

## Petrography and Geochemistry of Black-Coloured Cuddapah Limestone Hosted with Barite, South India

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**Abstract:** EDAX spot-analyzes of 22 minerals in a black-coloured limestone core sample in a barite mine in Cuddapah Basin, South India show that they are extremely enriched in CaO and silica undersaturated minerals. They are normative calcite, monticellite, kalsilite, Ca bearing silicate-perovskite and anhydrous portlandite (CaO). The abnormal petrographical and geochemical characteristics indicate that the rock *might have been derived from inherent lower mantle source of the Earth. The flushing out of H-O-H, O-H-O from hydrous minerals like brucite and portlandite and O-C-O from carbonate minerals from lower mantle frequently happened along boundaries of several subduction (converging) and diverging creep (horst and graben) microplate movements in lower mantle. This phenomenon creates instability and flushing out of deep-seated H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub> and other phases reaching to higher levels up to crust and surface of the Earth causing periodic crustal evolution.*

**Keywords:** Cuddapah-Basin, Black-coloured limestone, Microplates of converging and diverging slabs, Lower mantle, Carbonatite.

### 1. INTRODUCTION

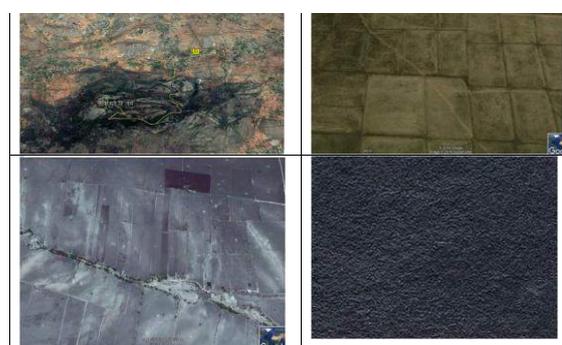
A drillhole sample of limestone from a barite mine belonging to Tiffin's Barytes & Asbestos and Paints Ltd in Cuddapah Basin, South India is studied. In this basin, basalt, trap, rhyolite, rhyo-dacite, gabbro and dolerite occur as lava flows, sills and dykes [1-5] along discontinuity of different lithological formations in this basin. The crescent shaped Cuddapah Basin extends 445 km N-S and convex towards W for 145 km [1-5] E-W. Shale imperceptibly grades into slate in this basin. Low angle dipping lithological units and thrust faults towards east and arc-shaped structure may be formed by sliding down NE-SW trending Precambrian half graben [6]. It is subsequently subjected volcano-tectonic sedimentation and deformation [1-5].

### 2. METHODOLOGY

The core sample in a black limestone was examined under High-resolution Scanning Electron EDAX Microscope and their elemental compositions were determined in the Department of Metallurgy and Material Sciences, Indian Institute of Technology, Madras. The actual elemental compositions individual grains to their oxide forms and their anhydrous oxides were recalculated [7] as normative proportions.

### 3. PETROGRAPHY AND GEOCHEMISTRY

The limestone appears to be very similar to mode occurrence of slate in this area. It is a very fine-grained compact massive holocrystalline rock.



**Fig.1** Mode of field occurrences of black coloured limestone. 1 Cuddapah limestone quarry near Cuddapah Town, 2 Kota limestone exhibiting cubical blacks by jointing 3 Kyra-limestone, subjected to faulting and shearing, 4 polished limestone slab showing different orientations of mineral grains.

The spot analysis represents the composition of some of other mineral grains intimately associated with it. Some mineral grains orient towards a particular direction and some others orient cross-cutting relationship with subophitic texture. Most grains are inequigranular and idiomorphic habit. Inequigranular grains ranging from 12 x 4 and 2 x 1 μm with thickness of platelets <0.1 μm. Conchoidal fracture is seen in this fine-grained slab. Globular crystal of 1 μm dimension is found. Coalesced pits of 3-2 μm gas-cavities are seen on the surface of a linear calcite skeletal crystal. Most grains are interpenetrated and euhedral slender prism with length and breadth ratio exceeding over 4. Calcite platelets are very flat and they are less than 2 μm thick. Aggregates of cylindrical or tubular / hallow crystals of (8x4 μm) are commonly seen. Some grains are rounded by re-crystallization along peripheral portions (Plate 1). Inter-penetrating twinned calcite crystals of 30x5 μm and 20x4 μm are abundantly seen in fine-grained carbonate matrix.

