Rare earth element resources on Fuerteventura, Canary

Islands, Spain: a geochemical and mineralogical approach 2

3

1

Marc Campeny¹, Inmaculada Menéndez², Luis Quevedo^{2,3}, Jorge Yepes², Ramón 4 Casillas⁴, Agustina Ahijado⁴, Jorge Méndez-Ramos³, José Mangas² 5

6

- 7 8 9 10 ¹ Departament de Mineralogia, Museu de Ciències Naturals de Barcelona, Passeig Picasso s/n, 08003 Barcelona, Spain
- ² Instituto de Oceanografía y Cambio Global, IOCAG, Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Spain
- 11 12 13 14 15 16 17 ³ Instituto de Materiales y Nanotecnología, Departamento de Física, Universidad de La Laguna, apartado correos 456, 38200 La Laguna, Tenerife, Spain
- ⁴ Departamento de Biología Animal, Edafología y Geología, Universidad de La Laguna, apartado correos 456, 38200 La Laguna, Tenerife, Spain.

Correspondence to: Marc Campeny (mcampenyc@bcn.cat)

Abstract. Rare earth elements (REEs) play a pivotal role in the ongoing energy and mobility transition challenges. Given their critical importance, governments worldwide and especially from the European Union, are actively promoting the exploration of REE resources. In this context, alkaline magmatic rocks (including trachytes, phonolites, syenites, melteigites and ijolites), carbonatites and their associated weathering products were subjected to a preliminary evaluation as potential targets for REE exploration on Fuerteventura Island (Canary Archipelago, Spain) based on mineralogical and geochemical studies. These lithologies show significant REE concentrations. However, only carbonatites exhibit the potential to host economically viable REE mineral deposits. REE concentrations in carbonatites of about 10,300 ppm REY (REEs plus yttrium) have been detected, comparable to other locations hosting significant deposits of these critical elements worldwide. Conversely, alkaline magmatic rocks and the resulting weathering products display limited REE contents. Notably, REEs in carbonatites are associated with primary accessory phases such as REE-bearing pyrochlore and britholite, and secondary monazite. The carbonatites of Fuerteventura hold promise as prospective REE deposits within a non-conventional geological setting (oceanic island). However, due to intricate structural attributes, the irregular distribution of these mineralizations and possible land use and environmental constraints, additional future detailed investigations are imperative to ascertain their viability as substantial REE resources.

Keywords. Rare earth elements, Carbonatites, Fuerteventura, Canary Islands, Weathering

18

19

20

21

22 23 24

30

31

32

33

1 Introduction

37

38 The implementation of actions to mitigate climate change is one of the major global challenges facing 39 society today. In this regard, the European Commission (EC) has adopted a series of economic and 40 technological proposals aimed at reducing greenhouse gas emissions and transforming Europe into the first 41 climate-neutral continent by 2050. These guiding principles, encompassed in the European Green Deal 42 (EGD) (European Commission, 2019), are directly linked to the establishment of an energy and mobility 43 transition based on green technologies that will replace the current fossil fuel-based model. However, in 44 order to achieve the ambitious targets, other finite resources will be essential: metals. Some of them, 45 commonly referred to as green metals, will play a crucial role in a successful energy and mobility transition 46 and, consequently, in achieving the neutrality goals outlined by the EGD (Graedel et al., 2015; Jyothi et al., 47 2020). Among the green metals is the group of rare earth elements (REEs) that are critical for a wide range 48 of high-tech applications such as wind turbines, electric vehicles, rechargeable batteries, energy-efficient 49 lighting, optical telecommunications, photovoltaic cells, solar energy harvesting or artificial photosynthesis 50 for "green hydrogen" (H₂) generation (Méndez-Ramos et al., 2013; Acosta-Mora et al., 2018; Wondraczeck 51 et al, 2015). Such elements are also commonly known as the vitamins of modern industry (Alonso et al., 52 2012; Chakhmouradian and Wall, 2012; Massari and Ruberti, 2013; Charalampides et al., 2015; Weng et 53 al., 2015; Balaram, 2019). 54 According to the International Union of Pure and Applied Chemistry (IUPAC), REEs comprise a group of 55 17 chemical elements: scandium (Sc), yttrium (Y) and the 15 members of the lanthanide series (Connelly 56 et al., 2005). The term "rare" is confusing because, even though REEs seldom occur in pure mineral phases, 57 their average concentration in the Earth's crust is around 125 ppm, surpassing other common industrial 58 metals such as copper, gold or platinum (Long et al., 2010; Rudnick and Gao, 2014). 59 Given their pivotal role in modern industry and green technologies, as well as the projected increase in 60 demand for REEs in the coming years, governments worldwide are actively promoting the exploration of 61 new REE resources (Barteková and Kemp, 2016). In line with this, the EC included light rare earth elements 62 (LREEs) and heavy rare earth elements (HREEs) in the 2023 list of critical raw materials (CRMs), 63 acknowledging them as essential and considering HREEs as the material with the highest supply risk 64 (European Commission, 2023a).

65 On March 16, 2023, the EC presented a bold initiative to the European Parliament: The European Critical 66 Raw Materials Act. This regulation aims to establish a comprehensive framework to ensure a secure and 67 sustainable supply of CRMs, including REEs, in the coming years (European Commission, 2023b). 68 The search for REEs in the geological environment has primarily centred on investigating non-conventional 69 HREE sources such as soils and weathering products (Braun et al., 1993; Wang et al., 2010, Wang et al., 70 2013; Berger et al., 2014; Aiglsperger et al., 2016; Torró et al., 2017; Reinhardt et al., 2018; Borst et al., 71 2020), but also traditional and well-known LREE-bearing lithologies, such as carbonatites (Goodenough et 72 al., 2016; Yang et al., 2019; Pirajno and Yu, 2022). 73 Carbonatites are igneous rocks formed by carbonate mantle melts and are genetically associated with a 74 wide range of mafic, ultramafic, and alkaline silicate rocks (Yaxley et al., 2002). Although carbonates such 75 as calcite or dolomite are their main forming minerals, a significant portion of carbonatites contain 76 accessory phases enriched in critical metals such as REEs (Christy et al., 2021). REEs can be contained in 77 fluorcarbonates (e.g., bastnäsite, parisite, huanghoite, synchysite), phosphates (e.g., monazite, 78 rhabdophane), silicates (e.g., allanite), or even oxides (e.g., REE-bearing pyrochlore, cerianite). These 79 accessory minerals make carbonatites the main current REE source, representing 86.5% of the deposits 80 under exploitation for these elements (Liu et al., 2023). However, although carbonatites are rare rocks, 81 predominantly found in continental rifts associated with cratons (Humphreys-Williams et al., 2021), they 82 have exceptionally been described in other geological contexts, most notably oceanic islands associated 83 with hotspots, such as Cape Verde (Mourão et al., 2010; De Ignacio et al., 2018;) or Fuerteventura in the 84 Canary Islands (Mangas et al., 1996; Carnevale et al., 2021). 85 The petrogenesis of carbonatites is still a debated topic (Anenburg et al., 2021; Yaxley et al., 2022). 86 Different processes have been proposed for their formation, although there is a consensus that they originate 87 from primary fusion processes derived from a carbonated mantle (Kamenetsky et al., 2021). For the specific 88 case of the oceanic carbonatites, this debate is even more lively. Doucelance et al. (2010) suggested a 89 shallow origin from low-degree partial melting at the base of the oceanic lithosphere. Other authors have 90 proposed the involvement of unmixing process linking to alkaline magma suites (Weidendorfer et al., 91 2016), the action of hydrothermal fluids of marine origin enriched in Ca that would have serpentinized the 92 mantle (Park and Rye, 2013) or even the contribution of recycled marine carbonates through subduction or 93 assimilated in shallow magma chambers (Démeny et al., 1998; Hoernle et al., 2002; Doucelance et al., 94 2014).

The present work concentrates on the mineralogical and geochemical study of carbonatites and associated alkaline igneous rocks, along with their weathering products, in three different sectors in the western region of Fuerteventura (Canary Islands, Spain; Figure 1). The primary goal of this research is to conduct an initial evaluation of these materials, which are genetically associated with a volcanic island linked to an oceanic intraplate magmatism. This assessment aims to enhance our understanding of REE accumulation while appraising the potential of this peculiar geological environment as a non-conventional source of REE.

2 Geological setting

2.1 The Canary Island Seamount Province

The Canary Islands archipelago, located between 27°N and 30°N of latitude, is part of the Canary Island Seamount Province (CISP). This volcanic region forms a band of approximately 1300 km in length and 350 km in width, running parallel to the African continental margin. Within the CISP, there are over 100 seamounts and up to 8 emerged islands: El Hierro, La Palma, La Gomera, Tenerife, Gran Canaria, Lanzarote, Fuerteventura and Savage islands (Courtillot et al., 2003; Schmincke and Sumita, 2010; van den Bogaard, 2013). Based on magnetic anomaly measurements and dating of both emerged and submarine igneous materials, volcanic activity in the CISP spans more than 142 Ma, from the Early Cretaceous to the present day (Frisch, 2012; van den Bogaard, 2013; Longpré and Felpeto, 2021).

2.2 Fuerteventura Island

Fuerteventura, the easternmost island of the Canarian archipelago, along with Lanzarote, forms the emergent crest of the Eastern Canarian Volcanic Ridge, which is located approximately 100 km offshore from the Moroccan coast (Figure 1). Fuerteventura is the oldest island in the archipelago, with its initial stages of formation linked with submarine volcanic activity, dating to the Oligocene (~34 Ma). The first episodes of subaerial volcanism occurred around ~23 Ma (Coello, 1992; Ancochea et al., 1996; Pérez-Torrado et al., 2023).

Fuerteventura is characterized by the occurrence of three distinct main geological units, arranged in order

from oldest to youngest: the Fuerteventura basal complex (FBC), the Miocene subaerial volcanic units, and the Pliocene-Quaternary volcano-sedimentary facies (Fúster et al., 1968; Le Bas et al., 1986; Muñoz et al.,

122 2005; Gutiérrez et al., 2006; Troll and Carracedo, 2016).

2.2.1 The Fuerteventura basal complex

The FBC unit mainly outcrops in the western part of the island (Figure 1). Two different groups of lithofacies may be distinguished: (1) Early Jurassic to Late Cretaceous oceanic crust materials (Steiner et al., 1998), constituted by mid-ocean ridge basalts and oceanic sediments; (2) Oligocene submarine and transitional volcanic rocks associated with plutonic bodies and dyke swarms (Feraud et al., 1985; Hobson et al., 1998; Gutiérrez et al., 2006). In this second group, a set of lithologies can be distinguished related to an ultra-alkaline-carbonatitic magmatic pulse that occurred ~25 Ma (Le Bas, 1981; Barrera et al., 1986; Balogh et al., 1999). Additionally, alkaline ultramafic, mafic and felsic plutonic rocks such as wehrlites, pyroxenites, gabbros and syenites intruded the previously existing Oligocene materials, forming distinctive ring complexes (Muñoz et al., 2005). These magmatic rocks, predominantly of Oligocene age, have been interpreted as episodes of submarine and transitional growth in Fuerteventura (Le Bas et al., 1986; Gutiérrez et al., 2006).

In general, outcrops related with the FBC intrusive assemblage exhibit significant variations and four distinct morphologies and characteristic textures can be identified (Fúster et al., 1968; Barrera et al., 1986; Le Bas et al., 1986; Fernández et al., 1997; Mangas et al., 1992, 1994, 1997; Ahijado 1999; Ancochea et al., 2004; Ahijado et al., 2005; Muñoz et al., 2005):

- 140 (1) Basaltic, alkaline and carbonatitic dykes and veins of meter-scale, decimeter-scale, and 141 centimeter-scale, that are randomly distributed, resulting in a chaotic arrangement (Figure 2a, b). 142 Related to the carbonatite veins and dikes, an intense fenitization may occur.
 - (2) Shear zones (Fernández et al., 1997), characterized by gradual or diffuse boundaries, which display assimilation structures between different rock bodies, along with the presence of mylonites, and brecciated textures resulting from deformation (Figure 2c).
 - (3) Pegmatitic textures developed within certain rock bodies, often containing centimeter-sized crystals of rock-forming minerals (Figure 2d).
 - (4) Contact metamorphism and metasomatism, as well as skarn zones that occur in deformed or undeformed carbonatites, influenced by subsequent hydrothermal fluid circulation (Ahijado et al., 2005; Casillas et al., 2008, 2011).

