Carbonates and REE bearing barite from Carbonatite complex of Tiruppattur, Tamil Nadu, India

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Abstract— A barite sample collected from 200 m SE of Onnakarai village located in the ultramafic alkaline carbonatite complex of Tiruppattur is studied under polarizing microscope, scanning electron microscope and carried out X-ray diffraction analyses and Energy Dispersive X-ray micro Analyses (EDAX). Conventional wet gravimetric analyses are also made. EDAX analyses show presence of significant quantity of normative alkali-carbonates and niobium bearing rutile minerals. The carbonatitic barite is composed of significant proportion of $(SrSO_4)_{2.88-18.26\%}$ replacing barite molecules. Though barite incorporates significant amount of TiO_2, no rutile needles are found within barite crystals, indicating that it is crystallized above eutectic temperature of ~1200°C $BaO-TiO_2$ system under atmospheric conditions. Petrographic studies of fluids inclusions presence primary and secondary fluid inclusions carrying H_2O, liquid CO_2 and CO_2 phases with maximum peak of decrepitating pulses at 280°C indicate that the mineral is consolidated relatively at very high pressure condition much above atmospheric pressure. It is also enriched with incompatible elements like Ti, Nb, Zr, Hf, Y, Sc and REE constituents. The analyses show that the structural formula of the barite on the basis of 4 (O) ions is $Ba_{0.95-0.32}Sr_{0.10-0.03}P_{0.00-0.04}Ti_{0.35-0.28}Si_{0.17-0.01}Al_{0.02-0.00}Fe_{0.01-0.00}Mg_{0.02-0.00}Ca_{0.04-0.01}Na_{0.08-0.00}K_{0.03-01}CO2_{0.35-0.03}SO4_{0.97-0.66}$. The EDAX analyses show that barite has enriched with significant amount of CO_2 and SO_3. In the field it occurs in the form of small vein lets (< 3 x 0.3m) and lenses in ultramafic rock at the contact ultrapotassic garnetiferous syenites. It is closely associated with benstonite-riebeckite carbonatite, ferro-carbonatites, monazite-riebeckite bearing albitite and ilmenorutile-apatite veins.

Index Terms—Carbonate barite, carbonatite of Tiruppattur, alkali syenites, benstonite, ferro-carbonatite, nioborutile.

I. INTRODUCTION

Carbonatites are defined as magmatic carbonate rocks Johansen [1]. Many carbonatite complexes are genetically associated with barite deposits [2]. Barite generally occurs as late magmatic deposits and hydrothermal deposits in carbonatite complexes. Barite genetically related with carbonatite-alkaline complex is generally enriched with Sr, Ti, Sc, Y, Nb, Ta, Zr, Hf and REE. Apatite, zircon, monazite, nioborutile and pyrochlore mineralization is common in the co-magmatic alkali syenites and carbonatites. In addition to this, sulphide and carbonate mineralization are also prominent. A thin vein-let of barite (3 m length and <30 cm

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width) is exposed amidst an ultramafic body comprised with coarse grained pyroxenes, amphiboles and biotite flakes in a prospecting pit located 200 m SSE of Onnakarai village (12°16'50"N-78°26'37"E). An occurrence of benstonite ($BaCO_3CaCO_3$) was reported from the carbonatite complex of Tiruppattur near Jogipatti village [3] located at 1.5 km NE of Samalpatti Railway Station (12°18'43"N-78°29'03"E). The benstonite body is attributed by them to be formed at high temperature condition by the presence of anorthoclase bearing ultramafic rocks. Similar type of pale yellowish benstonite and riebeckite bearing carbonatite was exposed during pitting and prospecting investigation carried by the Department of Geology and Mining, Government of Tamil Nadu during the year 1993. The pits are located about at 1.5 km SE of Onnakarai village. Thin veins of apatite-nioborutile bearing rocks are exposed about 1 km NE of Mottusulakkarai village (12°15'56"N-78°25'28"E). Floats of nioborutile are strewn for more than 5 ha of land located south of Onnakarai village. Monazite-riebeckite bearing albitite is exposed adjacent to a skarn rock exposure in which ferro-carbonatite is emplaced at about 1 km east of Garigaipalli Railway Gate (12°17'05"N-78°27'30"E). The sketch map shows that a major portion study area, the part of carbonatite complex of Tiruppattur [4,5] is comprised of ultamafic rocks. At the contact of northern portion of ultramafic rocks potash feldspar enriched garnetiferous syenites are exposed and in the southern portion granitic gneisses are exposed. North of Dasampatti Railway station (12°14'58"N-78°26'26"E) pink biotite granite outcrops (Fig. 1). The ultramafic rock is carbonatized in the eastern side and vermiculite is mineralized on the western side of the ultramafic rock.
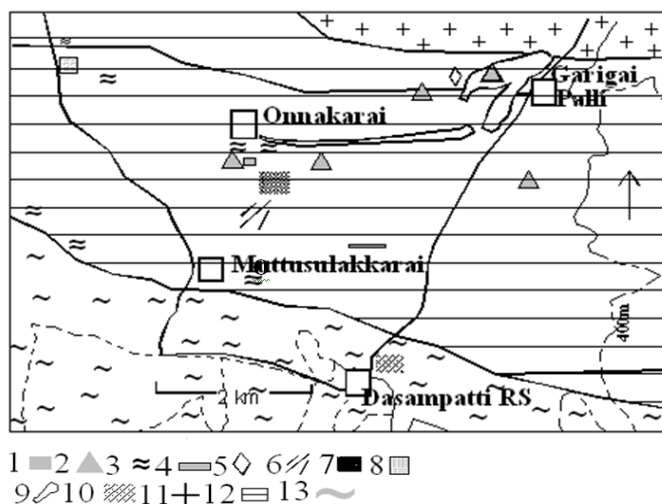