Hardness ranges between 3 and 4 and density between 2.5 and 2.7 g / cm<sup>3</sup> but lower than calcite (2.9-3.0 g / cm<sup>3</sup>), Compressive strength is 60 -170 N mm<sup>2</sup> and has low water absorption quality >1 with quite low

porosity. Sizes of gas cavities range around 10x10µm and rarely 25x10µm with depth of 5 µm. Gas-cavities of sizes 1 to 3 µm<sup>2</sup> are also seen on the surfaces of mineral grains. Skeletal grains and tubular calcite grains are commonly found. This feature indicates that rapid growth of mineral grains from a magma. However, most grains appear to be isolated. Slender prisms of contact twins of 20x5µm are seen. Hexagonal prisms and rhombohedrons are commonly found. Without high resolution polarizing microscope using only SEM images and spot chemical compositions, it is very difficult to identify individual minerals. The chemical compositions within the site captured show presence a mixture of Ca-silicate perovskite [8] Ca-periclase, calcite and others. The thickness of mineral grains in the matrix boundaries is very limited. The chemical compositions and their normative [7] proportions are given the Table 1. All anhydrous mineral grains have very high CaO with limited SiO<sub>2</sub> and CO<sub>2</sub>.

The silica content of mineral grains ranges between 0.85 and 23.26% and alumina varies from 0.21 to 1.21%. The CaO varies between 54.28 and 81.96%. CO<sub>2</sub> varies between 1.32 and 21.84 %. All these grains show low values of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, MgO, and CO<sub>2</sub>%. This is characteristic feature of the rock but it is not matching with any ordinary sedimentary limestone. P<sub>2</sub>O<sub>5</sub> is significantly is high in some samples. Alkali carbonates (Na-K)<sub>2</sub> CO<sub>3</sub> present up to 14.94%. Salts of Na-K and Ba or Sr are present indicating alkaline affinity of the rock. K<sub>2</sub>O is higher than Na<sub>2</sub>O. All these minerals are distinctly enriched in Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Rb<sub>2</sub>O, SrO, P<sub>2</sub>O<sub>5</sub> and SO<sub>3</sub>.

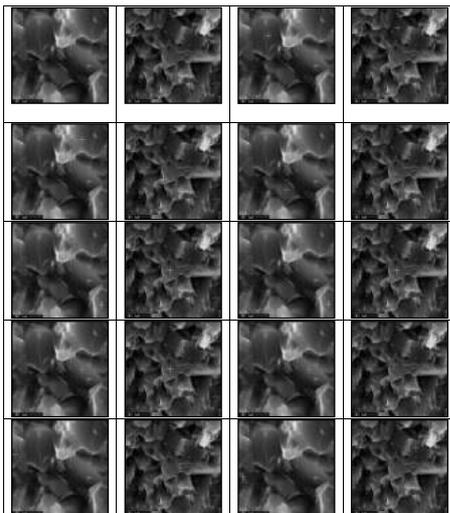


Fig. 2 SEM images black limestone according to the number listed in the Table-1. Crystals with euhedral prisms and rhombohedrons are commonly oriented towards different directions but towards the centre (rosette).

Radiating rosettes calcium bearing minerals of a dimension of 10µm is seen. One or two places show peripheral re-crystallization. The normative coexistence of both silica undersaturated mineral kalsilite with potash feldspar transform them into biotite by local enrichment of water. By these phenomena kalsilite and nepheline are distinctly absent. The norm of the analysis 7, SiO<sub>2</sub> is utilized to produce clinopyroxene which is also considered to be equivalent to silicate perovskite under HPTX condition [8]. In the analyses listed in the Table 1. CO<sub>2</sub> is too low to form required carbonate minerals or any other non-silicate minerals. The positive correlation (Fig. 2) of portlandite against calcite suddenly transits to negative correlation at about 16.5% of calcite. Portlandite develops at the expense of calcite. A negative correlation between potash feldspar and anhydrous portlandite is also seen. The specific gravity of Ca silicate perovskite and Ca-post perovskite [9] occurring at lower mantle portion at Core-Mantle Boundary exceeds over 4. Ca-silicate perovskite is stable at high pressure and temperature condition at lower mantle [8, 9].