152 In addition, during Miocene magmatic pulses, alkaline plutons were formed in the central-western part of 153 Fuerteventura Island north of the locality of Pájara (sector 2, Figure 1). These intrusions constitute typical 154

ring complexes of alkaline magmatic rocks, including nepheline syenites, syenites, and trachytes (Muñoz,

1969). They are regarded as the most recent rocks in the FBC (Figure 1) and have been dated using the K-

156 Ar method, yielding an approximate age of 20.6 ± 1.7 Ma (Le Bas et al., 1986; Holloway and Bussy, 2008).

2.2.2 Miocene subaerial volcanic unit

143

144

145

146

147

148

149

150

151

155

157

158

159

160

161

162

163

164

165

166

167

168

169

During the Miocene, Fuerteventura witnessed the formation of up to three volcanic edifices (Figure 1; Coello et al., 1992; Ancochea et al., 1996). The northern volcanic structure, referred to as the Tetir edifice, experienced two volcanic construction phases between 22 and 12.8 Ma (Balcells et al., 1994). These episodes involved the eruption of basalts, picritic basalts, oceanic basalts, trachybasalts and trachytes. In the central part of the island, the Gran Tarajal edifice developed three different construction phases spanning from 22.5 to 14.5 Ma (Balcells et al., 1994). On the Jandía Peninsula, in the southern part of the island, a volcanic edifice comprising both basaltic and trachybasaltic materials emerged. It formed three successive construction episodes occurring between 20.7 and 14.2 Ma ago (Balcells et al., 1994). Based on their mineralogical and petrological features, the lithologies comprising this unit have not been considered as potentially containing significant concentrations of REEs. Therefore, they have not been included in the evaluation conducted in the present study.

2.2.3 Pliocene and Quaternary volcano-sedimentary facies

After the subaerial volcanic activity during the Miocene, a period of volcanic quiescence ensued, leading to the erosion of the previously formed volcanic edifices. Subsequently, during the Pliocene (between 5.3 and 2.6 Ma), a phase of magmatic rejuvenation began, characterized by scattered Strombolian eruptions (Figure 1). Concurrently, various sedimentary formations emerged across the entire island, including littoral and shallow-water marine deposits, as well as aeolian, colluvial, and alluvial subaerial sediments and paleosols from the Pliocene to the Quaternary (Fúster et al., 1968; Zazo et al., 2002; Ancochea et al., 2004). The soils on Fuerteventura are predominantly classified as eutric cambisols and lithosols-vitric andosols, according to the FAO/UNESCO (1970) nomenclature. However, the current arid and deforested conditions have led to extensive erosion of the weathered rock profiles present in different areas of the island. Edaphic calcretes are abundant in Fuerteventura (Alonso-Zarza and Silva, 2002; Huerta et al., 2015), with their primary source of calcium believed to be the Pliocene paleodunes formed by calcarenites, rather than the parent igneous rock itself (Chiquet et al., 1999; Huerta et al., 2015; Alonso-Zarza et al., 2020). Interestingly, the aeolian dust deposits predominantly originate from the Sahara Desert (Goudie and Middleton, 2001; Menéndez et al., 2007; Scheuvens et al., 2013).

3 Materials and Methods

3.1 Sampling

Alkaline magmatic rocks and especially carbonatites are considered potential targets for the exploration of rare earth elements (Goodenough et al., 2016; Balaram et al., 2019; Anenburg et al., 2021; Beland and Jones, 2021). In Fuerteventura, these types of lithologies are found in two distinct geological areas: the Oligocene (sectors 1 and 3; Figure 1) and the Miocene lithologies related with the FBC (sector 2, Figure 1).

Considering that weathering profiles may concentrate REE in larger quantities than primary bedrocks (Bao

and Zhao, 2008; Menéndez et al., 2019, Braga and Biondi, 2023; Chandler et al., 2024), these lithological formations were included in the present evaluation study and sampling was conducted on a selection of six

different profiles: (1) Agua Salada ravine (sector 1) and (2) Aulagar ravine (sector 3), developed on carbonatites, (3) the FV-30 road, (4) Las Peñitas quarry, (5) Palomares ravine and (6) the Pájara profiles, on syenite bedrock (Figure 1; Table S1).

Accordingly, a systematic sampling campaign was conducted in three different sectors of Fuerteventura, targeting alkaline and carbonatitic igneous rocks and their associated weathering products. The specific locations of these predetermined sectors are outlined in Figure 1. As a result, a set of 29 representative samples of potentially REE-enriched magmatic rocks, along with 21 samples of associated weathering products, were collected for further analysis and evaluation (Table S1). For the weathering products, we conducted six sampling profiles (labelled A to F; Figure 1) at various suitable points to compare the mineralogical and geochemical changes resulting from weathering of the primary magmatic rocks.

3.2 Petrographic and mineralogical studies

Selected samples of magmatic rocks were prepared in thin sections for textural and mineralogical analysis at the Laboratory of Geological and Paleontological Preparation of the Natural Sciences Museum of Barcelona (LPGiP-MCNB; Barcelona, Spain). A representative subset of these samples was also examined using a JEOL JSM-7100 field emission scanning electron microscope (FE-SEM) at the Scientific and Technological Centers of the Universitat de Barcelona (CCiTUB). The FE-SEM system is equipped with an INCA Pentaflex EDS (energy dispersive spectroscopy) detector (Oxford Instruments, England), which allowed for the acquisition of semi-quantitative analyses of mineral phases. The general operating conditions for the FE-SEM were a 15-20 kV accelerating voltage and a 5 nA beam current. To achieve accurate and precise mineralogical identification and characterization of the weathering magmatic rocks and calcretes, X-ray powder diffraction (XRPD) measurements were performed using a PANalytical Empyrean powder diffractometer equipped with a PIXcel1D Medipix 3 detector at the Integrated XRD Service of the General Research Support Service of La Laguna University, Spain. The diffractometer employed incident Cu K_α radiation at 45 kV and 40 mA, along with an RTMS (real-time multiple strip) PIXcel1D detector with an amplitude of 3.3473° 20. The diffraction patterns were obtained by scanning random powders in the 2θ range from 5° to 80°. Data sets were generated using a scan time of 57 seconds and a step size of 0.0263° (20), with a 1/16° divergence slit. Mineral identification and semiquantitative results were obtained using the PANalytical's HighScore Plus search-match software (v. 4.5) with a PDF+ database.

3.3 Geochemical analyses

The major elements composition of carbonates from carbonatites was studied using an electron probe microanalyzer (EPMA) system. The EPMA analyses were conducted on a JEOL JXA-8230 electron microprobe, equipped with five wavelength-dispersive spectrometers and a silicon-drift detector EDS, located at the CCiTUB. The spot mode was employed for the analyses and the electron column was set to an accelerating voltage of 15 kV and a beam current of 10 nA. Standard counting times of 10 seconds were used, along with a focused beam, to achieve the highest possible lateral resolution. The analytical standards employed during the analysis process were: celestine (PETJ, Sr K_{α}) wollastonite (PETL, Ca K_{α}), periclase (TAPH, Mg K_{α}), hematite (LiFH, Fe K_{α}), rhodonite (LiFH, Mn K_{α}) and albite (TAPH, Na K_{α}). Bulk-rock geochemical data of major and trace element composition were obtained by X-ray fluorescence (XRF) and inductive coupled plasma (ICP)-emission spectrometry. The samples were prepared by lithium metaborate/tetraborate fusion and nitric acid digestion at the ACTLABS Activation Laboratories Ltd. (Ancaster, Canada).

4 Results

4.1 Petrography and mineralogy

247 4.1.1 Alkaline magmatic rocks and carbonatites

as well as Miocene alkaline lithologies (K-Ar age of 20.6±1.7 Ma; Le Bas et al., 1986), that form part of the FBC. Their outcrops extend across kilometer-scale areas but exhibit high heterogeneity at a detailed level due to the occurrence of numerous small intrusions, ranging in size from metric to decimetric dimensions (Figs. 2a, b). At a mineralogical level, separation of the different types of alkaline rocks found in the FBC is complex because these lithologies are intimately associated and infiltrate diffusely, leading to the formation of hybrid intrusions. The materials with the most mafic composition correspond to pyroxenites and melteigites, and their formation is associated with the earliest magmatic fractions. However, these are commonly spatially associated with more differentiated rocks, mainly ijolites, nepheline syenites, and syenites. All these lithologies have a relatively simple mineralogy, characterized by varying proportions of nepheline (10-30%) modal) and potassium feldspar (50-80% modal), associated with aegirine-augite and biotite (10-30%

The primary lithologies under study, consist of Oligocene (~25 Ma) alkaline igneous and carbonatitic rocks,

260 modal). A set of accessory minerals with varying proportions (always less than 5% modal) also occur, 261 including ilmenite, titanite, zircon, and fluorapatite. 262 At a textural level, the alkaline series lithologies of the FBC present granular textures with millimeter-sized 263 euhedral grains. However, in some of the intrusions in sectors 2 and 3, pegmatitic syenites-ijolites were 264 detected with centimeter-sized grains characterized by the presence of large aegirine-augite crystals. 265 Some of the intrusions described in the three sectors show aphanitic textures caused by faster cooling, 266 resulting in rocks with similar mineralogy but extrusive-type textural characteristics. Therefore, due to their 267 textural features, some dikes and apophyses, although mineralogically equivalent, should be classified as 268 trachytes and phonolites. 269 Carbonatitic intrusions commonly co-occur with the alkaline rocks, sharing similar morphology, textures, 270 and spatial distribution within the outcrops (Figure 2e). Furthermore, alkaline and/or carbonatitic intrusions 271 can be occasionally associated with mafic intrusions, primarily pyroxenites and alkaline gabbros. In 272 addition, a subsequent set of mafic dikes with basaltic composition overlaps the previous intrusive bodies 273 (Figs. 2a, b). 274 All carbonatites described in different outcrops from sectors 1 and 3 are predominantly composed of calcite 275 (95% modal) and can thus be classified as calciocarbonatites (Le Maitre, 2005). None of the studied samples 276 shows the occurrence of ferromagnesian carbonates such as ankerite, dolomite, and/or siderite, as well as 277 REE carbonates. Texturally, calcite occurs as euhedral crystals ranging in size from millimetres to 278 centimetres, often recrystallized and exhibiting polysynthetic twinning. In some cases, a secondary micritic 279 calcite matrix is present, filling interstitial spaces and fractures. 280 The major element composition of calcite is relatively consistent across all the carbonatite samples. 281 Notably, there are significant contents of SrO, with values of up to 5.43 wt%, while REEs are absent from 282 the carbonate composition (Table S2). 283 The accessory mineralogy (~5% modal) comprises disseminated phases within the calcium carbonate. 284 Among them, the occurrence of minerals from the spinel group, including magnetite (Figure 3a), and 285 primarily jacobsite, occurring as subhedral crystals of up to 50 µm (Figure 3b). Another characteristic 286 mineral is perovskite, occurring as subhedral crystals of up to 100 µm. These grains are remarkable for 287 their significant Nb contents, as described in other carbonatitic localities worldwide (Torró et al., 2012). 288 Britholite also occurs as subhedral crystals of up to 100 µm (Figure 3b). This primary britholite contains 289 significant LREE content (Figure 4), and its alteration leads to the formation of secondary REE-enriched phosphates, mainly monazite-Nd (Figure 3c), which also contains substantial amounts of La and Ce (Figure 4). REEs, in addition to occurring in primary britholite and secondary monazite, were also detected in tiny pyrochlore grains, heterogeneously disseminated in the calcite groundmass (Figure 3b). In some cases, pyrochlore forms euhedral crystals of up to 20 µm, also included in calcite (Figure 3d). This pyrochlore shows slight zoning towards plumbopyrochlore (Christy and Atencio, 2013), with significant enrichment in Pb observed at grain borders (Figure 3d). Carbonatites can be affected by certain contact metamorphism, especially in sectors 1 and 3 (Figure 1) and may exhibit a slightly different mineralogy from the one described thus far. This is characterized by the occurrence of skarn-type metamorphic minerals, formed due to the interaction between carbonatites and spatially associated silica-rich rocks. Among these minerals, there are subhedral crystals of andradite, up to 30 µm in size, implanted in a matrix of secondary calcite and phlogopite, exhibiting pronounced zoning with kerimasite cores (Figure 3e). In these areas, the occurrence of REE mineralizations associated with allanite (Figure 3f) is also typical. Allanite occurs as granular aggregates associated with hydrothermal secondary sulfates, primarily baryte (Figure 3f), but occasionally celestine (Figure 3c). This particular mineralogy, typically associated with skarn formations, emerges from the interaction between a carbonatite intrusion and surrounding silicate rocks, in contrast to the typical process. It has recently gained attention from several researchers in various carbonatite locations worldwide, who have

308

309

310

311

312

313

314

315

316

317

318

290

291

292

293

294

295

296

297

298

299

300

301

302

303

304

305

306

307

4.1.2 Weathering products

In certain areas within the three studied sectors (Figure 1), there is evidence of the development of characteristic shallow geological formations consistently associated with weathering, which affect the outlined magmatic lithologies (Figs. 5, 6). These geological products were studied through the analysis of six alteration profiles, developed on carbonatites (Agua Salada and Aulagar) and syenites (Palomares ravine, FV-30 road, Las Peñitas quarry, and Pájara) (Figure 1).