Fig. 1 Geological sketch map showing occurrence and association of barite vein-let. 1 barite, 2 ferro-carbonatite, 3 Sovite, 4 benstonite, 5 monazite –riebeckite-albite rock,

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6 nioborutile,7 nioborutile floats, 8 vermiculite pocket 9 skarn, 10 granite, 11 syenite 12 ultramafic rock 13 granite gneiss.

Fig.2 Quartz feldspar-barite deposit in Alangayam at the SE of Elagiri Hill in the Alangayam rift valley
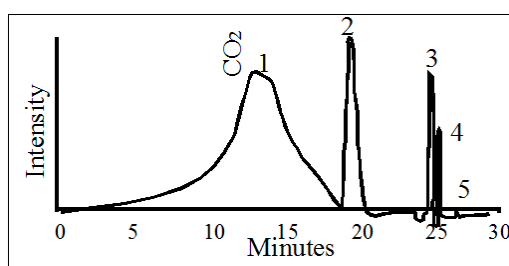

Fig. 3 Chromatograph showing peaks of 1. CO_2 and 2, 3, 4, 5 unknown gas phases in barite.

Veins of riebeckite and schistose riebeckite are found along shear zones in the ultramafic rocks. Numerous pegmatites and aplites are emplaced in the ultramafic rock showing kimberlitic affinities [4,5]. The geological setting, mineralogical composition and geochemistry of the carbonatite complex of Tiruppattur reveal extensive magmatic differentiation from common parent magma of shonkinitic composition [6]. Barite is generally considered to be formed as late magmatic mineral or hydrothermal product in the range of 200° to 450^oC. However, the geochemical and trace element composition, petrographical studies and BaO-TiO_2 system, it appears to be formed at high temperature magmatic stage[7] at 1320^oC under atmospheric pressure conditions (without pressure correction)[8]. Compositional variation of barite sample collected provides additional support to its high temperature late magmatic origin under this geological setting.

