2 . Geology, Genesis, Mode of Occurrence and Classification

2.1 GENERAL GEOLOGY

2.1.1 Geologically, barytes deposits are found in rocks ranging from Archaean crystalline to late Tertiary sediments. Barytes occurs most commonly as veins either singly or associated with chalcopyrite, galena, pyrite, sphalerite, quartz, fluorite, siderite, calcite and dolomite, and also rarely with allanite, monazite, columbite, marcasite, magnetite, tetrahedrite, etc.

2.1.2 On account of its insolubility it forms residual deposits under favourable conditions. The deposits sometime are of large dimensions and economically mineable, although of rather low grades. Sedimentary deposits from under special conditions and are of large dimensions and high grades. These are considered as the most important ones. There are four types of occurrences, viz., (i) Vein deposits, (ii) Residual deposits, (iii) Bedded deposits, and (iv) Replacement deposits. Barytes deposits, of different types, are encountered in specific areas so that distinct barytes districts can be identified.

2.2 GENESIS[1]

2.2.1 Geo-chemical Aspects : Natural barium is a mixture of seven stable isotopes. Its atomic number, weight and radius are 56, 137.33 and 1.34 A°, respectively. A very small amount of short lived barium occurs in nature as a fission product of U^{238}.

2.2.1.1 Barium is one of the most common tracer elements of the alkaline earth metals in the upper lithosphere with strong oxygen affinity but, unlike the more abundant elements such as calcium, it rarely forms independent minerals in igneous rocks. It forms an element in certain rock-forming minerals, replacing potassium diodochically in felspars and micas, e.g. celsian, hyalophane, sanidine (in volcanic rocks) and kolla cherite (barium muscovite). Barium biotites in diorites and potash felspars in alkaline rocks are the chief hosts of barium. Finish granites rich in rare earth metals, as a general rule, contain relatively much barium, but the converse is not true. Barium is sometimes considerable in alkaline rocks. Some coals are also relatively rich in barium.(1)

2.2.1.2 In general, in igneous rocks, the highest content of barium occurs in acidic rocks, syenites and nepheline syenites. In hydrothermal deposits, barytes is a common constituent in many metalliferous veins. Hydrothermal solutions may also extract barium from surrounding rocks. Barium is readily removed by fluorine bearing gases and solutions become concentrated therein, finally giving rise to fluorite-barytes veins. In the biosphere, barium is not taken up by animals in significant proportions. It has not become enriched in the shells of lower organisms while the content is low in radiolarian and globigerina oozes. Barytes nodules are known to occur in the ocean bottom and manganese nodules from the ocean bottom show significant barium content.(1)

2.2.2 Source of Barium

2.2.2.1 It is widely agreed that the source of many barytes deposits is magmatic. One of the earliest studies on this subject was by T.H. Holland (1897) on the genesis of quartz barytes veins containing galena in Archaean crystalline at Alangayam, India. Holland came to the conclusion that this had a magmatic source and F.W. Clarke (1924) however, pointed out that the association of $BaSO_4$ was incompatible in a magma belt. It is now universally recognized that such mineral assemblages with sulphides, fluorides, etc. do form in veins from the residual solutions of igneous activity.[1]

2.2.2.2 Recent works on the Alangayam quartz vein deposits have suggested that these are genetically controlled by the large Yelagiri syenite intrusive which outcrops a few kilometres to the west of these deposits and similar veins (Sugavanam et al 1970). However, N. Leelananda Rao has carried out detailed studies on Yelagiri syenite and adjacent rocks and considered that Alangayam quartz barytes veins to be older than syenites and associated carbonatites. He further considers that these "veins are genetically related to pink granite and have intruded along the shear planes of the older rocks". As further evidence, he points out that "the syenites of Yelagiri carry xenoliths of quartz veins and granites and therefore, the barium content of syenites can be ascribed to contamination".[1]