The carbonatite-calcrete sections generally consist of centimetre-scale calcrete veins injected into the bedrock, seemingly without any apparent connection to the current upward lithosol (Figure 5). In general, the development of soils or weathering products was not detected on carbonatites in any of the studied sectors of the FBC.

coined the term antiskarn to describe it (Anenburg and Mavrogenes, 2018; Yaxley et al., 2022).

Weathering products developed on syenite bedrock are generally more abundant, and the corresponding alteration profiles are better preserved than in carbonatites. The cambic B horizon displays reddish to yellowish colorations (5YR6/6), with a thickness of up to 20-30 cm. Additionally, it is common to find BC horizons instead of B horizons, while the C horizon is well-developed, reaching a 30-40 cm thickness at certain levels of the profile (Figure 6). Furthermore, except for the Las Peñitas profile (E profile, Figure 1), centimetre-scale calcrete bands (Bk; Jahn et al., 2006) were also detected in deeper layers across all the studied profiles.

In terms of mineralogical composition, carbonatite profiles exhibit significant changes due to weathering. In general, weathering processes lead to a reduction in calcite, the disappearance of fluorapatite, and the formation of secondary minerals like palygorskite (Figure 7). The contribution from lateral slope movement is also evident through the presence of residual plagioclase and clinopyroxene.

In the case of syenite weathering profiles, illite/chlorite and kaolinite are the predominant secondary products, followed by muscovite and palygorskite (Figure 7). Other minerals such as quartz were also detected, even in the C horizons.

4.2 Bulk-rock and mineral geochemistry

Chemical analysis of the major, minor and trace elements were carried out in order to evaluate the geochemical features and the distribution of REEs, on 25 representative samples of igneous rocks from the FBC, including trachytes, phonolites, syenites, ijolites and carbonatites (Table S3). In addition, we also analysed 21 samples of weathering products (Table S4).

The total REY (REEs plus yttrium) content in the FBC igneous rocks exhibits widespread and significant enrichment in comparison to the average crustal values (~125 ppm, Rudnick and Gao, 2014). Notably, the extrusive and magmatic alkaline lithologies (trachytes and phonolites as well as syenites and ijolites) show variable REY values ranging between about 230 and 1,400 ppm (Table S3). In contrast, the carbonatitic rocks exhibit REY content more than ten times greater than the alkaline lithologies, with specific samples reaching maximum values of up to about 10,300 ppm, as evidenced in sample 85a sourced from a carbonatite outcrop in sector 1 (Table S3).

The weathered magmatic rocks, though moderately significant in REY content relative to the average crustal values (Table S4), still exhibit slightly lower levels compared to the content observed in the associated alkaline and carbonatitic protoliths (Table S3). A contrasting pattern emerges in the calcretes,

349 where REY values experience a sharp reduction, presenting virtually negligible values ranging between 20 350 and 72 ppm REY. These levels are significantly below the average Earth's crust values (Rudnick and Gao, 351 2014) and are markedly lower than those observed in both the alkaline lithologies and, particularly, the 352 carbonatites of the FBC. 353 REE normalized diagrams further underscore this distribution, portraying elevated content in the 354 carbonatites, followed by the alkaline rocks (Figure 8a). Meanwhile, the weathered magmatic rocks and 355 calcretes (Figure 8b) display significantly lower values. All studied lithologies exhibit clear negative 356 patterns, indicative of enrichment in LREEs relative to HREEs. Notably, carbonatites and alkaline rocks 357 (Figure 8a) exhibit a flattening of these negative patterns in the final segment, indicating a certain degree 358 of HREE enrichment. 359 The FCB carbonatites exhibit a depletion in some critical elements commonly associated with this lithology 360 such as Nb or Ta (Table S3). Negative anomalies of both Nb and Ta are clearly observed in the multi-361 element diagrams of carbonatite samples (Figure 9a). However, given the presence of pyrochlore in the 362 carbonatites, these anomalies in Nb and Ta are likely not indicative. We interpret that the low concentrations 363 of these elements could be attributed to an analytical artifact that would underestimate the contents of High 364 Field Strength Elements (HFSE) due to the challenge of pyrochlore dissolution in the analytical digestion 365 protocols employed. These protocols have been primarily devised to assess the contents of REEs rather 366 than HFSE. Additionally, alkaline rock patterns also show a distinctive negative anomaly in Sr (Figure 9b). 367 As for the weathering products, their contents of other minor elements do not indicate significant 368 concentrations of metals or critical elements like Nb or Ta (Table S4). The multi-element diagrams for the 369 calcretes exhibit a negative Ta anomaly (Figure 9c), while the patterns of weathered magmatic rocks do not 370 reveal notable anomalies in any group of elements (Figure 9d). 371 A specific geochemical study of REE distribution in the six studied weathering profiles was also conducted 372 (Figure 10). The main objective was to evaluate the geochemical interactions between the protolith and the 373 related weathering lithologies, with the aim of detecting potential REE enrichments or depletions caused 374 by weathering processes. 375 In the exchange patterns of calcretes spatially associated with carbonatitic protoliths, as analyzed in the 376 Agua Salada and Aulagar ravine profiles (Figs. 10A, B), REE concentrations are two orders of magnitude 377 lower than in the carbonatite (Figure 10A), as also previously determined from the REE diagrams (Figure 378 8). Notably, it was found that the REE concentration is directly proportional to the distance from the protolith (Figure 10B), and calcrete samples with the highest REE concentrations (sample 14; Figure 10) were found in closer proximity to the primary carbonatites than more REE depleted samples (samples 15 and 18; Figure 10B). In addition, although the values of all elements are depleted in the calcrete patterns, there is a greater depression in LREE than in HREE relative to the protolith, resulting in typically positive patterns, except for sample 76 from the Agua Salada ravine, where a clear inverse trend is observed (Figure 10A).

In general, the diagrams in Figure 10 show that weathering products on syenites exhibit enrichment relative to the protolith (green areas in Figs. 10C, D, E). However, calcrete samples, whether derived from carbonatites or syenites, consistently show depletions compared to the protolith contents (reddish areas in Figs. 10C, D, F). The diagrams corresponding to the weathering products generated on syenites exhibit similar morphologies (Figs. 10C, D, E, F). Overall, these lithologies are characterized by enrichment in

REEs relative to the protolith as well as V-shaped patterns, featured by the presence of a negative anomaly

in Eu, which is also reported in all C and B horizons developed on syenites, except sample 61 (Figure 10C),

394 5 Discussion

5.1 REE evaluation of the FBC magmatic rocks

and is likely related to plagioclase crystallization.

The FBC magmatic rocks, in the three study sectors, encompass alkaline lithologies (trachytes, phonolites, syenites, melteigites, and ijolites) as well as carbonatites. Regarding the group of alkaline rocks, the detected REE content varies between 214 and 1,330 ppm (Table S3), significantly higher than the average concentration determined in the Earth's crust (~125 ppm, Rudnick and Gao, 2014). However, this finding is not surprising, and the observed values in Fuerteventura are not anomalous, as these types of lithologies typically exhibit REE concentrations within this range (Dostal, 2017). Therefore, the measured REE concentrations are neither significant nor sufficiently elevated to hypothetically consider these lithologies as a potential non-conventional deposit of these critical elements in the FBC.

On the other hand, FBC carbonatites present significantly higher values in terms of REE content. In the studied carbonatite samples from sectors 1 and 3 (carbonatites do not outcrop in sector 2), REE content ranges between about 1300 ppm and 10,300 ppm. The latter value corresponds to the richest REE-detected sample in the entire FBC, which is located in the Agua Salada ravine area of sector 1 (Table S3; Figure 1).

408 The reported REE content values in the FBC carbonatites are similar to the general average concentrations 409 found in other locations worldwide where carbonatites are exploited for REE extraction. This is the case, 410 for example, of Bayan Obo, the largest REE mine in the world in terms of reserves and production (Lai et 411 al., 2015; Liu et al., 2018). In this locality, high-grade carbonatites exhibit average concentrations of 2880 412 ppm (Wu et al., 2008; Smith et al., 2015, 2016), which are equivalent to those measured in some of the 413 samples from Fuerteventura. It should be noted that low-grade carbonatite ore from Bayan Obo presents 414 extremely high values in comparison to the FBC, with REE concentrations reaching 30,750 ppm (Chao et 415 al., 1997; Smith et al., 2016). 416 Another significant example is the Mountain Pass carbonatite in California, USA, regarded as the largest 417 REE mine in the American continent, intermittently in operation for REE extraction since 1954 (Olson et 418 al., 1954; Haxel, 2005). In this REE deposit, average value across the whole complex are around 2580 ppm 419 (Castor et al., 2008; Mariano and Mariano, 2012; Smith et al., 2016), also in line with REE concentrations 420 detected in the present study for the FBC carbonatites. 421 This comparative analysis can also be carried out using normalized REE values (Figure 11). In this regard, 422 FBC carbonatites are significantly depleted in LREE compared to those from Bayan Obo (Yang et al., 423 2019) and Mountain Pass (Castor et al., 2008), although they show similar values to other REE deposits 424 associated with carbonatites, such as those in Ashram, Canada (Beland and Jones, 2021) and Bear Lodge, 425 USA (Moore et al., 2015; Smith et al., 2016; Figure 11). However, the pattern of the Fuerteventura 426 carbonatites exhibits a slightly less pronounced slope, indicating a higher relative content of HREE, which 427 are considered the materials with the highest risk of supply among all the CRMs defined by the EC 428 (European Commission, 2023a). In fact, in the FBC carbonatites, the normalized HREE values are 429 equivalent to those reported in the primary carbonatitic rocks from the deposits of Bayan Obo (China) and 430 Mountain Pass (USA) (Figure 11). The relative significant HREE content reported in FBC carbonatites 431 holds particular significance for several economic and technological reasons. The use of HREEs, such as 432 Yb, Er, and Tm, is of particular interest in cutting-edge photonic and nanotechnology applications. 433 At the mineralogical level, it was observed that, in the FBC carbonatites, the main REE-hosting minerals 434 are accessory phases; primarily minerals from the pyrochlore group, found as disseminated euhedral micro-435 crystals implanted in primary calcite (Figs. 3b, d). Another REE-bearing mineral in the FBC carbonatites 436 is britholite, which exhibits significant LREE content. However, this mineral is commonly altered to monazite (Figs. 3c, 4), interpreted as a secondary phase but also a carrier of these critical elements (Chen et al., 2017).

Another noteworthy aspect is the lack of REE fluorcarbonates like bastnäsite REE(CO₃)F, parisite Ca(REE)₂(CO₃)₃F₂, synchysite Ca(REE)(CO₃)₂F or huanghoite Ba(REE)(CO₃)₂F. They do not occur in the FBC, as they do in other REE deposits associated with, for example, the Bayan Obo carbonatite or the Sulphide Queen carbonatite from Mountain Pass (Castor et al., 2008; Smith et al., 2015, 2016). This point

is crucial for a future hypothetical evaluation of the FBC carbonatites, as the processing of oxides and

phosphates for REE extraction is a much more complex and expensive treatment process than for REE-

bearing carbonates (McNulty et al., 2022).

