

A comparison of the fenites at the Chilwa Island and Kangankunde carbonatite complexes, Malawi

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Abstract

Carbonatites are igneous carbonate rocks. They are the main source of the rare earth elements (REE) that are essential in low carbon and high technology applications.

Exploration targeting and mine planning would both benefit from a better understanding of the processes that create the almost ubiquitous alkaline and rare earth (RE)-bearing metasomatic aureoles in the surrounding country rocks.

Using SEM-based analysis and whole rock geochemistry, we investigated the composition and mineralogy of the fenite aureoles developed around the RE-poor Chilwa Island carbonatite and the RE-rich Kangankunde carbonatite, which intrude similar country rocks in the Chilwa Alkaline Province of Southern Malawi. Although common characteristics and trends in their mineralogy and composition may be typical of fenites in general, there are significant differences in their petrography and petrogenesis. For instance, the mineralogically diverse breccia at Kangankunde contrasts with the intensely altered potassic breccia of Chilwa Island. This may be caused by differing sequences of fluids expelled from the carbonatites into the aureoles. The main RE-bearing mineral in fenite is different at each complex, and reflects the key RE-bearing mineral of their main carbonatite, being fluorapatite at Chilwa Island, and monazite at Kangankunde. Each fenite

has distinctive mineral assemblages, in which the relative abundance of the RE-bearing minerals appears to be determined by the mineralogy of their respective host carbonatites.

At both localities, the RE minerals in fenite are less enriched in lanthanum and cerium than their equivalents in carbonatite, a characteristic that we attribute to REE fractionation within fluids in the aureole.

Identifying the mineral assemblages present in fenite and understanding the sequence of alkaline and mineralising fluid events could therefore be useful in predicting whether a fenite is associated with a RE-rich carbonatite. Detailed studies of other aureoles would be required to assess the reliability of these characteristics.

Keywords: fenite, carbonatite, rare earth elements, exploration, metasomatism

Introduction

Carbonatites are the most important source of rare earth elements (Wall, 2013; Goodenough *et al.*, 2016), which are essential for new and green technology applications. For the purposes of this paper, the REE are divided into the light rare earth elements (LREE) La to Pm, the middle rare earth elements (MREE) Sm to Dy, and the heavy rare earth elements (HREE) Ho to Lu, including Y. Carbonatites are generally particularly enriched in the LREE (Chakhmouradian and Wall, 2012; Weng *et al.*, 2015; Verplanck *et al.*, 2016; Goodenough *et al.*, 2018).

Carbonatite complexes are also the main source of niobium (Mitchell, 2015) and important sources of fluor spar, apatite, baddeleyite, and potential ores for iron (magnetite), lime

(calcite) as well as vermiculite and baryte. Intrusions are typically surrounded by aureoles of country rock which have undergone alteration by alkaline fluids associated with the cooling magma. These rocks are termed fenites (Bardina and Popov, 1994). Previous studies of the fenitisation process include Garson and Campbell Smith (1958); McKie (1966); Woolley (1969); Morogan and Woolley (1988); Andersen (1989); Morogan (1989); Platt and Woolley (1990); Verschure and Majer (2005); Carmody (2012). Reviews of fenite have been provided by Le Bas (2008) and Elliott *et al.* (2018).

The REE are defined as ‘critical metals’ (European Commission, 2017), with current production almost entirely dependent on China (Brown *et al.*, 2017; European Commission, 2017). Exploration and development at carbonatite centres in other countries, and thus greater security of supply, could be facilitated by an improved knowledge of the fluid regimes associated with enrichment in rare earths at carbonatite complexes. A key aspect here is the evolution of fluids exsolved from the magma, of which the fenitisation process is an important component. A better understanding of fenitisation will therefore improve our knowledge of carbonatitic magma composition and evolution.