2.2.2.3 The world's largest barytes mine, at Chamberlain Creek Arkansas lies adjacent to the Magnet cove syenite-carbonatite complex (Scull 1958) and has promoted speculation in other countries, raising the possibilities of locating large barytes deposits close to syenites and carbonatites. The proximity of syenite-carbonatite complex to barytes deposits is considered to be perhaps fortuitous (T. Deans in Carbonatites edited by Tuttle, O.F. and Cittins, J,1967). Barytes occurring as crystals in vesicles in a rhyolite porphyry at Pilot Knob in Missouri is considered to be of magmatic origin (Frank and Moynihan, 1963) and the barytes deposits of South-Kasteru Missouri are ascribed to a magmatic origin (Tarr, 1933).[1]

2.2.2.4 The controls of barytes mineralisation in the western United States which contains the world's largest known reserves of the mineral occurring as veins, beds and residual deposits (from veins) have been analysed by Dunham and Hanor (1967). They came to the conclusion that formation of barytes deposits was due to (a) large scale uplifted features, either domal or linear and (b) proximity to non-basaltic or non-alkaline igneous provinces.[1]

2.2.2.5 It has been concluded that there is strong correlation between the occurrence of barytes and regions characterized by quartz-diorite, granodiorite and adamellite intrusives. It has been further suggested that both the igneous rocks and the barytes deposits are controlled by magmatic activity at depth, barium being enriched in melts that crystallise plagioclase first thus making it available for incorporation in the vapour phase of magmatic activity. The diodochy of barium and potassium in the formation of barium minerals is well known. Analyses of plagioclase and potash felspars of granitic rocks by X-Ray emission micro-analysis, have shown that in the plagioclase series, barium may be present in amounts up to a few hundred parts per million (ppm) at the time of crystallisation but on cooling barium becomes exsolved in the potash phase. The potash felspars from non-alkaline areas show an average of 2,500 ppm of barium for potash felspars containing up to 40 percent albite by weight.[1]

2.2.2.6 Similar studies have not been carried out on potash felspars from alkaline rocks. From the results of experimental studies by Tuttle and Dowen (1958) and Smith et al (1964) on granitic rocks, it has been shown that the genesis of a barium vapour phase is dependent on the composition of the early formed crystals, the time at which a vapour phase is evolved and the nature of distribution of Barium between the various phases. The distribution co-efficients for barium between vapour and melt and vapour and crystals are unknown and remain to be studied. From these studies Dunham et al (1967) concluded that a barytes district is developed if there is regional magmatic activity in an area which is also subjected to large scale uplifts both domal and linear, that facilitate the creation of openings, for passage of vapours and their precipitation. It is considered that mineralisation may begin during or soon after the uplift which may actually be caused by the igneous intrusion, to form syngenetic and epigenetic deposits. Subsequently, there may be further periods of mineralisation.[1]

2.2.2.7 Studies on the occurrence of barytes in the Paleogene flysch of the Western Carpathians (Burtan, J et al, 1971) have revealed that the mode of development of barytes and associated minerals suggest a hydrothermal origin while the composition and structure of the matrix indicate that they were formed in a marine environment in the zone of the continental shelf edge. The deposits contain pyroclastic quartz grains which have been partly destroyed. The source of Barium is related to hydrothermal solutions derived from not very distant magma zones.[1]

2.2.2.8 The possibility of Barium transport through hydrous gas phase was demonstrated by Stuvel (1967) and Naboleo (1945). Barium is adsorbed from solutions by clays, hydroxides and organic carbon.

2.2.3 Sedimentary Barytes

2.2.3.1 While the occurrence of barytes in small quantities as veins replacements, etc. can be explained due to deposition from hydrothermal solutions, the mode of formation of the very few but immense deposits of sedimentary bedded barytes is clearly governed by special conditions. Such deposits came to notice only during the last twenty years and until quite recently some of the largest of these in U.S.A. were considered to have been formed by metasomatic replacements of particular sedimentary strata such as shales and siltstones of Mississippian age Stanley Formation (Scull, 1968, Ketner, 1963). These conclusions were arrived at even though field studies had shown that the barytes layers were interbedded with chert and minor limestone bands, which were almost entirely mono-mineralic, occurred concordantly with the members of the sedimentary formation and did not show any wall rock alteration. Detailed study of sedimentary characters including small scale sedimentary features has now clearly established their sedimentary origin.[1]