446

447

448

449

450

451

452

453

454

455

456

457

458

459

460

461

462

463

464

465

466

437

438

439

440

441

442

443

444

5.2 REE evaluation of associated weathering products

The weathering materials developed on magmatic rocks, also analysed for their REE concentrations, constitute the remnants of soils that were interpreted as developed under wetter conditions during a humid phase of the oxygen isotope stage 2, spanning from 29 to 20 thousand years BP (Huerta et al., 2016). This period aligns with the last glacial maximum, marked by heightened humidity in the Canary Islands, resulting in slope erosion and the formation of talus flatiron (Gutiérrez-Elorza et al., 2013). Over time, these materials have undergone substantial volume reduction due to human-driven deforestation and erosion, primarily before the 15th century (Machado-Yanes, 1996). Notably, topography plays an essential role in the distribution of these weathering profiles and influences specific physical attributes such as slope (FAO/UNESCO, 1974). The studied weathering products developed on syenite rocks (profiles C, D, E, F; Figs. 1, 7) are classified by FAO/UNESCO (1974) as eutric cambisols, reflecting a Mediterranean climate condition. Indeed, on the African continent, which is adjacent to the Canary Islands, eutric cambisols are primarily found within the tropical subhumid zone, gradually transitioning into the semi-arid zone (FAO/UNESCO, 1974). These syenite weathering profiles exhibit better-preserved characteristics and a more significant extent compared to those studied in carbonatites (profiles A and B; Figs. 1, 7). In general, intensive weathering plays a crucial role in the formation of REE deposits, as these elements tend to be concentrated in such geological formations compared to others leached during the weathering process. This phenomenon is exemplified in several locations worldwide, where REE deposits associated with weathering products occur: for instance, Bear Lodge in the USA (Andersen et al., 2017), Chuktukon and Tomtor in Russia (Kravchenko and Pokrovsky, 1995; Kravchenko et al., 2003; Chebotarev et al., 2017), Las Mercedes in the Dominican Republic (Torró et al., 2017), Araxá in Brazil (Braga and Biondi, 2023), and Mount Weld in Australia (Zhukova et al., 2021; Chandler et al., 2024), among many others. However, the weathering processes on Fuerteventura are characterized by fluctuating climatic conditions and intense erosion in the context of a typical Mediterranean climate, which is in turn characterized by drier conditions and a lower propensity for intense weathering compared to tropical climates. The weathering processes on Fuerteventura do not therefore typically lead to the development of laterites and mature weathering profiles, since these conditions do not favor the formation and subsequent preservation of these products, particularly within the carbonatite bedrock areas. Consequently, this constraint substantially reduces the capacity of the FBC to potentially contain economically valuable REE concentrations within the associated weathering products.

5.3 Fuerteventura carbonatites as potential REE source

Based on the mineralogical and geochemical data, it can be concluded that, among the lithologies studied in the FBC, only the carbonatites are favorable targets for further characterization and evaluation of their potential economic viability as an REE source. Therefore, the primary alkaline rocks, as well as the entire suite of corresponding secondary weathering products, can be ruled out. The geochemical data obtained from the oceanic carbonatites of Fuerteventura, exemplified in multielement and REE diagrams (Figure 8), suggest a petrogenetic affinity with carbonatites associated with intracontinental rift geological settings. This similarity has also been previously highlighted by other authors such as Carnevale et al. (2021) who, based on stable isotope data (δ^{13} C and δ^{18} C) and noble gases isotopic composition (He, Ne, Ar), suggested that oceanic and continental carbonatites were comparable in petrogenetic terms. Therefore, despite the lingering questions about the formation processes of oceanic carbonatites, their assessment as a possible source of critical metals, especially REEs, should be fully considered in the same way as their continental counterparts. However, when considering a more detailed assessment of the sectors where the FBC carbonatites outcrop, it is essential to note that the distribution of these outcrops and thus potential REE mineralization is not straightforward. The carbonatite outcrops have a very limited surface distribution, in the order of meters (Figure 2e), and exhibit complex structural features influenced by shear metamorphism (Figure 2c) and

overlapping episodes of intrusive activity that resulted in swarms of dikes with intricate distributions (Figs.

2a, b). Hence, these general features of the carbonatite outcrops make it imperative to validly estimate their volume and to carry out more precise studies of their depth distribution, which likely involve drilling and geophysical techniques. These prospective hypothetical findings would provide a deeper understanding of the morphology and dimensions of the carbonatitic bodies, enhancing the ability to calculate resources and reserves while refining the general metallogenic modeling.

However, it is important to highlight that any attempt to assess potential REE deposits linked to FBC carbonatites must consider the irregular distribution of these mineralizations. In addition, it should also be considered the existence of regulatory constraints that may stem from the allocation of land for strategic military activities, as well as environmental considerations to safeguard natural and marine-coastal areas, especially bearing in mind that Fuerteventura is a UNESCO biosphere reserve territory. This latter point is particularly pertinent for a specific area within sector 3 (Figure 1). Therefore, any comprehensive analysis of the potential of FBC carbonatites as REE sources must also factor in these potential restrictions tied to land use regulations aimed at upholding the broader socio-economic, environmental, and societal interests inherent to a distinctive site like the island of Fuerteventura.

6 Conclusions

- A preliminary evaluation of rare earth element (REE) content was conducted through a mineralogical and geochemical study of alkaline and carbonatitic igneous rocks within the Fuerteventura basal complex (FBC), along with associated weathering products. Based on the gathered data and their corresponding interpretations, our findings can be summarized as follows:
- (i) The concentrations of REEs present in the alkaline and carbonatitic rocks of the FBC are significant and exceed the average values attributed to the Earth's crust.
 - (ii) The weathering products developed on these magmatic rocks do not exhibit significant REE enrichment.
 - (iii) Calcified horizons (Bk, calcretes), spatially related with carbonatites, have practically negligible concentrations of REE elements. Colluvial processes may have influenced the lateral transport and accumulation of REEs in Pleistocene-Holocene deposits distant from the source area.
- 525 (iv) Among the magmatic rocks, carbonatites are the only lithology studied within the FBC with a real potential to host REE mineral resources. The detected concentrations of REY in

carbonatites range up to about 10,300 ppm, which is a comparable concentration to other locations hosting significant deposits of these critical elements worldwide.

- (v) Within carbonatites, REEs are primarily hosted in two accessory mineral phases: (1) oxides belonging to the pyrochlore group; and (2) phosphates. In this second group, primary phases such as REE-bearing britholite can be distinguished, as well as monazite generated as a secondary product from the britholite alteration.
- (vi) Primary calcite in the Fuerteventura carbonatites is not the predominant host of REEs. It displays a highly homogeneous composition with insignificant Fe-Mg content and negligible REEs.
- 536 (vii) The carbonatites within the FBC could be considered potential REE resources associated with
 537 a non-conventional geological setting. However, the complex structural features of the studied
 538 FBC outcrops (deformation, metamorphism, swarms of dikes from different intrusive
 539 pulses...) make it essential to conduct more detailed studies to quantify the real economic
 540 possibilities of this lithology as an REE source.
 - (viii) All the studied sectors contain outcrops located in restricted areas due to environmental or military use concerns. Any further detailed evaluation of the FBC carbonatites must take into account the environmental, socio-economic, and geostrategic factors that will significantly limit the real potential extension of REE deposits, considering a hypothetical exploitation.

Acknowledgements

This research was funded by the "Tierras Raras" project (SD-22/25) and the "MAGEC-REEmounts" project (ProID-20211010027) of the Canarian Agency for Research, Innovation and Information Society (ACIISI by its initials in Spanish) of the Canary Islands Government. Funding support was also provided by the project "Materials for Advanced Energy Generation" (ENE2013-47826-C4-4-R), "3D Printed Advanced Materials for Energy Applications" (ENE2016-74889-C4-2-R) and "Estudio de los procesos magmáticos, tectónicos y sedimentarios involucrados en el crecimiento temprano de edificios volcánicos oceánicos en ambiente de intraplaca" (CGL2016-75062-P), all funded by the Government of Spain. The collection of samples in specific protected areas required authorization from the Fuerteventura Island Government. We appreciate the cooperation and assistance provided by the Spanish Army, especially by the soldier Liberto Yeray Puga Acosta, who facilitated our access to the Pájara CMT restricted military

| 557 | area to carry out sampling. We also thank Gerard Lucena from the LPGiP-MCNB for his thorough work in |
|-----|---|
| 558 | the elaboration of polished thin sections. |
| 559 | |
| 560 | Statements and Declarations |
| 561 | Data availability statement |
| 562 | The authors confirm that the data supporting the findings of this study are available within the article and |
| 563 | its supplementary materials. |
| 564 | |
| 565 | Competing interests |
| 566 | The authors declare no competing interests. The funders had no role in the design of the study, in the |
| 567 | collection of samples, the analyses, the interpretation of data, the writing of the manuscript nor the decision |
| 568 | to publish these results. |
| 569 | Author contributions |
| 570 | Conceptualization: MC, IM, LQ, JY, JM; fieldwork and sampling: MC, IM, LQ, JY, RC, AA, JM; |
| 571 | methodology: MC, IM, JY, JM; validation of results: MC, IM, LQ, JY, RC, JMR, JM; data curation: MC, |
| 572 | IM, JM; writing-original draft preparation: MC, IM, JY, JM; writing-review editing: MC, IM, LQ, JY, RC, |
| 573 | JMR, JM; supervision: IM, JY, JM; project administration: JMR, JM; funding acquisition: IM, JY, RC, |
| 574 | JMR, JM. |
| 575 | |
| 576 | Additional information |
| 577 | Supplementary tables are available in the online version at https: XXXXX |

- 578 References
- Acosta-Mora, P., Domen, K., Hisatomi, T., Lyu, H., Méndez-Ramos, J., Ruiz-Morales, J. C., Khaidukov,
- N. M.: "A bridge over troubled gaps": up-conversion driven photocatalysis for hydrogen generation
- and pollutant degradation by near-infrared excitation, Chem. Commun, 54, 1905 -1908
- 582 <u>https://doi.org/10.1039/C7CC09774C</u>, 2018.
- Aiglsperger, T., Proenza, J. A., Lewis, J. F., Labrador, M., Svojtka, M., Rojas-Purón, A., Longo, F.,
- 584 Ďurišová, J.: Critical metals (REE, Sc, PGE) in Ni laterites from Cuba and the Dominican Republic,
- 585 Ore Geol. Rev., 73, 127–147, https://doi.org/10.1016/j.oregeorev.2015.10.010, 2016.
- 586 Ahijado, A.: Las intrusiones plutónicas e hipoabisales del sector meridional del Complejo Basal de
- Fuerteventura, Doctoral Thesis, Universidad Complutense de Madrid, 392 p., 1999.
- Ahijado, A., Casillas, R., Nagy, G., Fernández, C.: Sr-rich minerals in a carbonatite skarn, Fuerteventura,
- Canary Islands (Spain), Mineralogy and Petrology, 84, 107–127, https://doi.org/10.1007/s00710-005-
- 590 0074-8, 2005.
- Alonso, E., Sherman, A. M., Wallington, T. J., Everson, M. P., Field, F. R., Roth, R., Kirchain, R. E.:
- 592 Evaluating Rare Earth Element Availability: A Case with Revolutionary Demand from Clean
- 593 Technologies, Environ. Sci. Technol., 46, 3406–3414, https://doi.org/10.1021/es203518d, 2012.
- Alonso-Zarza, A. M., Silva, P. G.: Quaternary laminar calcretes with bee nests evidences of small-scale
- 595 climatic fluctuations, Eastern Canary Islands, Spain, Palaeogeogr. Palaeoclimatol. Palaeoecol., 178,
- 596 119–135, https://doi.org/10.1016/S0031-0182(01)00405-9, 2002.
- 597 Alonso-Zarza, A. M., Rodríguez-Berriguete, Á., Casado, A. I., Martín-Pérez, A., Martín-García, R.,
- Menéndez, I., Mangas, J.: Unravelling calcrete environmental controls in volcanic islands, Gran
- 599 Canaria Island, Spain, Palaeogeogr. Palaeoclimatol. Palaeoecol., 554, 109797,
- 600 https://doi.org/10.1016/j.palaeo.2020.109797, 2020.
- Ancochea, E., Brändle, J. L., Cubas, C. R., Hernán, F., Huertas, M. J.: Volcanic complexes in the eastern
- 602 ridge of the Canary Islands: the Miocene activity of the Island of Fuerteventura, Journal of
- Volcanology and Geothermal Research, 70, 183–204, https://doi.org/10.1016/0377-0273(95)00051-
- 604 8, 1996.
- Ancochea, E., Barrera, J. L., Bellido, F.: Canarias y el vulcanismo neógeno peninsular. Geología de España,
- 606 635-682. In: Aparicio, A., Hernán, F., Cubas, C. R., Araña, V., 2003, Fuentes mantélicas y evolución
- del volcanismo canario, Estudios Geológicos, 59, 5–13, https://doi.org/10.3989/egeol.03591-477,
- 608 2004.
- Andersen, A. K., Clark, J. G., Larson, P. B., Donovan, J. J.: REE fractionation, mineral speciation, and
- supergene enrichment of the Bear Lodge carbonatites, Wyoming, USA, Ore Geology Reviews, 89,
- 611 780–807, https://doi.org/10.1016/j. oregeorev.2017.06.025, 2017.
- Anenburg, M., Mavrogenes, J.A., Carbonatitic versus hydrothermal origin for fluorapatite REE-Th
- deposits: experimental study of REE transport and crustal "antiskarn" metasomatism, American
- Journal of Science, 318, 335–366, https://doi.org/10.2475/03.2018.03, 2018.
- Anenburg, M., Broom-Fendley, S., Chen, W.: Formation of Rare Earth Deposits in Carbonatites, Elements,
- 616 17, 327–332, https://doi.org/10.2138/gselements.17.5.327, 2021.

