Field Relationship and Petrogenesis of the Brecciated Unit of Jangalgali Formation, Jammu, India

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PREFACE

The brecciated unit of the Jangalgali Formation in Jammu region, NW Himalaya has been explored and studied at five different localities (Kalakot, Khargala, Beragua, Tattapani and Kanthan) at the same stratigraphic level. The whole Jangalgali Formation is lying in an unconformity zone and found sandwiched between the underlying Precambrian Sirban Limestone and overlying Late Palaeocene-Mid Eocene Subathu Formation. In the present work, the brecciated unit has been evaluated for its origin based on field, petrographic and geochemical studies.

Breccias in all five localities are having fine-grained matrix and with textures varying from tight, fitted fabric geometry to more open and chaotic packing. There are very few or no calcareous materials present in it; and also no fossils were noticed in these units. The Jangalgali breccia unit is 2–10 m thick and dominantly comprises with phenocrysts of quartz and feldspars of different shapes and sizes distributed randomly in a glassy matrix, along with < 2% by volume of accessory minerals like zircon, rutile, hematite, biotite, hornblende, tourmaline, pyrite, plagioclase and feldpathoids. Bipyramidal, angular and skeletal morphologies are common in quartz. Quartz shows resorption features and contains inclusions of negative crystals. Presence of euhedral hexagonal dipyramidal quartz phenocrysts and irregularly shaped inclusions with high volatile contents indicates its volcanic origin.

Zircon and rutile grains from Jangalgali breccia unit (JBU) were studied by SEM-EDX, EPMA and Raman spectroscopy for their morphology and chemistry to get insights into their origin. Varied morphology and textures were found in both zircon and rutile; which are euhedral, prismatic and sub rounded. Zircons are showing magmatic trend in Raman spectroscopy and also exhibits inherited magmatic cores in CL images. The observed irregular fractures and scratches on few zircon grains may be due to long-term corrosion, metamictization and alteration processes. The Raman spectroscopy of the zircons show magmatic trend, and also exhibits inherited crystals in CL studies. It is dominantly comprised of high silica (~90 wt. %). Their A/CNK ratio’s are quite high (>6), suggesting highly peraluminous nature. The average concentrations of ΣREE and trace elements are quite low (~38 ppm and ~500 ppm respectively). The field, mineralogy, textural relation as well as geochemistry of the JBU suggest rhyolitic character.
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(Matsyendra Kumar Shukla)
HIMALAYA, the world’s youngest and loftiest mountain chain forms the northern limit of the Indian subcontinent. From east to west it has an extension of 2400 km and occupies an area of nearly 750,000 km$^2$. Geographically, the Himalayan range lies between its eastern and western syntaxis as represented by the Namche Barwa and Nanga Parbat peaks. The northern boundary of the Himalayan range is the east-flowing Yalu Tsangpo (Tsangpo-big River in Tibetan) and west-flowing Indus River. The southern boundary of the Himalayan range is the Main Frontal Thrust (MFT) that marks the northern limit of the Indo-Gangetic depression. Immediately to the west of the Himalayan range are the Hindu Kush Mountains, to the east the Indo-Burma Ranges, and to the north the Karakorum Mountains and the Gangdese Shan (also known as the Trans-Himalaya in Heim and Gansser, 1939).

Himalaya is a classic example of an orogenic system created by continent–continent collision (e.g., Dewey and Bird, 1970; Dewey and Burke, 1973). The classic reviews of the Himalayan geology by Wadia (1953), Gansser (1964) and LeFort (1975) laid the foundation for productive geologic research in the next several decades to follow. Gansser (1974) classified Himalaya into five physiographic divisions from south to north, i.e. Outer Himalaya, Lesser Himalaya, Higher Himalaya, Tethys Himalaya and Trans Himalaya. The history of the Himalayan evolution has been generally divided into two stages: the Eohimalayan event that occurred during the middle Eocene to Oligocene (45–25 Ma) and the Neohimalayan event that occurred since the early Miocene (LeFort, 1996; Hodges, 2000). The timing of the India-Asia collision responsible for the evolution of Himalaya is well known and was interpreted by many workers e.g. ~ 57 Ma by Leech et al., (2005), ~50 Ma by Najman et al. (2010) and Wang et al. (2011), at ~54 Ma by Gaetani and Garzanti (1991) and by Beck et al. (1995) it was inferred between 66 - 55.5 Ma.

Stratigraphically, the major lithologic units in the Himalayan orogen consist of the Neogene Siwalik Group, the Proterozoic Lesser Himalayan Sequence (LHS), the Proterozoic–Ordovician Greater Himalayan Crystalline Complex (GHC), and the Proterozoic to Eocene Tethyan Himalayan Sequence (THS) (e.g., LeFort, 1996). The major tectono-stratigraphic units in the Himalayan orogen are defined (from south to north) as the Main Frontal Thrust (MFT) hanging wall, Main Boundary Thrust (MBT)
hanging wall, Main Central Thrust (MCT) hanging wall, and South Tibetan Detachment (STD) hanging wall (LeFort, 1996; Hodges, 2000; Yin, 2006).

The potential of the Himalaya as a guide to decipher the feedback processes between lithospheric deformation and atmospheric circulation has motivated intense research in recent years on the history of the Himalayan–Tibetan orogen, its role in global climate change, and its interaction with erosion (e.g., Harrison et al., 1992, 1998a; Molnar et al., 1993; Royden et al., 1997; Ramstein et al., 1997; Tapponnier et al., 2001; Beaumont et al., 2001; Yin et al., 2002).

In Northwest Himalaya a sequence of lithounits comprising of brecciated unit overlies by bauxite/laterite units, known as the Jangalgali Formation, is found. This formation lies south of Main Boundary Thrust (MBT) and is sandwiched between Neoproterozoic Sirban Limestone and Late Palaeocene to Mid Eocene Subathu Formation (Raha, et.al 1978 and Raha, 1984; P. Singh, 1970 & 1973; Singh and Andotra 2000; Nanda and Kumar, 1999; Bhat et. al, 2008) and the exposures of this formation are seen in Kalakot and Riasi areas (Fig. 1.1).

![Fig. 1.1 Location and road map of the study area.](image-url)
The exposures of the Jangalgali Formation are reported at five localities which include Kanthan, Kalakot, Beragua, Khargala and Tattapani in the Jammu region of J&K State, India (Fig.1.2). Bhatia (1982) reported that a chert-breccia, similar to the one at Kalakot, do occur in Bidhalna and Pharat windows where Subathus rest unconformably over Shimla Slate (equivalent to Sirban Limestone). However, the details of this rock unit are still to be explored.

![Location map of the study area where Jangalgali Formation is exposed](modified after Singh, 2003).

The Jangalgali Formation was earlier, included within the Subathu Group along with its two members i.e. Khargala Chert breccia and Lain Bauxite (Singh, 1973). But, since the Jangalgali Formation is represented by entirely different lithotypes; hence it has been later designated as a separate lithounit. The Lain Bauxite, which conformably overlies Khargala Chert Breccia, is named after the village Lain and it is represented by pisolithic and massive varieties of bauxite. Also at few places, laterite occurs where bauxite is not developed (Singh, 1980).
Breccia in general is a “rock composed of broken fragments of minerals or rock cemented together by a fine grain matrix (Glossary of meteoritical terms) that may be similar to or different from the composition of the fragments”. By virtue of their stratigraphic position in Northwest Himalaya, breccia units bring out attention of many workers regarding their origin and relation to India-Asia collision. Medlicott (1876) was probably the first, who discussed the siliceous breccia overlying the carbonate rocks. He termed these underlying carbonate rocks as Great Limestone, also compared it with the Infra-Trias limestone of Mt. Sirban, Hazara district (Pakistan) and later named it as “Sirban Limestone”.

Wadia (1928) expressed his views on the origin and occurrence of chert breccia along with overlying bauxite occurring between the Sirban Limestone and Nummulitic Limestone in Jammu region. He recognized two facies within the Eocene Strata i.e. i) Hazara facies and ii) Subathu facies and further classified the Hazara facies under Laki series (Chharat) while the rocks of the Subathu facies contain only Upper Laki and Lower Kirthar horizons. Wadia (1937) assigned Sirban Limestone to Permian or Permo-carboniferous age on account of indirect evidence, i.e. association of some volcanic rocks near the base of the Devigah inlier (now in Pakistan administered territory of J&K).

Anon (1979) reported rhyolitic volcanic breccia from the bauxite unit of lower Subathu sequence at the Chenab river section near Kanthan bridge, Salal. Presence of minor rhyolite has also been recorded by Acharyya (1999a, b, 2000) from the Eocene sediments of the Himalayan frontal belt. There are different opinions put forth by earlier workers regarding the origin of these units (Singh, 2003 & 2012; Bhat et. al, 2008). Singh (2003 & 2012) proposed a sedimentary model for the origin of this breccia and suggested that this breccia is formed by silicification of the Sirban Limestone. According to him, the breccia facies in the basal interval of the Palaeogene succession of the Jammu area is entirely composed of basement-derived sediments, which suggest activation of growth faults hundreds of kilometres away from the collision zone (India- Eurasia) and erosion of the hanging walls vis-a-vis deposition in the fault depressions. He inferred that, the breccia sedimentation in the fault zone with the pebble size clasts suggests rapid subsidence followed by sedimentation. He projected the breccia unit as an important proxy for India-Eurasia collision in the foreland basin and also used it as a marker horizon in the unconformity zone that lies between Neoproterozoic Sirban Limestone and Palaeocene to Mid Eocene Subathu Formation.
Bhat et al. (2008) advocated that this brecciated unit is the erosion products of the underlying litho units of the Sirban Limestone. In the Himalayan foothill belt of Jammu region, Sirban Limestone occurs as inliers within the Tertiary expanse, forming prominent high mountain ranges amongst the low-lying Tertiary hills, the best exposures of it occur in Reasi inlier (Reasi, Bidda, Salal, Muthal, Katra and Talwara). The Sirban Limestone is composed of thickly bedded highly jointed, hard, dark grey dolostone with beds of ooid and pellooidal limestones (Bhat et al., 2008) the unconformity between the Sirban Limestone and the Subathu is marked by widespread occurrence of chert-dolomite breccia with a bauxite bed above it forming the base of the Subathu.

However, recently based on preliminary study of field, mineral, texture and geochemical data on the chert breccia, it has been suggested that it is a high-silica rhyolitic tuff breccia (Siddaiah, 2011; Shukla and Siddaiah, 2011; Siddaiah and Shukla 2012). In the literature very little is available on the mineral chemistry and geochemical characteristics of this brecciated unit which could help to understand the nature and origin of these breccias. Although several biostratigraphic studies have been carried out on syn-orogenic sediments of the Subathu Formation because of their abundant and well-preserved fauna and hydrocarbon potential (Singh, 1970; Singh & Vimal, 1970; Acharyya et al, 1979; Karunakaran & Ranga Rao, 1979; Singh, 2003, 2012; Bhat et al, 2009) but there are no systematic studies on the lithounits that make up the Jangalgali Formation.

The breccia is one of the important lithounits of Jangalgali Formation and not much is known about it. Since there are no absolute ages yet available in the unit of architectural elements of the Jangalgali Formation. Its stratigraphic age may likely go to anywhere between Neoproterozoic to Late Palaeocene; therefore these breccia units may hold key to fill the huge time gap between Sirban Limestone and Subathu Formation. It may also be helpful to build a model for the geodynamic evolution of this part of the Himalayan region. These brecciated units have been reported to be of different origin (sedimentary and volcanic) by different workers. The proposed detailed study shall give new and modern inputs to settle the controversy regarding the origin of the same.

Hence, keeping in mind the importance of breccia units in the Jangalgali Formation, this study was under taken to understand the origin of these breccias and its relation to India-Eurasia collision (if exists). The main focus is to shed light on the Petrogenetic character of the brecciated units of Jangalgali formation and its related problems and their understandings e.g. stratigraphic position, time and nature of the formation.
GEOLOGICAL SETTING AND FIELD RELATIONSHIP

In Northwest Himalaya, a sequence of lithounits (breccia and bauxite/laterite) known as Jangalgali Formation occurs in the Jammu region. The Jangalgali Formation lies south of the Main Boundary Thrust (MBT) and is sandwiched between Neoproterozoic Sirban Limestone (Raha, et al., 1978 and Raha, 1984) and basal part of Thanetian Subathu Formation (P. Singh, 1970 & 1973; Singh and Andotra 2000). The most important exposed litho-units, in the study area, mainly belong to the Subathu (Late Palaeocene to Middle Eocene) Group (Table-2.1). In general, the foreland succession of the Jammu region comprises of the Subathu, Murree and Siwalik groups from bottom to top respectively.

The exposures of the breccia unit can be followed for more than 100 km in the northwestern part of the Indian Himalaya including five localities in Jammu region viz., Kanthan, Kalakot, Beragua, Khargala and Tattapani (Fig-2.1). Thickness of the Jangalgali breccia unit (JBU) ranges between 2 - 10m (Figs-2.2 & 2.3). The whole sequences of Jangalgali Formation i.e. breccia and bauxite/laterite units are found only in Kanthan area, rest of localities have only breccia units unconformable with the Subathu shales. Few detached outcrops of nodular chert (2-3 m thick) were also found at Beragua and Tattapani overlain by Subathu shale which has no relation either textural or chemical with underlying Jangalgali breccia unit.
**Table-2.1** Geological sequence of the Subathu Group and Jangalgali Formation in Jammu Himalaya (Modified after Singh, 1973, 1980).

<table>
<thead>
<tr>
<th>Age</th>
<th>Group</th>
<th>Formation</th>
<th>Member</th>
<th>Lithology</th>
<th>Thickness (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early Eocene</td>
<td>Subathu</td>
<td>Arnas Limestone</td>
<td>Chinab Limestone</td>
<td>Greenish grey limestone</td>
<td>2-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Chinkah Limestone</td>
<td>Grey shelly limestone</td>
<td>4-6</td>
</tr>
<tr>
<td>Late Early Eocene</td>
<td>Subathu</td>
<td></td>
<td>Ans Limestone</td>
<td>Grey fossiliferous limestone</td>
<td>5-20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Kalakot</td>
<td>Olive, green, grey or khaki needle shales interbedded with dark grey fossiliferous limestone bands, lenticular to nodular limestones, and marls containing pyrite and phosphatic nodules. Shales contain thin bands of siltstones, clay and lenses of red / purple shales</td>
<td>10-85</td>
</tr>
<tr>
<td>Late Palaeocene</td>
<td></td>
<td>Beragua</td>
<td></td>
<td>Quartz-wacke, quartz-arenite, carbonaceous shales, coal seams, pyrite concretions and ferruginous shales</td>
<td>6-54</td>
</tr>
<tr>
<td>Early Palaeocene - Cambrian (?)</td>
<td>Jangalgali</td>
<td>Lain- Bauxite Khargala Chert Breccia</td>
<td></td>
<td>Bauxite pisolitic and massive Chert breccia/ Brecciated unit</td>
<td>1.8-2</td>
</tr>
</tbody>
</table>

---------------------------------------------------------------------------------UNCONFORMITY---------------------------------------------------------------------------------
Fig-2.1 Geological map of the study area (modified after Rao and Rao 1979; Nanda and Kumar 1999).
Fig-2.2 Generalized litholog of the study area showing the stratigraphic position of the Jangalgali breccia unit (modified after Singh, 1980).
2.1 Subathu Formation, the upper contact of the Breccia

The upper contact of Jangalgali Formation is with carbonaceous shale of Subathu Formation, which is followed by the Murree Group of rocks (Raha, et.al 1978; Singh P 1980; Najman and Garzanti 2000). The contact of breccia units with Subathu Formation is sharp (Fig-2.4a & Fig-2.4b). Thanetian age was assigned to the lowermost limestone band of basal Subathu Formation based on foraminifers namely, *Ranikothalia nuttalli*
The breccia as well as the bauxite/laterite unit, which is non-fossiliferous, is being considered as an unconformity (Singh, 2003).

**Fig-2.4a** Upper contact of breccias at A) Kalakot B) Beragua C) Khargala D) Tattapani (Hammer = 35 cm, Arrow indicate sample collection point).

**Fig-2.4b** Upper contact of breccias at Kanthan A) before new bridge B) near old bridge

The term ‘Subathu’ was first used to include a thick succession of conformable strata comprising the ‘Nummulitics’ or Subathus, the Dagshais and the Kasaulis, exposed near the Subathu Cantonment in the Solan District of Himachal Pradesh (Medlicott, 1864).
Singh (1980) assigned a ‘Group’ status to the Subathu succession of Jammu and Kashmir and recognized three formations within this group. In ascending order, these formations are Beragua, Kalakot and Arnas Limestone (with three members- Ans, Chinkah and Chinab; Table-2.1). In recent years, the lower part of the Subathu succession has been equated with the Palaeocene ‘Kakara Series’ of Srikantia and Bhargava (1967) and it has been formally named as the Kakara Formation; the name Subathu Formation has now been restricted for the middle and upper parts of the succession (Juyal and Mathur, 1990, 1992; Nanda and Kumar, 1999).

