

## Rare earth minerals in carbonatites of Basal Complex of Fuerteventura (Canary Islands, Spain)

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**ABSTRACT:** The Fuerteventura calcicarbonatites appear in the Basal Complex as veins, breccias and shear bands along the coastline between Puerto de la Peña and Cueva de Lobos, and in the area around the Barranco of Esquinzo. These carbonatites are essentially made up of calcite and to a lesser extent apatite, aegirine-augite, albite, orthoclase-sanidine, biotite, ore minerals and epidote with accessory minerals such as sphene, zircon, garnet, celestite, barite, britholite, allanite, pyrochlore and monazite. Geochemical analysis of these carbonatites show high values of REE of between 511 and 7,372 ppm with a high relation of LREE/HREE. Microprobe studies reveal that these elements are mainly associated with phosphates (britholite, monazite, and apatite), silicates (allanite and titanite), oxides (pyrochlore), carbonates (bastnäesite) and sulphates (barite). The carbonatites were generated in the last magmatic-hydrothermal crystallization phases of the alkaline intrusive complexes of Fuerteventura and some of them were emplaced along shear zones showing important plastic deformation structures.

### 1. REGIONAL GEOLOGY

Two large geological units have been defined in Fuerteventura (Fuster et al. 1968): the Basal Complex (BC) made up of plutonic and volcanic rocks and underwater sediment, and the later group of surficial volcanic rocks. In the BC, we have descriptions of pelagic sediment dating back to the Cretaceous and Oligocene periods, together with submarine hyaloclastites and alkaline basaltic lava. This lower volcanic-sedimentary sequence was intruded by ultramafic plutons, tholeiitic-alkaline gabbros, syenites and an ijolitic-syenitic-carbonatite complex ( $\approx 60$  Ma., Le Bas et al. 1986) which cropped out along the Central West coastline of Fuerteventura (the complex which we shall denominate as of now the Puerto de la Peña-Cueva de Lobos, PP-CL). However, carbonatite and syenite veins of PP-CL complex has been dated at Early Miocene ( $\approx 25$  Ma., Cantagrel et al. 1993) These rocks are traversed by abundant NNE-SSW dykes and subvolcanic plutons of varying compositions and with ages of between 48 and 12 Ma. There is a second ijolitic-syenitic-carbonatite complex in this intrusive episode ( $\approx 25$  Ma., Le Bas et al. 1986) which appears in the North-West of the island (the Esquinzo complex, E) and which is traversed, again, by a network of dykes and posterior plutons. The subaerial volcanic activity was centred around the Miocene epoch with the characteristic eruptive rifts of the same and around the Pliocene-Quaternary, with strombolian characteristics.

### 2. RARE EARTH MINERALS

The carbonatites are to be found close to the ultra-

mafic and salic intrusive rocks in the complex and they crop out in the shape of dykes and irregular veins some centimetres or even metres thick similar to those to be found along the coastline between Punta de Nao and Caleta Mansa (PP-CL). There are metrical breccias with heterogeneous angular elements such as the ones to be found in the Barranco de los Encantados (E), bands of ductile shear characterised by spectacular mylonite textures, with thicknesses below 50 metres, in the direction NW-SE and subverticals, such as exist between Caleta de la Cruz, Punta del Peñón Blanco and other small shear in the near zones (PP-CL).

The chemical analysis of the major and minor elements which have been carried out on representative samples of carbonatites from both complexes, allow us to define these as mainly calcicarbonatites (Mangas et al. 1994). These analyses overall indicated fair concentrations of Sr, Ba and light REE (Ce, La, Nd and Sm) and to a lesser extent Nb, Zr, Y and V. The concentrations of maximum and minimum REE as measured by the carbonatites of the E complex fluctuated between 511 and 4,974 ppm and in the PP-CL complex, between 697 and 7,372 ppm, with positive values in the proportion of light REE/heavy REE and the concentration of  $Ce > La > Nd > Sm$ .