- Balcells, R., Barrera, J. L., Gómez, J. A., Cueto, L. A., Ancochea, E., Huertas, M. J., Ibarrola, E., Snelling,
- N.: Edades radiométricas en la Serie Miocena de Fuerteventura (Islas Canarias), Bol. Geol. Min., 35,
- 619 450–470, 1994.
- Balaram, V.: Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling,
- 621 and environmental impact, Geoscience Frontiers, 10, 1285–1303,
- https://doi.org/10.1016/j.gsf.2018.12.005, 2019.
- Balogh, K., Ahijado, A., Casillas, R., Fernández, C.: Contributions to the chronology of the Basal Complex
- of Fuerteventura, Canary Islands, Journal of Volcanology and Geothermal Research, 90, 81–101,
- 625 https://doi.org/10.1016/S0377-0273(99)00008-6, 1999.
- Bao, Z., Zhao, Z.: Geochemistry of mineralization with exchangeable REY in the weathering crusts of
- granitic rocks in South China, Ore Geol. Rev., 33, 519–535,
- 628 <u>https://doi.org/10.1016/j.oregeorev.2007.03.005, 2008.</u>
- Barrera, J. L., Fernández-Santín, S., Fúster, J. M., Ibarrola, E.: Ijolitas-Sienitas-Carbonatitas de los Macizos
- del Norte de Fuerteventura, Bol. Geol. Min., TXCII-IV, 309–321. ISSN 0366-0176, 1993.
- Barteková, E., Kemp, R., National strategies for securing a stable supply of rare earths in different world
- regions, Resources Policy, 49, 153–164, https://doi.org/10.1016/j.resourpol.2016.05.003, 2016.
- Beland, C. M. J., William-Jones, A. E.: The mineralogical distribution of the REE in carbonatites: A
- 634 quantitative evaluation, Chemical Geology, 585, 120558,
- https://doi.org/10.1016/j.chemgeo.2021.120558, 2021.
- Berger, A., Janots, E., Gnos, E., Frei, R., Bernier, F., Rare earth element mineralogy and geochemistry in
- a laterite profile from Madagascar. Applied Geochemistry 41, 218–228,
- https://doi.org/10.1016/j.apgeochem.2013.12.013, 2014.
- Borst, A. M., Smith, M. P., Finch, A. A., Estrade, G., Villanova-de-Benavent, C., Nason, P., Marquis, E.,
- Horsburgh, N. J., Goodenough, K. M., Xu, C., Kynický, J., Geraki, K.: Adsorption of rare earth
- elements in regolith-hosted clay deposits, Nat. Commun., 11, 4386, https://doi.org/10.1038/s41467-
- 642 020-17801-5, 2020.
- Braga, J. M., Biondi, J. C.: Geology, geochemistry, and mineralogy of saprolite and regolith ores with Nb,
- P, Ba, REEs (+ Fe) in mineral deposits from the Araxá alkali-carbonatitic complex, Minas Gerais
- state, Brazil, Journal of South American Earth Sciences, 125, 104311,
- 646 https://doi.org/10.1016/j.jsames.2023.104311, 2023.
- Braun, J. J., Pagel, M., Herbilln, A., Rosin, C.: Mobilization and redistribution of REEs and thorium in a
- 648 syenitic lateritic profile: A mass balance study, Geochem. Cosmochim. Acta, 57, 4419–4434.
- 649 https://doi.org/10.1016/0016-7037(93)90492-F, 1993.
- 650 Carnevale, G., Caracausi, A., Correale, A., Italiano, L., Rotolo, S.G., An Overview of the Geochemical
- Characteristics of Oceanic Carbonatites: New Insights from Fuerteventura Carbonatites (Canary
- 652 Islands), Minerals, 11, 203. https://doi.org/10.3390/min11020203, 2021.
- 653 Casillas, R., Nagy, G., Demény, A., Ahijado, A., Fernández, C.: Cuspidine-niocalite-baghdadite solid
- solutions in the metacarbonatites of the Basal Complex of Fuerteventura (Canary Islands). Lithos
- 655 105:25–41. https://doi.org/10.1016/j.lithos.2008.02.003, 2008.

- Casillas, R., Démeny, A., Nagy, G., Ahijado, A., Fernández, C.: Metacarbonatites in the Basal Complex of
- Fuerteventura (Canary Islands). The role of fluid/rock interactions during contact metamorphism and
- anatexis, Lithos, 125, 503–520, https://doi.org/10.1016/j.lithos.2011.03.007, 2011.
- Castor, S. B.: The Mountain Pass rare-earth carbonatite and associated ultrapotassic rocks, California, The Canadian Mineralogist, 46, 779–806, https://doi.org/10.3749/canmin.46.4.779, 2008.
- Chakhmouradian, A. R., Wall, F.: Rare Earth Elements: Minerals, Mines, Magnets (and More), Elements, 8, 333–340, https://doi.org/10.2113/gselements.8.5.333, 2012.
- Chao, E. C. T., Back, J. M., Minkin, J. A., Tatsumoto, M., Wang, J., Conrad, J. E, McKee, E. H., Hou, Z.
- L., Meng, Q. R., Huang, S. G.: The sedimentary carbonate-hosted giant Bayan Obo REE-Fe-Nb ore
- deposit of Inner Mongolia, China: a corner stone example for giant polymetallic ore deposits of
- hydrothermal origin, USGS Bulletin, 2143, 65, https://doi.org/10.3133/b2143, 1997.
- Chandler, R., Bhat, G., Mavrogenes, J., Knell, B., David, R., Leggo, T.: The primary geology of the
- Paleoproterozoic Mt Weld carbonatite complex, Western Australia, Journal of Petrology, 65, 2,
- https://doi.org/10.1093/petrology/egae007, 2024.
- 670 Charalampides, G., Vatalis, K., Baklavaridis, A., Benetis, N. P.: Rare Earth Elements: Industrial
- Applications and Economic Dependency of Europe, Procedia Economics and Finance, 24, 126–135,
- 672 <u>https://doi.org/10.1016/S2212-5671(15)00630-9</u>, 2015.
- 673 Chebotarev, D. A., Doroshkevich, A., Klemd, R., Karmanov, N.: Evolution of Nb- mineralization in the
- Chuktukon carbonatite massif, Chadobets upland (Krasnoyarsk Territory, Russia), Periodico di
- 675 Mineralogia, 86, 99–118, https://doi.org/10.2451/2017PM733, 2017.
- 676 Chen, W., Honghui, H., Bai, T., Jiang, S.: Geochemistry of Monazite within Carbonatite Related REE Deposits, Resources, 6, 51, https://doi.org/10.3390/resources6040051, 2017.
- 678 Chiquet, A., Michard, A., Nahon, D., Hamelin, B.: Atmospheric input vs in situ weathering in the genesis
- of calcretes: an Sr isotope study at Gálvez (Central Spain), Geochim. Cosmochim. Acta, 63, 311–323,
- 680 https://doi.org/10.1016/S0016-7037(98)00271-3, 1999.
- Christy, A. G., Atencio, D.: Clarification of status of species in the pyrochlore supergroup, Mineralogical
- Magazine, 77, 13–20, https://doi.org/10.1180/minmag.2013.077.1.02, 2013.
- Christy, A.G., Pekov, I.V., Krivovichev, S.G., The Distinctive Mineralogy of Carbonatites, Elements, 17,
- 684 333–338, https://doi.org/10.2138/gselements.17.5.333, 2021.
- Coello, J., Cantagrel, J. M., Hernán, F., Fúster, J. M., Ibarrola, E., Ancochea, E., Casquet, C., Jamond, C.,
- Díaz-de-Terán, J. R., Cendrero, A.: Evolution of the Eastern volcanic ridge of Canary Islands based
- on new K-Ar data, Journal of Volcanology and Geothermal Research, 53, 251–274,
- 688 https://doi.org/10.1016/0377-0273(92)90085-R, 1992.
- 689 Connelly, N. G., Hartshorn, R. M., Damhus, T., Hutton, A. T.: Nomenclature of Inorganic Chemistry
- 690 IUPAC Recommendations 2005, RSC Publishing, Cambridge, ISBN-0-85404-438-8, 2005.
- 691 Courtillot, V., Davaille, A., Besse, J., Stock, J.: Three distinct types of hotspots in the Earth's mantle, Earth
- 692 Planet. Sci. Letters, 205, 295–308, https://doi.org/10.1016/S0012-821X(02)01048-8, 2003.
- De Ignacio, C., Muñoz, M., Sagredo, J., Carbonatites and associated nephelinites from São Vicente, Cape
- Verde Islands, Min., Mag., 76, 311–355, doi:10.1180/minmag.2012.076.2.05, 2012.

- Demény, A., Ahijado, A., Casillas, R., Vennemann, T.W., Crustal contamination and fluid/rock interaction
- in the carbonatites of Fuerteventura (Canary Islands, Spain): A C, O, H isotope study, Lithos, 44, 101–
- 697 115, https://doi.org/10.1016/S0024-4937(98)00050-4, 1998.
- Dostal, J.: Rare Earth Element Deposits of Alkaline Igneous Rocks, Resources, 6, 34–46, https://doi.org/10.3390/resources6030034, 2017.
- Doucelance, R., Hammouda, T., Moreira, M., Martins, J.C., Geochemical constraints on depth of origin of
- 701 oceanic carbonatites: The Cape Verde case, Geochim. Cosmochim. Acta, 74, 7261–7282,
- 702 https://doi.org/10.1016/j.gca.2010.09.024, 2010.
- Doucelance, R., Bellot, N., Boyet, M., Hammouda, T., Bosq, C., What coupled cerium and neodymium
- isotopes tell us about the deep source of oceanic carbonatites, Earth Planet. Sci. Lett., 407, 175–186,
- 705 https://doi.org/10.1016/j.epsl.2014.09.042, 2014.
- European Commission: European Green Deal, https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal en, 2019.
- 708 European Commission: Study on the Critical Raw Materials for the EU 2023 Final Report,
- 709 <u>https://op.europa.eu/en/publication-detail/-/publication/57318397-fdd4-11ed-a05c-01aa75ed71a1</u> -
- 710 <u>https://doi.org/10.32873/725585</u>, 2023a.
- Furopean Commission, Regulation of the European Parliament and of the Council establishing a framework
- for ensuring a secure and sustainable supply of critical raw materials and amending Regulations (EU)
- 713 168/2013, (EU) 2018/858, 2018/1724 and (EU) 2019/1020, https://eur-lex.europa.eu/legal-
- 714 <u>content/EN/TXT/?uri=CELEX%3A52023PC0160</u>, 2023b.
- 715 FAO/UNESCO: Soil Map of the World Project 1:5000000, Chart VII, https://www.fao.org/soils-
- 716 <u>portal/data-hub/soil-maps-and-databases/faounesco-soil-map-of-the-world/en/</u>, 1974.
- Feraud, G., Giannerini, G., Campredon, R., Stillman, C.J.: Geochronology of some canarian dike swarms:
- 718 contribution to the volcano-tectonic evolution of the archipielago, J. Volcanol. Geotherm. Res., 25,
- 719 29–52, https://doi.org/10.1016/0377-0273(85)90003-4, 1985.
- 720 Fernández, C., Casillas, R., Ahijado, A., Perelló, V., Hernández-Pacheco, A.: Shear zones as a result of
- intraplate tectonics in oceanic crust: the example of the Basal Complex of Fuerteventura (Canary
- 722 Islands), Jour. Struct. Geol., 19, 41–57, https://doi.org/10.1016/S0191-8141(96)00074-0, 1997.
- Frisch, T.: In: Schmincke, H. U., Sumita, M.: Geological evolution of the Canary Islands: a young volcanic
- archipelago adjacent to the old African continent, Bull Volcanol., 74, 1255–1256,
- 725 https://doi.org/10.1007/s00445-012-0605-1, 2012.
- Fúster, J. M., Cendrero, A., Gastesi, P., Ibarrola, E., López-Ruiz, J.: Geología y volcanología de las Islas
- 727 Canarias- Fuerteventura, Instituto "Lucas Mallada", Consejo Superior de Investigaciones Científicas,
- 728 Madrid. 239 pp, 1968.
- Goodenough, K. M., Schilling, J., Jonsson, E., Kalvig, P., Charles, N., Tuduri, J., Deady, E. A., Sadeghi,
- 730 M., Schiellerup, H., Müller, A., Bertrand, G., Arvanitidis, N., Eliopoulos, D. G., Shaw, R. A., Thrane,
- K., Keulen, N.: Europe's rare earth element resource potential: An overview of REE metallogenetic
- provinces and their geodynamic setting, Ore Geol. Rev., 72, 838–856,
- 733 https://doi.org/10.1016/j.oregeorev.2015.09.019, 2016.