I. FIELD RELATIONSHIP

Barite is mineralized at very late magmatic stages in association of galena, pyrite and pyrrhotite sulphide minerals accompanied with very late magmatic ferro-carbonatite and apatite-ilmenorutile veins about 200 m south of Onnakarai village located 3 km NW of Dasampatti Railway station, Dharmapuri District, Tamil Nadu. It is associated with wollastonite-grossularite bearing skarn rock carrying ultrabasic nodules of varying dimensions from < 1 cm to >30 cm. The barite vein hardly extends 3 m in length and a width less than 30 cm as a lensoidal body. The depth persistence is limited 30 to 50 cm. Thin vein lets of riebeckite and calcite are seen within the barite. It is a very dense and heavy mineral and it is distinct from calcite by its absence of reaction with dilute HCl. It occurs in the form of tabular crystals and it is transparent to translucent in nature. The accessory minerals associated with barite are riebeckite, calcite, biotite and quartz. It also occurs as thin veins and lenses near Kodamandapatti village at the contact of ultramafic rock and alkali syenites. Barite also occurs at the south-eastern foot hill of Elagiri near Alangayam village. The barite deposit is located at about 15 km NE of the carbonatite complex of Tiruppattur 2 km NNW of Andiyappanur. In Alangayam[9] ($12^o37'38"$N-$78^o44'58"$E)-Andiyappanur ($12^o18'43"$N-$78^o29'03"$E) barite is associated (Figure 2) with quartz and potash feldspars with accessory minerals of galena and pyrite. Barite is mineralized in pegmatites and aplites in the matrix of fine-grained quartz. It is associated with potash feldspars and quartz in pegmatite veins. It is exposed in 7 seven hillocks of 600 m high as tabular bodies with a shallow dip of 15° towards NE (Figure. 2). The maximum thickness of quartz-barite bed is 60 m. The colour of the barite varies from white to pale brownish yellow due to ferric oxide stains. Quartz is the main gangue mineral in this deposit and the reserve is estimated to be more than 5 million tones with quartz: barite ratios varying from[9] 2:7 to 1:12. Barite occurs in the form of tabular crystals in this area. Ground truth studies and Google Earth map interpretation, it is known that quartz-barite pegmatites and aplites is exposed in a vast area covered by thick forests at the foot hillocks of Elagiri (Fig. 2).

II. METHODOLOGY

In order to study the mineralization of barite, a single fragment of barite (2mm x 2mm x1mm) is subjected to "High Resolution EDAX" probe analyses in the Department of Material and Metallurgical Engineering, Indian Institute of Technology Madras, Chennai. About 5 barite EDAX (Energy Diffusive X-ray micro- analyses) analyses were made among them the first one represents bulk composition of the mineral. Four EDAX were carried out from the fragment of the barite at different portions showing morphological variations up to a magnification of 5000 x. Counts versus electron energy levels of elements are measured (SEM Images & Figure. 3). Trace element concentrations of these minerals are also detected with the help of EDAX probe analyses. They represent the chemical composition at the site of cursor positions where the electron diffusive micro analysis is made (EDAX images Plate 1 and 2). The major elements are recalculated into their oxide forms from the values of elemental output. Structural formulae of barite grains are re-calculated on the basis of 4 (O) (Table 1). In the EDAX analyses, only total iron is reported in the form of FeO and it is not possible to know the per cent of ferric iron present. Further H_2O and other volatiles like CO_2, CH_4 etc may not be possible to detect precisely. Hence the moisture content and loss of ignition around 2% may be experimental error. However, this 2% error does not affect much of the bulk composition the minerals at its specific sites. Back scattered images were taken under High Resolution Scanning Electron microscope. The sample exhibits well developed platelets of barite. Before doing EDAX the barite samples were studied under polarizing microscope and under the scanning electron microscope. The sample analyzed is very pure and there no mineral inclusions are identified. However, the barite sample analyzed by normal gravimetric analyzes in the geochemical laboratory, Geology Faculty of Moscow State Lomonosov University, has

inclusions of riebeckite needles and biotite flakes with epitaxial calcite grains. The sample collected from Alangayam was analyzed in the Tamil Nadu State Geology Department by wet gravimetric analytical method. Under microscopic examination, the mineral is composed of only pure barite without any admixtures of any other mineral impurities. X-ray diffraction and wet gravimetric analyses were carried out in the laboratories of Geochemical Analyses and X-ray crystallography in the Department of Petrology, Geology Faculty of Moscow State University, Russia. Using wide diaphragm fitted high power objective in a polarizing microscope, presence of primary and secondary fluid inclusions of varying sizes from 3µm to 15 µm were identified filled with brine solutions, liquid CO_2 enclosed with gaseous CO_2 are identified. The volume percentage of CO_2 widely vary from 10 to 30% of the total volume of the inclusions, however, the volume of liquid CO_2 phase is limited to 5-10% and the volume of saline solution is 60 -90 and the water vapour varies between 10 to 20% in volume. Stray occurrences of magnetite daughter minerals are found in some primary inclusions. However no heating and freezing experiments were conducted to estimate homogenization temperature to identify the mineral is formed by hydrothermal or pneumatolytic conditions. Barite powders of 60-80 mesh mono-fractions (US standard sieve (0.250 to 0.175mm) were separated and volume of one cubic centimeter fractions were analyzed in a decrepitometer by step-heating process at every 20° intervals from room temperature 20^oC to 450^oC and the maximum pulses of decrepitations were counted at 280^oC. Again one cubic meter mono-fraction of barite was subjected to step heating process between 100 to 350^oC in a solid state gas chromatograph at the geothermo-barochemical laboratory in the Geological Faculty of Moscow State University, Russia. Only CO_2 and H_2O contents in the fluid inclusions present in the mineral were determined. Argon was used as the carrier gas. Gaseous constituents along with argon carrier gas were allowed to flow through a narrow tube at different rates depending on their various physicochemical properties by step heating process. The rate at which gaseous constituents flow is directly proportional to the temperature of the narrow tube. The higher the temperature of the narrow tube, the faster the gaseous constituents move through the tube. Before, the gas of CO_2 is determined, water is removed in a cold trap because the presence of water disturbs the measurement. The detector outputs the data in the form of a graph of detector response (intensity y- axis) against retention time (x-axis) as chromatogram. The area under a peak is proportional to the amount of gaseous constituents present in the chromatogram (Figure 3). By calculating the area of the peak using the mathematical function of integration, the concentration of gaseous constituents in the barite sample was determined. Only the molar volume of CO_2 and H_2O were calculated. The CO_2 content is 0.664 mole/l and the ratio of CO_2 / H_2O is 0.0292. The results show the partial pressure of CO_2 in volatile pressure plays a significant role in the formation of barite.