The lower age limit of the Subathu Group (Kakara-Subathu succession) is generally considered to be the Late Palaeocene (Thanetian). However, many sections also extend into the Early Palaeocene (Danian) and Late Cretaceous (Maastrichtian). The basal fossiliferous shales of the succession, in most sections, yield characteristic index fossils of the Daviesina tenuis-Lockhartia conditiae assemblage zone (Mathur and Juyal, 1999) indicating a Thanetian age. The upper age limit of the Subathu Group is considered as Early Lutetian on the basis of invertebrate fossils of faunal zone VIII of Mathur and Juyal (1999), and the mammalian fauna including rodents which are specifically similar to those known from the well dated Kuldana Formation in Pakistan (Kumar and Sahni, 1985; Kumar 1991, 1992; Kumar et al., 1997).

The deposition of basal black-grey unit of the Subathu Group was probably initiated under coastal marshy conditions and in a reducing environment as indicated by the formation of coal seams (Fig-2.5) and also the presence of foraminiferids. The green shale-limestone unit or the middle part of the Subathu Group, according to Nanda and Kumar (1999), is predominantly marine as indicated by the dominance of foraminiferids, ostracodes, echinoids and marine vertebrates including sharks, rays, tetraodons, pycnodons, etc. The top of this unit includes oyster-bearing coquinites, which are suggestive of brackish water conditions gradually changing into fresh water environment during the deposition of red beds of the upper Subathu. The bone bed at the top of green shale-limestone unit also shows a mixing of typical marine and continental vertebrates in the Triyath locality (Kumar, 1999).

The red bed unit constituting the upper part of the Subathu Group represents the first continental sediments in the foreland basin, which was gradually transgressing the Tethyan shoreline following the withdrawal of this sea. This is suggested by the complete dominance of land dwelling and fresh water vertebrates including fish, reptiles and...
mammals in well marked bone beds, which are traceable in several localities across the border in Pakistan (Nanda and Kumar, 1999).

Fig-2.5 Coal seams from basal Subathu Formation at A) Beragua B) Kanthan.
In the study area Subathu Group is followed by the Murree Group of rocks. The Murree Group is divisible into the Lower and Upper Murree Formations (Karunakaran and Ranga Rao, 1976; Rao and Rao, 1979). The Lower Murree sediments are mainly argillaceous and consist of deep purple or chocolate coloured mudstones interbedded with sandstones, while the Upper Murree sediments are arenaceous and form continuous sandstone ridges.

2.2 Sirban Limestone, the lower contact of the Breccia

Sirban Limestone is at the lower contact of the Jangalgali Formation on which breccia unit occurs, above which bauxite and laterite layers are found at few places (Nanda and Kumar, 1999; Singh, 2003, 2012; Bhat et al., 2008). The base of the Sirban Limestone is not well exposed anywhere in the type locality. However, at Kalakot a detached block was found near the river bridge showing both the lower as well as upper contact of the breccia but not reported in-situ (Fig-2.6).

![Image of Sirban Limestone and Breccia](image.jpg)

**Fig-2.6** Lower and upper contact of breccia at Kalakot (Found in a detached block).

In the Himalayan foothill belt of Jammu region, Sirban Limestone occurs as inliers within the Tertiary expanse, forming prominent high mountain ranges amongst the low-lying Tertiary hills. Some of the best exposures of the Sirban Limestone occur at Reasi,
Salal, Talwara, Muthal, Katra, Bidda and Jotipuram localities in the Reasi inlier. The Katra-Reasi-Jotipuram-Salal inlier is the largest of the Sirban Limestone; it is surrounded by the rocks of Subathu and Murree Group. The Subathu and Murree Groups along with their basement Sirban Limestone was folded up on an approximately east-west axis though a post-Murree tectonic activity; later on these rocks were thrustted / faulted against the already folded Siwalik strata in the late Pleistocene times (Bhat et al., 2008). The Sirban Limestone standout in relief in the background of the low lying Outer Himalayan foothills comprising Murree and Siwalik strata in Jammu and surrounding areas. The base of this carbonate sequence is nowhere exposed in the region which poses problem in placing a proper stratigraphic order. However, these rocks are unconformably overlain by the Subathu Group which forms the autochthonous basement of the Tertiary sediments. Medlicott (1876) termed these carbonate rocks as ‘Great Limestone’.

The Sirban Limestone is composed of thickly bedded highly jointed, hard, dark grey dolostones and pelloidal limestones and is also characterized by algal mats and stromatolites (Rao and Rao 1979). Gupta and Dixit, (1970) reported for the first time an extensive occurrence of algal stromatolites from the Sirban Limestone. However, later Cynobacterial mats, microbiota and an assemblage of Neoproterozoic microflora, in the stromatolitic succession of the Sirban Limestone/ Vaishnodevi Limestone or Great Limestone (Venkatachala & Kumar, 1997, 1998; Bhat et al 2009), have also been reported. Based on the microflora reported by Venkatachala and Kumar (1998) from a well exposed chert bed near Bidda and a shale bed near Muthal, Palaeo-Mesoproterozoic age was assigned to the Sirban Limestone of Bidda. However, since the Muthal microflora comes from the top most unit of the Sirban Limestone, therefore at Muthal Neoproterozoic age was assigned for the same. Earlier, Wadia (1937) considered Sirban Limestone to be of Permian or Permo-carboniferous age.

2.3 Field characteristics of the Jangalgali breccia unit

The Jangalgali breccia is found within the unconformity zone between Sirban Limestone and Subathu Group of rocks. Its thickness, however, is variable; at its type localities (Kanthan and Khargala) it is up to 10 m thick while at Kalakot, Beragua and Tattapani it is reduced to ~5 m. The lower contact of the JBU with Sirban Limestone is not sharp and is observed only at few places, while its upper contact with Subathu is sharp in all five localities (where bauxite/ laterite unit is not present). The overlying bauxite/ laterite unit of
Jangalgali Formation is absent in most of localities and is observed only in Kanthan area (Fig-2.7). In Kanthan, about 10 m thick breccia unit having sharp contact with Subathu shales was explored. This exposure is lying along the Chenab River with almost East-West trend. The JBU is mainly consisting of rhyolite clasts with a dominantly clastic matrix of gray to dark gray in colour; it is relatively impermeable. The average fragment size of breccia ranges from approximately 2 to 30 cm in diameter. However, the fragments are variable from sub millimetre to metre-sized. Larger fragments occur more frequently; angular to sub angular fragments are characteristic in all localities and can often be refitted into each other.
**Fig-2.7** Field Photograph showing the exposures of bauxite of Jangalgali Formation at A) Kanthan B) Salal.

In few breccia fragments vesicles of size between 0.5 to 1.5 cm have also been noticed (Fig-2.8 Hand specimen). All the fragments are arranged in a fine to medium grain siliceous matrix. However, careful examination of the fragments as well as matrix indicates that many of the displaced fragments have no preferred relative orientation and also have no or very little proportion of calcareous materials. The JBU is distinctly of porphyritic (~25 to 45 volume % phenocrysts at few horizons) texture with quartz as the dominant proportion. Phenocrysts of quartz and K-feldspar are set in a fine-grained glassy matrix and lack preferred orientation.

![Breccia fragment showing vesicles](image)

**Fig 2.8** Hand specimen of breccia fragment showing vesicles collected from Kalakot.

Freshly exposed outcrop surfaces appear glassy with conchoidal fracture. Throughout the lateral extent of the Jangalgali breccia, the rhyolite clast range from unbroken to highly fracture. There is hardly any significant evidence of transport or reworking of phenocrysts
prior to deposition. A brief description of all the sections of Jangalgali breccia unit, exposed in different areas is presented in Table-2.2.

**Table-2.2** Field features of breccia unit at different localities in Jammu region.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Field description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kalakot</strong> (~120 km northwest of Jammu city)</td>
<td>Breccia is exposed on either side of the bridge on the stream (Sair Tawi) draining country on the west side of the village. It is ~5 m thick, lavender to grey, weathers tan to brown, and consists of phenocrysts ranging in size from few mm to a couple of cm. GPS reading: 33° 12' 58&quot; N, 74° 24' 58&quot; E; elevation 625 m.</td>
</tr>
<tr>
<td><strong>Beragua &amp; Khargala</strong> (~11 km west of Kalakot)</td>
<td>About 10 m thick, breccia is exposed along the Kalakot–Rajauri road. It is porphyritic with ~10 % phenocrysts of mainly quartz and sanidine enclosed in a glassy matrix. The size of phenocrysts ranges from few mm to a couple of cm. GPS reading: 33° 12' 55&quot; N; 74° 24' 04&quot; E, elevation 825.5 m for Beragua; and 33° 14' 10&quot; N; 74° 23' 48&quot; E, elevation 900 m for Khargala.</td>
</tr>
<tr>
<td><strong>Tattapani</strong> (~6 km west of Beragua)</td>
<td>Breccia is exposed along the right side of the road. It is ~5 m thick. The size of phenocrysts ranges from few mm to a couple of cm. GPS reading: 33° 14' 25&quot; N; 74° 24' 41&quot; E, elevation 798 m.</td>
</tr>
<tr>
<td><strong>Kanthan</strong> (~20 km from Reasi town)</td>
<td>Breccia occurs ~1 km before the Kanthan village on the left bank of the Chenab river, near the bridge. It is grey to pale red and ~10 m thick. It is phophyrritic, with 10-15 % phenocrysts of quartz, sanidine and minor plagioclase and biotite set in a glassy groundmass. GPS reading: 33° 10' 14&quot; N; 74° 51' 04&quot; E; elevation 525.5 m.</td>
</tr>
</tbody>
</table>

**2.3.1 Kalakot Section**

In the Kalakot section which is about ~120 km northwest of Jammu city (GPS reading: 33° 12' 58" N, 74° 24' 58" E; elevation 625 m.), the breccia unit known as Khargala Chert Breccia is exposed on either side of the bridge on the stream (Sair Tawi) draining country on the west side of the village. It is ~5 m thick, lavender to grey, weathers tan to brown, and consists of phenocrysts ranging in size from few mm to a couple of cm (Fig-2.9).
Fig 2.9 Field photographs (1-10) showing the characteristic features of the exposures of breccia unit at Kalakot: 1- lateral extension of JBU along one side of the river, 2- bifurcated breccia unit exposed due to river cutting action, 3- breccia exposure showing boulder size angular clast, 4- various angular phenocryst of different size occur with random orientation, 5- angular phenocryst with fine to medium grain matrix, 6- breccia with fine grain siliceous matrix, 7- top oxidised layer of breccia with fresh exposure below it, 8- flow like texture with randomly arranged fine to medium grain quartz phenocryst, 9- fractured layer of breccia comprises with angular quartz phenocryst, 10- breccia used as a foundation rock for the river bridge pillar (indicating how strong it is). 

In certain sections, the breccia unit is followed by an impersistent lateritic bed, designated as Lain Bauxite Formation (Singh, 1980). The thickness of lateritic part below the carbonaceous shales varies in different sections (Nanda and Kumar, 1999); these have been identified from inadequate material (Ranga Rao, 1986; Mehta & Jolly, 1989).
The Kalakot-Jgni-Sialsui Road runs along the southern limb of the Kalakot Inlier (Anticline). The complete section of the Subathu Group can be observed while passing along this road starting from near Sair (Kalakot) Bridge where the basal beds of the Subathu are exposed just above the Jangalgali Breccia unit. The exposures of the northern limb of the anticline can be seen at Tattapani and Dali Villages, close to Kalakot.

2.3.2 Beragua and Khargala Section

Along the road towards Rajauri (~11 km west of Kalakot, between Beragua and Khargala), about 1 m above the road level, a thick bed (~10 m) of breccia and the upper part of the green shale-limestone unit of the Subathu Group are exposed (GPS reading: 33° 12’ 55” N; 74° 24’ 04” E, elevation 825.5 m for Beragua; and 33° 14’ 10” N; 74° 23’ 48” E, elevation 900 m for Khargala). The breccia units here are porphyritic with ~10 % phenocrysts of mainly quartz and sanidine enclosed in a glassy matrix. The size of phenocrysts ranges from few mm to a couple of cm (Fig-2.10 and Fig-2.11).

![Breccia](image1.jpg)

![1m](image2.jpg)

![Beragua](image3.jpg)

![Khargala](image4.jpg)
Fig-2.10 Field photographs (1-4) showing the exposures of breccia unit at Beragua; 1-lateral extension of breccia, 2-breccia comprises with rhyolitic clast, 3-fine to medium angular phenocryst arranged in siliceous matrix, 4-rhyolitic breccia with very fine matrix.

The rocks of the Beragua member are best developed at village Beragua. Near the Beragua village, an abandoned coal mine (named as Beragua coal mine) is situated. A composite succession of the Subathu Group consists of basal carbonaceous shale beds intercalated with semi anthracitic coal seams which are often lensoid and impersistent, is exposed here. This member is mainly composed of ferruginous shale, dark grey shale, carbonaceous shale, coal seams, quartzwacke and quartzarenite. Pyrite concretions are fairly distributed.

Fig-2.11 Field photographs (1-2) showing the exposures of breccia unit at Khargala, 1-lateral extension of JBU, 2-breccia comprises with fine grain rhyolitic clasts exposed along the road towards Tattapani.

2.3.3 Tattapani Section
In the Tattapani section (~ 6 km west of Beragua), breccia is exposed along the right side of the road (GPS reading: 33° 14’ 25” N; 74° 24’ 41” E, elevation 798 m). It is up to 5 m thick. The size of phenocrysts ranges from few mm to a couple of cm (Fig-2.12). In this area the northern limb of the anticline of Kalakot inlier is exposed. Few detached outcrops of nodular chert (2-3 m thick) were also observed at Tattapani overlain by
Subathu shale. However, it has no relation, neither textural nor chemical, with underlying Jangalgali breccia unit.

Fig-2.12 Field photographs (1-6) showing the exposures of breccia unit at Tattapani, 1-lateral view of breccia, 2-breccia comprises with angular phenocryst, 3-breccia showing angular clast with vesicles present in both matrix as well as in phenocryst, 4-fine to medium angular phenocryst arranged in siliceous matrix, 5-detached outcrop of breccia
with fine grain matrix, 6-breccia exposure having planar deformation features and fine grain matrix.

2.3.4 Kanthan Section

In Kanthan section (~20 km from Reasi town), breccia unit occurs about 1 km before the Kanthan village. It is up to 10 m thick and having sharp contact with overlying Subathu shales. The exposures of the breccia unit are lying along the left bank of the Chenab River near the bridge with almost East-West trend (GPS reading: 33° 10’ 14” N; 74° 51’ 04” E; elevation 525.5 m). It is grey to pale red and varies from 2-10 m in thickness (Fig-2.13). It is prophyritic, with 10-15 % phenocrysts of quartz, sanidine and minor plagioclase and biotite set in a glassy groundmass. A bauxite band of Jangalgali Formation also occurs below the carbonaceous shales of Subathu Formation near Kanthan village (right bank of the Chenab River).
Fig-2.13 Field photographs (1-12) showing the exposures of breccia unit at Kanthan

1- fine grain massive block of reddish brown breccia, 2- breccia comprises with angular clast, 3- fine grain breccia overlain by secondary deposits, 4- breccia showing angular clasts with vesicles present in both matrix as well as in phenocryst 5- greyish breccia with fine to medium angular clasts arranged in siliceous matrix, 6- outcrop of breccia with fractured clasts and fine grain matrix, 7- dark grey breccia with fine grain texture and vesicles in the matrix, 8- reddish brown fractured block of breccia with angular clasts, 9- lateral extension of breccia along the Chenab river, 10- breccia comprises with greenish angular clast, 11- massive block of light grey breccia containing voids and vesicles, 12- block of breccia with different size of randomly oriented angular clast.