2.2.3.2 Comparative studies of sedimentary features in the Meggen barytes-pyrite-sphalerite deposit, Germany, with the Arkansas barytes deposit have been carried out. Analysis of the layering feature of stratigraphic sections, hand specimens, thin and polished sections from the Meggen mine levels, revealed fabrics characteristic of a formation by sedimentary and diagenetic processes. Particular features in the barytes include the lenticular form and arrangement of the lenses of fine grained barytes. In the pyrite zones, the Meggen and Leonenschiefer display geopetal features, rhythmic banding, compaction structures and a succession of layers which would suggest a normal deposition by sedimentation similar to that found in the Arkansas deposit U.S.A. Zimmermann, R.A. (1970).[1]

2.2.3.3 Barytes enrichment in rocks takes place by direct contribution of barium / barium sulphate by volcanic source in the form of flows or exhalations and pyroclastic material (Neelkantam, 1987). According to Devore (1981) that cold circulating ground water at ambient temperatures extract barium from tuffs or allied rocks containing accessory amounts of barium, which on mixing with the sulphur of the sea water precipitates $BaSO_4$. Evaporation, neutralisation and increase in concentration of sulphate ion favours precipitation of $BaSO_4$, with loss of carbon dioxide from the solution results in precipitation of $BaCO_3$.[8,9]

2.2.3.4 Several theories have been put forward to account for the immense quantities of barium that concentrate into the formation of these bedded deposits. Since most bedded deposits contain carbonaceous matter (organic) and pyrite and emit a fetid odour when crushed, it has been contended that micro-environments to produce $BaSO_4$ may develop in the ocean around decaying organic matter, although it is known that ocean waters are undersaturated in $BaSO_4$. This is in contradiction to the general observation of lack of precipitation of $BaSO_4$, in globigerina and radiolarian oozes and in shells of organisms, mentioned earlier. However, present day pelagic oozes of east central Pacific Ocean contain as much as 10 per cent barytes. $BaSO_4$, is a sparingly insoluble substance; consequently the possibility of barytes beds being formed under normal conditions of deposition by chemical precipitation has to be ruled out. Detrital accumulation is similarly impossible because of the low hardness of the mineral. Based on these characteristics, Twenhofel (1950), Rankama and Sahama (1949) Pettijohn (1956) and others concluded that barium minerals of sedimentary origin do not make rock masses, occurrences being limited to mineral particles, nodules and aggregates. The fact, however, remains that sedimentary beds constitute the largest and most valuable deposits of the mineral.[1]

2.2.3.5 Experimental studies on the solubility of $BaSO_4$ has shown (Morey and Hesselgesser, 1951) that $BaSO_4$ which is nearly insoluble in water, increase in solubility to 40 mg. per litre of condensate in superheated steam under pressure 500° C at 1000 bars. The solubility of barytes is also increased by the presence of chlorides; 105 mg. of $BaSO_4$ dissolves in 1 litre of water containing 100 gm of NaCl (Saidl, 1958). Experimental studies on the solubility of barytes in concentrated solutions of chlorides of some metals at elevated temperatures showed that solubility varied with the nature and concentration of the chloride solutions. The solubility curve has an ascending pattern with increasing temperature within certain limits for normal and dilute solutions of NaCl, KCl, etc.[1]

2.2.3.6 The study of liquid inclusions in barytes crystals showed that temperatures higher than 200°C are unfavourable for deposition of barytes. The source of the enormous quantities of Barium required to form large bedded deposits needs examination. Dunham and Hanor(1967) have indicated the relationship of acid igneous rocks and structural uplifts to the unique concentration of barytes deposits in the Western United States. Much of the evidence from the geological features of all barytes deposits point to a magmatic origin in particular to acid igneous activity.[1]