- Goudie, A. S., Middleton, N. J.: Saharan dust storms: nature and consequences, Earth Sci. Rev., 56, 179–204, https://doi.org/10.1016/S0012-8252(01)00067-8, 2001.
- Graedel, T. E., Harper, E. M., Nassar, N. T., Reck, B. K.: Criticality of metals and metalloids, Proceedings of the National Academy of Sciences, 112 4257–4262, https://doi.org/10.1073/pnas.1500415112, 2015.
- Gutiérrez, M., Casillas, R., Fernández, C., Balogh, K., Ahijado, A., Castillo, C., Colmenero, J. R., García-Navarro, E.: The submarine volcanic succession of the basal complex of Fuerteventura, Canary Islands: A model of submarine growth and emergence of tectonic volcanic islands, Bulletin of the Geological Society of America, 118, 785–804, https://doi.org/10.1130/B25821.1, 2006.
- Gutiérrez-Elorza, M., Lucha, P., Gracia, F. J., Desir, G., Marín, C., Petit-Maire, N.:_Palaeoclimatic considerations of talus flatirons and aeolian deposits in Northern_Fuerteventura volcanic island (Canary Islands, Spain), Geomorphology, 197, 1–9, https://doi.org/10.1016/j.geomorph.2011.09.020, 2013.
- Haxel, G. B.: Ultrapotassic mafic dikes and rare earth element- and barium-rich carbonatite at Mountain Pass, Mojave Desert, southern California: summary and field trip localities, U.S. Geol. Surv. Open-File Rep., 1219. http://pubs.usgs.gov/of/2005/1219/, 2005.
- Hobson, A., Bussy, F., Hernández, J.: Shallow-level migmatization of gabbrosin a metamorphic contact
 aureole, Fuerteventura Basal Complex, Canary Islands, Journal of Petrology, 39, 1025–1037,
 https://doi.org/10.1093/petroj/39.5.1025, 1998.
- Hoernle, K., Tilton, G., Le Bas, M.J., Duggen, S., Garbe-Schönberg, D., Geochemistry of oceanic carbonatites compared with continental carbonatites: Mantle recycling of oceanic crustal carbonate, Contrib. Mineral. Petrol., 142, 520–542, https://doi.org/10.1007/s004100100308, 2002.
- Holloway, M. I., Bussy, F.: Trace element distribution among rock-forming minerals from metamorphosed to partially molten basic igneous rocks in a contact aureole (Fuerteventura, Canaries), Lithos, 102, 616–639, https://doi.org/10.1016/j.lithos.2007.07.026, 2008.
- Huerta, P., Rodríguez-Berriguete, A., Martín-García, R., Martín-Pérez, A., La-Iglesia-Fernández, A.,
 Alonso-Zarza, A.: The role of climate and eolian dust input in calcrete formation in volcanic islands
 (Lanzarote and Fuerteventura, Spain), Palaeogeogr. Palaeoclimatol. Palaeoecol., 417, 66–79,
 https://doi.org/10.1016/j.palaeo.2014.10.008, 2015.
- Humphreys-Williams, E.R., Zahirovic, S.: Carbonatites and Global Tectonics, Elements, 17, 339–344, https://doi.org/10.2138/gselements.17.5.339, 2021.
- Jahn, R., Blume, H. P., Asio, V. B., Spaargaren, O., Schad, P.: Guidelines for soil description, FAO, Rome
 97 p, https://www.fao.org/3/a0541e/a0541e.pdf, 2006.
- Jyothi, R. K., Thenepalli, T., Ahn, J. W., Parhi, P. K., Chung, K. W., Lee, J. Y.: Review of rare earth elements recovery from secondary resources for clean energy technologies: grand opportunities to create wealth from waste, J. Clean. Prod., 267, 122048, https://doi.org/10.1016/j.jclepro.2020.122048, 2020.
- Kamenetsky, V.S., Doroshkevich, A.G., Elliot, H.A.L., Zaitsev, A.N., Carbonatites: Contrasting, Complex, and Controversial, Elements, 17, 307–314, https://doi.org/10.2138/gselements.17.5.307, 2021.

- Kravchenko, S. M., Pokrovsky, B. G.: The Tomtor alkaline ultrabasic massif and related REE-Nb deposits,
- northern Siberia, Economic Geology, 90, 676–689, https://doi.org/10.2113/gsecongeo.90.3.676,
- 775 1995.
- Kravchenko, S. M., Czamanske, G., Fedorenko, V. A.: Geochemistry of carbonatites of the Tomtor massif,
 Geochem. Int., 41, 545–558, ISSN: 0016-7029, 2003.
- Lai, X., Yang, X., Santosh, M., Liu, Y., Ling, M.: New data of the Bayan Obo Fe-REE-Nb deposit, Inner
- Mongolia: Implications for ore genesis, Precambrian Research, 263, 108–122,
- 780 https://doi.org/10.1016/j.precamres.2015.03.013, 2015.
- Le Bas, M. J.: The pyroxenite-ijolite-carbonatite intrusive igneous complexes of Fuerteventura, Canary
- 782 Islands, J. Geol. Soc. London, 138, 496, https://doi.org/10.1144/gsigs.138.4.0493, 1981.
- Le Bas, M. J, Rex, D. C., Stillman, C. J.: The early magmatic chronology of Fuerteventura, Geol. Mag.,
- 784 123, 287–298, https://doi.org/10.1017/S0016756800034762, 1986.
- Le Maitre, R.W., Igneous Rocks: a Classification and Glossary of Terms, Cambridge University Press, Cambridge, U.K, 2002.
- Le Maitre, R. W., Streckeisen, A., Zanettin, B., Le Bas, M. J., Bonin, B., Bateman, P., Bellieni, G., Dudek,
- A., Efremova, S., Keller, J., Lameyre, J., Sabine, P. A., Schmid, R., Sorensen, H., Woolley, A. R.:
- Igneous Rocks: A Classification and Glossary of Terms, 2nd Edition, Cambridge, UK, Cambridge
- 790 Univ. Press, ISBN: 9780521619486, 2005.
- Liu, Y. L., Ling, M. X., Williams, I. S., Yang, X. Y., Wang, C. Y., Sun, W.: The formation of the giant
- Bayan Obo REE-Nb-Fe deposit, North China, Mesoproterozoic carbonatite overprinted Paleozoic
- dolomitization, Ore Geology Reviews, 92, 73-83, https://doi.org/10.1016/j.oregeorev.2017.11.011,
- 794 2018.
- Long, K. R., Van Gosen, B. S., Foley, N. K., Cordier, D.: The principal rare earth elements deposits of the
- 796 United States: A summary of domestic deposits and a global perspective,
- 797 https://pubs.usgs.gov/sir/2010/5220/, 2010.
- Longpré, M. A., Felpeto, A.: Historical volcanism in the Canary Islands; part 1: A review of precursory
- and eruptive activity, eruption parameter estimates, and implications for hazard assessment, Journal
- 800 of Volcanology and Geothermal Research, 419, 107363,
- 801 <u>https://doi.org/10.1016/j.jvolgeores.2021.107363</u>, 2021.
- 802 Machado-Yanes, M. C.: Reconstrucción paleoecológica y etnoarqueológica por medio del análisis
- antracológico.La Cueva de Villaverde, Fuerteventura, In: Biogeografía Pleistocena-Holocena de la
- Península Ibérica, 261274, Ramil-Rego, P., Fernández-Rodríguez, C., Rodríguez-Guitián, M. (Eds.),
- 805 ISBN 84-453-1716-4, 261 p, 1996.
- 806 Mangas, J., Pérez-Torrado, F. J., Reguillón, R. M., Cabrera, M. C.: Prospección radiométrica en rocas
- 807 alcalinas y carbonatitas de la serie plutónica I de Fuerteventura (Islas Canarias). Resultados
- preliminares e implicaciones metalogénicas, Actas del III Congreso Geológico de España y VIII
- 809 Congreso Latinoamericano de Geología. Salamanca, 3, 389–393, ISBN: 84-600-8114-1, 1992.
- 810 Mangas, J., Pérez-Torrado, F. J., Reguillón, R. M., Martin-Izard, A.: Mineralizaciones de tierras raras
- 811 ligadas a los complejos intrusivos alcalino-carbonatíticos de Fuerteventura (Islas Canarias), Bol. Soc.
- 812 Esp. Min., 17, 212–213, 1994.

- Mangas, J., Pérez-Torrado, F. J., Reguillón, R. M., Martin-Izard, A.: Rare earth minerals in carbonatites of
- Basal Complex of Fuerteventura (Canary Islands, Spain), In: Mineral Deposit: Research and
- Exploration, where do they meet? Ed. Balkema, Rotterdam, 475–478, ISBN-13: 978-9054108894,
- 816 1997.
- Mariano, A. N., Mariano, Jr. A.: Rare earth mining and exploration in North America, Elements, 8, 369-
- 818 376, https://doi.org/10.2113/gselements.8.5.369, 2012.
- Massari, S., Ruberti, M.: Rare earth elements as critical raw materials: Focus on international markets and
- future strategies, Resour. Policy, 38, 36–43, https://doi.org/10.1016/j.resourpol.2012.07.001, 2013.
- 821 McDonough, W., Sun, W.: The composition of the Earth, Chemical Geology, 67, 1050-1056,
- 822 https://doi.org/10.1016/0009-2541(94)00140-4, 1995.
- McNulty, T., Hazen, N., Park, S., Processing the ores of rare-earth elements, MRS Bulletin, 47, 258–266,
- 824 https://doi.org/10.1557/s43577-022-00288-4, 2022.
- Méndez-Ramos, J., Acosta-Mora, P., Ruiz-Morales, J. C., Hernández, T., Morge, M. E., Esparza, P.:
- 826 Turning into the blue: materials for enhancing TiO₂ photocatalysis by up-conversion photonics, RSC
- 827 Advances, 3, 23028–23034, https://doi.org/10.1039/C3RA44342F, 2013.
- 828 Menéndez, I., Díaz-Hernández, J. L., Mangas, J., Alonso, I., Sánchez-Soto, P. J.: Airborne dust
- 829 accumulation and soil development in the North-East sector of Gran Canaria (Canary Islands, Spain),
- J. Arid Environ., 71, 57–81, https://doi.org/10.1016/j.jaridenv.2007.03.011, 2007.
- Menéndez, I., Campeny, M., Quevedo-González, L., Mangas, J., Llovet, X., Tauler, E., Barrón, V., Torrent,
- J., Méndez-Ramos, J.: Distribution of REE-bearing minerals in felsic magmatic rocks and paleosols
- from Gran Canaria, Spain: Intraplate oceanic islands as a new example of potential, non-conventional
- sources of rare-earth elements, Journal of Geochemical Exploration, 204, 270–288,
- 835 https://doi.org/10.1016/j.gexplo.2019.06.007, 2019.
- Moore, M., Chakhmouradian, A., Mariano, A. N., Sidhu, R.: Evolution of Rare-earth Mineralization in the
- 837 Bear Lodge Carbonatite, In: Ore Geology Reviews, 64, Mineralogical and Isotopic Evidence,
- Wyoming, 499, 521, http://dx.doi.org/10.1016/j.oregeorev.2014.03.015, 2015.
- Mourão, C., Mata, J., Doucelance, R., Madeira, J., da Silveira, A.B., Silva, L.C., Moreira, M., Quaternary
- extrusive calciocarbonatite volcanism on Brava Island (Cape Verde): A nephelinite-carbonatite
- 841 immiscibility product, Journal of African Earth Sciences, 56, 59–74,
- https://doi.org/10.1016/j.jafrearsci.2009.06.003, 2010.
- 843 Muñoz, M.: Ring complexes of Pájara in Fuerteventura Island, Bulletin Volcanologique, 33, 840–861,
- 844 https://doi.org/10.1007/BF02596753, 1969.
- Muñoz, M., Sagredo, J., de Ignacio, C., Fernández-Suárez, J., Jeffries, T. E.: New data (U-Pb, K-Ar) on the
- geochronology of the alkaline-carbonatitic association of Fuerteventura, Canary Islands, Spain,
- 847 Lithos, 85, 140–153, https://doi.org/10.1016/j.lithos.2005.03.024, 2005.
- Olson, J.C., Shawe, D. R., Pray, L.C., Sharp, W. N.: Rare-Earth Mineral Deposits of the Mountain Pass
- District, San Bernardino County, California, Science, 119, 325–326,
- https://doi.org/10.1126/science.119.3088.325, 1954.
- Park, J., Rye, D.M., Broader Impacts of the Metasomatic Underplating Hypothesis, Geochem. Geophys.
- 852 Geosyst., 20, 4180–4829, https://doi.org/10.1029/2019GC008493, 2019.