In order to distinguish the carrier minerals of REE in these carbonatites, we carried out an optical mineralogical study together with an electronic microprobe (Camebax AX 50 in the Universities of Oviedo, Spain and Paris VI, France). The carbonatites are essentially made up of heterogranular (sövite-alkalite) white or reddish-grey calcite (>70%) with high SrO content (<13%) and low REE<sub>2</sub>O<sub>3</sub>

Table 1 Representative analysis of microprobe of rare earth minerals in Fuerteventure carbonatites. 1-4: britholites of Punta del Peñón Blanco; 5-6: Monazites of Punta del Peñón Blanco and Caleta de la Cruz, respectively; 7-10: allanites (7-8 Punta de Nao and 9-10 Barranco de los Encantados); 11-12: pyrochlores of Punta del Peñón Blanco. n.a.: element non analyzed.

	1	2	3	4	5	6	7	8	9	10	11	12
	Wt%											
SiO <sub>2</sub>	2.21	6.83	16.08	21.37	0.53	0.21	34.73	32.21	35.67	27.80	0.44	0.00
TiO <sub>2</sub>	0.00	0.00	0.06	0.02	0.00	0.02	0.02	0.06	0.01	0.19	9.75	10.49
Al <sub>2</sub> O <sub>3</sub>	0.01	0.00	0.01	0.00	0.07	0.04	27.19	16.56	21.19	11.95	0.06	0.09
FeO	0.00	0.05	0.03	0.00	0.11	0.07	2.33	10.32	12.15	14.61	0.89	0.96
MnO	0.14	0.11	0.04	0.00	0.00	0.00	n.a.	n.a.	n.a.	n.a.	1.14	1.49
MgO	0.00	0.00	0.00	0.00	0.01	0.02	0.06	1.10	0.42	0.38	0.10	0.00
CaO	47.73	39.28	21.90	11.86	3.21	0.14	17.00	11.85	17.87	9.15	14.73	13.49
Na <sub>2</sub> O	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.07	0.01	0.01	0.10	3.50	3.50
K <sub>2</sub> O	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.01	0.00	0.02	0.00	n.a.	n.a.
P <sub>2</sub> O <sub>5</sub>	38.36	29.83	10.88	0.84	30.17	29.77	0.07	0.06	0.00	3.18	0.03	0.03
SO <sub>3</sub>	0.20	0.05	0.01	0.00	0.00	0.01	n.a.	n.a.	n.a.	n.a.	0.00	0.00
SrO	3.43	3.11	2.74	1.32	1.10	0.00	2.91	1.19	3.76	0.62	0.60	0.44
BaO	0.03	0.01	0.08	0.00	0.07	0.00	n.a.	n.a.	n.a.	n.a.	0.00	0.00
Nb <sub>2</sub> O <sub>5</sub>	0.00	0.00	n.a.	n.a.	0.00	0.00	n.a.	n.a.	n.a.	n.a.	45.34	43.43
ZrO <sub>2</sub>	0.03	0.03	n.a.	n.a.	0.01	0.00	n.a.	n.a.	n.a.	n.a.	0.36	0.34
TbO <sub>2</sub>	0.00	0.04	n.a.	n.a.	18.01	0.23	n.a.	n.a.	n.a.	n.a.	0.59	0.54
Y <sub>2</sub> O <sub>3</sub>	0.00	0.70	n.a.	n.a.	0.38	0.07	n.a.	n.a.	n.a.	n.a.	0.00	0.06
Ce <sub>2</sub> O <sub>3</sub>	2.56	8.16	20.77	28.11	20.18	32.09	4.97	11.43	2.44	13.79	8.38	10.10
La <sub>2</sub> O <sub>3</sub>	1.22	4.11	14.17	21.50	10.79	22.72	3.83	7.21	1.39	11.34	1.99	2.43
Nd <sub>2</sub> O <sub>3</sub>	1.24	4.55	7.93	9.85	12.13	12.42	0.54	1.72	0.93	3.00	3.04	3.84
Sm <sub>2</sub> O <sub>3</sub>	0.11	0.55	0.68	0.58	1.34	0.65	0.00	0.00	0.00	0.06	0.30	0.40
Total	97.27	97.41	95.38	95.45	98.11	98.46	93.73	93.72	95.86	96.17	91.24	91.24