The alkaline fluids that fenitise country rock around a carbonatite intrusion were originally a component of the carbonatite magma. Temporal and spatial segregation of Na- and K-rich fluids is common, with fenite aureoles frequently comprising an outer sodic zone and a, generally later, inner potassic fenite (Le Bas, 2008). Calcite and ankerite carbonatites can induce both Na- and K-rich fluids (Le Bas, 2008), which suggests that the composition of the parent magma may not be the main determining factor, although the magmatic evolution of any individual carbonatite may control the earlier preferential loss of Na over K (Woolley, 1982). A dependence on magma temperature appears to be important, with

sodic fenite being associated with magma at deeper levels in the complex, of higher temperature, and possibly with a lower CO₂ content. In contrast, potassic fenite may be produced from magma at higher levels and lower temperatures, and be richer in CO₂ (Woolley, 1982; Rubie and Gunter, 1983; Le Bas, 2008; Viladkar and Ramesh, 2014).

As carbonatite magmas undergo fractional crystallisation, a sequence of magma typically evolves from calcitic composition to dolomitic/ankeritic and then to sideritic composition (Heinrich, 1966; Le Bas, 1981; Wall, 2013). The carbonatite differentiation experiments of Anenburg *et al.* (2020) mimic this observed sequence. An associated increase in Fe, Ba, Mn and REE accompanies this trend, with the highest concentrations of these elements being found in late-stage carbonatites (Goodenough *et al.*, 2018). REE mobility in fluids is well established, with an early study by Martin, Whitley and Woolley (1978) identifying magma-derived REE enrichment of a barren quartzite rock during emplacement of the Borralan alkaline/carbonatite complex in Scotland. Bühn and Rankin (1999) commented on the high capability of these fluids to transport the high field strength elements (HFSE) and REE at the Kalkfeld carbonatite in Namibia. Further studies of fluid inclusions related to fenite have demonstrated that REE-HFSE-bearing fenitising fluids are generally aqueous-CO₂ alkali-bicarbonate brines of variable salinity (Palmer, 1998; Bühn and Rankin, 1999; Bühn *et al.*, 1999, 2001; Williams-Jones and Palmer, 2002; Carmody, 2012; Dowman *et al.*, 2017b). However, it is acknowledged that element partitioning in natural magma systems is highly complex and only reasonably well understood for a few geochemically simple systems (Chakhmouradian and Reguir, 2013).

Until recently, apatite was the only mineral mentioned in the literature on RE-bearing minerals in fenite aureoles around carbonatites (Kresten and Morogan, 1986; Morogan and

Woolley, 1988; Andersen, 1989; Morogan, 1989; Smith, 2007; Le Bas, 2008). However, growing interest in REE has been accompanied by increased reporting of rare earth mineralisation in altered rocks. Cordylite-(La), a new mineral species was found in fenite from the Biraya Fe-REE deposit in Irkutsk, Russia (Mills *et al.*, 2012), together with other RE-minerals, such as daqingshanite-(Ce),(La), monazite-(Ce) and bastnäsité-(Ce). Apatite associated with fenite at the Songwe carbonatite complex in Malawi can be HREE-enriched, and the fenite rocks contain occasional xenotime-(Y) (Broom-Fendley *et al.*, 2013). Xenotime-(Y) is the principal RE-bearing mineral at the carbonatite of Lofdal in Namibia, and is found in albitised fault zones (Wall *et al.*, 2008; do Cabo *et al.*, 2011; Loye, 2014). At Bandito in the Yukon, a fenite (associated with nepheline syenite rather than carbonatite) was found to be RE-rich, with up to 3.49% REE in areas of highly metasomatised syenite, contained in minerals such as monazite, bastnäsité and apatite (Endurance Gold Corporation, 2013).

This contribution compares the mineralogy and whole rock composition of fenites at two of the largest carbonatite complexes in Malawi, both of which have well-developed metasomatic aureoles located in broadly similar protoliths (Figs 1, 2). Kangankunde is considered a world-class rare earth deposit and Chilwa Island has pyrochlore, fluorapatite, magnetite-bearing calcite carbonatite (Garson, 1965; Simonetti and Bell, 1994). In selecting complexes situated in similar country rock, the effect of the protolith is minimised. In this study, as part of trying to achieve a better understanding of metasomatic processes at carbonatite complexes, we will comment on similarities seen at the two locations, but we are particularly interested in identifying any differences in the mineralisation and in the alteration of the fenites with respect to the contrasting RE-enrichment of their host carbonatite. We also consider how differences between the

carbonatites of the two complexes (in terms of relative size, composition, emplacement order) may influence the sequence and composition of metasomatic fluids expelled into the country rock.