Table 1 EDAX Chemical compositions of carbonate-lava sample. Trace elements were determined at magnified levels of 2 to 3 orders.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	
SiO2	15.58	0.92	2.06	1.24	23.26	1.27	57.66	0.27	1.66	0.95	1.11	2.81	2.02	1.45	1.43	2.62	2.17	2.04	6.51	3.27	14.82		
Al2O3	0.77	0.45	1.20	1.13	1.21	0.30	0.95	0.47	0.21	0.00	1.18	0.78	0.74	0.21	0.35	0.00	0.47	0.30	0.13	1.07	1.59	1.07	
MgO	0.29	0.27	0.00	0.17	0.27	0.28	0.24	0.20	0.00	0.00	0.26	0.26	0.21	0.26	0.32	0.21	0.46	0.76	0.15	0.46	0.68	0.22	
MnO	0.12	0.11	1.14	1.21	0.80	0.00	0.24	0.28	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
FeO	61.62	68.26	61.89	62.48	54.28	79.17	24.27	69.79	81.56	66.60	69.60	79.51	76.12	77.81	82.19	71.29	70.18	70.18	67.44	66.87	63.62		
CaO	0.00	0.00	0.54	0.19	0.51	0.00	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.41	0.00
CO2	0.42	0.42	0.00	0.00	0.00	0.00	0.23	0.00	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.41	0.00	0.36	0.00	0.00	0.00
Na2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Si	0.53	1.74	1.00	1.00	1.00	0.00	0.01	1.02	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Al	0.02	0.02	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mg	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.12	0.42	0.00	0.12	0.08	0.11	0.10	0.17	0.50	0.45	0.10	0.11	0.15	0.18	0.19	0.19	0.39	0.69	0.10	0.38	0.50	0.07	0.10
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Y	0.44	1.01	0.08	1.22	0.88	0.41	0.25	0.41	1.37	0.89	1.07	0.64	1.19	0.79	1.17	1.05	1.18	1.81	1.03	1.05	1.19	0.99	
Zr	0.60	0.40	0.60	0.61	0.51	0.61	0.52	0.48	0.64	0.62	0.62	0.60	0.61	0.62	0.60	0.62	0.60	0.62	0.60	0.62	0.60	0.62	0.60
Nb	12.69	12.75	21.84	17.15	8.36	4.31	8.64	13.43	13.20	8.00	9.75	5.00	2.62	2.41	5.82	3.74	8.20	3.77	8.68	10.70	13.10	14.20	
sum	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

The sample 7 indicates silica over saturated silicate perovskite, the intermittent stage of formation of silicate perovskite.

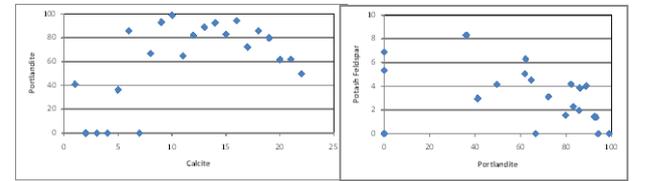


Fig. 3. Distribution of Portlandite and calcite: Potash feldspar and portlandite.

Fig. 3: Shows co-variants of positive and negative bi-components belonging to magmatic decent. The linear narrow positive correlation indicates that magmatic fluid-state of crystallization. The trend of negative correlations might be reversible state of crystallization showing environmental state of crystallization. Both stages of positive and negative correlations show that

chemical components of crystallizing minerals might be utilized to trace the evolutionary history of the magma and its fugitive components. The low content of Ba against high content of Sr in this carbonate rock might have been due to early crystallization of barite before calcite and the calcite exhibits carbonatite affinity [9,10].