(<0.6%). Subordinate minerals and intimately crystallized accessories consisted in apatite, aegirine-augite, albite (Ab 97-98%, An 0.7-2%, Or 0.7-2%), orthoclase-sanidine (Or 88-94%, Ab 3-10%, An 1-3%), biotite, ore minerals, epidote, titanite, zircon, garnet (Grs 68-75%, Alm 22-26%, Sps 3-6% and Prp 0.1-1%), celestite, barite, britholite, allanite, pyrochlore and monazite, with secondary minerals of sericite and chlorite. The main ore minerals were magnetite, ilmenite and pyrite and to a lesser extent, hematite, chalcopyrite, pyrrhotite and mock ore with secondary elements of hematite, needle ironstone, chalcosine and indigo copper. The specific minerals of REE in these carbonatites are, if ordered by abundance, britholite, allanite, pyrochlore and monazite, all of which have contents of light REE<sub>2</sub>O<sub>3</sub> of between 4 and 68% (see Table 1). We should also indicate that other paragenesis minerals bear traces of light REE<sub>2</sub>O<sub>3</sub> such as, for example, barite (3-5%), apatite (0.2-4%) and titanite (<1.6%). We shall now

proceed towards a description of the REE specific minerals.

The great affinity between REE and PO<sub>4</sub> is confirmed by the presence of phosphates such as britholite and monazite. The britholite is an isostructural type of apatite and is formed by clustered substitution of Ca + P for REE + Si with the REE taking the place of Ca. This is a mineral scarcely to be found in carbonatites and only registered in studies in Pilansberg (South Africa) and a rich variety of Th in Oka (Canada). In Fuerteventura, this mineral has been detected in the carbonatites in Punta del Peñón Blanco (PP-CL) and in Barranco de Agua Salada (E) which represent the first indications of the same in Spain (see Table 1, analyses 1-4). The britholite appears in the shape of individual crystals some 0.02 - 0.5 mm in size either to be found in polycrystalline mosaics or in seams with other paragenesis minerals (Fig. 1). Their outer appearance is similar to that of apatite: hexagonal, prismatic or globular in shape.

colourless or pale yellow, with moderate relief, first order grey double refraction, cleancut surfaces with few fractures and no exfoliation. From the chemical perspective, there is an important variance over the analyses carried out above all in the proportion of REE-Ca and Si-P but, as can be seen from Table 1, these differences correspond to perfectly coupled ionic substitutions. As regards the concentration of light REE, this fluctuates between 4.5 and 60% without ever reaching the theoretical level of 62% and always with a proportion of  $Ce > La > Nd > Sm$ .

Although britholites have been cited where the content in  $Ce_2O_3$  reaches 22.5%, some of the britholites analysed in Fuerteventura had up to 28%. The content in SrO varies from between 1.1 to 4.3% with this element in the Ca position so that the britholites with more Ca have less Sr. The proportion of MnO is slight varying between 0.04 and 0.1% with a Sr/Mn proportion of between 26 and 108. The content in  $SO_3$  is usually low, around 0.05 and yet in some of the britholites, values of around 2.7% have been registered. The concentration of  $ThO_2$  is always under 0.07% and  $Y_2O_3$  fluctuates between 0.04 and 1.3% with the  $Yb_2O_3$  under 0.2%. Lastly, we should indicate that we have analysed britholites with low concentrations of P, Si and Ca. In some crystals, these elements have totally disappeared and have been substituted by a carbonate thereby forming a fluorocarbonate of REE which is called bastnäesite. Bastnäesites are rare: they are usually yellowish hexagonal crystals, 0.05 - 0.1 mm in size with a relief which is superior to calcite and with REE concentrations of between 58.5 and 60%.