Geological background

The carbonatite complexes of Chilwa Island and Kangankunde lie in Malawi's Cretaceous Chilwa Alkaline Province (CAP), at the extreme southern end of the East African Rift system. The ~300 km² area experienced repeated episodes of emplacement of alkaline and carbonate magmas into amphibolite and granulite facies basement rocks (Bailey, 1977; Kröner *et al.*, 2001). Crustal extension and decompressional melting between 138 and 107 M.y. drove the most recent alkaline magmatism in the CAP (Eby *et al.*, 1995). This produced twenty-eight intrusions and vents of alkaline rocks and carbonatites (Woolley, 2001). These lie in two main belts: a western belt associated with lines of rifting and an eastern chain within a zone of depression (Garson, 1965).

Chilwa Island is located at the north end of the eastern chain and is the largest of the Malawi carbonatites. It is a ring structure ~4 km in diameter, surrounded by brecciated country rock and fenitised Precambrian granulites and gneisses, with the outer margins of country rock alteration hidden beneath the lake and its sediments at a distance of at least several kilometres. The fenite aureole comprises an inner zone of potassic feldspathic breccia surrounding the outermost sövite passing outwards to progressively less altered rock (Fig. 1). Outermost areas have mineralogy inherited principally from the basement, dominated by plagioclase and quartz, with a thin network of veins of mineralisation which include aegirine and riebeckite. Between these outer areas and the breccia lie rocks of

moderate alteration, where the vein network promoting alteration is more developed, with the replacement of basement minerals by orthoclase, aegirine and sodic amphiboles, such as arfvedsonite and riebeckite (Woolley, 1969).