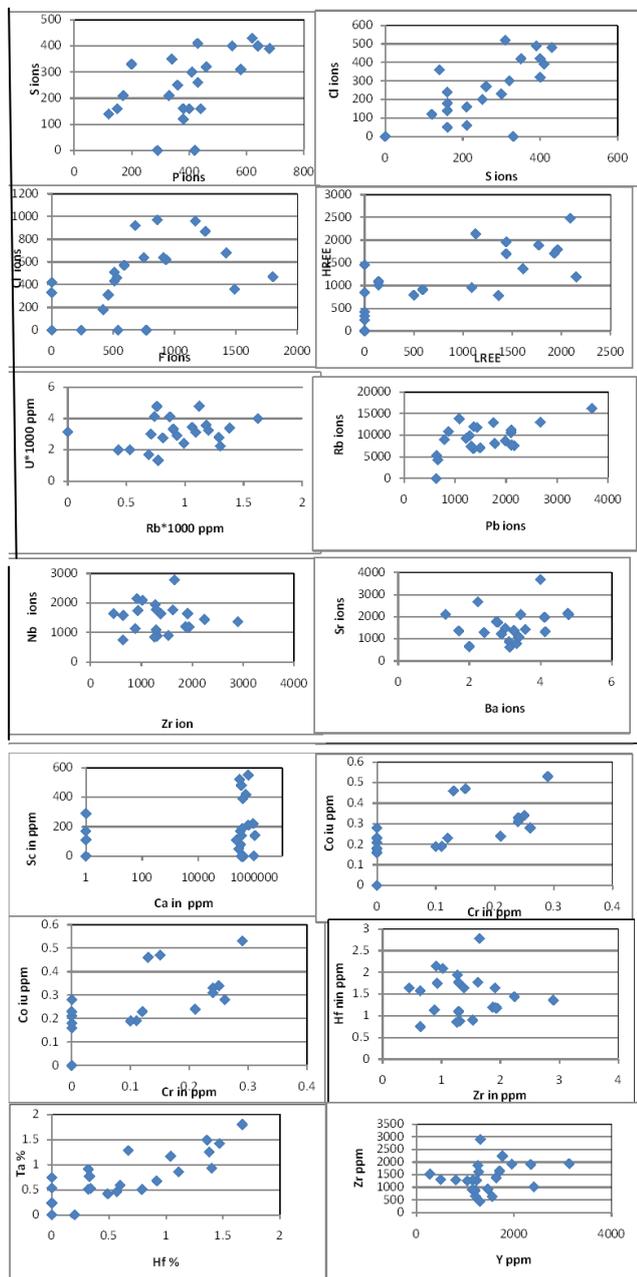


Fig. 4: Bi-component variation of major and trace elements in minerals.

#### 4. DISCUSSION

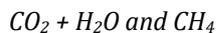
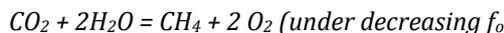
The normative composition of this rock shows that it has very rare mineral assemblage. It is enriched with calcium components like Ca-silicate perovskite and Ca-periclase. Such minerals are stable in lower mantle horizon. Ca-silicate perovskite is the fourth abundant mineral in the lower mantle [10, 11]. In addition to Ca-

silicate perovskite considerable amount of Ca-periclase phases may be present at ambient PTX condition in deep mantle. During rapid ascending of melt / magma  $CaSiO_3$  breaks down into  $CaO + SiO_2$ . By combination of  $CaO + SiO_2$  a reversible reaction might be possible at lower mantle to form  $CaSiO_3$

$CaO + SiO_2$  (Stishovite) =  $CaSiO_3$  at very high pressure above 500 GPa. Similarly, Ca-periclase forms from Ca silicate perovskite under high pressure [11].

Many authors reported that Cuddapah Basin is a sedimentary basin in which sediments of shale calcareous and dolostone are deposited and quartzite are found [4]. Some volcanic and magmatic rocks are emplaced. There are tectonic blocks of horst and graben making deep creep into the lower mantle which has significant amounts of inherent volatile phases. Along this deep creep, upwelling of magma and its volatile components escape to the surface [12]. Yet, some authors believe that Cuddapha Basin is formed by subduction forces associated tectonic movements with volcanic tuffs [13, 14, 15]. Subduction wedge is heterogeneous in its rigidity [16]. It is subjected to tension and compression at different parts of the wedge.