III. RESULTS AND DISCUSSION

The structural formula calculated on the basis of 4 (O) ions represents, $Ba_{(0.95-0.32)}Sr_{(0.10-0.03)}P_{(0.00-0.04)}Ti_{(0.35-0.28)}$ $Si_{(0.17-0.01)}Al_{(0.02-0.00)}Fe_{(0.01-0.00)}Mg_{(0.02-0.00)}Ca_{(0.04-0.01)}Na_{(0.08-0.00)}$ $K_{(0.03-1)}CO2_{(0.35-0.03)}SO4_{(0.97-0.66)}$. Though EDAX analyses indicate presence of high TiO_2, and CO_2 optical investigation or back scattered images do not show any presence of rutile needles. Rittmann's norm[10] (Rittmann.1973) indicates formation of alkali carbonates (from 3.6 to 10.9%) and normative proportion of rutile is also very high in the range of 19 to 26% (wt.). Celestite substitutes for barite from 2.9% to 18.3%. The wet gravimetric analyses show enrichment of ferric iron with absence of ferrous iron and the oxidation potential of the mineral is very high. The CO_2 content is so high Ca, Mg, and Fe unable to compensate to form carbonates and the enrichment alkalies particularly Na forms as sodium carbonates. This indicates its carbonatitic affinity of its course of mineralization. Field occurrences of galena, pyrite, scapolite, barite, benstonite, nioborutile, apatite, vermiculite biotite and amphiboles indicate that the ultramafic, alkali syenites and carbonatites are formed under SO_3, CO_2, P_2O_5, F and H_2O rich conditions. The unit cell dimension a = 8.717Å, b= 5.643Å and c= 7.278Å and cell volume is 358 $Å^3$ which is slightly higher than the volume given for the barite given (a = 8.88Å, b= 5.45Å and c= 7.15Å and cell volume[11,12] is 343 $Å^3$ by Deer et.al. This may be due to accommodation of more of Ti, Nb, Zr and other incompatible elements in its lattices.

High Sr/Ba ratios are characteristic of early formed co-magmatic rocks and differentiated rocks in a deep-seated zone and it is possible to discriminate the latter types by using higher K values at constant Sr/Ba values. Highly differentiated alkali-syenites have emplaced in late magmatic stages have successively lower Sr/Ba ratios and higher K values compared with their early co-magmatic counter parts[13]. BaO is incorporated in potassium feldspars up to 2% (wt.%). Highly differentiated pegmatite and aplite veins of ultra-potassic syenites are found at the contact of ultramafic rocks. Compared to Sr, Ba is more reactive and tends to behave as stronger incompatible element and tends to concentrate in residual liquids than that of Sr. Therefore, early magmatic rocks have enriched in Sr than Ba and Ba is enriched in late magmatic syenites with relatively high values of Zr/Hf, Nb/Ta and Sc/Y. Though EDAX analyses are spot specific under higher magnification, the analyses represent the compositions of microcrystals. The calculation of Rittmann's norm indicates presence of excessive constituents of CO_2, SO_3 and P_2O_5 ions. In the gravimetric analyses no ferrous iron is present. The excessive CO_2, SO_3, and P_2O_5 may be consumed by carbonates, sulphates and phosphates of unknown minerals, probably some anglesite $PbSO_4$ may substitute into the barite crystals. Ca ion is insufficient to form calcite or apatite. After formation of sodium and potassium carbonates, excessive CO_2 is remaining. Similarly excessive SO_3 remains after formation of barite and celestite. Celestite replaces barite at the maximum of 18%. Since, SO_3 in excess with insufficient Si ions, the possibility of formation of barioperovskite ($BaOTiO_2$) or benitoite ($BaO TiO_2 3SiO_2$) could be possible. Normative proportion of rutile extends from 19 to 26%. However no rutile crystals are identified in thin section or under scanning electron microscope. The distribution of excessive SO_3 with depletion excessive CO_2 ions is seen in the course of barite mineralization (Figure 4a) and two different linear trends of magmatic crystallization is seen between SO_3 and CO_2 ions in Figure 4b. In the Figure 4c, there appears two separate fields of barite crystallizations with common magmatic trend from early formed silica-poor and carbonate rich barites towards for immiscible separation into carbonate rich and silica rich late magmatic end. At an optimum enrichment of silica and carbonate phases