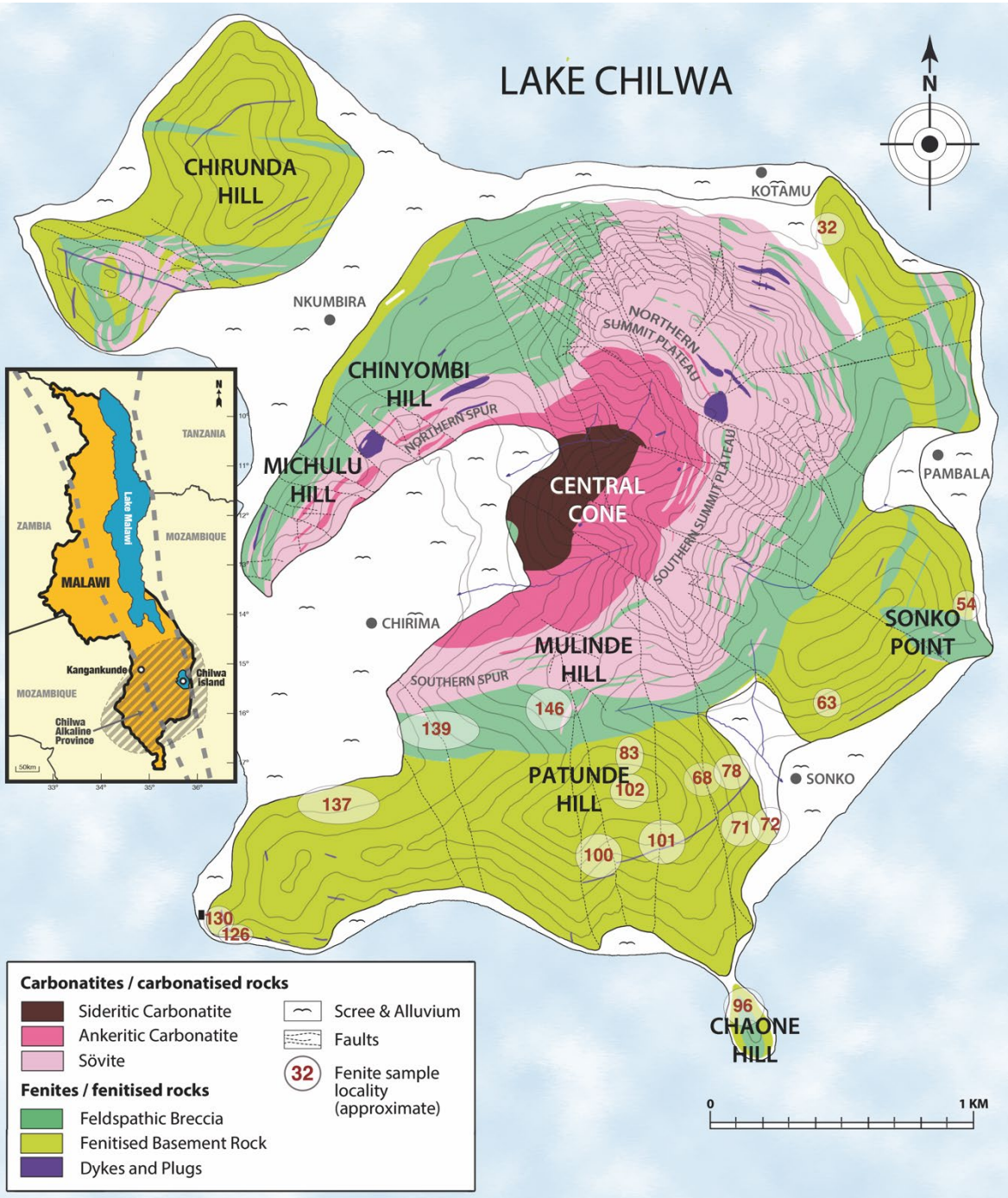


Fig. 1. Geological map of Chilwa Island (adapted from Garson and Campbell Smith, 1958)

Chilwa Island carbonatites were surveyed comprehensively by Garson and Campbell Smith (1958), with further descriptions by Garson (1965); Le Bas (1981) and Woolley (2001). The complex consists of multiple carbonatite intrusions, with structural relationships indicating sequential emplacement from earlier outer calcite carbonatite, called 'sövite' by Garson (1965) inwards to ankerite carbonatite and the youngest central 'sideritic' carbonatite. Sövite varies from almost pure calcite to compositions containing apatite and/or pyroxene and pyrochlore. Garson and Campbell Smith (1958) suggested that areas of sövite may have been replaced by more ankeritic carbonatite. The 'sideritic' carbonatite was reclassified as ankerite by Buckley and Woolley (1990) but consists of an alteration assemblage of calcite and iron and manganese oxides, with substantial quartz (Garson and Campbell Smith, 1958; Woolley, 2001; Dowman, 2014). For convenience, we continue to use the term sideritic carbonatite in this manuscript.

A late-stage hydrothermal and silicification event partially altered the carbonatite, creating quartz and quartz-fluorite veins and introducing secondary minerals into the sideritic carbonatite.

Kangankunde is situated in the western chain of carbonatites, in the western Shire Valley. It is the largest carbonatite vent complex in Malawi, forming a hill rising 180 m above the plain. Together with the two knolls at its northern and southern ends, it forms an elongated structure of ~0.80 km by 0.65 km, the shape being influenced by its location in a zone of weakness parallel with, and related to, the main rift fault in the west (Garson, 1965). The carbonatite is surrounded by fenitised granulites, gneisses and amphibolites, extending out to a distance of over a kilometre from the foot of the hill (Fig. 2). The innermost part of the aureole comprises breccia which is less shattered than that of Chilwa Island. Outer areas of

184 the aureole are more fractured than at Chilwa Island and have a more extensive network of
185 veins of mineralisation. These veins are formed of aegirine, commonly intergrown with
186 sodic amphibole, and iron oxides, reported as limonite and goethite by Garson (1965).
187 Carbonate is evident throughout the aureole, and is concentrated within, or adjacent to,
188 fenite veins (Woolley, 1969; Dowman, 2014).
189

Fig. 2. Geological map Kangankunde (adapted from M S Garson Geological Survey Dept. Nyasaland, 1963)

The Kangankunde carbonatite is unusual due to the dominance of ferroan dolomite and ankerite carbonatite, and the lack of calcite carbonatite and major associated silicate rocks (Garson, 1965; Woolley, 1969; Wall, 2000). All ferroan dolomite/ankerite carbonatite, apart from occasional dark brown veins, contains rare earth minerals, and Kangankunde has the highest concentration of light REE in the Chilwa Alkaline Province.