- Pérez-Torrado, F. J., Carracedo, J. C., Guillou, H., Rodríguez-González, A., Fernández-Turiel, J. L.: Age,
- duration, and spatial distribution of ocean shields and rejuvenated volcanism: Fuerteventura and
- Lanzarote, Eastern Canaries, Journal of the Geological Society of London, 180,
- 856 https://doi.org/10.1144/jgs2022-112, 2023.
- Pirajno, F., Yu, H.C.: The carbonatite story once more and associated REE mineral systems, Gondwana Research, 107, 281–295. https://doi.org/10.1016/j.gr.2022.03.006, 2022.
- Reinhardt, N., Proenza, J., Villanova-de-Benavent, C., Aiglsperger, T., Bover-Arnal, T., Torró, L., Salas,
- $R., Dziggel, A.: Geochemistry \ and \ Mineralogy \ of \ Rare \ Earth \ Elements \ (REE) \ in \ Bauxitic \ Ores \ of \ the$
- 861 Catalan Coastal Range, NE Spain, Minerals, 8, 562, https://doi.org/10.3390/min8120562, 2018.
- Rudnick, R.L., Gao, S.: Composition of the Continental Crust, In: Holland, H.H., Turekian, K.K. (editors):
- 863 Treatise on Geochemistry, 4, 1–51, https://doi.org/10.1016/B978-0-08-095975-7.00301-6, 2014.
- Scheuvens, D., Schütz, L., Kandler, K., Ebert, M., Weinbruch, S.: Bulk composition of northern African
- dust and its source sediments—a compilation, Earth Sci. Rev., 116, 170–194,
- 866 <u>https://doi.org/10.1016/j.earscirev.2012.08.005</u>, 2013.
- Schmincke, H., Sumita, M.: Geological evolution of the Canary Islands: a young volcanic archipelago adjacent
- 868 to the old African Continent, Ed. Görres, Koblenz, 200 p, ISBN: 978-3-86972-005-0, 2010.
- 869 Smith, M. P., Campbell, L. S., Kynicky, J.: A review of the genesis of the world class Bayan Obo Fe-REE-Nb
- deposits, Inner Mongolia, China: multistage processes and outstanding qüestions, Ore Geology Reviews,
- 871 64, 459–476, https://doi.org/10.1016/j.oregeorev.2014.03.007, 2015.
- 872 Smith, M. P., Moore, K., Kavecsánszki, D., Finch, A. A., Kynicky, J., Wall, F.: From mantle to critical zone:
- A review of large and giant-sized deposits of the rare earth elements, Geoscience Frontiers, 7, 315–334,
- 874 <u>https://doi.org/10.1016/j.gsf.2015.12.006</u>, 2016.
- Steiner, C., Hobson, A., Favre, P., Stampli, G. M.: Early Jurassic sea-floor spreading in the central Atlantic
- 876 the Jurassic sequence of Fuerteventura (Canary Islands), Geological Society of American Bulletin,
- 877 110, 1304–1317, https://doi.org/10.1130/0016-7606(1998)110<1304:MSOFCI>2.3.CO;2, 1998.
- 878 Torró, L., Proenza, J. A., Aiglsperger, T., Bover-Arnal, T., Villanova-de-Benavent, C., Rodríguez-García,
- D., Ramírez, A., Rodríguez, J., Mosquea, L.A., Salas, R.: Geological, geochemical and mineralogical
- characteristics of REE-bearing Las Mercedes bauxite deposit, Dominican Republic, Ore Geol. Rev.,
- 881 89, 114–131, https://doi.org/10.1016/j.oregeorev.2017.06.017, 2017.
- Torró, L., Villanova, C., Castillo, M., Campeny, M., Gonçalves, A. O., Melgarejo, J. C.: Niobium and rare
- earth minerals from the Virulundo carbonatite, Namibe, Angola, Mineralogical Magazine, 76, 393–
- 409, https://doi.org/10.1180/minmag.2012.076.2.08, 2012.
- Troll, V., Carracedo, J. C.: The Geology of Fuerteventura, In: Troll, V., Carracedo, J. C., Weismaier, S.
- 886 (eds), The Geology of Canary Islands, Elsevier, 531-582. http://dx.doi.org/10.1016/B978-0-12-
- 887 809663-5.00008-6, 2016.
- van den Bogaard, P.: The origin of the Canary Island Seamount Province New ages of old seamounts,
- 889 Scientific Reports, 3, 2107. https://doi.org/10.1038/srep02107, 2013.
- Wang, Q., Deng, J., Liu, X., Zhang, Q., Sun, S., Jiang, C., Zhou, F.: Discovery of the REE minerals and its
- geological significance in the Quyang bauxite deposit, West Guangxi, China, J. Asian Earth Sci., 39,
- 892 701–712, https://doi.org/10.1016/j.jseaes.2010.05.005, 2010.

- 893 Wang, X., Jiao, Y., Du, Y., Ling, W., Wu, L., Cui, T., Zhou, Q., Jin, Z., Lei, Z., Wen, S.: REE mobility
- 894 and Ce anomaly in bauxite deposit of WZD area, Northern Guizhou, China, J. Geochem Explor., 133,
- 895 103–117, https://doi.org/10.1016/j.gexplo.2013.08.009, 2013.
- 896 Wang, Z.Y., Fan, H.R., Zhou, L., Yang, K.F., She, H.D., Carbonatite-related REE deposits: An 897 overview, Minerals, 10, 965. https://doi.org/10.3390/min10110965, 2020.
- 898
- Warr, L. N.: IMA-CNMNC approved mineral symbols, Mineralogical Magazine, 85, 291-899 320, https://doi.org/10.1180/mgm.2021.43, 2021.
- 900 Weidendorfer, D., Schmidt, M.W., Mattsson, H.B.: Fractional crystallization of Si-undersaturated alkaline
- 901 magmas leading to unmixing of carbonatites on Brava Island (Cape Verde) and a general model of
- 902 carbonatite genesis in alkaline magma suites, Contributions to Mineralogy and Petrology, 171, 43,
- 903 https://doi.org/10.1007/s00410-016-1249-5, 2016.
- 904 Weng, Z., Jowitt, S.M., Mudd, G.M., Haque, N.: A Detailed Assessment of Global Rare Earth Element
- 905 Resources: Opportunities and Challenges, Economic Geology, 1925–1952, 110,
- 906 https://doi.org/10.2113/econgeo.110.8.192, 2015.
- 907 Wondraczek, L., Tyystjärvi, E., Méndez-Ramos, J., Müller, F. A., Zhang. Q.: Shifting the Sun: Solar
- 908 Spectral Conversion and Extrinsic Sensitization in Natural and Artificial Photosynthesis, Advanced
- 909 Science, 2, 1500218, https://doi.org/10.1002/advs.201500218, 2015.
- 910 Woolley, A.R., Kjarsgaard, B.A. (2008): Carbonatites of the world: map and database. Mineralogical 911 Magazine 71, 718.
- 912 Wu, C.: Bayan Obo Controversy: Carbonatites versus Iron Oxide-Cu-Au-(REE-U), Resource Geology, 58,
- 913 348–354, https://doi.org/10.1111/j.1751-3928.2008.00069.x, 2008.
- 914 Yang, K., Fan, H., Pirajno, F., Li, X.: The bayan Obo (China) giant REE accumulation conundrum
- 915 elucidated by intense magmatic differentiation of carbonatite, Geology, 47, 1198-1202,
- 916 https://doi.org/10.1130/G46674.1, 2019.
- 917 Yaxley, G.M., Anenburg, M., Tappe, S., Decree, S., Guzmics, T.: Carbonatites: Classification, Sources,
- 918 Evolution, and Emplacement, Annual Reviews on Earth and Planetary Sciences, 50, 261-293,
- 919 https://doi.org/10.1146/annurev-earth-032320-104243, 2022.
- 920 Zazo, C., Goy, J. L., Hillaire-Marcel, C., Gillot, P. Y., Soler, V., González, J. A., Dabrio, C. J., Ghaleb, B.:
- 921 Raised marine sequences of Lanzarote and Fuerteventura revisited –a reappraisal of relative sea-level
- 922 changes and vertical movements in the eastern Canary Islands during the Quaternary, Quaternary
- 923 Science Reviews, 21, 2019–2046, https://doi.org/10.1016/S0277-3791(02)00009-4, 2002.
- 924 Zhukova, I. A., Stepanov, A. S., Jiang, S. Y., Murphy, D., Mavrogenes, J., Allen, C., Chen, W., Bottrill,
- 925 R.: Complex REE systematics of carbonatites and weathering products from uniquely rich Mount
- 926 Reviews, Weld REE deposit, Western Australia, Ore Geology 139, 104539,
- 927 https://doi.org/10.1016/j.oregeorev.2021.104539,2021.

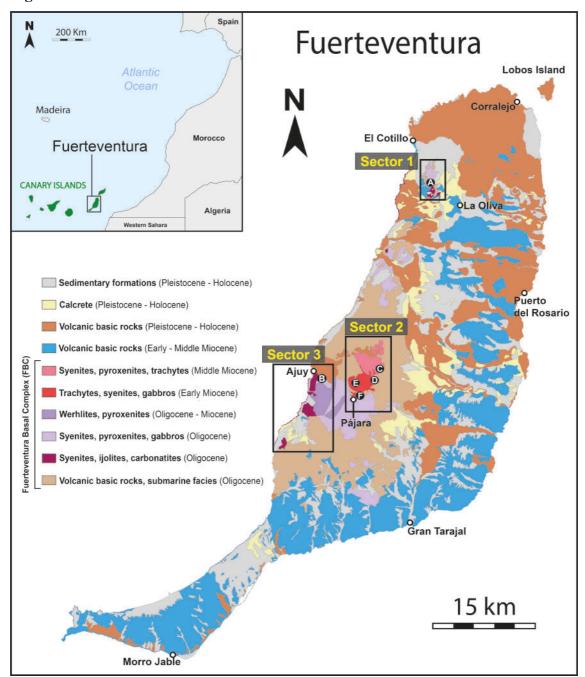


Figure 1: Simplified geological map of Fuerteventura Island (modified from Balcells et al., 2006) showing the location of the three study sectors for the assessment of REE content in the FBC. Additionally, the studied weathering profiles are also indicated, as: (A) Agua Salada ravine; (B) Aulagar ravine; (C) Palomares ravine; (D) FV-30 road; (E) Las Peñitas quarry; (F) Pájara.