Kanthan section displays beds of the Subathus in patches. In this section Subathu Group is represented by Kalakot member. The Subathu beds are composed of grey and carbonaceous shales with coal seams whose upper part is represented by Nummulitic limestone beds. In this area the Subathu beds occur as thin faulted inlier strips within the Murree Group and the contact of the Subathu with overlying Murree Group is apparently conformable. The limestone beds in the middle of the section document numerous mega oysters. The entire section contains foraminifera and oysters (Bhat et al 2008).
Chapter -3

METHODS AND MATERIALS

Ten lithological sections were investigated for their field characters. A total 127 thin sections (Table-3) of Jangalgali breccia unit were prepared using balsam and araldite (for EPMA study) and coated with carbon for SEM-Edx and EPMA studies. Around 40 representative samples were crushed and finely powdered using Jaw crusher and N.V.Tema Mill respectively, for making pressed powdered pellets and loss on ignition (LOI) test. For LOI calculation, the samples in glass vials were dried for 24 hours in an oven at 70-80°C before they were transferred into clean pre-weighed crucibles with weights recorded to the nearest 0.0001 gram. After cooling the samples for 30 minutes, the total weight of the sample and crucible were also recorded. The crucible and samples were placed in a furnace operating at ~1000°C for a period of one hour. The crucible and sample were removed and placed in a dessicator to fully cool. About two hours later, the crucible and ashed sample were reweighed. The percentage of LOI was then calculated by the formula:

\[
\% \text{ LOI} = 100\times(\text{weight change during ignition}) / (\text{fresh sample weight}).
\]

<p>| Table- 3 List of thin sections of JBU from different localities |
|---------------------------------|-----------------|-----------------|-----------------|
| Locality | With Balsam | With Araldite |
| Sample No. | No. of section | Sample No. | No. of section |
| Kalakot | | |
| KDR-1 | 2 | KDL-1 | 2 |
| KDR-2 | 2 | KDL-3 | 2 |
| KDR-3 | 5 | KDR-4 | 3 |
| KDR-4 | 4 | KDL-5 | 2 |
| KDR-5 | 4 | KL-3 | 2 |
| KDR-1P | 1 | KR-1 | 2 |
| KUL-3A | 1 | KR-3 | 2 |
| KUL-3B | 1 | KR-4 | 4 |
| KUL-3C | 1 | KR-5 | 8 |
| KDL-1 | 2 | Total | 27 |
| KDL-3 | 4 | | |
| Khargala | | |
| KH-0 | 2 | | |
| KH-1 | 2 | KH-8 | 1 |
| KH-2 | 2 | | |
| KH-3 | 2 | | |
| KH-7 | 1 | | |
| KH-6 | 2 | | |
| KH-3 | 2 | | |
| Total | 40 | Total | 01 |</p>
<table>
<thead>
<tr>
<th>Location</th>
<th>Sample Codes</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kanthan</td>
<td>KO-2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>KO-3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>KO-4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>KO-5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>KN-1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>KN-3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>KN-4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>KN-5</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>KN-6</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>KN-8</td>
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</tr>
<tr>
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<td>KN-10</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td><strong>22</strong></td>
</tr>
<tr>
<td>Beragua</td>
<td>BG-1</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>BG-3</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>BG-4</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>BG-7</td>
<td>3</td>
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<tr>
<td></td>
<td>BG-8</td>
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<td></td>
<td>BG-9</td>
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<td></td>
<td>BG-10</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>BGB-1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>BGB-2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td><strong>23</strong></td>
</tr>
<tr>
<td>Tattapani</td>
<td>TP-1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>TP-2</td>
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<tr>
<td></td>
<td>TP-3</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td><strong>14</strong></td>
</tr>
<tr>
<td><strong>Grand total</strong></td>
<td></td>
<td><strong>40+87=127</strong></td>
</tr>
</tbody>
</table>

All the laboratory studies (e.g. LOI test, Raman, SEM-EDX, XRF, ICPMS and EPMA) have been carried out at Wadia Institute of Himalayan Geology, Dehradun. Brief descriptions of various techniques used in the present study are as follows:

### 3.1 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman Effect. This shift provides information about
vibrational, rotational and other low frequency transitions in molecules. Raman spectroscopy can be used to study solid, liquid and gaseous samples and are very useful for the rapid identification of a wide variety of minerals (Hope et al., 2001; Das and Hendry, 2011).

A Raman system typically consists of four major components: 1) Excitation source (Laser); 2) Sample illumination system and light collection optics, 3) Wavelength selector (Filter); and 4) Detector (Photodiode array). The Raman Effect is based on molecular deformations in electric field ‘E’ determined by molecular polarizability ‘α’. The laser beam can be considered as an oscillating electromagnetic wave with electrical vector (E). Upon interaction with the sample it induces electric dipole moment $P = \alpha E$ which deforms molecules. Because of periodical deformation, molecules start vibrating with characteristic frequency $\nu_m$.

Amplitude of vibration is called a nuclear displacement. In other words, monochromatic laser light with frequency $\nu_0$ excites molecules and transforms them into oscillating dipoles. Such oscillating dipoles emit light of three different frequencies (Fig-3.1) when:

1) A molecule with no Raman-active modes absorbs a photon with the frequency $\nu_0$. The excited molecule returns back to the same basic vibrational state and emits light with the same frequency $\nu_0$ as an excitation source. This type of interaction is called an elastic Rayleigh scattering.

2) A photon with frequency $\nu_0$ is absorbed by Raman-active molecule which at the time of interaction is in the basic vibrational state. Part of the photon’s energy is transferred to the Raman-active mode with frequency $\nu_m$ and the resulting frequency of scattered light is reduced to $\nu_0 - \nu_m$. This Raman frequency is called Stokes frequency, or just “Stokes”.

3) A photon with frequency $\nu_0$ is absorbed by a Raman-active molecule, which, at the time of interaction, is already in the excited vibrational state. Excessive energy of excited Raman active mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to $\nu_0 + \nu_m$. This Raman frequency is called Anti-Stokes frequency, or just “Anti-Stokes”.

29
Fig-3.1 Raman transitional schemes.

About 99.999% of all incident photons in spontaneous Raman undergo elastic Rayleigh scattering. This type of signal is useless for practical purposes of molecular characterization. Only about 0.001% of the incident light produces inelastic Raman signal with frequencies $v_0 \pm v_m$. Spontaneous Raman scattering is very weak and special measures should be taken to distinguish it from the predominant Rayleigh scattering.

Raman spectroscopy unlike other analytical tools (e.g. XRD) can be used to investigate local molecular structure (over a few unit cells of a crystal lattice) with high spectral resolution (Roach and Reddy, 2004). It can provide information on elemental speciation in a mineral or in a compound, also provide estimates of crystallinity, and basic information on mineral symmetry (Pasteris et al., 2001). An additional advantage of Raman spectroscopy over XRD is that it can be used as a powerful tool to identify elements of concern, even at different oxidation states (Hope et al., 2001; Muller et al., 2010).

In the present study, Raman spectroscopic analysis of minerals like zircon, rutile, plagioclase, hematite and beta-quartz were carried out on thin sections of JBU without carbon coating. For this, Horiba JY-Lab RAM HR instrument equipped with Ar- laser (514.57 nm) and Lab spec software was used. The other specifications for most of the observations are: Power 20 MW; Accumulation 1; Exposure time 2 seconds.
3.2 Scanning Electron Microscopy (SEM)

In the SEM a beam of high energy electrons is focused to a point and scanned in a raster pattern across the surface of the sample. As these electrons hit the sample they enter the surface atom layers and are either inelastically or elastically scattered. Inelastically scattered electrons lose significant energy during collisions and therefore have low energy when they escape from the sample surface. These electrons are then known as secondary electrons (SE). Elastically scattered electrons lose little or no energy during their collisions. They escape with high energy and as there is a higher probability that their escape trajectories will be at a high angle, i.e. back in the direction of the electron gun that produced them, they are known as backscattered electrons (BSE). Backscattered electron imaging provides elemental composition variation as well as surface topography. The difference in the energies of the secondary and backscattered electrons allows them to be separated by different detectors to produce different signals and images of the sample being investigated.

To understand the difference between the images it is useful to consider the interaction volume from which each signal is produced. Because of their low energies secondary electrons (SE) are generated from a small volume around the point where the electron beam hit the sample. The depth from which this signal is generated is tens of nanometres. Backscattered detector (BSD) electrons, with their higher energies, are generated from larger volumes. The volume from which both signals are emitted is also dependent on the energy given to the electrons that were focused onto the surface (referred to as primary electrons). Reducing the energy of the primary electrons (by reducing the accelerating voltage applied to them) reduces the interaction volume, making the signals more surface specific (extracts, Cobham Technical Services).

Viewing three dimensional images of microscopic areas only solves half the problem in an analysis. It is often necessary to identify the different elements associated with the specimen. This is accomplished by using the “built-in” spectrometer called an Energy Dispersive X-ray Spectrometer (EDS or EDX). EDS is an analytical technique which utilizes x-rays that are emitted from the specimen when bombarded by the electron beam to identify the elemental composition of the specimen. To explain further, when the sample is bombarded by the electron beam of the SEM, electrons are ejected from the atoms on the specimen’s surface. A resulting electron vacancy is filled by an electron from a higher shell, and an x-ray is emitted to balance the energy difference between the two electrons. The EDS x-ray detector measures the number of emitted x-rays versus their
energy. The energy of the x-ray is characteristic of the element from which the x-ray was emitted. A spectrum of the energy versus relative counts of the detected x-rays is obtained and evaluated for qualitative and quantitative determinations of the elements present. Modern SEM/EDS instruments are operated using very sophisticated software. These software programs allow unattended feature analysis and “mapping” of the composition of the elements on the surface of the specimen (extracts, William R. Herguth).

In the present study, the Carl Zeiss SMT EVO 40 instrument, equipped with EDX, was used for the Scanning Electron Microscopic study and data was generated at the operating conditions (in most cases): WD 8mm; HV 25.0 kV; Image size: 1000 x 750; Magnification: 846 xs.

3.3 X-ray Fluorescence analysis

X-ray fluorescence analysis is a method that uses the characteristic X-ray (fluorescent X-ray) that is generated when X-ray is irradiated on a substance. The fluorescent X-ray is the excess energy irradiated as electromagnetic field, which is generated when the irradiated X-ray forces the constituent atom’s inner-shell electrons to the outer shell and the vacant space (acceptor) falls on the outer-shell electrons. These rays possess energy characteristic to each element and therefore qualitative analysis using Mosley's Equation and quantitative analysis using the energy's X-ray intensity (number of photons) are possible.

There are two types of X-ray fluorescence spectrometers: Wavelength-dispersive X-ray fluorescence (WDXRF) and Energy-dispersive X-ray fluorescence (EDXRF) spectrometers. WDX disperses the fluorescent X-ray generated in the sample using dispersion crystal and measures it using a goniometer, resulting in a large size. On the other hand, the detector in EDX has a superior energy resolution and requires no dispersion system, which enables downsizing of the device. X-ray fluorescence analysis can be considered as spectrochemical analysis of an X-ray region.

In defining X-ray fluorescence analysis, the wavelength of the characteristic X-ray and atomic number are used. Most devices are equipped with the automatic identification (definition) feature but it is important to note various interfering spectrums. Depending on the element types contained in the sample, energy position of characteristic X-rays may be close to each other or spectrums may overlap.

When conducting quantitative analysis with fluorescent X-ray, there are two basic methods: The first is to create a standard curve. This method involves measuring several
samples with a known element concentration, and finding the relationship between the intensity of the measured element's fluorescent X-ray and the concentration. By referring this relationship, element concentration of unknown sample is obtained only with information on its fluorescent X-ray intensity. The other method is known as the fundamental parameter method (FP) of theoretical calculation. With this method, if the type and properties of all elements that compose a sample are known, then the intensity of each fluorescent X-ray can be derived theoretically. By utilizing this method, the composition of unknown sample can be extrapolated by its fluorescent X-ray intensity of each element (extracts, Seiko Instruments).

For the bulk rock chemistry of JBU, 32 representative samples were powdered and made pellets using 6g of powder of each sample; X-ray Fluorescence analysis in present study was performed by Seimens SRS 3000 instrument. Reference standards [USGS (RGM-1 and G-2)] were used during the analysis, and the precision of major and trace element analyses is better than 2% and 5% respectively.

3.4 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

ICP-MS is an analytical technique used for elemental determinations, particularly for the rare-earth elements (REEs) because of its superior detection capabilities over other elemental analysis techniques. An ICP-MS combines a high-temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer. The ICP source converts the atoms of the elements in the sample to ions. These ions are then separated and detected by the mass spectrometer.

Argon gas flows inside the concentric channels of the ICP torch. The RF load coil is connected to a radio-frequency (RF) generator. As power is supplied to the load coil from the generator, oscillating electric and magnetic fields are established at the end of the torch. When a spark is applied to the argon flowing through the ICP torch, electrons are stripped off of the argon atoms, forming argon ions. These ions are caught in the oscillating fields and collide with other argon atoms, forming an argon discharge or plasma. The sample is typically introduced into the ICP plasma as an aerosol, either by aspirating a liquid or dissolved solid sample into a nebulizer or using a laser to directly convert solid samples into an aerosol. Once the sample aerosol is introduced into the ICP torch, it is completely desolvated and the elements in the aerosol are converted first into gaseous atoms and then ionized towards the end of the plasma. Generally, it is
recommended that samples have no more than 0.2% total dissolved solids (TDS) for best instrument performance and stability.

The ions formed by the ICP discharge are typically positive ions, $M^+$ or $M^{+2}$, therefore, elements that prefer to form negative ions, such as Cl, I, F, etc. are very difficult to determine via ICP-MS. The detection capabilities of the technique can vary with the sample introduction technique used, as different techniques will allow differing amounts of sample to reach the ICP plasma. Detection capabilities will vary with the sample matrix, which may affect the degree of ionization that will occur in the plasma or allow the formation of species that may interfere with the analyte determination.

Once the elements in the sample are converted into ions, they are then brought into the mass spectrometer via the interface cones and are then separated by their mass-to-charge ratio. The most commonly used type of mass spectrometer is the quadrupole mass filter (having 4 rods, ~1 cm in diameter and 15-20 cm long). In this filter, alternating AC and DC voltages are applied to opposite pairs of the rods. These voltages are then rapidly switched along with an RF-field. The result is that an electrostatic filter is established that only allows ions of a single mass-to-charge ratio (m/e) pass through the rods to the detector at a given instant in time (extracts, USGS).

ELAN DRC-e instrument was used for ICPMS analysis of REE’s of the JBU. Solutions of the 0.1g of each of the 13 samples were prepared using mixture of HF and HClO$_4$ followed by HNO$_3$ acids. Reference standards [USGS (RGM-1 and G-2)] were used during the analysis, and the precision of trace and REE’s is better than 5%. Chondrite-normalised REE diagram of JBU have been made on Petrograph2beta software using normalizing values after Nakamura (1974).

3.5 Electron Probe Microanalysis (EPMA)

Electron probe microanalysis (EPMA) is an analytical technique that is used to know the composition of small areas on specimen of solid materials. It is considered a spot analytical technique, which means compositional information is collected from only a small volume, not the entire sample. The beam electrons interact with a volume usually between one and nine cubic micrometers. This volume is known as the interaction volume of the electrons. Within an interaction volume, numerous electron-specimen interactions occur, such as X-ray production.

EPMA works by bombarding a micro-volume of a sample with a focused electron beam (typical energy = 5-30 keV) and collecting the X-ray photons thereby emitted by
the various elemental species. Because the wavelengths of these X-rays are characteristic of the emitting species, the sample composition can be easily identified by recording WDS spectra (Wavelength Dispersive Spectroscopy). WDS spectrometers are based on the Bragg's law and use various moveable, shaped monocrystals as monochromators.

EPMA is a fully qualitative and quantitative method of non-destructive elemental analysis of micron-sized volumes at the surface of materials, with sensitivity at the level of ppm. Routine quantification to 1% reproducibility is obtained over several days. It is the most precise and accurate micro-analysis technique available and all elements from B to U and above can be analyzed. It is fully compatible with routine analysis sessions, with easy and direct interpretation of the results. EPMA instruments are equipped with a complete kit of built-in microscopy tools that allow simultaneous X-ray (WDS and EDS), SEM and BSE imaging, plus sophisticated visible light optics; they provide very flexible sample inspection with image magnification ranging from 40 to 400,000. Determination of thickness and elemental composition from nm to mm thick layers in stratified materials can also be made possible through EPMA.

EPMA provides much better results than standard SEM/EDS systems. Because of the internal properties of WDS, the general sensitivity, analysis of light elements and risks of erroneous interpretation of qualitative spectra are all superior with EPMA. Spectral resolution and detector dead time are much better than EDS. The excitation beam regulation system and sophisticated sample stage capabilities guarantee that this technique provides outstanding stability and measurement repeatability (extracts, Cameca).

In the present study, six different minerals (quartz, plagioclase, zircon, rutile, hematite and ilmenite) of JBU were analysed through Electron microprobe analyser (EPMA). CAMECA SX-100 electron microprobe analyser was used for the EPMA study with operating conditions, voltage: 15 kV; current: 20 n A with a beam diameter of 1 μm. Following mineral standards were used during elemental analysis - Kyanite for Si & Al; Orthoclase for K; jadeite for Na; wollastonite for Ca; diopside for Mg; Almandine for Fe; Rhodonite for Mn; Apatite for P; Chromite for Cr; Barite for Ba; Zircon for Zr and Rutile for Ti. The precision was better than 2% for majority of the elements.

3.6 Cathodoluminescence (CL) microscopy
Luminescence is a common phenomenon in inorganic and organic substances resulting from an emission transition of anions, molecules, or a crystal from an excited electronic
state to a ground or other state with lesser energy (Marfunin, 1979). According to the methods of excitation several types of luminescence can be distinguished such as photo-, cathodo-, thermo- or X-ray luminescence. Because of the wide range of individual luminescence behaviour of mineral species, luminescence techniques are used for the investigation and interpretation of the composition and structure of minerals and materials (Götze, 2002).