In addition to the main RE-rich carbonatite, the complex hosts two older intrusions of medium-grained, apatite-rich dolomite carbonatite, which are not related petrographically or by mineral chemistry to the main carbonatite (Wall, 2000). Isotope studies also suggested no direct link with REE mineralisation (Broom-Fendley *et al.*, 2017), although this carbonatite did experience a subsequent influx of REE mineralising fluids from the main carbonatite (Wall and Mariano, 1996).

Carbonate-free, monazite-bearing quartz rocks were mapped and described by Garson and Campbell Smith (1958) both within the main area of carbonatite and in the fenite aureole. In these rocks, strontianite is absent and florencite-goyazite is more abundant than in the carbonatite. Further rare earth-bearing quartz-rich rocks occurring in the outer fenite aureole (Wall and Mariano, 1996; Wall, 2000) are quartz-florencite rocks and quartz-apatite rocks. In contrast, quartz-fluorite rocks, located at 1.5 km from the carbonatite, contain accessory crystals of strontianite and baryte, but lack REE minerals. At Chilwa Island, rare-earth bearing rocks of secondary quartz were identified in fenite by Dowman (2014). These contain a variety of minerals including monazite, fluorapatite, bastnäsite, xenotime and a Th-REE phase (possibly thorian synchysite) and are considered to be highly altered.

217

218 Fenites at both Chilwa Island and Kangankunde contain fluid inclusions, with quartz being
219 the most important host mineral (Dowman, 2014). The fluid inclusions of both complexes
220 were found to have similar patterns and characteristics. They are secondary, small and
221 heterogeneous, forming cross-cutting trails probably representing different fluid inclusion
222 assemblages, suggesting that multiple fluid events occurred during metasomatism.
223 Aqueous and/or CO₂-bearing inclusions are present, and daughter minerals such as
224 nahcolite, burbankite, rutile and apatite were identified. Methane, nitrogen and chloride all
225 appear to be absent, as does halite.

226

227 At Chilwa Island, a time bracket for the complex is provided by Snelling (1965) whose
228 date of 138 Ma was from K-Ar dating of biotite in early sövite, and by Eby *et al.* (1995)
229 who used titanite fission-track analysis to date a nepheline-syenite plug intruding
230 carbonatite at 126 Ma, with apatite fission-track dates of 87±9 Ma from the same rock. An
231 apatite fission-track central age of 99±4 Ma was obtained from fluorapatite in low-grade
232 fenite (Dowman *et al.*, 2017a).

233

234 At Kangankunde, a date of 123±6 Ma was obtained from K-Ar dating of phlogopite in
235 carbonatite by Cahen and Snelling (1966). Wall *et al.* (1994) reported a date of 136±11 Ma
236 from Sm-Nd isotopes for the main carbonatite, with an isochron linking monazite and
237 secondary apatite from the carbonatites with monazite, florencite and REE-rich apatite
238 from the quartz rocks. However, the quartz fluorite rock did not plot on the same isochron,
239 and although the date is not of high precision, this rock appears to be considerably younger
240 at 80±45 Ma. The technique failed for the apatite-dolomitic carbonatite, and thus no Sm-
241 Nd data are available for this rock (Wall, 2000).

Key aspects regarding the two complexes are summarised in Table 1.