2.2.3.7 Barytes is deposited either from a primary source or by leaching of suitable wall rocks or by dissolution of barytes from the sediments by bacterial sulphate reduction in a suitable diagenetic environment or by metamorphic reactions. Barytes is deposited from fluids with a high oxidation potential where sulphur is present as sulphide. Suitable conditions of this kind occur close to the earth's surface or in sub-surface areas where sulphate solutions mix with reduced Barium containing waters. In solution Barium migrates to the region of sulphate stability and this is often bound to a narrow zone close to the earth's surface.[10]

2.2.3.8 In the case of Cuddapah basin in India, the source of vein barytes within the metasediments has been considered to be the basic volcanic of middle or late Cuddapah age which are so closely associated with the vein and replacement bodies ramifying through the area. Some tempting evidence leaning towards this view is provided by a few chemical analyses of basic volcanics in the Cuddapahs which gave barium content ranging from 150 to 450 ppm (Sankaran, 1964) which may represent Barium residual in the consolidated lava sills from which the specimens had been collected.

2.2.3.9 A detailed petrographic study of barytes and associated strata in Mangampeta sedimentary barytes, India has shown that typically in the mid-section of the lenticular body, the barytes is underlain by carbonaceous (bituminous) shale with abundant pyrite in cubes and stringers parallel to stratification. Near the end of the barytes lens, the basal strata are crystal tuff interbedded with softer tuffs both containing minor quantities of barytes. The lowest barytes layers also contain minor intercalations near the base of pyritiferous carbonaceous shale. The barytes in the lower layers is dense, finely crystalline and massive and is of the best quality analysing 90 to 97 percent $BaSO_4$.[1]

2.2.3.10 Overlying the finely crystalline, massive barytes is interbanded with thin (2 cm) layers of soft tuff consisting of quartz with grains of pyrite, barytes and felspars. This in turn is overlain by a succession of bands of rosette barytes in a matrix of buff or grey tuff, alternating with bands of grey tuffaceous layers containing minor barytes, pyrite and bands of vesicular tuff, (Karunakaran, 1970). These layers are seen to be overlain at one place by layers of fine grained tuff containing abundant volcanic lapilli, of roughly ellipsoidal or elongated stringy shapes in sizes ranging from 2 mm to 10 mm scattered irregularly in the tuff. The whole sequence thus indicates an acid volcanic sequence. Volcanic emanations, through cracks in the ocean bottom deposited the barytes as a chemical precipitate while pyroclastic material from the same source released sub-aerially contributed to part of the sequence.(1)

2.2.3.11 The carbonaceous shale rich in pyrite which underlies the barytes beds and occurs sparingly higher in the sequence may represent euxinic conditions obtaining in partially enclosed sea basins, like the back waters seen near shore lines or may indicate the abrupt extermination and entombing of all marine life in a restricted area by submarine and subaerial volcanism. Much of the pyrite may be of later development while the large crystals aggregates which have caused sags in the strata below may represent devitrified volcanic lapilli.(1) Granular, lapilli, vein and replacement are the four genetic types of barytes found in the area, the first two being economically significant. It is opined that a granular barytes is a product of exhalative volcanic action and the lapilli barytes represents the pyroclastic phase of the same volcanism. The vein barytes is considered to be of hydrothermal origin.(2)

2.2.3.12 The genesis of barytes in Vinjamur area of Nellore district, A.P. India is considered to be of volcanic origin by (Vasudevan and Neelakantam) on the basis of, flow layering seen in the barytes; the overlying and underlying rocks being metarhyolitic and other associated rock units being meta andesites, tuffs and agglomerates; the magnetite being titaniferous and exhibiting exsolution textures (euhedral crystals of magnetite occuring in association with barytes); welded nature of the barytes and magnetite; petrology indicating co-magmatic status of barytes with carbonates, magnetite and quartz (manganese is also associated with magnetite); barytes being always associated with magnetite as interlayered units.(3,9)

2.2.3.13 In Kodandarama mine area, the igneous and metamorphic rocks are exposed and they overlie unconformably on high grade schist. The strike of the formations is NNW-SSE. The dip ranges from 30° to 50° with local steep dips upto 65° towards south west and west. In Kodandarama mine the width of barytes is 8-10 m. In this mine, it is associated with magnetite and silica.(4)