immiscible separation is possible. The extension of the fields, qz : NakCc immiscible fraction may take place at 20:120 (i.e. 1:6). However, more analytical data are required to define the boundary of immiscible fields. A linear correlation is seen with decreasing Ti ions with increasing SO_3 ions during the course of barite mineralization (Figure d). Early magmatic barites are enriched with high content of $SrSO_4$ and during progressive differentiation substitution of celestite molecules in barite decreases[14] (Figure. 4e). Figure 4f and 4g indicate the paths of progressive differentiation towards enrichment of Zr - Nb and also Zr/Hf - Nb/Ta. Assuming the bulk composition of barite representing as melt composition partition coefficients of the distribution of High Field Strength Elements are calculated by dividing the trace elemental concentration by trace element composition of bulk of the sample and plotted in the Figure 4h. The diagram shows superimposition of composition of sample with another with maximum range of two orders of variations of heavy elements particularly for Hf, Eu, Dy, Y, Yb and Lu with smooth curves. This indicates that bulk sample also well crystallized and enclosed with minute barite grains with absence of significant amount of fine-grained matrix consolidated after crystallization of well developed barite crystals.

In the system $BaO-TiO_2$, from the component enriched more than 80 mol% of TiO_2, TiO_2 crystallizes[15] below 1550^oC leaving residual liquid enriched with BaO and it crystallizes $BaTi_4O_9$ with TiO_2 below 1446^oC. When temperature falls further below 1393^oC, $Ba_2Ti_9O_{20}$ crystallizes with TiO_2 from that component. The same component on cooling, crystallizing titanium rich phases incorporate more BaO from the residual liquid. On the other hand crystallization starts with increasing BaO mol% concentration, sequences of $Ba_2Ti_9O_{20}$, $BaTi_4O_9$, $Ba_4Ti_{13}O_{30}$, $Ba_6Ti_{17}O_{40}$ and cubic $BaTiO_3$ crystallize up to BaO and TiO_2 mol% 50 each. The diagram reveals that BaO rich phases crystallize at lower temperatures and TiO_2 rich phases crystallize and fractionate at higher temperatures[15]. In the present study, the barite with high concentration of TiO_2 with absence of any TiO_2 rich phases indicates that it might have formed at higher temperature as first generation before exsolution of Ti phases such as $BaTi_2O_5$ under reducing state[16] above 1200° C. With increasing degree of oxidation potential ($Ox^o = 100*Fe^{+3}/(Fe^{+3}+Fe^{+2} =100$; absence of ferrous iron in the wet chemical analyses) TiO_2 is liberated as rutile, ilmenite and nioborutile. After crystallization and fractionation Ti rich nioborutile, ilmenite and Ti-magnetite with concentration of barite molecules, barite of second generation was crystallized at about 300^oC.

V. CONCLUSION

It seems that there are two generations of barite Ti, CO_2 and REE bearing barite formed at very high temperature conditions around 1200^oC and the others which poor with these constituents formed relatively at low temperature hydrothermal conditions around 300° C. The ultramafic rock is extensively altered with ubiquitous development of biotite and amphibole with sporadic mineralization of pyrite and pyrrhotite along shear planes in ultramafic rocks at the contact of syenites. Trace element concentrations indicate that the barite is mineralized in the carbonatite-alkali syenite complex at late magmatic stages during rapid ascending of residual magmatic fluids carrying subsolidus barite crystals.