Luminescence processes can be described based on a scheme of the energy levels in a crystal. In insulators and semiconductors, a band gap (forbidden band) exists between the valence and conduction bands (Fig-3.2). A precondition for luminescence is the existence of activators (impurity ions, lattice defects), which occupy discrete energy levels in this forbidden zone between the valence and conduction bands. These luminescence centres in minerals are defect centres which may be intrinsic (e.g. electron-hole centres) or impurity-related extrinsic ones, which are classified according to electronic structure: 1) transition metal ions (e.g. Mn$^{2+}$, Cr$^{3+}$, Fe$^{2+}$), 2) Rare earth elements (REE), 3) Actinides (especially uranyl UO$_2^{2+}$), 4) Heavy metals (e.g. Pb$^{2+}$), 5) Electron-hole centres (molecular ions S$^{2-}$, O$^{2-}$, F-centres) and 6) Crystallophosphors of the ZnS type (sphalerite, cinnabar, realgar) (Marfunin, 1979). More extended defects such as dislocations and clusters may also take part in the luminescence production process (Marfunin, 1979; Waychunas, 1988).

The occurrence of luminescence can be related to three elementary processes: excitation (absorption), emission and radiationless transitions. When exciting the crystal with various kinds of energy, the ions with unfilled shells pass from the ground state to the excited state, which is attended by the appearance of an absorption band in the optical spectrum (excitation/absorption). The ions can return from the excited to the ground state by emissive transitions or through radiationless transitions (absorption or emission of lattice vibrations = phonons). In the case of emissive transition, the wavelength of the emitted light (photon energy) depends on the energy difference between excited and ground state.
**Fig-3.2 (a–c)** Process of charge transfer and luminescence production in insulator crystals: **a)** excitation of several energy levels by absorption of photons and resulting radiative transitions (luminescence emission); **b)** excitation of an electron by high-energy particles or photons from the valence band to the conduction band and recombination with an activator resulting in luminescence emission (1) or trapping of the electron (2); **c)** thermal or optical stimulation of a trapped electron to the conduction band and recombination with an activator (e.g. thermoluminescence) (after Götze, 2002).

CL can be observed on a wide variety of electron beam instrumentations due to the irradiation of a solid surface with an electron beam. The penetration depth of electrons and accordingly, the excitation depth of a crystal depend on the energy of the electrons (10–20 keV) and are in the range of 2–8 μm. The CL intensity is proportional to the acceleration voltage and current density, but is limited due to the destruction of the specimen under electron bombardment (Waychunas, 1988; Remond G et al. 1992). CL has developed into a standard technique for investigations in several fields of geosciences and material sciences (Remond G et al. 1992; Marshall, 1988; Pagel et al. 2000; Götze, 2000). Important fields of application are the identification of minerals and the quantification of phase distribution in rocks and technical products, the analysis of real
structure and crystal chemistry of solids (defects, zonal growth, internal structures, and trace elements), microstructural characteristics of rocks and materials or the reconstruction of processes of mineral formation and alteration.

In the present work CL microscopic study was carried out on various zircon grains with the help of GATAN CHROMA CL2 UV model 788 and the operating condition for most of the case was: Probe current- 5nA; Beam current- 100μA and voltage- 20kV.
Chapter 4
MINERALOGY AND PETROGRAPHIC CHARACTERS OF JANGALGALI BRECCIA UNIT

4.1 Minerals and their abundance

The Jangalgali breccia units (JBU) are generally of porphyritic (~ 10–15 volume % phenocrysts) in nature and consist of mainly with phenocrysts of quartz and K-feldspar, setting in a fine grained glassy matrix and lack preferred orientation (Fig-4.1). Freshly exposed outcrop surfaces appear glassy. The rock breaks with conchoidal fracture. In thin-sections, the Jangalgali breccia units from all five localities consist of random aggregates of light and dark gray crystallites, exhibiting weak pleochroism.

![Outcrop of brecciated unit from Jangalgali Formation showing porphyritic texture](image)

Fig-4.1 Outcrop of brecciated unit from Jangalgali Formation showing porphyritic texture (pen is ~ 15 cm).

The major mineral constituents of JBU are quartz and feldspar but it also contains accessory minerals (<2 vol %) such as zircon, rutile, hematite, pyrite, biotite and hornblende. Sanidine, ilmenite, tourmaline and feldspathoid group of minerals are also present in lesser amount.

Phenocrysts of JBU are of large angular and euhedral to subhedral quartz and plagioclase with subsidiary sanidine dispersed in a microcrystalline to glassy groundmass.
Among the phenocrysts, quartz is the most abundant. Most of the larger crystals are sharp and fresh in appearance, but edges of the smaller grains are corroded or rounded. Accessory minerals such as zircon, rutile, hematite and tourmaline occur as small euhedral to subhedral crystals. The groundmass constitutes a major component of the rhyolite. Light yellowish-brown, 50–150 μm prismatic crystals of zircon, large (often larger than 100 μm) brownish/reddish rutile, quartz eyes and Negative crystal having sharp contact with host quartz phenocryst occur in the glassy matrix (Fig- 4.2).

![Photomicrographs of JBU showing- A). Euhedral zircon (PPL), B). Rutile (PPL), C). Type 1 quartz eyes (CN), D). Negative crystal having sharp contact with host quartz phenocryst (CN). PPL- Plane polarized light; CN- Crossed nicols.](image)

Since quartz is the dominant phase of these breccia units, therefore the major attention is given to its texture and other petrographic characteristics.

**4.2 Morphological characters of prominent minerals**

**4.2.1 Quartz**

Quartz in the studied JBU exhibits several distinct types of texture such as quartz-eye, partially resorbed/embayed, skeletal in addition to negative crystals and hexagonal
bipyramidal forms. These striking textural features provide valuable information about how the magma crystallized. A brief description of these is as follows:

i) Quartz-eye
Two distinct types of quartz-eye are found in JBU. Type-1 consists of typical quartz phenocrysts (Fig-4.2C) which are large (up to 8 mm in diameter), rounded and irregular. Individual crystals with distinct edges are dispersed throughout the groundmass. Type-2 quartz-eye is elliptical, small (< 2 mm) and consists of sugary aggregates of anhedral quartz crystals. These are different from type-1 and are interpreted as miarolitic pods. The quartz-eye represents quartz formed from an exsolved magmatic aqueous fluid during initial stages of its separation from a silicic magma (Candela and Blevin, 1995; Harris et al, 2003). Further, cooling during the course of crystallization of rhyolitic melts can lead to the generation of quartz-eye due to its ease of nucleation relative to other minerals (Piccoli et al 1996).

ii) Negative crystals
The melt inclusions observed in the quartz phenocrysts are randomly distributed in the host crystal. They vary from sub-rounded to negative crystal shapes with sizes ranging from < 5 to > 200 μm. Negative crystals often occur in clusters rather than individually and are commonly devitrified. The boundary between the negative crystal (melt inclusion) and the host quartz is sharp, and there is no trace of reaction between the two (Fig-4.2D). Negative crystal inclusions are not present in all quartz phenocrysts; conversely, some quartz phenocrysts contain several inclusions of negative crystals. Based on their mode of occurrence, these inclusions are interpreted to be of primary origin. Similar observations have been reported by Lowenstern (1994) and Clocchiatti (1975) for naturally and experimentally heated volcanic rocks and by Frezzotti (1992) for partly crystallized melt inclusions in granites. Skirius et al. (1990) observed the transition of initially rounded melt inclusion into negative crystal shape during prolonged heating experiments. In addition, the observed negative crystals at the centre of quartz phenocrysts of the JBU from Jammu region may help constrain the primary chemical composition of the magma.

iii) Bipyramidal quartz
Beta-quartz occurs as euhedral mostly hexagonal bipyramidal crystals (Fig-4.3A). Some beta phases are highly spherical probably due to partial fusion in a liquid melt that was changing due to rapid cooling during a volcanic eruption (Fig-4.3B). Their presence as unstrained, single crystals up to 2 mm in size but without evidence of granulation
indicates that they have a magmatic origin. This quartz morphology, especially the distinct bipyramids, is consistent with it being high-temperature beta-quartz commonly observed in volcanic rocks (Lowenstern and Sinclair, 1996).

iv) Embayed/resorbed quartz

Embayed and rounded quartz phenocrysts are common in the samples of JBU. Re-entrants and in some cases embayments, along with irregular overgrowths, imply resorption. The general explanation is that rounded and embayed quartz is a product of decompression-induced stability field shift for quartz that occurs during magma ascent (McPhie et al, 1993). Some quartz grains develop highly angular and skeletal shape, and display jigsaw features which are attributed to in situ quench fragmentation (Fig-4.3C). Embayed quartz has been interpreted to result from (i) adiabatic or sub isothermal decompression making melt quartz undersaturated and leading to quartz resorption by the melt, and (ii) thermal disequilibrium by mixing with relatively high temperature magma (Nakamura, 1995; Sato, 1996). Nekvasil (1991) showed that decrease in pressure can cause resorption texture in quartz, K-feldspar and plagioclase (Fig-4.3D).

**Fig-4.3** Photomicrographs of JBU showing- A) Hexagonal bipyramidal quartz crystals (CN), B). Beta phase, spherical due to partial fusion in the melt (CN), C). Quartz with skeletal texture (PPL), D). Prismatic plagioclase with straight multiple albite twins (CN).
Based on petrographic studies the observed populations of various forms of quartz crystals in JBU are hexagonal dipyramidal, angular, rounded to sub rounded, skeletal and mosaic interlocking; of which the euhedral hexagonal dipyramids and angular crystals of quartz are more common.

Thin section photomicrographs of quartz exhibits many textures (Fig-4.4) such as packet of hexagonal quartz phenocrysts occur in a fine grain matrix, euhedral hexagonal quartz phenocrysts arranged in similar orientation (Fig-4.4-1-5), hexagonal quartz crystal occurs within quartz phenocrysts (Fig-4.4-6), pair of quartz phenocrysts resembling like twins (Fig-4.4-7), mosaic of quartz eyes in a fine grain glassy matrix, skeletal texture (Fig-4.4-8), dogtooth quartz (Fig-4.4-12), fine-grained aggregates of quartz, mosaic of quartz within a phenocryst and mosaic of tiny (50 - 100 µm) hexagonal quartz phenocrysts (Fig-4.4-9-22); spherules and inclusions are also noticed in the quartz grains of JBU (Fig-4.4-23-26).
Fig-4.4 (1-26) Photomicrographs of JBU showing various textural and morphological features of quartz crystals, 1- euhedral angular quartz phenocrysts along with pair of hexagonal bipyramidal quartz phenocrysts (CN), 2- packet of hexagonal quartz phenocrysts occur in a fine grain matrix (CN), 3- euhedral hexagonal quartz phenocrysts (PPL) 4- euhedral hexagonal quartz phenocrysts (CN), 5- euhedral hexagonal quartz phenocrysts arranged in similar orientation (CN), 6- hexagonal quartz crystal occurs within quartz phenocrysts (CN), 7- pair of quartz phenocrystals resembling like twins, 8- euhedral quartz phenocryst with skeletal texture surrounded by fine grain matrix (PPL), 9- angular and sub rounded quartz phenocryst in a fine grain matrix (CN), 10- mosaic of quartz eyes in a fine grain glassy matrix (CN), 11- mosaic of sub rounded quartz crystals in a fine grain glassy matrix (CN), 12- quartz phenocryst with dogtooth texture surrounded by fine grain matrix (CN), 13- mosaic of angular and sub angular quartz phenocryst along with fine grain matrix (CN), 14- mosaic of euhedral, hexagonal, angular, sub angular and sub rounded quartz crystals along with fine grain glassy matrix (CN), 15-
mosaic of sub angular and sub rounded quartz crystals with in fine grain glassy matrix (CN), 16- Fine-grained aggregates of quartz crystals (CN), 17- sub angular, rounded and sub rounded quartz crystals arranged in a fine grain matrix (CN), 18- angular and euhedral quartz phenocryst occur haphazardly (CN), 19- sub angular, rounded and sub rounded quartz crystals randomly oriented (CL), 20- mosaic of quartz within a phenocryst surrounded by fine grain matrix (CL), 21- mosaic of tiny (50 - 100 μm) hexagonal quartz phenocrysts in a glassy matrix (CL), 22- mosaic of tiny euhedral, sub angular, rounded and sub rounded quartz phenocrysts in a glassy matrix (CL), 23- spherules in a sub rounded quartz phenocrysts (PPL), 24- inclusions with in a euhedral hexagonal quartz phenocrysts (PPL), 25- inclusions with in a angular quartz phenocrysts (PPL), 26- inclusions with in a sub angular and sub rounded quartz phenocrysts (PPL).

The phenocryst of quartz having euhedral hexagonal dipyramidal texture shows the basal section, few of them occur within euhedral hexagonal quartz, the length of inner euhedral quartz ranges between 300-500 μm while outer one is up to 1 mm in length. Outlines of few quartz grains showing various shapes are presented in the form of schematic diagram (Fig-4.5). Raman analysis of both the quartz i.e. quartz within quartz (inner and outer, Fig-4.5a) was carried out to confirm the exact phase of both the crystals (Fig-4.6.1 & 4.6.2), which is found similar. Some individual euhedral quartz crystal shows variation in colour and extinction with surrounding ground mass. Most of the individual phenocryst of euhedral quartz lies between 200 - 600 μm, arranged in the groundmass without any preferred orientation and the crystal faces of these phenocrysts are very sharp. Paired crystals of quartz (200 - 500 μm) formed in a fine grain ground mass, shows parallel extinction. Few anhedral phenocrysts of quartz grains of 0.5-1.0 mm in size occur in different shapes like triangular, angular with multifaceted, zigzag, nib shape and needle like crystals.
Fig-4.5 Schematic diagrams of the outline of the quartz crystals of JBU showing different morphologies.
Fig-4.6.1 Raman Spectra of the inner crystal of quartz occurring within quartz.

Fig-4.6.2 Raman Spectra of the outer crystal of quartz.
Detailed scanning electron microscopic (SEM) investigations were carried out for the groundmass as well as quartz phenocryst of thin sections from all parts of JBU; few tiny quartz crystals (10-30 µm) with euhedral hexagonal texture displayed by secondary electron (SE) image (Fig-4.7) were found in the fine grain ground mass; crystal inclusions (<1 µm) in angular shape were also noticed in these euhedral hexagonal quartz, which may have formed during its crystallization.
Fig-4.7 (1-10) Secondary electron (SE) images of quartz grains showing different textures and morphology: 1- euhedral hexagonal quartz phenocryst in a glassy matrix with tiny inclusions, 2- euhedral hexagonal bipyramidal quartz phenocryst, 3- mosaic of angular and sub rounded quartz crystals with tiny inclusions, 4- euhedral angular crystal of quartz surrounded by glassy matrix, 5- angular and sub rounded quartz crystals with inclusions, 6- euhedral bipyramidal quartz phenocryst surrounded by glassy matrix, 7- mosaic of quartz eyes in a fine grain glassy matrix, 8- mosaic of euhedral, angular and sub angular quartz crystals in a fine grain glassy matrix, 9- angular and lenticular quartz grain arranged in glassy matrix, 10- mosaic of tiny euhedral hexagonal quartz grains.
Quartz grains from breccia units also contain some melt inclusions, these are opaque in nature. The size of inclusion range between 10 to 125 μm occurs in both phenocryst and fine grained ground mass. Few irregular and non mature type of melt is found in a fine grain silicic matrix (Fig-4.8).

![Fig-4.8 SE- image of quartz grain showing melt in fine grain siliceous matrix (1 and 2 are the Edx analysis point).](image)

Melt component has been studied at two points (1 and 2) through SEM-EDX (Table-4.1), it is rich in volatiles and contain Cl (2.17-2.21 wt %), S (0.11-0.21 wt %) and Cr (0.45-2.17 wt %).
**Table-4.1** EDX data of melt in fine grain quartz matrix (Sample no- KDL-3a, Kalakot).

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<thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td>[wt.-%]</td>
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<td>[%]</td>
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<tr>
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**Edx data of point-2**

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Mineral characteristics of quartz grains of JBU have been analyzed through Electron microprobe analyzer (EPMA) and the data are presented in (Table-4.2.1). It shows very high percentage of SiO₂ (>95%) with very less amount of other major oxides (>1%).
Table 4.2.1 Electron microprobe analysis data (major oxides wt. %) of quartz from JBU.