2.3 MODE OF OCCURRENCE

2.3.1 Minerals bear a genetic relationship with the rock types in association with which they are formed. This is generally true except in the case of some minerals which are not formed in the places where they occur now. Barytes has been observed to occur in the form of veins, stringers, lenses and disseminations, which, in general, follow certain definite lines of fracture, i.e joints and fault fissures, with the single exception of the bedded barytes deposits in Mangampeta area.(5)

2.3.2 Earlier it was considered that the barytes veins were to be both of the nature of the fissure veins and replacement veins. But the sharp contact of the veins, their regular tabular form, lack of protuberances, emplacement into the country rock, the presence of rectangular shaped intrusions of the limestone with sharp limestones, and even the general disposition of stringers along joint planes in the country rock favour the view that the barytes deposits, are more of the nature of fillings than replacement deposits. At some places, red bands of calcite with ill-defined boundaries are met with. This indicates that some limestone might have been dissolved and recrystallised or the calcite may belong to a younger generation of hydrothermal minerals. In either case, replacement is only of minor consequence and the deposits are more of the nature of fissure veins.(5)

2.3.3 The association of vein barytes with basic volcanics and the presence of traces of BaO in the trap has led to the belief that barytes mineralisation is related to basic intrusions. But the absence of basic intrusives in other barytes bearing areas in Upper Cuddapah rocks has raised doubts about the possibility of the barytes being genetically related to the basic magma. Neelakantam and Roy(1979) believed that the barytes in Cuddapah basin both vein and bedded are the products of extreme barium rich volcanism. However, considering the mode of occurrence, disposition of the veins and basic assoication, it is more probable that vein barytes is hydrothermal in origin and possibly, the basic magma is the carrier of barium rich fluid. Although, basic volcanism in Lower Cuddapah time has affected the calcareous and argillaceous sediments, overlying Gulcheru Quartzite, the mineralisation is confined only to the calcareous horizon. The localisation of mineralisation to the dolomite/limestone may be attributed to the following reasons : (i) The Vempalle dolomitic limestone had more structural weak planes i.e. open fissures, fractures and joint planes and also solution cavities, compared to compact quartzite and shale, which might have served as paths for mineralising solution to get in and loci for ore deposition. The shale being plastic would have flown under pressure and does not give rise to fissure fractures as in the case of the limestone. The controls for mineralisation are, therefore, both structural and lithological, and (ii) the volcanism in Lower Cuddapah times occurred in three phases : (a) towards the end phase of the Vempalle formation in the form of subaerial basic lava flows, (b) basic and acidic volcanic activity contemporaneous with the sedimentation in the higher Tadpatri succession and (c) dolerite, gabbro and serisite sills intruding the Vempalle and Tadpatri Formations. The thrid phase of igneous activity is considered responsible for mineralisation in the Vempalle Formation.[10]

2.3.4 Occurrences of barytes in Mangampeta area are considered to be of sedimentary origin. The radiating platy aggregate of barytes containing inclusions of euhedral crystals, microlites unaltered feldspar, outlines of the wavy barytes lapalli, angular to sub-angular nature of quartz grains exhibiting embayed margins, the presence of minute dark dust like particles in quartz and barytes grains sagging of the tuff laminae beneath the quartz, pyrite and barytes lapalli indicate a pyroclastic origin of the crystal and devitrified glass tuffs and lapalli (rosette) barytes. The granular barytes is formed by the precipitation of the volcanic exhalative under sub-marine/subaqueous condition. The intercalations of the rosette barytes within the granular barytes and vice-versa may be attributed to deposition of pyroclastic material within the chemical sedimentary type. The intimate association of the barytes derived from the pyroclastic and exhalative phase of volcanic activity indicates them to be the products of same volcanism.[5]

2.4 CLASSIFICATION

2.4.1Deposits of barytes can be classified into three main groups, viz. (a) vein and cavity filling deposits, (b) bedded deposits, and (c) residual deposits.[5]