Figure 2: (a), (b) Images showing typical outcrops of the FBC in the southern area of Ajuy (sector 3; Figure 1). The images highlight characteristic swarms of alkaline and carbonatitic intrusions (whitish) intersected by later-intruded basaltic dikes (black colour). (c) Detailed view of a carbonatitic dike located in a shear zone of sector 3, exhibiting distinct linear sigmoidal structures resulting from deformation. (d) Detailed view of centimetre-sized phlogopite crystals within a carbonatitic dike outcropping in sector 3, displaying a typical pegmatitic texture. (e) Overview of an outcrop of metric-scale carbonatitic dikes in the sector 1 area.

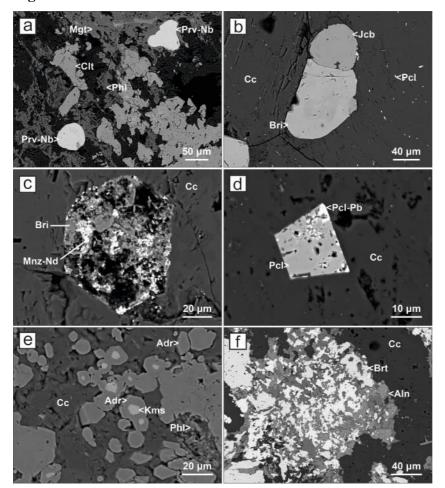


Figure 3: SEM (backscattered electron, BSE) images of the Fuerteventura carbonatites. (a) Subhedral crystals of niobium-rich perovskite (Prv-Nb) associated with phlogopite (Phl) and magnetite (Mgt) aggregates. The association has been affected by secondary hydrothermal processes, leading to the formation of celestine (Clt). (b) Typical subhedral crystal of jacobsite (Jcb) associated with britholite (Bri). Both crystals are hosted in magmatic calcite (Cc), with numerous disseminated microcrystals of pyrochlore (Pcl). (c) Partially altered subhedral grain of britholite (Bri) hosted in magmatic calcite (Cc). The alteration process led to the formation of secondary REE phosphates such as monazite-Nd (Mnz-Nd). (d) Euhedral crystal of pyrochlore (Pcl) hosted in calcite (Cc). Brighter areas developed on the grain's borders correspond to plumbopyrochlore (Pcl-Pb) zonation. (e) Typical mineral association related to small skarn like areas associated with carbonatites. Subhedral zoned crystals of andradite (Adr), hosted in calcite (Cc) and phlogopite (Phl), with a significant Zr zoning leading to kerimasite (Kms) cores. (f) Typical low-metamorphic alteration developed on carbonatites composed of allanite (Aln) aggregates hosted in calcite (Cc) and associated with secondary baryte (Brt). Abbreviations of mineral names in all the pictures follow the criteria proposed by Warr (2021).

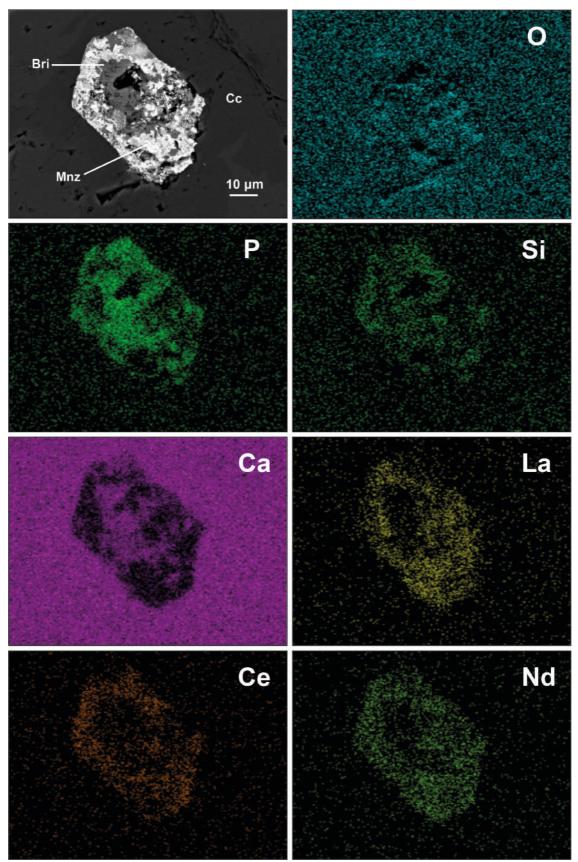


Figure 4: Wavelength-dispersive X-ray maps of representative compositional elements for an altered grain of britholite (Bri) hosted in calcite (Cc) and partially transformed into secondary monazite (Mnz).



Figure 5: **(a)** General view of a typical surface outcrop of Quaternary calcrete located in the Aulagar ravine area (profile B, sector 3; Fig.1). **(b)** Centimetre-thick calcrete layer filling a fracture between two carbonatitic dikes in the Aulagar ravine area (profile B, sector 3; Fig.1). **(c)** Calcrete layer developed within fractures between carbonatitic rocks in the Agua Salada ravine area (profile A, sector 1; Fig.1).

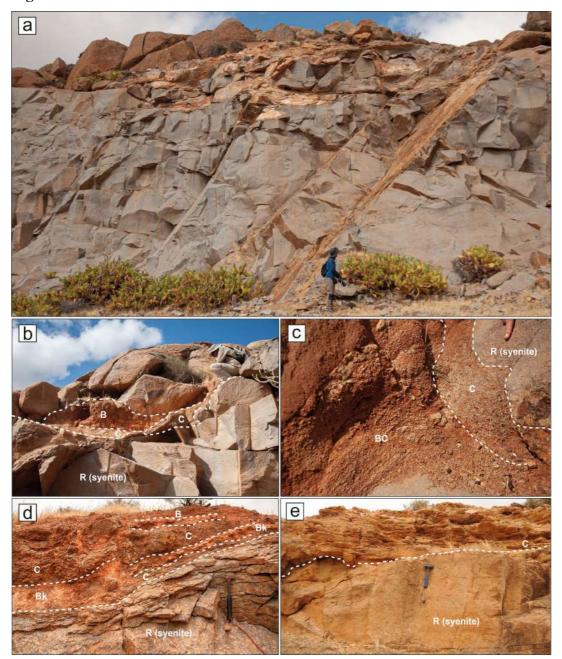


Figure 6: (a) General view of Las Peñitas quarry syenite outcrop (profile E, sector 2; Fig.1) where it is possible to distinguish different fractures filled by injected secondary weathering products. (b) Syenite weathering profile in Las Peñitas quarry (profile E, sector 2; Figure 1) showing surface erosion and B, BC and C horizons injected in the syenite bedrock (R). (c) Weathering profile displaying the development of C and BC horizons associated with a syenite protolith (R), located in Las Peñitas quarry (profile E, sector 2; Figure 1). (d) Weathering profile developed on syenite in the FV-30 road area (profile D, sector 2), exhibiting the development of C, B and calcrete (Bk) horizons. (e) Weathering profile on syenite protolith (R) displaying a metric sized C horizon in the Pájara area (profile F, sector 2; Figure 1).

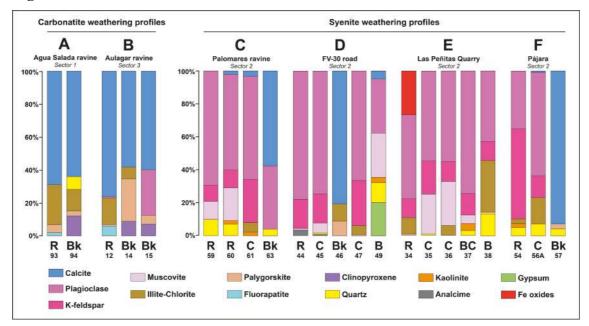


Figure 7: Graphical mineralogical quantification of the studied weathering profiles: (A) Agua Salada ravine; (B) Aulagar ravine; (C) Palomares ravine; (D) FV-30 road; (E) Las Peñitas quarry; (F) Pájara. The corresponding class assigned to the edaphic horizons (B, BC, Bk, C, R) and the sample number are shown at the foot of the columns.

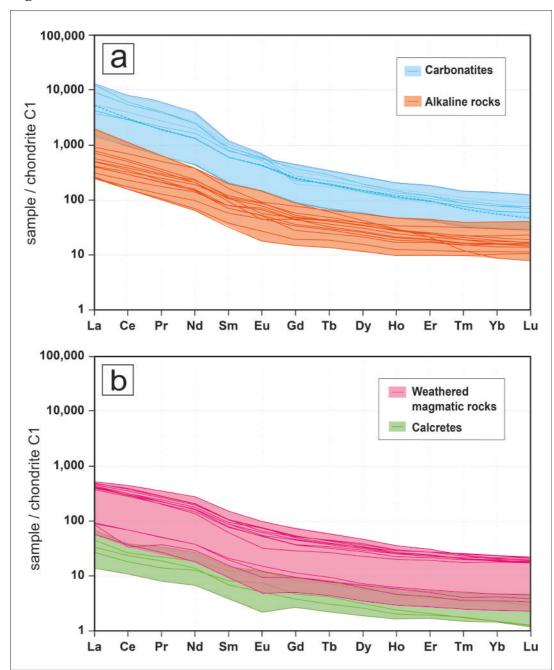


Figure 8: REE plots of the studied Fuerteventura lithologies normalised to C1 chondrites. Normalisation values are from McDonough and Sun (1995).

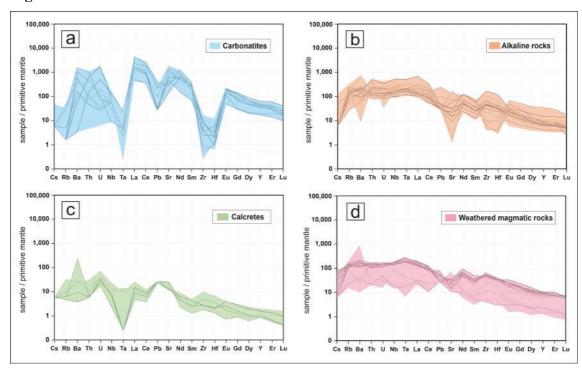


Figure 9: Multi-elemental trace element plots of Fuerteventura intrusive lithologies normalised to the primitive mantle. Normalisation values from McDonough and Sun (1995).

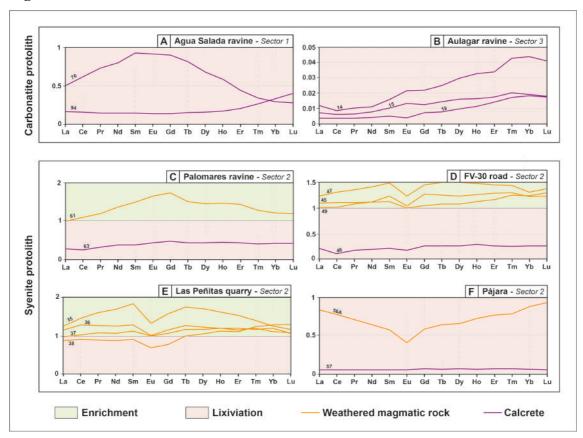


Figure 10: REE weathering enrichment/leaching diagrams between primary magmatic protoliths (carbonatites and syenites) and the associated weathering products from the studied profiles (Figure 1). The sample number is labelled on the corresponding pattern line.

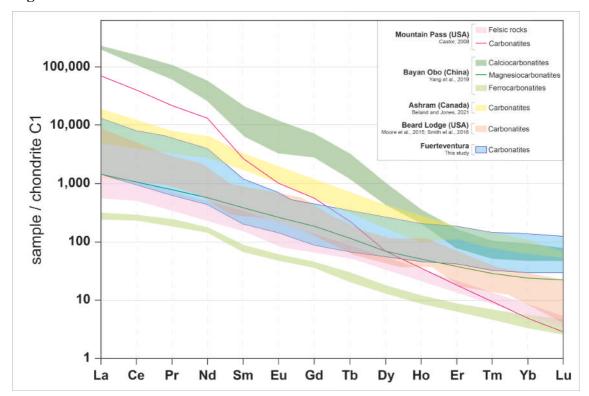


Figure 11: REE plot of the studied Fuerteventura carbonatites compared to other carbonatitic localities worldwide where REE deposits have been reported. REE contents for comparison are from Castor (2008), Yang et al. (2019), and Beland and Jones (2021). Normalisation values are from McDonough and Sun (1995).