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<tr>
<th>Oxide</th>
<th>KH7-1</th>
<th>KH7-2</th>
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<th>BG-9A 2</th>
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<tr>
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</tr>
<tr>
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4.2.2 Feldspar

Feldspars are the second most common phenocrystic phases after quartz in the studied breccia units. They occur as euhedral to subhedral grains in brown, glassy groundmass. Sanidine occurs with euhedral to subhedral form and exhibits Carlsbad twinning. Carlsbad twinning in the feldspar phenocrysts indicates that K-feldspar is primary. Plagioclase is present as prismatic crystals up to 700 µm in length and exhibits straight multiple albite twins. Microphenocryt of Plagioclase (~80-400 µm) feldspars invariably shows multiple (polysynthetic) twinning which appears as dark and light bands in crystals observed with crossed polars; microlitic texture of plagioclase grains with quartz eyes in fine grain matrix occurs as well (Fig-4.9.1).
Fig-4.9.1 (1-6) Photomicrographs of thin sections showing different morphologies of feldspar grains occurring in the fine grain siliceous matrix of JBU, 1- Prismatic plagioclase with straight multiple albite twins (CN), 2- euhedral to subhedral grains of feldspar in a glassy groundmass (CN), 3- Plagioclase phenocryst with multiple (polysynthetic) twinning (CN), 4- Plagioclase feldspar (Sanidine) with Carlsbad twinning (CN), 5- euhedral crystal of feldspar in brown, glassy groundmass (PPL), 6- microlitic texture of plagioclase grains in fine grained matrix (PPL).
Feldspar phenocrysts were also studied through Scanning electron microscopy (SEM). The Secondary electron (SE) images of K-feldspar shows various textural and morphological features (Fig-4.9.2).

**Fig-4.9.2 (1-3)** Secondary electron (SE) images of feldspar grains showing different texture and morphologies, 1- feldspar phenocryst surrounded by tiny quartz grains, 2- prismatic plagioclase in glassy groundmass, 3- subhedral plagioclase in glassy groundmass.

Mineral characteristics of K-feldspar grains have been analyzed through EPMA (Table-4.2.2). It contains ~53-55 % SiO₂, ~26-27% Al₂O₃, 9.6-9.7% K₂O and 3.4-4.4% FeO.
### Table 4.2.2 Electron microprobe analysis data (major oxides wt. %) of feldspar from JBU.

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<th>Oxide</th>
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**4.2.3 Zircon**

Several zircon grains were located in thin sections of JBU to study their textural properties through optical microscopy (Fig-4.10) as well as Scanning electron microscopy (SEM) (Fig-4.11) and Cathodoluminescence (CL) microscopy.
Fig-4.10 (1-5) Photomicrographs of thin section showing different morphologies of Zircon grains, 1- equi-dimensional zircon with altered, rough and patchy surface (CN), 2- ellipsoidal zircon with rainbow shades (CN), 3- euhedral ellipsoidal zircon with inclusions (PPL), 4- sub rounded zircon with fracture and halos (PPL), 5- prismatic zircon with resorbed texture (PPL).

Zircon here exhibits varied texture such as euhedral, prismatic and sub rounded crystals. Its size ranges between 40–180 µm; however majority of crystals are between 40-70 µm. It usually shows light yellow to reddish brown colour having rainbow shades while observing it under cross polarized microscopy.
Fig. 4.11 a-h SEM images of zircon crystals a) Subdued / rounded external appearance, irregular fractures, hollows or incompletely grown crystals, hairline cracks, growth zoning patterns b) Subdued / sub rounded edges, highly altered, rough surfaces, c) Euhedral shape, smooth surface, alteration at outer rim d) Prismatic, altered containing hairline cracks and scratches e) Subdued / sub rounded edges, hollows, hairline cracks, inclusions, irregular fractures f) Rounded shape, irregular fractures, alteration, rough surfaces g) Highly resorbed, fractured with rough surface h) Equidimensional shape having fracture, hollows, highly altered with rough and patchy surface.
The Cathodoluminescence images of zircon display various growth patterns and resorbed textures; few inherited zircon crystals (or inherited cores) have also been noticed (Fig-4.11.1).

Fig.4.11.1 Cathodoluminescence (CL) images of zircon exhibiting different zoning patterns including inherited zircon crystals (or inherited cores).
The energy dispersive x-ray (EDX) spectrum of zircon shows minor proportions of trace elements Hf and Sc (Fig-4.12).

![EDX Spectrum](image)

**Fig-4.12** Edx Spectra along with SEM image of the studied zircon grain (spot1C).

The Raman spectra of zircons show the overall decreasing pattern in terms of wavenumber (cm$^{-1}$) from 353.45 to 1002.75, which exhibit a magmatic trend (Fig-4.13). As we know Raman spectroscopy is a non-destructive in situ analytical technique to investigate the origin of zircon whether it is magmatogenic or metamorphogenic (Bao 1995; Bao et.al.1998). In addition, it is a powerful tool to measure the degree of radiation damage, crystallinity and irregularities in bond lengths of zircons (ZrSiO$_4$) by interpreting the systematic changes in observed wavenumbers and intensity of the Raman bands (Nasdala et.al, 1995, 2008).
**Fig-4.13** Raman Spectra of zircon showing magmatic trend.

EPMA data of zircon shows high percentage of ZrO$_2$ (~66%) with 30-32 % of SiO$_2$, while the other oxides contribute only less than one percent (**Table-4.2.3.1**).

**Table-4.2.3.1** Electron microprobe analysis data (major oxides wt. %) of zircon from JBU

<table>
<thead>
<tr>
<th>Oxide</th>
<th>KH7-1</th>
<th>KH7-2</th>
<th>BG9A1</th>
<th>BG9A2</th>
<th>BG9A3</th>
<th>BG9A4</th>
<th>KO4A1</th>
<th>KO4A2</th>
<th>KO4A3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0</td>
<td>0</td>
<td>0.03</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>31.39</td>
<td>32.11</td>
<td>30.45</td>
<td>30.92</td>
<td>31.32</td>
<td>30.99</td>
<td>31.03</td>
<td>31.35</td>
<td>31.58</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0</td>
<td>0.01</td>
<td>0.02</td>
<td>0</td>
</tr>
<tr>
<td>CaO</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>0.01</td>
<td>0</td>
<td>0.03</td>
<td>0</td>
<td>0.03</td>
<td>0</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0</td>
<td>0</td>
<td>0.02</td>
<td>0.06</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.04</td>
<td>0</td>
</tr>
</tbody>
</table>
In the present study the Raman spectral patterns in a single grain of zircon have been investigated, from core to rim along X and Y axis respectively to understand its metamorphic conversion from parent magmatic crystal. Zircon crystal used in this study is from the breccia unit of Jangalgali Formation at Kalakot. It is ~125 µm in size with equidimensional crystal habit, and contains features like hollow prisms or incompletely grown crystals, irregular fractures, resorbed texture, rare inclusions (melt), chemical alteration and growth zoning patterns. Zircon crystals are enclosed within fractured coarse-grained quartz phenocrysts and fine to medium grain siliceous matrix. It usually show light yellow to reddish brown colour having rainbow shades under cross polarized light.

Raman spectral analyses of zircon demonstrate that at the centre, the overall trend of intensity, from band ∆355 to band ∆1000, is decreasing; that suggests its primary magmatic nature. Since magmatogenic zircons, generally formed due to decreasing temperature from liquid to solid rocks, exhibit highest intensity at wavenumber ∆355 and second highest intensity for wavenumber ∆1000; hence, it gives decreasing trend while observing from ∆355 to ∆1000 band in Raman spectrum (Fig-4.14.1; Table-4.2.3.2; spot 1C, 4V to 6V; Bao 1995; Bao et.al.1998).
Fig-4.14.1 Raman Spectra of studied zircon (spot1C) along with optical photomicrograph

On the other hand, the metamorphogenic zircon, which normally form due to increasing temperature, show highest intensity at wavenumber $\Delta 1000$ band and after that $\Delta 355$ value come; therefore, it exhibit an increasing trend from $\Delta 355$ to $\Delta 1000$ band while observing towards periphery along X-axis (Fig-4.14.2; Table-4.2.3.2; spot 1C, 2H and 3H).

Table-4.2.3.2 Intensity and Raman shift of top two peaks of each spot from core to rim.

<table>
<thead>
<tr>
<th>Spot for Raman analysis</th>
<th>Intensity (a.u)</th>
<th>Raman shift (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ist</td>
<td>IInd</td>
</tr>
<tr>
<td>1C</td>
<td>5500</td>
<td>5000</td>
</tr>
<tr>
<td>2H</td>
<td>1150</td>
<td>1100</td>
</tr>
<tr>
<td>3H</td>
<td>2500</td>
<td>2000</td>
</tr>
<tr>
<td>4V</td>
<td>1200</td>
<td>850</td>
</tr>
<tr>
<td>5V</td>
<td>1500</td>
<td>1100</td>
</tr>
<tr>
<td>6V</td>
<td>2500</td>
<td>2000</td>
</tr>
</tbody>
</table>
Along X-axis, from centre to periphery (spot 1C & 3H), the intensities of both of two prominent bands (i.e. Δ355 and Δ1000) is decreasing. For wavenumber Δ355, the intensity decreases from 5500 a.u to 2000 a.u (spot 1C & 3H) and for wavenumber Δ1000, it goes down from 5000 a.u to 2500 a.u (Fig-4.14.3; Table-4.2.3.2).
Fig-4.14.3 Raman spectral trend along X-axis.

However, along Y-axis towards periphery (spot 4V to 6V) the trend is in ascending order; from 1200 a.u to 2500 a.u for band $\Delta$355 and 850 a.u to 2000 a.u for $\Delta$1000 band (Fig-4.14.4 ; Table-4.2.3.2). The difference in the intensities of both the prominent Raman bands from centre to periphery (spot 1C, 3H & 6V) is constant (500 a.u).

Fig-4.14.4 Raman spectral trend along Y-axis.
The concentration of zirconium (Zr) and hafnium (Hf), analyzed by EDX, varies from centre to periphery; along X-axis (1C to 3H), Zr concentration increases from 67.85 to 67.95 wt. % while Hf decreases from 2.32 to 2.16 wt. %; which is a characteristic of metamorphic zircon (Bao 1995; Bao et.al.1998; Nasdala et al, 1995, 2008). While reverse trend is observed along Y-axis (1C, 4V to 6V), as Zr concentration decreases from 67.85 to 66.35 wt. % and Hf increases from 2.32 to 2.62 wt. %, which is a typical characteristic of magmatic origin of zircon (Bao 1995; Bao et.al.1998; Nasdala et al, 1995, 2008; Zhang et al, 2000; Fig. 4.12; Table-4.2.3.3).

Table-4.2.3.3 Core to rim concentration of Zr and Hf in zircon analyzed through EDX.

<table>
<thead>
<tr>
<th>Spots from centre to periphery</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1C</td>
</tr>
<tr>
<td>Zirconium</td>
<td>67.85</td>
</tr>
<tr>
<td>Hafnium</td>
<td>2.32</td>
</tr>
</tbody>
</table>

Since, the zircon grain in this study has got metamorphosed only in one direction (X-axis), while the other side of the crystal did not suffer any metamorphic effects and thus retaining its original magmatic/igneous signature. Such kind of variation in Raman spectrum occurred, because of different nature attained by zircon grain, at centre and periphery respectively. This is probably due to the specific position of grain in the host rock that plays a key role in different p-t condition; and perhaps that is the reason, why such type of Raman spectral trend were not observed in several other zircon grains from the same rock and thus making the studied zircon specific and rare.

Raman Spectral analyses on a single grain of zircon from Kalakot showed two contrasting trends, one is a metamorphic and the other is a magmatic. This result is not usually observed from a single grain of zircon. This study revealed that Raman Spectroscopy can be successfully applied to evaluate not only the origin but also to predict or estimate the degree of metamorphic alteration from a single zircon grain.

4.2.4 Rutile

Rutile grains of various shapes from sub rounded to rounded, ellipsoidal and euhedral crystals are found, most of them are equidimensional with halos at their outer rim; size of it ranges from 30 to 200 µm (Fig-4.15).
Fig-4.15 (1-2) Thin section photomicrographs of rutile grains 1- euhedral grain with halos at its outer rim, 2- a pair of rutile crystals resembling like twins occurring in the fine grain siliceous matrix of JBU.

Like zircon, rutile crystals are also enclosed by fine to medium grain siliceous matrix and coarse-grained quartz phenocrysts. SEM analysis has been carried out on various grains of rutile (Fig-4.16) followed by EDX analysis.

The EDX spectra of rutile grains (Fig-4.17) showed the presence of Fe, Al and Rb as minor amounts despite Ti and O as primary. The mineral chemistry of major oxides of rutile, analyzed through EPMA (Table-4.2.4), shows variation in TiO$_2$ (wt %) with lowest of ~78% and maximum of ~95%, the FeO values also have high range (0.8-10%); however, other oxides are less than 0.2%. Raman analysis of various rutile crystals were identified by four bands (Fig-4.18) at wavenumbers 145, 257, 454 and 627.784 cm$^{-1}$ (maximum peak), which confirmed their diagnostic features as explained by Meinhold (2010).
Fig. 4.16 a-f SEM images of rutile crystals

a) Euhedral crystal showing rough surface, highly altered at the middle, and embayed at corners
b) Prismatic with subdued edges, solution/precipitation surfaces,
c) Highly resorbed, altered at corners with rough surface and dissolution features
d) Euhedral and ellipsoidal grain of rutile containing hairline cracks, inclusions (linear black dots at bottom), alteration at the middle
e) Sub rounded grain of rutile having smooth surface with no signs of alteration
f) A small euhedral grain with smooth surface and sharp edges.
**Fig-4.17** Energy dispersive x-ray spectra (Edx) of the rutile grain along with SE-image.

**Fig-4.18** Raman spectra of the euhedral rutile grain.
Table 4.2.4: Electron microprobe analysis data (major oxides wt. %) of rutile from JBU

<table>
<thead>
<tr>
<th>Oxide</th>
<th>BG9c 1</th>
<th>BG9c 2</th>
<th>KH7-1</th>
<th>KH7-2</th>
<th>BG9A 1</th>
<th>BG9A 2</th>
<th>BG9A 1</th>
<th>BG9A 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>0.03</td>
<td>0</td>
<td>0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0</td>
<td>0.01</td>
<td>0.03</td>
<td>0.01</td>
<td>0.09</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.17</td>
<td>0.08</td>
<td>2.61</td>
<td>3.2</td>
<td>0.81</td>
<td>0.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
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<td>0.03</td>
<td>0.5</td>
<td>0.65</td>
<td>0.75</td>
<td>0.78</td>
<td></td>
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</tr>
<tr>
<td>P$_2$O$_5$</td>
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<td>0.01</td>
<td>0.03</td>
<td>0</td>
<td>0.05</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0</td>
<td>0.01</td>
<td>0.02</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.03</td>
<td>0.02</td>
<td>0.13</td>
<td>0.14</td>
<td>0.38</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>93.39</td>
<td>94.88</td>
<td>84.55</td>
<td>78.02</td>
<td>91.04</td>
<td>89.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.02</td>
<td>0</td>
<td>1.62</td>
<td>1.97</td>
<td>0.44</td>
<td>0.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0</td>
<td>0.02</td>
<td>0</td>
<td>0</td>
<td>0.09</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>2.22</td>
<td>0.87</td>
<td>5.68</td>
<td>10.2</td>
<td>1.96</td>
<td>2.86</td>
<td></td>
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</tr>
<tr>
<td>BaO</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0.14</td>
<td>0.14</td>
<td>0.43</td>
<td>0.36</td>
<td>0.43</td>
<td>0.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>96.06</td>
<td>96.08</td>
<td>95.62</td>
<td>94.57</td>
<td>96.08</td>
<td>95.60</td>
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<td></td>
</tr>
</tbody>
</table>

4.2.5 Other accessories

Two different types of hematite crystals, reddish gray to dark brown in colour have been noticed; one of elliptical (~210 µm) while another is of pentagon (~100 µm) in shape, both occur simultaneously in few slides (Fig-4.19) surrounded by medium grain quartz phenocryst.
Fig-4.19 (1-3) Thin section photomicrographs of hematite grains showing different morphologies 1- Quadrilateral shape (CN), 2- Pentagon shape (CN), 3- Ellipsoidal along with pentagon crystals of hematite (CN).

Raman spectroscopic analysis of hematite confirmed its diagnostic properties (Fig-4.20). In general, haematite is bright red, occurs as well-developed rhombohedral crystals and as embayed grain disseminations within the matrix. Its presence suggests oxygen-rich nature of the magma.
Fig-4.20 Raman spectra of euhedral pentagon shape of hematite grain.

The Electron microprobe analysis data (major oxides wt. %) of hematite from Kanthan breccia unit shows very high range of FeO (~64-83%); SiO₂ ranges between 1.1-11%; Al₂O₃ ranges 0.5-7%; rest contributes less than 2% (Table-4.2.5).