Table 1. Summary of characteristics of the Chilwa Island and Kangankunde carbonatites

Characteristic	Chilwa Island	Kangankunde
Location in East African rift	In eastern belt, part of an irregular chain of igneous rocks in a zone of depression passing into a down faulted zone	In western belt, associated with lines of rifting in the Shire Rift Valley
Size	Largest Malawi carbonatite, 2.3 km by 2.4 km, rising 400m above Lake Chilwa	Largest vent and fourth largest Malawi carbonatite, 0.80 km by 0.65 km, now forms a hill, rising 180m above plain
Structure	Ring complex of igneous centres on a vertical axis interpreted as extending more than 2,400m below present lake level. Substantial shattering at carbonatite/country rock junction	Vent in zone of weakness parallel to, or related to fault to the west. Shallower erosion level than Chilwa Island
Country rocks	Gneisses and granulites	Gneisses, granulites and amphibolites
Carbonatite types	Calcite through ankerite to ferromanganiferous sideritic carbonatite	Dominant RE-rich ferroan dolomite and ankerite, minor presence of unrelated apatite-rich dolomite
Silicate intrusives	Minor olivine-nephelinite, rare ijolite, dolerite and nepheline syenite	Virtually none
RE-bearing and RE minerals	Apatite with minor monazite, bastnäsite and parisite-synchysite in calcite carbonatite and ankerite; florencite and minor Th-REE phase in sideritic carbonatite (Dowman, 2014)	Significant monazite deposit, minor bastnäsite, florencite and apatite
Nb-bearing minerals	Pyrochlore in calcite and ankerite, niobian rutile occurs infrequently in carbonatite	Rare pyrochlore

Methodology

Thirty one fenite samples from the Natural History Museum, London collection BM1968 P37 were studied. Mineralogy assemblages and compositions were determined at Kingston University using an Oxford Instruments INCA EDS system and a Gatan Chroma CL system, both hosted on a Zeiss EVO50 SEM. Whole rock analyses were carried out at the Natural History Museum, London. Tables S1 - S8, providing details of the samples, analyses and analytical techniques, including quality control, have been deposited with the Principal Editors of *Mineralogical Magazine*, and are available as supplementary data.

Fenite terminology

Elliott *et al.* (2018) noted that fenites are described as a metasomatic family by the International Union of Geological Sciences (IUGS) (Zharikov *et al.*, 2007), forming at high temperatures and possessing a characteristic suite of minerals. The IUGS do not provide a more detailed nomenclature. Attempts at classification include those based on spatial relationship to the source intrusion (Kresten, 1988); ratios of Na and K (Verwoerd, 1966); or by adding ‘fenitised’ to the name of the protolith (Arzamastev *et al.*, 2011; Kozlov and Arzamastsev, 2015) or by adapting the scheme used by the IUGS for metamorphic rocks (Elliott *et al.*, 2018). In this paper, we adopt the method used by Morogan (1994) where fenites are classified using a continuous scale of fenitisation intensity into low-grade, medium-grade and high-grade fenite. Low-grade and medium-grade fenites approximately match the earlier petrographic descriptions of Garson and Campbell Smith (1958) and Woolley (1969) of ‘quartz fenite’ and ‘syenite fenite’. The term ‘high-grade fenite’ is used to refer to breccia and other altered monophasic rock.

SEM identification of matrix minerals and assemblages

Low-grade fenite

At both complexes, low-grade fenite has a matrix of quartz and feldspar in similar proportions. The feldspar is mostly plagioclase (albite to oligoclase) with orthoclase forming in cracks and at margins of grains, as noted by Woolley (1969). The perthitic textures noted at Chilwa Island were not seen at Kangankunde.

Fenite veins typically represent up to 10 modal % of low-grade fenite at both sites. These contain aegirine, accompanied by orthoclase at Chilwa Island, and by iron oxides at Kangankunde. Rutile and fluorapatite are also components of the veins, particularly at Kangankunde, where zoned rutile grains can be seen as segregations in areas of iron oxide, or intergrown with aegirine. Fluorapatite at Kangankunde can exhibit zoning and associate with monazite-(Ce) and sub-micron-sized zircon. Veins at Kangankunde (Fig. 3a,b) have a more diverse mineral assemblage than those at Chilwa Island, with calcite and ankerite as common components. Strontianite and fluorite occur in most Kangankunde sections, with pyrochlore found occasionally in carbonate-rich samples.