REFERENCES

[1].A. Johannsen, . A descriptive petrography of the Igneous rocks, v.1, Chicago University Press, 1931, 267pp.

[2].E. Wm. Heinrich. Geology of carbonatites, Rand McNally, Chicago University Press, Chicago, 1966

[3]. E.I. Semenov, V. Gopal and V. Subramaniyan, A note on the occurrence of Benstonite, a carbonate of calcium and barium from the carbonatite complex of Jogipatti, near Samalpatti, Dharmapuri District, Tamil Nadu, *Current Science*, 40, (10) 1971, 254-256.

[4]. R. Ramasamy, R., SP. Subramanian, and R. Sundaravadivelu, (2010) Compositional variations of olivine in shonkinite and its associated ultrabasic rock from the carbonatite complex of Tiruppattur, Tamil Nadu, *Current Science*. 99, 2010, 1428-1433

[5]. R. Ramasamy, Crystallization, fractionation and solidification of co-magmatic alkaline series sequentially emplaced in carbonatite complex of Tiruppattur, Tamil Nadu, India, Book on *Crystallization*- Science and Technology, Edrs Marcello Rubens, Barsi Andreeta, ISBN, pp. 535-564, 12th Sept. 2012, INTECH, Austria.

[6]. S. Saravanan, and R. Ramasamy, Geochemistry and petrogenesis of shonkinite and associated alkaline rocks of Tiruppattur carbonatite complex. Tamil Nadu, *J. Geol. Soc. India* v. 46, 1995, 235-243

[7]. D.E. Rase, Phase equilibria in the system $BaO-TiO_2$, Journal of the American Ceramic Society, 38 (3) 1955, 102- 1 13.

[8]. W. Wong-Ng,, R.S. Roth, T.A. Vanderah, and H.F. McMurdie, Phase Equilibria and Crystallography of Ceramic Oxides, *J. Res. Natl. Inst. Stand. Technol.*. 106,2001.1097–1134..

[9]. N.K.N. Aiyengar, Minerals of Madras, Dept. of Industries and Commerce, Govt. of Tamil Nadu, Chennai, 1964

[10]. A. Rittmann, *Stable Mineral Assemblage of Igneous Rocks*, Springer-Verlag, Berlin, 1973, p.262

[11]. D. Slovenoc, D. Siftar, M. Haksic and I. Jurkovic, Strontium dependence on the lattice constants of barites from the Kreaevo Area in Central Bosnia (Bosnia and Herzegovina), Geol. Croat., 50/1,1997 27-32, Zagreb.

[12]. W.A. Deer, R.A. Howie, and J. Zussman, An Introduction to the Rock Forming Minerals 1992, 2nd edn, Pearson Prentice Hall, London 696p.

[13].R. Ramasamy and L.G. Gwalani, Strontium and Barium in carbonatites and alkaline rocks of Tirupattur, Indian Geological Congress, 1996 Abstact.vol. p. 59,

[14]. J.S. Hanor, Barite-Celestine geochemistry and environments of formation; in Sulfate Minerals - crystallography, geochemistry and environmental significance; Reviews in Mineralogy and Geochemistry; 40; 2000 193-275;

[15].K.W. Kirley and B.A. Wechesler Phase relations in the Barium titanate- titanium oxide system , J. Am. Ceram.Soc. 74, 1991. 1841-47.