Table-4.2.5 Electron microprobe analysis data (major oxides wt. %) of hematite from JBU

<table>
<thead>
<tr>
<th>Oxide</th>
<th>KO4A 1</th>
<th>KO4A 2</th>
<th>KO4A 3</th>
<th>KO4A 4</th>
<th>KO4A 5</th>
<th>KO4A 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>0.17</td>
<td>0.07</td>
<td>0.12</td>
<td>0.08</td>
<td>0.07</td>
<td>0.12</td>
</tr>
<tr>
<td>MgO</td>
<td>2.23</td>
<td>0</td>
<td>1.34</td>
<td>0.05</td>
<td>1.41</td>
<td>1.25</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7.13</td>
<td>0.57</td>
<td>4.14</td>
<td>0.63</td>
<td>4.43</td>
<td>4.62</td>
</tr>
<tr>
<td>SiO₂</td>
<td>11.6</td>
<td>1.18</td>
<td>7.95</td>
<td>1.98</td>
<td>6.48</td>
<td>6.54</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.09</td>
<td>0.06</td>
<td>0.05</td>
<td>0.06</td>
<td>0.15</td>
<td>0.16</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.98</td>
<td>0.05</td>
<td>0.47</td>
<td>0.02</td>
<td>0.22</td>
<td>0.25</td>
</tr>
<tr>
<td>CaO</td>
<td>0.26</td>
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<td>0.17</td>
<td>0.07</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.38</td>
<td>0.21</td>
<td>0.21</td>
<td>0.44</td>
<td>0.14</td>
<td>0.25</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.2</td>
<td>0.16</td>
<td>0.28</td>
<td>0.06</td>
<td>0.03</td>
<td>0.07</td>
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<tr>
<td>MnO</td>
<td>0</td>
<td>0.01</td>
<td>0.06</td>
<td>0.04</td>
<td>0.07</td>
<td>0</td>
</tr>
<tr>
<td>FeO</td>
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<td>82.07</td>
<td>74.66</td>
<td>72.7</td>
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<tr>
<td>BaO</td>
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<td>0.06</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>ZrO₂</td>
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<td>0.06</td>
<td>0.04</td>
<td>0</td>
<td>0.04</td>
<td>0</td>
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<tr>
<td><strong>Total</strong></td>
<td><strong>87.84</strong></td>
<td><strong>85.58</strong></td>
<td><strong>85.79</strong></td>
<td><strong>85.54</strong></td>
<td><strong>87.81</strong></td>
<td><strong>86.17</strong></td>
</tr>
</tbody>
</table>
Few crystals of ilmenite have been found in the Khargala breccia unit and analyzed through EPMA for their chemical characteristics (Table 4.2.6), indicating its pristine nature.

Table 4.2.6 Electron microprobe analysis data (major oxides wt. %) of ilmenite from JBU

<table>
<thead>
<tr>
<th>Oxide</th>
<th>KH7-1</th>
<th>KH7-2</th>
<th>KH7-3</th>
<th>KH7-4</th>
<th>KH7-5</th>
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<th>KH7-7</th>
<th>KH7-8</th>
<th>KH7-9</th>
<th>KH7-10</th>
<th>KH7-11</th>
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<tr>
<td>Na₂O</td>
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<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
<td>0.07</td>
<td>0.08</td>
<td>0.01</td>
<td>0.06</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
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<tr>
<td>MgO</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.41</td>
<td>3.41</td>
<td>3.05</td>
<td>2.4</td>
<td>2.38</td>
<td>2.06</td>
<td>3.2</td>
<td>4.09</td>
<td>3.75</td>
<td>3.8</td>
<td>3.46</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.68</td>
<td>0.66</td>
<td>0.58</td>
<td>0.54</td>
<td>0.49</td>
<td>0.52</td>
<td>0.65</td>
<td>0.68</td>
<td>0.69</td>
<td>0.63</td>
<td>0.85</td>
</tr>
<tr>
<td>P₂O₅</td>
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<td>0.01</td>
<td>0.08</td>
<td>0.01</td>
<td>0</td>
<td>0</td>
<td>0.04</td>
<td>0.07</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>K₂O</td>
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<td>0.03</td>
<td>0</td>
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</tr>
<tr>
<td>CaO</td>
<td>0.13</td>
<td>0.21</td>
<td>0.18</td>
<td>0.2</td>
<td>0.17</td>
<td>0.2</td>
<td>0.14</td>
<td>0.15</td>
<td>0.15</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>TiO₂</td>
<td>71.41</td>
<td>70.94</td>
<td>73.92</td>
<td>78.83</td>
<td>79.81</td>
<td>79.47</td>
<td>78.02</td>
<td>70.76</td>
<td>72.18</td>
<td>72.73</td>
<td>75.83</td>
</tr>
<tr>
<td>Cr₂O₃</td>
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<td>0.25</td>
<td>0.25</td>
<td>0.4</td>
<td>0.3</td>
<td>0.45</td>
<td>1.97</td>
<td>2.41</td>
<td>2.42</td>
<td>2.34</td>
<td>2.33</td>
</tr>
<tr>
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Altered biotites in a matrix of fine-grained quartz were found in many samples (Fig 4.21).
Fig-4.21 (1-3) Thin section photomicrographs of biotite grains 1- euhedral grain with halos at its outer rim (CN), 2 and 3- altered biotite grain surrounded by fine grain matrix (CN).

Few crystals of hornblende (~200 µm) with brown colour absorption in thin section enclosed by fine to medium grain quartz phenocryst were found (Fig-4.22).

Fig-4.22 Thin section photomicrograph of hornblende grain (plane polarised view).

Tourmaline crystals have also been found in few sections of JBU (Fig-4.23.1) and are confirmed with the help of Raman spectroscopic analysis (Fig-4.23.2).
Fig-4.23.1 Thin section photomicrograph of tourmaline crystal (plane polarised view)

In the matrix of majority of JBU samples, feldspathoid minerals such as analcime, leucite and petalite were also present; of which petalite (occurs as colourless, grey, yellowish
grey, to white tabular crystals and columnar masses) is more common in these rocks (Fig-4.24).

![Fig-4.24 Thin section photomicrograph of petalite crystal occurring in the fine grain siliceous matrix of JBU (plane polarised view).](image)

However, few opaque crystals of pyrite (~210 µm) were noticed (Fig-4.25) and also analyzed through SEM and Raman spectroscopy (Fig-4.26); but due to confining in specific location and not commonly occurring in majority of samples; it may be considered as secondary product.

![Image of petalite crystal](image)
Fig-4.25 Thin section photomicrograph of pyrite crystal, 1- optical image (CN) and 2- optical image (PPL), 3- SE image.

Fig-4.26 Raman spectra of the pyrite crystal.
Chapter 5
GEOCHEMISTRY OF WHOLE-ROCK/BULK SAMPLES

5.1 Major elements

The average loss on ignition (LOI) in all the samples is ~2 wt %. The SiO$_2$ content in the JBU is very high and varies from 68.4 to 96.9 wt % with an average of 90.11 wt % (Table-5.1). The Al$_2$O$_3$ values range from 0.92 to 5.17 wt % with an average of 2.46% and K$_2$O content varies from 0.01 to 1.13% with an average of 0.42 wt %; both show negative correlation with SiO$_2$ (Fig-5.1 (3 & 5)). MgO (0.10- 2.63 wt %; average 0.39 wt %) displays independence from SiO$_2$ (Fig-5.1 (2)).

The proportions of Na$_2$O, P$_2$O$_5$, CaO and MnO are very less (~0.01-0.25 wt %) and are almost independent from SiO$_2$ and occupying a scattered pattern on Harker’s plot (Fig-5.1 (1, 4, 6 & 8)); TiO$_2$ contents are also very less (0.06-0.42 wt %; average 0.19%) and are showing a scattered pattern against SiO$_2$ (Fig-5.1 (7)). Except few samples (four), the Fe$_2$O$_3$ contents are low (<4.0 wt %) with overall averages of 3.83 wt % showing negative trend with silica (Fig-5.1 (9)).

The A/CNK ratio (molar Al$_2$O$_3$/ (CaO + Na$_2$O + K$_2$O)) is high with an average of 6.81 which shows peraluminous nature of JBU and having scattered pattern on Harker’s diagram (Fig-5.1 (10)). However, CNK has negative trend against silica (Fig-5.1 (11)).

In all samples K$_2$O (average 0.42) content is always in greater proportion than Na$_2$O (average 0.02) suggesting preponderance of potassium-rich alkali feldspar in JBU.
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Table 5.1: Major (wt. %) and trace (ppm) element composition of the whole-rock/bulk samples from different parts of JBU.
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Fig. 5.1 (1)

X= SiO2
Y= Na2O

X= SiO2
Y= MgO

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The K₂O and CNK values are showing good positive relation with Al₂O₃ and occupy an increasing diagonal pattern when plotted on binary diagram against Al₂O₃ (Fig-5.2 (2 & 9)), however, MgO also exhibit little positive trend with Al₂O₃ (Fig-5.2 (3)). Na₂O and TiO₂ having scattered trend with Alumina (Fig-5.2 (1 & 6)), while CaO, MnO and Fe₂O₃ are showing straight pattern i.e independent from Al₂O₃ (Fig-5.2 (5, 7 & 8)).
Fig-5.2 (1)

2

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Fig-5.2 Binary variation diagram of alumina ($\text{Al}_2\text{O}_3$) against major oxides (1-9): 1- $\text{Al}_2\text{O}_3$ vs. $\text{Na}_2\text{O}$; 2- $\text{Al}_2\text{O}_3$ vs. $\text{K}_2\text{O}$; 3- $\text{Al}_2\text{O}_3$ vs. $\text{MgO}$; 4- $\text{Al}_2\text{O}_3$ vs. $\text{P}_2\text{O}_5$; 5- $\text{Al}_2\text{O}_3$ vs. $\text{CaO}$; 6- $\text{Al}_2\text{O}_3$ vs. $\text{TiO}_2$; 7- $\text{Al}_2\text{O}_3$ vs. $\text{MnO}$; 8- $\text{Al}_2\text{O}_3$ vs. $\text{Fe}_2\text{O}_3$; 9- $\text{Al}_2\text{O}_3$ vs. CNK.

Binary diagram of $\text{Fe}_2\text{O}_3$ against $\text{MgO}$ also indicates positive co-relation (Fig-5.2.1).

Fig-5.2.1 Binary variation diagram of $\text{Fe}_2\text{O}_3$ against $\text{MgO}$. 
In the triangular diagram of AFM (Al$_2$O$_3$, Fe$_2$O$_3$ and MgO) the maximum values are along A-F line indicating its felsic nature (Fig-5.3).

![Triangular diagram of AFM (Al$_2$O$_3$, Fe$_2$O$_3$ and MgO).](image)

**Fig-5.3** Triangular diagram of AFM (Al$_2$O$_3$, Fe$_2$O$_3$ and MgO).

### 5.2 Trace elements

Trace element (Ba, Cr, V, Co, Ni, Cu, Zn, Ga, Pb, Th, Rb, U, Sr, Y, Zr and Nb) concentrations are listed in Table-5.1. The average concentration of all above mention sixteen trace elements in 31 samples are ~500 ppm. Among all trace elements, only Cr has average concentration (167 ppm) of greater than 100 ppm. In few samples Ba and Zr have also reported above 100 ppm but on an average it accounts not more than 45 and 81 ppm respectively. Although Co, Zn and Pb also contributed significantly in overall trace element composition and have maximum values (in one or two samples) above 100 ppm but its averages are below 50 ppm. Almost all trace elements (sixteen) are exhibiting a scattered pattern against SiO$_2$ that means these are all independent from silica (Fig-5.4.1 (1-16)); Cr shows inverse relation with SiO$_2$ (Fig-5.4.1 (2)), while Co occupies a straight line showing independency from SiO$_2$ (Fig-5.4.1 (4)).
Fig-5.4.1 (1)

Fig-5.4.1 (2)

\[ X = \text{SiO}_2 \]
\[ Y = \text{Ba} \]

\[ X = \text{SiO}_2 \]
\[ Y = \text{Cr} \]

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- ✡ Khargala
- ■ Beragua
- ✤ Tattapani
- ○ Kanthan
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X = SiO2
Y = V

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X = SiO2
Y = Ca

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Fig-5.4.1 Binary variation diagram of Silica (SiO$_2$) against trace elements (1-16):

1- SiO$_2$ vs. Ba; 2- SiO$_2$ vs. Cr; 3- SiO$_2$ vs. V; 4- SiO$_2$ vs. Co; 5- SiO$_2$ vs. Ni; 6- SiO$_2$ vs. Cu; 7- SiO$_2$ vs. Zn; 8- SiO$_2$ vs. Ga; 9- SiO$_2$ vs. Pb; 10- SiO$_2$ vs. Th; 11- SiO$_2$ vs. Rb; 12- SiO$_2$ vs. U; 13- SiO$_2$ vs. Sr; 14- SiO$_2$ vs. Y; 15- SiO$_2$ vs. Zr; 16- SiO$_2$ vs. Nb.
Ba, Cu, Ga, Rb, Y and Zr are showing a fair relation with $\text{Al}_2\text{O}_3$ (Fig-5.4.2 (1, 4, 6, 8, 11, 14 & 15)), as these have the correlation coefficients value ranging between 0.7-0.9 with it (Table-5.2). Rest (Fig-5.4.2 (2, 3, 5, 7, 9, 10, 12, 13 & 16)) are showing independent character from $\text{Al}_2\text{O}_3$. 

Fig-5.4.2 (1)
Fig-5.4.2 Binary variation diagram of alumina (Al₂O₃) against trace elements (1-16):
1- Al₂O₃ vs. Ba; 2- Al₂O₃ vs. Cr; 3- Al₂O₃ vs. V; 4- Al₂O₃ vs. Co; 5- Al₂O₃ vs. Ni; 6- Al₂O₃ vs. Cu; 7- Al₂O₃ vs. Zn; 8- Al₂O₃ vs. Ga; 9- Al₂O₃ vs. Pb; 10- Al₂O₃ vs. Th; 11- Al₂O₃ vs. Rb; 12 Al₂O₃ vs. U; 13- Al₂O₃ vs. Sr; 14- Al₂O₃ vs. Y; 15- Al₂O₃ vs. Zr; 16- Al₂O₃ vs. Nb.
Table 5.2 Correlation coefficient matrix of major, trace and REE elements of JBU.

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Binary plots of twelve immobile elements (Zr, Ba, Th, U, Y, Sr, Ga, La, Sm, Yb, Rb/Sr and TiO$_2$/Zr) have been plotted against Nb, in which only three elements Zr, Th and U show positive trend with Nb (Fig-5.5 (1, 3 & 4)), while other nine elements are showing their independent character (Fig-5.5 (2, 5-12)).
2

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Fig-5.5 Binary variation diagram of Nb against immobile elements (1-12):

1-Nb vs. Zr; 2- Nb vs. Ba; 3- Nb vs. Th; 4- Nb vs. U; 5- Nb vs. Y; 6- Nb vs. Sr; 7- Nb vs. Ga; 8- Nb vs. La; 9- Nb vs. Sm; 10- Nb vs. Yb; 11- Nb vs. Rb/Sr; 12- Nb/Y vs. TiO$_2$/Zr.

Few other nine binary variation diagrams (Ba vs. Rb/Sr; Rb vs. Rb/Sr; Sr vs. Rb/Sr; TiO$_2$/Zr vs. Co; Zr vs. P$_2$O$_5$; Zr vs. Th; Zr vs. TiO$_2$; Rb/Sr vs. TiO$_2$/Zr and A/CNK vs. TiO$_2$/Zr) have also been interpreted (Fig-5.6 (1-9)), in which only three (Rb vs. Rb/Sr; Zr vs. Th and Zr vs. TiO$_2$) have positive trend (Fig-5.6 (2, 6 & 7)). The variation diagram of Rb/Sr with Ba, Rb and Sr occupy a diagonal pattern with Rb (Fig-5.6 (2)) and scattered with rest of two (Fig-5.6 (1&3)).
Fig-5.6 (1)

Fig-5.6 (2)

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\( X = \text{Sr} \)
\( Y = \text{Rb/Sr} \)

\( X = \text{TiO}_2/\text{Zr} \)
\( Y = \text{Co} \)

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- Beragua
- Tattapani
- Kanthan
Fig-5.6 Binary variation diagram of other trace elements of JBU (1-9):

1- Ba vs. Rb/Sr; 2- Rb vs. Rb/Sr; 3- Sr vs. Rb/Sr; 4- TiO₂/Zr vs. Co; 5- Zr vs. P₂O₅; 6- Zr vs. Th; 7- Zr vs. TiO₂; 8- Rb/Sr vs. TiO₂/Zr; 9- A/CNK vs. TiO₂/Zr.