Rare earth minerals are scarce in this zone at both complexes. Monazite-(Ce) is most common, particularly at Kangankunde, where it is seen in most sections. Parisite-(Ce) was detected in one section at each site. Bastnäsite-(Ce) was seen in several sections from Kangankunde, but appears to be absent in Chilwa Island low-grade fenite.

Medium-grade fenite

In the matrix of medium-grade fenite sections, orthoclase continues to develop at the expense of plagioclase. The proportion of primary quartz is less than 25% of sections but secondary quartz occurs more frequently in mineralised veins. The vein network becomes more extensive in medium-grade fenite at both complexes. This trend is more marked at

299 Kangankunde, where veins typically comprise 15%-25 modal% compared to 10%-20% at
300 Chilwa Island.

301

302 Minerals common in veins in medium-grade fenite at both complexes include orthoclase
303 (commonly located at vein margins) and aegirine together with sodic amphibole
304 (magnesioarfvedsonite and richterite). Iron oxide is a major component of veins at
305 Kangankunde.

306

307 The components of the accessory mineral assemblages in veins in medium-grade fenite
308 differ between the two complexes. At Chilwa Island, veins of orthoclase and aegirine
309 typically contain micro-assemblages comprising zircon, fluorapatite and ilmenite (Fig. 4a).
310 Ilmenite grains contain areas of dissociation into rutile and magnetite. Rutile grains
311 increase in size and frequency with alteration and may fringe ilmenite grains. Zoning,
312 when present, is caused by variations in Nb content (Dowman, 2014). Fluorapatite is the
313 most important RE-bearing mineral, typically with complex concentric zoning and
314 sometimes with monazite inclusions. Back-scattered electron images show bright and dark
315 zones. Bright zones contain REE whereas in dark zones, the REE are below detection
316 (Dowman, 2017b). In more altered areas of this grade, apatite zoning and the mineral
317 microassemblages disappear and fluorapatite associates with aegirine, orthoclase and
318 occasionally carbonate (Fig. 4b). The carbonate is generally calcite, although ankerite was
319 also detected. Apart from fluorapatite, rare earth-bearing minerals are not abundant, but
320 monazite-(Ce) and bastnäsite-(Ce) are found in most medium-grade samples except in the
321 more altered parts of this zone, where they become rare to absent, and instead, parisite-
322 (Ce) forms part of the mineral assemblage. Rutile grains tend to porosity here and can
323 contain parisite and inclusions of submicron zircon.

324

325 At Kangankunde, a more diverse range of accessory minerals occur in veins (Fig. 4c,d).

326 These include rutile, strontianite, fluorite (sometimes intergrown with aegirine), carbonate

327 as well as fluorapatite and the rare earth minerals, dominantly monazite-(Ce) but also

328 bastnäsite-(Ce). Parisite-(Ce), pyrochlore and ilmenite are occasional members.

329 Fluorapatite is much less common than at Chilwa Island. It may still be zoned but is often

330 porous in appearance, frequently contains submicron zircon grains and its abundance

331 declines with increasing fenitisation. Alteration promotes carbonate, chiefly dolomite and

332 ankerite rather than calcite. The rare earth minerals, monazite-(Ce) and, to a lesser extent,

333 bastnäsite-(Ce) are also favoured by alteration, and were found in every rock section of this

334 grade. Both these minerals are more abundant than at Chilwa Island.

335

336 ***Breccia***

337 The greatest contrast in mineral assemblages in fenite at the two complexes is in their

338 breccias. Breccia at Chilwa Island is almost monophase orthoclase with a few assemblages

339 of pyrochlore and ragged resorbing zircon (Fig. 5a). A Th-REE phase, with grains too

340 small to analyse was also noted.

341

342 Orthoclase, together with quartz and carbonate (calcite less common than dolomite,

343 ankerite and sideritic), form the matrix of the breccia at Kangankunde. Plagioclase is very

344 rare.