[16]. Na Zhu, A.R. West, Formation and stability of ferroelectric $BaTi_2O_5$ Online publication23rd Nov 2009, J. Am. Ceram.Soc. vol 93 (1) 2010 .295-300.
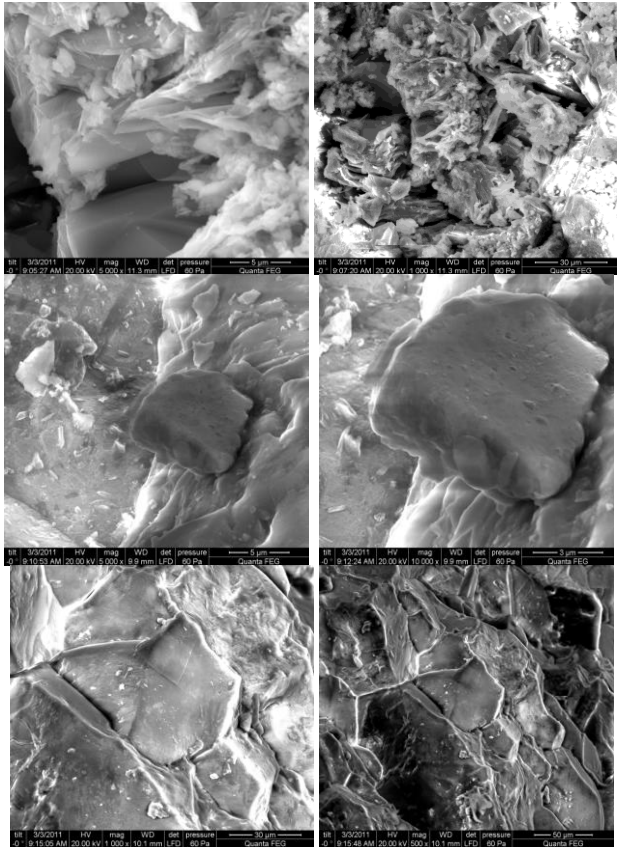
BSE images of barite crystals of varying sizes from <0.5 x 2 µm to 150 x 50 µm are seen. Square shaped platelets 5 µm sides are also seen at higher magnification. Both needle like barite and lath shaped barite grains with interlocking mosaic textures are seen. Plates, prisms and acicular crystals of barite are seen.
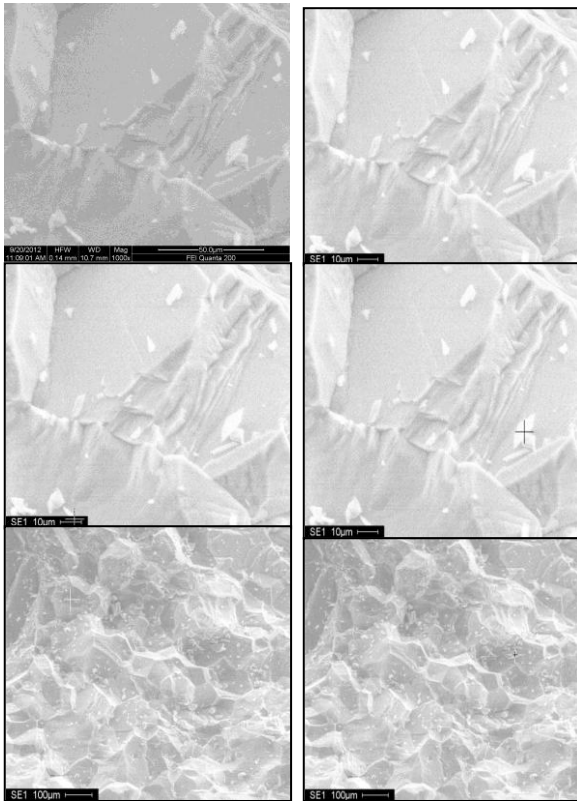
Barite with smooth surface 001 faces are seen as large platelets.

Table 1 Chemical composition of Barite from Carbonatite complex of Tiruppattur

	1	2	3	4	5	6	7	XRD2θ	Å
SiO_2	0.23	1.53	2.03	1.52	1.83	0.50	4.56	19.91	4.4593
Al_2O_3	0.00	0.00	0.44	0.63	0.00	0.00	0.17	20.35	4.3639
Fe_2O_3						0.10	0.06	20.95	4.2402
FeO	0.00	0.29	0.00	0.32	0.00	0.00	0.00	22.75	3.9086
MgO	0.00	0.22	0.00	0.37	0.00	0.05	0.00	24.83	3.5857
CaO	0.37	0.68	0.88	1.02	0.94	0.60	1.00	25.83	3.4491
Na_2O	0.80	1.38	0.00	0.62	0.77	0.05	0.00	26.78	3.3285
K_2O	0.21	0.74	0.90	0.78	0.81	0.00	0.00	27.15	3.2844
TiO_2	16.45	13.00	15.41	16.79	16.16	0.00	0.00	28.64	3.1168
P_2O_5	0.00	1.56	1.68	1.66	1.58	0.00	0.00	29.13	3.0655
SO_3	34.51	35.80	34.98	32.77	33.86	33.40	30.66	31.45	2.8444
BaO	36.58	34.26	32.80	30.27	31.65	62.68	58.74	32.69	2.7393
SrO	2.97	4.65	4.34	3.56	4.76	1.20	4.54	36.11	2.4873
CO_2	7.88	5.88	6.53	9.71	7.64	0.53	0.05	38.68	2.3278
H_2O						0.80	0.08	40.74	2.2147
Co/Ni	0.00	1.00	2.00	0.92	1.17			42.49	2.1275
Sr/Ba	0.08	0.13	0.13	0.11	0.14	0.03	0.11	43.97	2.0592
Sc/Y	0.02	0.07	0.08	0.11	0.09		a		8.717
Nb/Ta	9.70	6.05	4.06	3.21	6.08		b		5.643
Zr/Hf	20.45	11.81	22.23	11.56	16.55		c		7.278