Subduction zone is formed by sinking of a colder wedge down into the Earth [12]. Upwelling zone is developed at the boundaries of subduction zone where diverging hotter zone prevails. Lower mantle is composed of significant quantities of  $H_2O$ ,  $CO_2$  and other volatiles. Magma enriched with such volatile constituents flushing out from lower mantle is transformed crustal rocks [15]. Major components flushing out from lower mantle are  $CO_2$  and  $H_2O$ . *H-O-H* and *O-H-O* are derived from hydrous minerals like brucite and portlandite and *O-C-O* components from carbonate minerals [17].



Ca-silicate perovskite in lower mantle is composed of significant amount of inherent  $H_2O$ ,  $CO_2$  and other volatiles.

Lower mantle is composed heterogeneous layers and accompanied with both micro platelets of several converging and diverging platelets [12, 18]. Deep creep extended by rifted horst and graben blocks associated diverging micro platelets movements [12] in lower mantle.  $CH_4$  forms in more reduced parts carbonate layers of the mantle. Partial melting of these layers might have been produced [17] carbonatite magma. Seismic studies reveal that the lower mantle is not homogeneous. It has been revealed that there are several subduction and diverging micro platelets. They are subjected to both compression and tension forces at different parts of the same layers or along the deep creep formed along the boundaries of horst and graben

[18]. They might have been absorbed more volatiles H<sub>2</sub>O, CO<sub>2</sub> etc. The absorption or flushing out of such volatile constituents changes density and viscosity of mantle leading to local plate movements. According to Anderson [19] carbonate rocks in the lower mantle might have been partially melt and cause plate movements. Denser and colder slab sinks down into mantle. Therefore, carbonate-bearing mantle plays a critical role in plate tectonic movement.

Di calcium silicate perovskite (monticellite) + Stishovite = 2 Ca SiO<sub>3</sub> Perovskite

Ca-silicate perovskite is composed of significant amount of water to meet structural deficiency of oxygen atoms which generally utilized to form polymorphous Ca-periclase (CaO) minerals. The oxygen deficient hydrogen rich olivine polymorphs are composed of water up to 3 per cent. The silicate perovskite accommodate calcium in the place of Mg or Fe at ambient PTX condition 700 km below the Earth's surface. Nearing to lower mantle, oxygen is released and a a state is prevailed and CaO is present excessively. The present study reveals that minerals present in Cuddapah limestone slabs exhibit some characteristic features of silicate perovskite with sheet structure with growth of b-axis by compressive forces showing lower symmetry. They exhibit distinct carbonatitic affinity in such chemo-tectonic settings.

## 5. CONCLUSIONS

The Cuddapah Basin is regarded as a sedimentary basin in association with shale and limestone with slate cleavage. These rocks might have been subjected to transformation of high grade metamorphic events. However, enrichment of a silicate perovskite and CaO indicate that it might have been derived from mantle source. The EDAX images show gas-cavities and idiomorphic crystals in a fine-grained matrix. These features indicate that the crystal present in the rock might have been crystallized from magmatic stage. Drillhole sample might have been struck on carbonatite lava. More studies are required that on the sample belongs to carbonatite-lava. The close association of volcanic rocks in this basin, the black-coloured limestone might have been derived from deep mantle source. The very large barite deposit associated with this limestone with kimberlite, lamproite, [4] carbonatitized bodies [19, 20] of alkali feldspars and Fe-Ti-Nb enriched silicate- perovskite [8] in limestone might have shown carbonatite affinity. Lower mantle has numerous dynamic activities of micro platelets subjected to either tensional or compression forces leading to partial melting of carbonate materials and phase modifications in the lower mantle in space and time as density and viscosity increase with depth. Sudden upwelling magmas along diverging micro platelets or along boundaries of convergent plate margins under reduced state partial melt of carbonate material might have been produced carbonatite magma

[19] along converging or diverging microplate [20, 21, 22] during space and time. No definite conclusion is made and many researches are going on this field.

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## ACKNOWLEDGEMENT

The author expresses his sincere thanks for co-operation of Thiru. T. Ragavaiyya during EDAX analyses of limestone samples in the Department of Material Sciences and Metallurgical Engineering, Indian Institute of Technology, IITM, Chennai, 600 036.

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