2.4.2The barytes deposits in the country were earlier considered to belong to first category and it is only recently that a bedded deposit of barytes has been recognised in the Mangampeta area of Cuddapah District. The occurrences in the two important states namely Andhra Pradesh (A.P.) and Rajasthan with reference to the above classification are given below :

(1) ANDHRA PRADESH

Barytes occurs in the various lithostratigraphic units of Cuddapah Super Group of rocks right from the oldest Gulcheru Quartzite of the Papaghni group of Srisailam Quartzite of the youngest Krishna group. An occurrence of vein barytes deposit has also been reported from the Banganapalle conglomerate horizon of the Kurnool group.[5]

The occurrences in Anantpur district are in the form of veins which generally follow some definite lines of fractures, i.e. joints and fault fissures. Few veins have also been noticed along the zone of brecciation. The barytes occupying the planes of stratification is not uncommon, whereas in Kurnool district barytes mineralisation in the form of veins is confined to the upper horizon of

Vempalle Formation comprising dolomite, limestone, chert bands and chert breccia.[5]

In Pulivendla taluk of Cuddapah district barytes occurs in the Lower Cuddapah sequence of rocks as veins, stringers, lenses and disseminations. Although most of the barytes veins are confined to the contact, faulted/fissured zone between the Vempalle limestone and basic volcanics, a few veins are also reported at the trap (Volcanic) quartzite contact. The mineralisation has followed the shear, fissure and joint planes of limestone, which are concordant with the general trend of formation. The veins are of the swell and pinch types, having restricted strike lengths of few metres to about 400 m. These are usually narrow, ranging from a few centimetres to maximum of 2 m in thickness. The veins have sharp contact with the basic volcanic or limestone, which are the host rocks. The vein barytes is usually crystalline and white to snow white in colour, though some of the coloured varieties may be stained. The gangue minerals associated with the barytes are quartz, calcite, pyrite, chalcopyrite, limonite and malachite as disseminations or as thin films and coatings along the cleavage planes of the barytes in a number of veins and often in the country rock close to the contact. There is a general increase in the quartz content both along the strike and dip.[5]

In the Rajampet taluk of Cuddapah district, thickly bedded barytes deposits have been reported at Mangampeta. These deposits have undergone minor folding and cross folding. They generally occur below tuff cover of 2 to 180 m in thickness up to a maximum depth of 200 m below the ground surface. The ore is generally associated with thin bands of tuff. Low grade varieties composed of rossette barytes with tuff intercalations and having a specific gravity 3.8 to 4.2 occur at the top followed by granular variety of barytes of high grade having a specific gravity of 4.22 and above.[5] Typical section showing the grade wise disposition of barytes is shown in Plate I.

(2) RAJASTHAN

In Rajasthan, barytes mineralisation is associated with igneous metamorphic and sedimentary rocks. It occurs as veins, cavity filling, bedded, flout and residual deposits. The most important and economically viable area in Rajasthan is Alwar district which contributes about 90 percent of total barytes production of the State. In this district the barytes deposits fall in two distinct zones, one passing from Bhagat-Ka-Bas and the other Sainpuri to Akbarpur. These zones are commonly known as Rajgarh and Alwar belts. The geological setting in both the zones is identical. In Rajgarh belt the barytes deposits/occurrences are located at number of places in quartzites and at the contact with granite. The litho units in Khora Makhora area in Alwar district belong to the upper formation of Alwar Group. Barytes occurs as veins and veinlets in quartzite along the shear planes and fold closures. The localisation of barytes mineralisation is seen guided by structural control.

The other districts which contain barytes deposits/occurrences are Bharatpur, Bhilwara, Bundi, Chittor, Pali, Sikar, Jalor and Udaipur. In Bharatpur district near Hahori, barytes veins are emplaced along strike joints and mineralisation is confined to the volcanic rocks. In Bhilwara district near Jawar Kalan and Rawatbhata concentration of bedded barytes has been recorded from the Vindhyan sediments and occurs as small veins, stringers vugfilling and leminations in the shales of the lower part of Rewa Group known as Panna shales. In Udaipur district near Relpataliya the barytes occurs in granite gneisses of banded gneissic complex of Archean Group.

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