Number of ions on the basis of 4 (O)

	1	2	3	4	5	6	7
Si	0.007	0.043	0.056	0.041	0.050	0.019	0.173
Al	0.000	0.000	0.014	0.020	0.000	0.000	0.008
Fe	0.000	0.000	0.000	0.000	0.000	0.003	0.002
Mg	0.000	0.009	0.000	0.015	0.000	0.003	0.000
Ca	0.011	0.021	0.026	0.029	0.028	0.025	0.041
Na	0.044	0.076	0.000	0.032	0.041	0.004	0.000
K	0.007	0.027	0.032	0.027	0.028	0.000	0.000
Ti	0.349	0.276	0.320	0.337	0.333	0.000	0.000
P	0.000	0.037	0.039	0.038	0.037	0.000	0.000
S	0.731	0.759	0.724	0.656	0.697	0.966	0.873
Ba	0.404	0.379	0.354	0.317	0.340	0.947	0.874
Sr	0.049	0.076	0.069	0.055	0.076	0.027	0.100
C	0.304	0.227	0.246	0.354	0.286	0.028	0.003

HFSE ppm	Bulk	1	2	3	4
Rb	134	213	162	173	222
Ba	21030	18900	17680	17190	16890
Nb	320	442	349	263	450
Ta	33	73	86	82	74
Ce	596	402	546	679	600
Pb	46	113	199	184	149
Sr	1610	2420	2210	1910	2400
Zr	225	378	289	289	331
Hf	11	32	13	25	20
Eu	9	79	91	98	103
Dy	0	0	58	0	36
Y	177	272	327	292	294
Yb	0	46	35	0	0
Lu	0	49	74	70	62

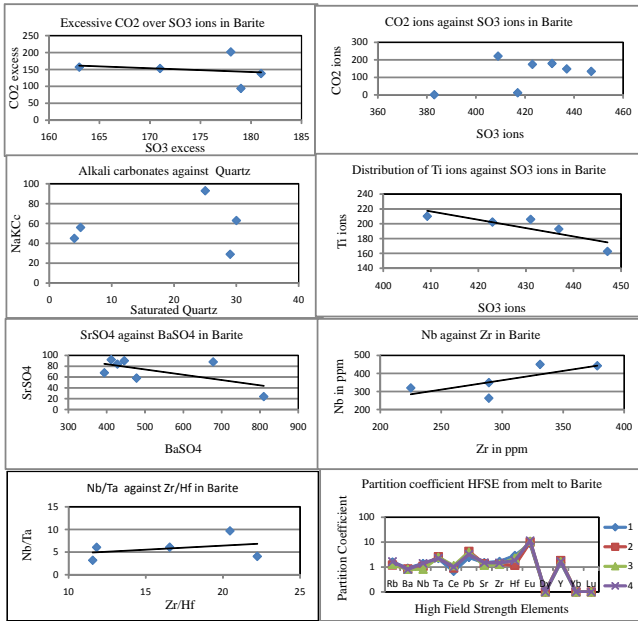| R Norm	1	2	3	4	5	6	7
ru	25.59	19.09	24.03	25.99	24.46		
ap		2.22	3.24	3.59	3.27		
ank		2.11					
cc	1.74					2.63	0.22
nakc	5.59	10.89	3.61	6.93	7.63		
cels	7.20	10.54	10.46	8.42	11.14	2.75	9.68
bar	59.38	52.22	53.30	48.76	49.88	92.78	84.27
rieb						1.72	4.51
bio		1.74	5.69				
qz	0.50	2.93	3.61	0.62	3.63	0.11	1.32
Barite	89.19	83.21	83.59	85.27	81.74	97.12	89.70
cels	10.81	16.79	16.41	14.73	18.26	2.88	10.30

Figure 4 Geochemical variation diagrams showing magmatic differentiation during the course of crystallization of barite from the late magmatic fluids.