Monazite is scarce and is to be found in the shape of colourless individual anhedral or euhedral crystals with very high relief and between 0.05 and 0.1 mm in size. Monazites have been found in the carbonatites in Punta del Peñón Blanco, Caleta de la Cruz and Punta Nao (PP-CL) (Table 1, analyses 5 and 6). As was to be expected, the monazites analysed revealed high concentrations of light  $REE_2O_3$ , between 44 and

68%, with Ce/La values of between 1.1 and 1.9 when the maximum theoretical concentration of this mineral is 69.73% and the normal Ce/La proportion is 1. The Th is usually to be found in monazites and substitutes REE with values of even up to 20%. In the Fuerteventura analyses, this element was to be found in concentrations of between 0.2 and 18%. Magmatic-hydrothermal monazites have been described in carbonatites in Kangankunde Hill (Malawi) and Bayan Obo (Mongolia).

The allanite, which is an epidote rich in REE, has been studied in carbonatites in Punta Viento and Punta Nao (PP-CL) and in the Barrancos de Agua Salada and Encantados (E) (Table 1, analyses 7 through to 10). It is found in the shape of idiomorphic (prismatic) or aliotriomorphic crystals of between 0.05 and 0.3 mm in size. These allanites are colourless or slightly yellowish and some have zoning of colour and relief with the areas of zoning most pronounced around the centre to the edge. The central areas are metamictic and the analyses indicate a high level of REE and composition of britholite (Fig.2). The proportions of REE in these analyses varied between 4.5 and 28% with values of  $Ce > La > Nd > Sm$ . These maximum data of REE in allanites are indeed rare although similar findings have been registered in allanites of carbonatites in Mountain Pass (California, USA). The geochemical zoning from the centre to the edge of some of the crystals of allanite is characterised by decreases in  $REE_2O_3$ , FeO and MgO or increases in CaO,  $Al_2O_3$ ,  $SiO_2$ ,  $PO_4$  and SrO. Therefore, it is probable that there may be coupled substitutions of REE and Fe by Al and Ca.

Pyrochlore, which is an oxide of Nb and REE, has been found in carbonatites in Punta del Peñón Blanco and Caleta de la Cruz (PP-CL). These pyrochlores are idiomorphic (square or octahedron) or aliotriomorphic (round or irregular) and are to be found scattered or in bands. The size of the crystals varies between 0.03 and 0.2 mm and they are bright

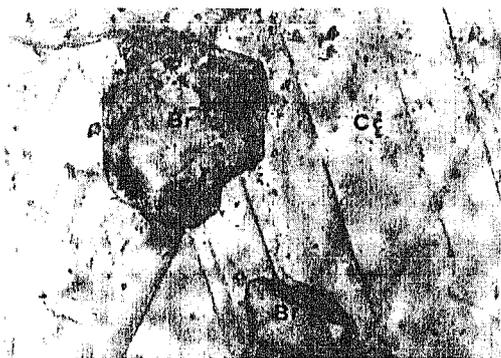


Fig. 1 Britholite crystals (51% of  $REE_2O_3$ ) in the carbonatite of Punta del Peñón Blanco, with greater relief than the calcite. Thin section X 200 PPL.

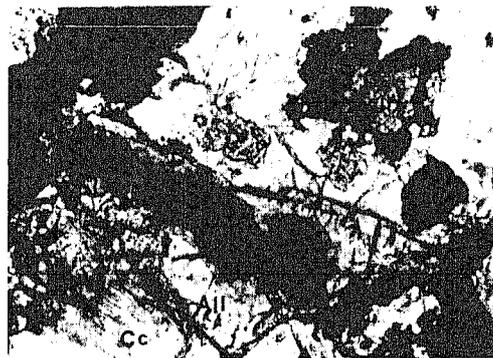


Fig. 2. Zoned allanite crystal. The central area is metamictic with high content of  $REE_2O_3$  and composition of britholite. Thin section X 200 PPL.