The ternary plot of Ba-Rb-Sr shows the Ba enrichment trend (Fig-5.7 (1)) and Rb is found enriched in Th-Rb-Zr/10 variation diagram (Fig-5.7 (2)), while in Th-Sr-Zr/10 ternary plot, Zr/10 is enriched (Fig-5.7 (3)).
Fig. 5.7 Ternary diagrams: 1- Ba-Rb-Sr; 2- Th-Rb-Zr/10; 3- Th-Sr-Zr/10.
5.3 Rare earth elements
The concentration of ΣREE in the studied samples (Table-5.3) shows a significant variation (i.e., a minimum of 4.26 ppm, a maximum of 93.89 ppm and an average of 37.90 ppm). The Chondrite-normalised REE diagram (Fig-5.8 (1-6)) of JBU as a whole-rock, exhibits LREE (La_N/Sm_N = 1.73–9.53) with descending slope and relatively flat HREE distribution, with a ubiquitous negative Eu anomaly; the average value of Eu/Eu* is 0.74. All samples of JBU show an overall light rare earth element (LREE) enriched pattern with an average value of (La/Sm)_N 4.13, similar to the pattern of tuff samples from the Singhora Basin, Chattisgarh (Das et.al.2009).
**Table-5.3** Major (wt. %) trace (ppm) and REE (ppm) compositions of representative samples of JBU

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<td>2.90</td>
<td>7.59</td>
<td>2.37</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>(Eu/Eu*)</td>
<td>0.55</td>
<td>0.12</td>
<td>0.08</td>
<td>0.15</td>
<td>0.22</td>
<td>0.61</td>
<td>3.66</td>
<td>1.35</td>
<td>0.19</td>
<td>0.21</td>
<td>0.14</td>
<td>1.48</td>
<td>0.84</td>
<td></td>
</tr>
</tbody>
</table>

\[
\text{Eu/Eu}^* = \frac{(\text{Eu}_N)}{\left[(\text{Sm}_N)(\text{Gd}_N)\right]^{1/2}};
\]
(The ratio between the 'expected' Eu concentrations as interpolated between Sm and Gd, and the observed value)
Fig-5.8 (1)
Fig-5.8 Chondrite-normalised REE diagram of the 13 representative samples of JBU from different localities (1-6): 1- Combined; 2- Kanthan; 3- Kalakot; 4- Beragua; 5- Khargala; 6- Tattapani.
The binary variation diagram of major oxides against ΣREE (Fig-5.9 (1-12)); exhibiting either no promising trends (Na$_2$O, SiO$_2$, Al$_2$O$_3$, TiO$_2$ and Fe$_2$O$_3$) or a linear trend (MgO, P$_2$O$_5$, CaO, MnO) indicating independency from each other, however K$_2$O have fair positive correlation with total REE (Fig-5.9 (6)).
Fig-5.9 Binary variation diagram of total REE against major oxides (1-12):

1- Total REE vs. Na₂O; 2- Total REE vs. MgO; 3- Total REE vs. Al₂O₃; 4- Total REE vs. SiO₂; 5- Total REE vs. P₂O₅; 6- Total REE vs. K₂O; 7- Total REE vs. CaO; 8- Total REE vs. TiO₂; 9- Total REE vs. MnO; 10- Total REE vs. Fe₂O₃; 11- Total REE vs. CNK; 12- Total REE vs. A/CNK.
The trace elements such as Ba, Co, Cr, Nb, Ga, Ni, Pb, Rb, Th, U, and Zr are giving no notable trend against ΣREE (Fig-5.10 (1, 2, 3, 4, 5, 7, 8, 9, 11, 12 & 16)); however excluding few values, Cu and Zn obtains a linear trend (Fig-5.10 (4 & 15)); while Sr, V and Y exhibits good positive correlation (~0.9), having increasing diagonal trend with ΣREE (Fig-5.10 (10, 13 & 14)).
**Fig-5.10** Binary variation diagram of total REE against trace elements (1-16):

1- Total REE vs. Ba; 2- Total REE vs. Co; 3- Total REE vs. Cr; 4- Total REE vs. Cu; 5- Total REE vs. Ga; 6- Total REE vs. Nb; 7- Total REE vs. Ni; 8- Total REE vs. Pb; 9- Total REE vs. Rb; 10- Total REE vs. Sr; 11- Total REE vs. Th; 12- Total REE vs. U; 13- Total REE vs. V; 14- Total REE vs. Y; 15- Total REE vs. Zn; 16- Total REE vs. Zr.
In this work the breccia unit of Jangalgali Formation has been studied, for its field relationship, mineralogy and geochemical characteristics of bulk rock as well as individual minerals. Since, little is available in the literature on the petrographic and geochemical aspects of this breccia unit, therefore the main focus of this work was on these aspects.

6.1 Discussion on Breccias of different origin

Breccia is a general term used for a rock consisting of broken fragments of rocks or different types of minerals cemented together by a fine grain matrix, some time glassy matrix, which may or may not be similar to the composition of those broken fragments (Glossary of meteoritical terms). Breccia has diverse origins; it can be formed in variety of ways and defined accordingly. Here breccias formed due to common possible source of origin are discussed.

There are six most common terms volcanic breccia, chert breccia, collapse breccia, fault breccia, impact breccia and seismic breccia; which have been used in the literature to describe various kinds of breccia or brecciated units. The detail descriptions of these units are given as follows:

i) Volcanic breccia

Volcanic breccia according to Fisher (1958, 1966) is a “rock composed predominantly of angular volcanic fragments > 2 mm in size set in a subordinate matrix of any composition and texture, or with no matrix; or composed of fragments other than volcanic set in a volcanic matrix”. Volcanic breccia can also be referred as breccia of igneous origin (Reynolds, 1928); a term pyroclastic breccia is also used by Macdonald, (1953) for such type of rocks. Wentworth and Williams (1932) and Twenhofel (1950) defined a volcanic breccia as a pyroclastic rock composed of angular volcanic fragments > 32 mm. Norton (1917) subdivided volcanic breccias into flow breccia, which is formed by fragmentation of lava during its flow, and tuff breccia made up of fragmental products of explosive eruptions. However, the term tuff breccia was restricted to volcanic breccias of pyroclastic origin with abundant tuff matrix (Wentworth and Williams, 1932).

It is not necessary that the fragments of a volcanic breccia are composed of volcanic material; a rock fragment of any origin may be incorporated within brecciated regime, after
being solidified, it may be composed of non volcanic fragments set in a volcanic matrix. Therefore, depending upon the composition of matrix, it may be sedimentary in origin, if it has sandy matrix; also these may be referred as pyroclastic in origin with a tuffaceous matrix or vesicular and pumiceous matrix.

Fisher (1958) proposed grade size limits for volcanic breccia (Table-6.1), ranging between 2 mm to >64 mm; on that basis it can be grouped into four classes, 1) between 2-4 mm which is named as tuff; 2) between 4-32 mm called as Lapilli tuff, 3), is between 32-64 mm known as Pyroclastic breccia and Agglomerate; and the last one of size grade >64 mm is referred as Bombs and Blocks.

<table>
<thead>
<tr>
<th>Grade size (mm)</th>
<th>Pyroclastic terminology</th>
<th>Sediment-volcanic terminology</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;64</td>
<td>Bombs and blocks</td>
<td>Volcanic breccia and volcanic conglomerate</td>
</tr>
<tr>
<td>32-64</td>
<td>Pyroclastic breccia and agglomerate</td>
<td></td>
</tr>
<tr>
<td>32-4</td>
<td>Lapilli (lapilli tuff and lapillistone)</td>
<td></td>
</tr>
<tr>
<td>4-2</td>
<td>Tuff</td>
<td></td>
</tr>
<tr>
<td>&lt;2</td>
<td>Ash</td>
<td></td>
</tr>
</tbody>
</table>

The basic difference between bombs and blocks is that during its formation the fragments of the former one are in a molten condition (wholly or partly), however, for later one it is in solid state (Schmid, 1981). The fragments of size <2 mm is called Ash. Fisher (1966) opposed to use prefix like sedimentary, epiclastic, pyroclastic or volcanic before the primarily size terms (i.e. ash, lapilli, blocks, bombs, tuff and agglomerate) applied to fragments in rocks of pyroclastic origin. A specific term volcaniclastic (Fisher, 1961) and sometimes volcanic clastic (Blokhina et al., 1959) are also used to embrace the entire field of clastic rocks composed in part of or entirely of volcanic fragments. Two approaches have been used to assign genetic names for primary volcaniclastic deposits; first, according to their mode of fragmentation (Fisher, 1961, 1966; Schmid, 1981) and second, based on their process of deposition (McPhie et al., 1993). Fisher (1960, 1961) have used three different types of genetic terms, namely, pyroclastic, epiclastic and autoclastic in his classification of volcaniclastic rocks, which refer to processes of fragmentation.
White and Houghton (2006) have classified primary volcanioclastics into four end-member group’s i.e. pyroclastic, autoclastic, hyaloclastites and peperite. According to them, pyroclastic deposits form from clasts deposited from subaerial, subaqueous, or subsurface jets, plumes, or currents; while an autoclastic deposit forms during effusive volcanism and the fragments are deposited under the influence of continued dome or lava flowage; however, hyaloclastites, formed during magma entry into lakes, glaciers, and oceans, with limited or no transport of fragments forming direct or indirect thermal response to magma chilling by water. Peperites form when hot magma interacts with unconsolidated water-saturated sediments or clastic materials; however, there is some debate about the use of the genetic term peperite (McPhie et al., 1993).

Anderson (1933) has reviewed the origin of volcanic breccias and has summarized their origin in two broad groups, one, which is not transported by water and another group contain volcanic breccias transported by water. The previous one is a result of, crumbling of a dome, intrusion, friction, crumbling of advancing lava flow and eruptions (vulcanian, pelean, ulavulanian and dry avalanche); the later one comprises of the breccias formed due to the transportation by water, which is further subdivided into two classes one, eruption related mechanism such as through a crater lake or melting of ice and snow, or accompanied by heavy rains; the second one is not related to eruption but formed due to the collapse of the dam of a crater lake or heavy rains falling on unconsolidated ejecta or rapid melting of snow and ice.

Based on mixtures of pyroclastic and sedimentary materials, Shatalov (1937) proposed three groups of rocks, named as pyroclastic rocks, tuffites and tuffogenic rocks (Table-6.2). This classification was later followed by Blokhina et al. (1959).

**Table-6.2** Rock types produced by mixtures of pyroclastic and sedimentary (epiclastic) material.

<table>
<thead>
<tr>
<th>Rock types</th>
<th>Mixture proportions (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pyroclastic fragments</td>
<td>sedimentary (epiclastic) materials</td>
</tr>
<tr>
<td>Pyroclastic rocks</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Tuffites</td>
<td>&gt; 50</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Tuffogenic rocks</td>
<td>&lt;50</td>
<td>&gt; 50</td>
</tr>
</tbody>
</table>
ii) Chert Breccia

Fairbridge (1978) defined the chert breccias as *autoclastic breccias*, in which both fragments and matrix consist of microcrystalline quartz. Chert is a common component of many carbonate sequences. It is a very good indicator of either the depositional environment or of the prevailing diagenetic conditions. In many cases, cherts are the results of replacement of pre-existing carbonate (Knauth, 1979 and 1994), therefore replacement textures are abundant and dissolved silica is generally ubiquitous. The clasts in chert breccias are penecontemporaneous with the matrix much like any other intraformational conglomerate or breccia. These clasts are the product of consolidated sediments, which later get fragmented, within a surrounding softer matrix, and finally become lithified. In many massive chert formations, the intraformational chert breccias are ubiquitous and can be used as an important proxy to reveal the complex history of diagenetic interactions between a siliceous sediment, seawater and fresh water (Kolodny et.al, 2005). Chatellier (1988) interpreted chert as a *seismic marker* in Mississippian successions, where it is associated with clinoforms and has been off in logs and in cuttings.

Chert, of white to light gray in colour, known as *Late diagenetic chert*, commonly occur at the interface between highly or fully dolomitized and partially dolomitized rocks. The coexistence of these units (white to gray cherts and dolomite) are indicative of hydrothermal events. Initially, in this case, hot fluids are associated with the precipitation of dolomite whereas the subsequent periods of cooling down are associated with chert precipitation (Chatellier, 2005). Since cherts do not precipitate under high temperature conditions, therefore, hydrothermal events will show a vertical change in diagenetic mineral assemblages. According to Chatellier (2005) the amount of chert decreases with depth, which indicate that the prevailing temperature is increasing with depth (i.e. Chert $\propto$ 1/depth; and Dolomite $\propto$ depth; Fig-6.1)

Knauth, (1979) has given a model for the origin of chert in limestone; he proposed that much of the chert replacement of limestone has occurred in *mixing zone* of the meteoric-marine coastal system, which is a near horizontal zone, extended many kilometres towards inland.
Chert can also be associated with volcanism; abundant cherts have been described associated with volcanism especially during the Eocene time (McGowran 1989, Lyons et al. 2000). Lilletveit et al (2002) have proposed a possible connection between deposition of volcanic tuffs and preservation of siliceous oozes.

However, Chert is the general term used for siliceous rocks as a group. Folk, (1974) divided it into three main textural types– Granular microquartz consisting of nearly equidimensional grains of quartz (8-10 µm), Chalcedony (fibrous silica), forming sheaf like bundles of radiating and extremely thin crystal about 0.1 mm long and Megaquartz, composed of equant to elongated grain (> 20 µm). Cherts are common rocks in geologic successions ranging in age from Precambrian to Tertiary. They are particularly abundant in Jurassic to Neogene (Tertiary) rocks, moderately abundant in Devonian and Carboniferous rocks and least abundant in Silurian and Cambrian deposits (Hein and Parrish, 1987).

**iii) Collapse Breccia**

Collapse breccias are formed as a result of karst processes in evaporitic successions (Friedman, 1997). It can also be named as solution-collapse breccia, because it is caused by dissolution of underlying soluble bedrock, i.e. carbonate rock such as limestone or dolomite (Middleton, 1961). Such type of breccias involving gypsum and/or anhydrite composed of calcite and/or dolomites have been known as rauhwackes i.e. rough stone (Friedman, 1997).

Typical diagnostic features of solution-collapse breccias are - V-structures (cave roof collapse), breccia pipes (collapse dolines), inverse grading and sharp flat base (Middleton,
1961; Park & Jones, 1985; Simpson, 1988). These breccias exhibit a close relationship to thick deposits of evaporites in the subsurface as well as to neighbouring surface exposures (Blount and Moore, 1969). It is important to note that collapse breccias developed only after the dolomitization and formation of chert nodules in the host rocks (Eliassen, 2002; Eliassen and Talbot, 2005). Collapse breccias are also of economic importance in exploration of hydrocarbon and ore deposits, as they are having good porosity and permeability.

iv) Fault Breccia

Fault breccias are resultant of the grinding action of two fault blocks. It is a common product along upper crustal fault zones. According to the classification of fault breccia given by Woodcock and Mort (2008), it is defined (for sedimentary rocks) as having at least 30% of its volume being clasts of > 2 mm in diameter; it can be cohesive or incohesive, foliated or not, and can contain small clasts, fine-grained matrix or a crystalline cement in any relative proportion. Further, he subdivided Fault breccia, according to the clast setting, into crackle, mosaic and chaotic breccia (Table-3). In crackle breccia, clasts are little rotated with respect to each other; in mosaic breccias, it show more separation and rotation in comparison to crackle breccia, however, in chaotic breccias, clasts are strongly rotated and have lost any geometric fit to formerly adjacent clasts (Woodcock et al, 2006).

**Table-6.3** Classification of fault breccia based on clast (>2 mm).

<table>
<thead>
<tr>
<th>Percentage of clasts ( &gt;2 mm)</th>
<th>Type of fault breccia</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;75</td>
<td>crackle</td>
</tr>
<tr>
<td>60-75</td>
<td>mosaic</td>
</tr>
<tr>
<td>30-60</td>
<td>chaotic</td>
</tr>
</tbody>
</table>

Another term in this group is known as Cataclasites (Wise et. al., 1984) which is a non-foliated rock, produced due to the micro or macrofracturing occurred during brittle faulting at high rates of strain and further sub-divided into breccia, microbreccia and gouge based on their particle size.

v) Impact breccia

Impact breccia as name suggest is formed during the process of impact cratering when large extraterrestrial body impact with the earth or any other planets. Breccia of this type may be
present on or beneath the floor of the crater and may be identified by its diagnostic features like planar deformation features (PDF), shatter cones, impact glasses, shocked minerals (e.g. quartz and feldspar), and the presence of extraterrestrial material such as iridium and osmium. A term Suevite has been referred for the impact breccia composed of a fine-grained groundmass containing both clastic and melt particles (Stahle, 1972; Stoffler, 1977; Stoffler and Grieve, 2007; Osinski et al, 2008; Reimold et al, 2012). Stahle, (1972) identified different type of impact glasses from the Suevite samples of the Nordlinger Ries (Table-6.4); these glasses show typical differences in their structures, despite of uniform chemical compositions of their matrix glasses.

**Table-6.4** Classification of the Ries impact glasses.

<table>
<thead>
<tr>
<th>Stages</th>
<th>Class</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Stage V</em> Vaporization</td>
<td>Homogeneous glass bodies</td>
<td>Small droplets of glass; dense homogeneous matrix glass; few grains of lechatelierite*, zircon and quartz fragments with glass rims; no &quot;fragment schlieren&quot; or rock inclusions.</td>
</tr>
<tr>
<td><em>Stage IV</em> Rock glasses</td>
<td>Normal glass bombs</td>
<td>Aerodynamical shapes; differently coloured matrix glass; light and dark glass schlieren; frequent mineral fragments and mineral glasses; &quot;fragment schlieren&quot;; many bubbles.</td>
</tr>
<tr>
<td></td>
<td>Glass bombs rich in crystalline rock fragments</td>
<td>Irregularly shaped glass crumbs; great portions of strongly shocked rock inclusions; plenty of Lechatelierite and diaplectic SiO₂ glass; nearly no quartz fragments.</td>
</tr>
<tr>
<td><em>Stage III</em> Strongly shocked rocks</td>
<td>Porous rock fragments</td>
<td>Deformed boulders of crystalline rocks; complete alteration of rock minerals, diaplectic coesite bearing SiO₂ glasses; selective melting of feldspars and opaque minerals.</td>
</tr>
</tbody>
</table>

(*Lechatelierite, an amorphous form of SiO₂, is silica glass, which forms naturally by very high temperature melting of quartz sand; also forms as the result of high pressure shock metamorphism during meteorite impact cratering).
The *Ries* impact structure in southern Germany is one of the world’s best preserved (i.e., least eroded), mid-size (25 km diameter), complex impact structures (Reimold et al, 2012). Another example of such type of breccia is *Chicxulub impact* breccia which is a result of an impact by an asteroid or comet with the northwestern Yucatan platform; these breccias are containing clasts of dolomite, limestone, and anhydrite, as well as *shocked mineral* (quartz and feldspar) fragments of basement rock, and altered melt rock (Ward et al 1995).

**vi) Seismic breccia**

Seismic breccia forms, as a result of *hydro fracturing* of rocks generated due to an earthquake and sometime associated with intrusive related ore deposits such as skarns, greisens and porphyry-related mineralization. In the case of earthquake triggering, original partially consolidated layers either become disturbed or disappeared due to hydro fracturing or liquefaction. As a result of plastic or brittle deformations the new layers formed consist of angular fragments which may still contain original sedimentary structures (Clague et al., 1992; Roep and Everts, 1992; Rodriguez- Pascua et al., 2000; Nygard et al., 2006; Gruszka and Van Loon, 2007). Such kind of plastic or brittle deformed layer has been described as “*intraclast breccias*” by Marco and Agnon (2005). An example of earthquake-induced breccia is found frequently in the glaciolacustrine sediments in central Poland (Gruszka and Van Loon, 2007).

A term *Seismites/ brecciated seismites* have been used in the literature to describe the deformed unconsolidated sedimentary layers associated with earthquakes (Seilacher, 1969, 1984). Some more related terms like *mixed layer, Mixtites and homogenites*; which are less in use, have also been reviewed by Agnon et al. (2006).

The common mode of formation of breccias, in general, can be grouped into three major classes igneous, sedimentary and tectonic; the most common sub classes representing them and their related features are described in Table-6.5.
Table 6.5 General classification of breccia and their related features.

<table>
<thead>
<tr>
<th>Types of breccia (in broad)</th>
<th>Sub-classes</th>
<th>Mode of formation (in general)</th>
<th>Field/Petrographic features (in general)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGNEOUS</td>
<td>Volcanic breccia (tuff breccia, flow breccia); Volcaniclastic (Pyroclastic, autoclastic, hyaloclastites &amp; peperite)</td>
<td>Formed by explosive eruption of a volcano during which clast fragments set in a subordinate matrix of any composition and texture.</td>
<td>Angular fragments (&gt;2 mm), hexagonal dipyramidal quartz, embayed quartz, mosaic of quartz, haphazardous arrangement of clast, highly compacted and common igneous minerals (e.g. qtz, plg, rutile, zircon etc.)</td>
</tr>
<tr>
<td></td>
<td>Chert breccia</td>
<td>Resultant of replacement of pre-existing carbonate rocks (limestone &amp; or dolomites).</td>
<td>Angular to sub angular clasts, poorly sorted, loosely compacted and immature fragments of rocks; fragments and matrix both consist of microcrystalline quartz</td>
</tr>
<tr>
<td>SEDIMENTARY</td>
<td>Collapse breccia</td>
<td>Formed by collapse of rocks in a karst landscape, when rocks are partly dissolved. Formed due to a) Grinding action of two fault blocks; b) Fracture of rocks by tectonic or gravitational stresses.</td>
<td>Dissolution textures</td>
</tr>
<tr>
<td></td>
<td>Fault breccia</td>
<td>Unoriented &amp; fractured grains, brittle deformation features, fault gauges.</td>
<td></td>
</tr>
<tr>
<td>TECTONIC</td>
<td>Seismic breccia</td>
<td>Formed by hydro fracturing of rocks generated due to an earthquake.</td>
<td>Associated with intrusive-related ore deposits such as skarns, greisens and porphyry-related mineralization. Shocked minerals (quartz &amp; feldspar), planar deformation features (PDFs), shatter cones &amp; impact glasses.</td>
</tr>
<tr>
<td></td>
<td>Impact breccia</td>
<td>Formed by the meteorite/comets impact on earth.</td>
<td></td>
</tr>
</tbody>
</table>

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6.2 Discussion on Jangalgali Breccia Unit

The breccia is one of the important members of the Jangalgali Formation (apart from the bauxite/laterite units) and was portrayed as chert breccia by earlier workers. In this study the brecciated unit from Jangalgali Formation is referred as Jangalgali breccia unit (JBU) and has been studied from five different localities (Kalakot, Khargala, Beragua, Tattapani and Kanthan) at same stratigraphic level. The occurrence of brecciated unit and overlying bauxite of the Jangalgali Formation is exposed only at Kanthan area, whereas at other localities the JBU is in direct contact with overlying Subathu Formation. This brecciated unit has been reported to be of different origin (sedimentary and volcanic) by different workers. For the bauxite in Jammu area, volcanic source was suggested by Singh et al. (2005, 2009); while Bhat, et.al, (2008) have mentioned the Kanthan breccia of rhyolitic nature that occurs interbedded with pre-Eocene bauxite beds in Riasi area and is composed of tuffaceous greywacke with glass, quartz and quartzite fragments. The stratigraphic position, chemical and mineralogical characteristics of the breccias at Kanthan and at Khargala and its surrounding areas (i.e. Kalakot, Beragua, and Tattapani) have been studied thoroughly and found with similar characteristics (Siddaiah, 2011; Siddaiah and Shukla, 2012).

Singh, (2003 & 2012) assigned Early Palaeogene age to these chert breccias and overlying bauxite based on his assumption (not yet confirmed) and suggested that it was formed during India-Asia collision and proposed that the chert breccias at the bottom of the Subathu Formation, are likely deposited by short-lived, small streams and consist of clasts which are silicified products of the underlying Precambrian dolomitic limestone, probably derived from the hanging walls of the faults locally developed in the basement. Bhatia (1982) mentioned in his paper that a chert-breccia, similar to the one at Kalakot also occurs in Bidhalna and Pharat windows where Subathus rest unconformably over Shimla Slate (equivalent to Sirban Limestone). However, the detail of this rock unit is still to be explored and studied.

For the origin of chert, one has to know the sources of the silica and the mechanism involved in the past to extract the silica from water, especially sea water to form chert. Rivers are generally believed to be the main transporting agent of silica to the oceans (Boggs, 2006). However, silica is also added to the ocean through reaction of sea water with hot volcanic rocks along mid-ocean ridges and by low temperature alteration oceanic basalts and detrital silicate particles on the seafloor. With regards to the studied brecciated unit (JBU), the source of silica and the possible mechanism involved for its origin is not clear and justified.
The present study reveals that the Jangalgali breccia unit is consisting mostly of angular fragments with fine-grained siliceous matrix tightly fitted fabric geometry and chaotic packing i.e. lacking a visible order or organization (Siddaiah, 2011; Siddaiah and Shukla, 2012); the textural pattern is more or less similar as described by Woodcock et al. (2006). Euahedral quartz phenocrysts described as ‘quartz eyes’ by Williams and Burr (1994) are the most common feature in all thin sections of JBU (Shukla and Siddaiah, 2011). Euahedral crystals of quartz usually develop with small amounts of degree of undercooling (ΔT< 55°C; Swanson and Fenn, 1986). The presence of hexagonal dipyramidal quartz in JBU, a typical habit of high temperature quartz, indicates volcanic source. The hexagonal dipyramidal quartz crystallize at small degree of initial undercooling and are replaced by skeletal quartz at moderate to large degree of initial undercooling (MacLellan and Trembath 1991). Such type of interrelation between quartz genesis and the specific properties developed at that time can be useful for the reconstruction of geological processes as discussed by Gotze (2009).

As quartz and feldspar are the dominant mineral constituents of JBU, the other accessory minerals present in JBU are magmatic zircon, igneous rutile, hematite, pyrite, biotite and hornblende; which contributed in less than 2% of volume and occur as small euahedral to subhedral crystals. In addition to this, sanidine, ilmenite, tourmaline and feldspathoid group of minerals are also noticed in lesser amount. Amongst the feldspathoid group of minerals, petalite is more common which occur as colourless, grey, yellowish grey, to white tabular crystals and columnar masses; in addition to analcime and leucite, the other feldspathoids.

Several distinct types of textures such as quartz-eye, partially resorbed/embayed, skeletal, negative crystals and hexagonal bipyramidal forms are found in quartz of studied JBU. Detailed investigations through scanning electron microscopy (SEM) were carried out for the groundmass as well as quartz phenocryst of various thin sections from all parts of JBU. Few tiny quartz crystals of size range between 10-30 µm with euahedral hexagonal texture displayed by secondary electron (SE) image were found in the fine grain glassy ground mass. Crystal inclusions of less than 1 µm with angular shape were also noticed in few euahedral hexagonal quartz grains, which might have formed during its crystallization. In few of thin sections of JBU, some melt inclusions of opaque nature with 10 to 125 µm in size have been noticed in both the phenocryst as well as fine grained ground mass. In addition to, few irregular and non mature type of melt is also noticed in a fine grain silicic matrix. Melt components have been studied through SEM-EDX for their chemical characteristics and reveals that it is rich in volatiles such as Cl (2.17-2.21 wt %), S (0.11-0.21 wt %) and Cr (0.45-2.17 wt %). The presence of irregularly shaped volatile rich inclusions in fine grained-
silicic matrix of JBU may have resulted due to magma trapping just before the eruption (Manley 1996). Mineral characteristics of quartz grains of JBU have also been analyzed through Electron microprobe analyzer (EPMA). It shows very high percentage of SiO$_2$ with very less amount of other major oxides, indicating its pristine nature.

Feldspars, the second most common phenocrystic phases after quartz in the studied JBU, occur as euahedral to subhedral grains in brown, glassy groundmass. Sanidine crystals with euahedral to subhedral form, exhibit Carlsbad twinning, which indicate that K-feldspar is of primary character. Plagioclase is present as prismatic crystals up to 700 μm in length and exhibits straight multiple albite twins. Mineral and morphological characteristics of K-feldspar grains analyzed through SEM, EDX and EPMA suggest its pristine nature.

Electron microprobe analysis of zircons displays chemically homogenous nature and contains 66.31 to 67.13 wt. % ZrO$_2$ and 30.45 to 32.11 wt. % SiO$_2$ which suggest its primary character. The energy dispersive X-ray (EDX) of zircon shows Zr and Si as prominent, while small peaks of Hf and Sc associated with the spectra considered as minor elements also supports the EPMA analysis (i.e. primary character). The Raman spectra of zircons exhibit a magmatic trend with relatively low background both at low and high frequencies (Shukla, 2013). The Cathodoluminescence (CL) analyses of zircon grains display various growth patterns and resorbed textures along with few inherited zircon crystals (or inherited cores) indicating its magmatic origin.

EPMA of major oxide concentration of rutile dominantly consist of TiO$_2$ (78.02-94.88 wt. %) with less amount of FeO (0.87-10.20 wt. %) and very little concentration of ZrO$_2$ (0.14-0.56 wt. %) and Al$_2$O$_3$ (0.17-3.20 wt. %) suggest its primary nature and is also supported by EDX analysis. The EDX spectra of rutile grains showed primarily the presence of Ti, O as well as minor amounts of Fe. The very small Al and Rb peaks associated with the spectra for rutile were also observed, as Rb is not an accessory phase of rutile crystallization, it can be formed through exsolution processes. Raman analysis of various rutile crystals have confirmed its diagnostic feature (i.e. primary origin) as its peak pattern occurred increasing from 220 to 627.784 cm$^{-1}$, few rutile crystals also show their polymorphic character of Anatase phase in raman bands.

The study of chemical characteristics of the bulk rock unit revealed that silica content in the JBU is very high (~90 wt % on an average) which is generally uncommon and indicates its high siliceous rhyolitic nature (Siddaiah, 2011; Siddaiah and Shukla, 2012); similar kind of high silica is also reported in Proterozoic Singhora tuff, Chattisgarh (Das et al., 2009). No significant trend has been observed between major oxides and SiO$_2$ except few (Al$_2$O$_3$ and
K₂O) due to high silica percentage. The A/ CNK ratio is high (>6) showing the peraluminous nature of JBU and the greater proportion of K₂O content than Na₂O, suggesting prevalence of potassium-rich alkali feldspar in JBU. The individual trace elemental compositions are very less (below 50 ppm on an average); except for Cr (average 167 ppm) and Zr (average 80 ppm). It shows no or less correlation with SiO₂ and Al₂O₃ because of low concentration as compare to them. The total REE contribution is not much (<40 ppm) and exhibits no prominent trend with major and trace elements except few (such as K₂O, V, Sr and Y). Overall this litho-unit is enriched in light rare earth elements (LREE) and in large ion lithophile elements i.e. LILE (K, Rb, Sr, Ba and Pb) and exhibits rhyolitic trend.

The chemical and petrographic characteristics of this lithounit (JBU), which was not studied earlier, was found of rhyolitic nature based on various textures in quartz such as hexagonal dipyramidal quartz, quartz eyes, mosaic of euhedral quartz phenocryst and bulk rock chemistry as well as the mineral assemblages like euhedral magmatic zircons, rutile, plagioclase and biotite (Siddaiah, 2011; Shukla and Siddaiah, 2011; Siddaiah and Shukla, 2012; Shukla, 2013).
Chapter -7

CONCLUSIONS

The present study is based on field, petrography and geochemical characteristics and provides several insights into the origin of Jangalgali breccia unit.

1. Absence of calcareous materials and fossils in the matrix and lack of visible order of orientation of the phenocrysts; contradicts the previous model of sedimentary origin of this unit.

2. The detached out crops of *nodular chert* occurs below Subathu shale, at Beragua and Tattapani and has totally different textural and chemical characteristics from underlying *Jangalgali breccia unit*. So, one should not intermingle these two different units.

3. Since the breccias at Kanthan and other places are at same stratigraphic position, so these units cannot be separated and must be considered as one unit.

4. The Jangalgali breccia unit is 2–10 m thick and chemically it consists of high silica (~70-90 wt. %) with phenocrysts of quartz and feldspars of different shapes and sizes distributed randomly in a glassy matrix. Zircon, rutile, biotite, tourmaline and haematite occur in minor amounts (<2 vol %). Bipyramidal, angular and skeletal morphologies are common in quartz. Quartz shows resorption features and contains inclusions of negative crystals.

5. The presence of various textures in quartz such as hexagonal dipyramidal quartz, quartz eyes, mosaic of euhedral quartz phenocryst and also the mineral assemblages like euhedral magmatic zircons, rutile, plagioclase, haematite and biotite; all support its volcanic characteristics.

6. Zircons are chemically homogenous and Raman analysis indicates its magmatic origin (Shukla, 2013). Rutile chemistry suggests involvement of low degree of alteration in their formation. The presences of ilmenite rim on the margin of rutile crystal indicate that it is a secondary igneous rutile formed by the oxidation of ilmenite. The morphology, textures and microstructures, present in zircons and rutiles, such as hollows or incompletely grown crystals indicate rapid growth from a vapor phase; irregular fractures and scratches in the crystals are due to long-term corrosion, metamictization and alteration.

7. The major, trace and REE compositional characteristics of this breccia unit (JBU) are pointing towards its high siliceous rhyolitic nature.

8. Based on various textures especially in quartz, zircon & rutile, and bulk rock chemistry as well as the mineral assemblages (e.g. euhedral magmatic zircons, igneous rutile,
plagioclase and biotite), the rhyolitic nature were suggested for Jangalgali breccia unit (Siddaiah, 2011; Shukla and Siddaiah, 2011; Siddaiah and Shukla, 2012; Shukla, 2013). But, the source of rhyolite is still not confirmed and yet to define and justify.

Recommendations

The widespread occurrence of rhyolitic breccia in Jangalgali Formation with distinct textures and its stratigraphic position particularly at the base of the Early Palaeogene shallow marine sediments of the Himalayan Foreland Basin make it an important proxy for exploring its relation with India–Eurasia primordial collision and basin-wide stratigraphic correlation studies in a region that generally lacks similar useful marker units/horizons. Therefore, knowledge on the origin and absolute age of this rock unit is warranted to understand better its significance in regional geology and India–Eurasia collision.

There are few other questions which are still remain unresolved e.g. -

- What are the exact sequences of the lithounits between Sirban Limestone and Subathu Formation in Jammu area; Shimla Slate and Subathu in Himanchal Pradesh and between Tal Quartzite and Subathu in Uttarakhand?
- Why there exists, unconformity of so long period (~500 Ma), between Neoproterozoic basement rock and Palaeogene succession, is it lack of information or sub-aerial deposition?
- Whether the breccias reported in Bidhalna and Pharat windows are of same nature and characteristics like Jangalgali breccia unit or not.
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