red or dark red, with no pleochroism and the double refraction masked by the natural colour. The analyses revealed values of Nb<sub>2</sub>O<sub>3</sub> of between 43.5 and 46.5% always in line with the proportion Nb+Ta>2 (see Table 1, analyses 11 and 12). As regards light REE<sub>2</sub>O<sub>3</sub> analysed, these elements varied between 3 and 16.5% with Ce most abundant (but not sufficient for it to be defined as Ce-pyrochlore) and the proportion of Nd always greater than La in a proportion of 1.5 and 1.7. The concentration of Na<sub>2</sub>O fluctuated between 2.5 and 4.5, that of ThO<sub>2</sub> between 0.6 and 0.8%, that of ZrO<sub>2</sub> between 0.2 and 0.4% and the Sr between 0.4 and 0.6%. There are no important substitutions of Ti by Nb, nor of REE, Th, Ba or Sr by Na and Ca. Magmatic hydrothermal pyrochlores have been cited in the carbonatites of Araxá (Brazil) and Panda Hill (Tanzania).

### 3. METALLOGENY

The characteristics of outcropping together with the mineralogical, petrological and geochemical features of the rocks which make up the alkaline complexes of Fuerteventura show that these are related spatially and genetically. Thus, the ultramafic and mafic materials of the complexes represent earlier magmatic fractions and are penetrated by far more differentiated silic elements which produce an alkaline metasomatism. The carbonatites are later manifestations and cut through the former rocks in the shape of dykes, breccias or shearbands.

The carbonatites which are the most evolved petrological facies of the complexes are residual magmatic carbonatites which were originated by fractioned crystallisation and immiscibility and where elements incompatible with REE were concentrated. These magma were low viscosity molten flows which were saturated in volatile elements (C, P, S and H<sub>2</sub>O amongst others) which transported some minerals which had been previously formed (aegirine-augite, feldspar Na-K, magnetite, garnet and zircon, etc.). These molten flows and fluids settled in cortical areas with varying physico-chemical characteristics, from late magmatic through to hydrothermal (with fluid inclusions in calcite and apatite in the carbonatites in Punta del Peñón Blanco and Punta Viento which contain slightly saline aqueous solutions -- T<sub>mice</sub>: -0.1/-0.9°C=<1.6% eq. wt. NaCl-- and with temperatures of homogenisation in liquid of between 330° and 390°C). In the deposit zone, the progressive crystallisation of heterogeneous paragenesis takes place (there may also be processes such as auto-metasomatism and recrystallisation), with minerals which are essentially carbonated together with silicates, phosphates, oxides, sulphides and sulphates, apart from precocious minerals. Logically, in the carbonatites found in the shear bands, we should also mention phenomena of deformation and metamorphism with processes of remobilisation, recrystallisation and neof ormation.

The current targets of REE exploration, with are the reflection of the market demands, are guided to high grade and purity mineralizations in specific

elements, more than to those containing remarkable concentrations in several REE. In Fuerteventura, the REE concentrations in the carbonatites described before are interesting (REE concentration range between 511 and 7,372 ppm), standing out those that appear in the Peñón Blanco, Caleta de la Cruz and Punta Nao within the PP-CL complex and in the headwater of Barranco de los Encantados in the E complex.

However, to define the economic-mining potential of the carbonatites of Fuerteventura is necessary to take into account other considerations:

1. The grades in REE of these rocks vary in the same outcrop and between one and the others, because the distribution of REE specific minerals (specially: britholite, allanite, pyrochlore and monazite) is irregular.

2. These minerals contain light REE (mainly Ce, La, Sm and Nd) with varying contents.

3. The volume occupied by the carbonatites bodies is minimum in the two alkaline complexes (PP-CL and E complex).

4. Some of these bodies are situated in areas protected by the Coast Law (intertid and coastal zones) and the Natural Environment Law of the Canary Islands (Betancuria Natural Park), or within the military shooting field of Pájara.

Thus, we can affirm that the actual economic-mining potential for REE of the carbonatites of Fuerteventura has low profitability. However, from a scientific point of view, these alkaline complexes with carbonatites are important because together with those of the Cape Verde Islands, are the only ones that appear subaerially in oceanic environments in the whole world.

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