345

346 The mineralogy of the breccia at Kangankunde is diverse (Fig. 5b,c). Although veins of

347 aegirine and iron oxides, characteristic of medium- and low-grade fenite, are largely

348 absent, fluorapatite is present, preferentially located in carbonate. It is usually porous,

containing grains of monazite and submicron zircon but may also occur with a cumulate habit. Strontianite is most common in this part of the aureole and is accompanied by newly appearing minerals such as daqingshanite-(Ce), $(\text{Sr,Ca,Ba})_3(\text{Ce,Lu})(\text{PO}_4)(\text{CO}_3)_3(\text{OH,F})$ and florencite-(Ce)-goyazite. Monazite-(Ce) is abundant, and bastnäsite-(Ce) is more common than further out in the aureole, although parisite appears to be absent. Pyrochlore and rutile occur in areas of carbonate, but fluorite is rare.

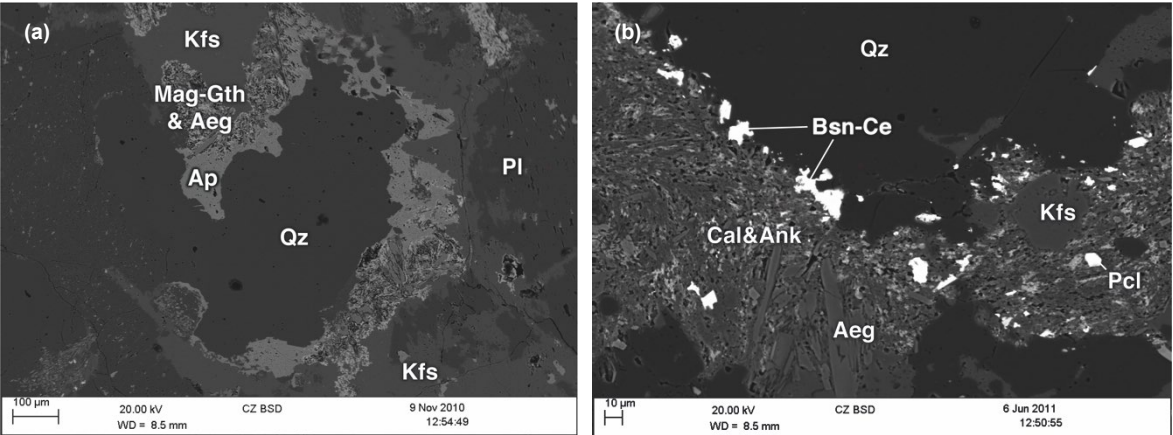
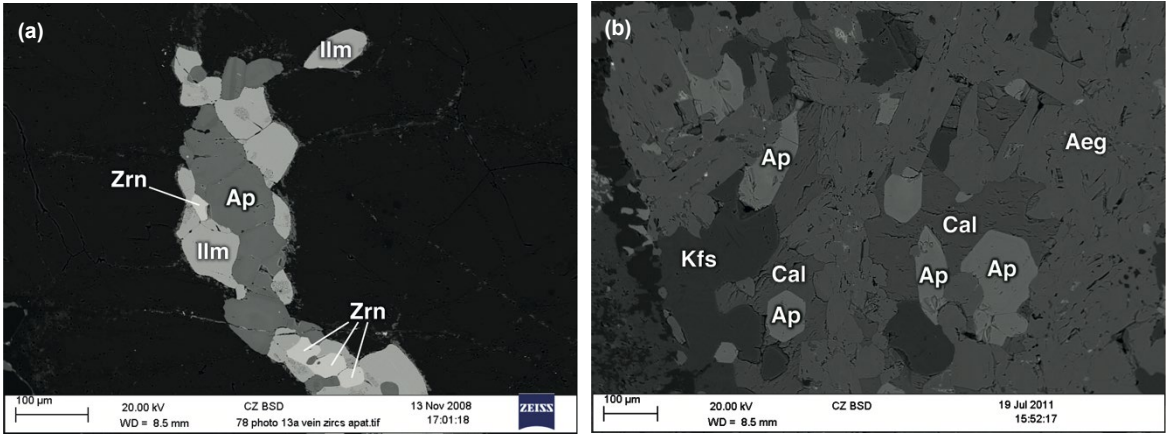


Fig. 3. Back-scattered electron images of mineralogy in low-grade fenite at Kangankunde:

(a) BM1968 P37 193 typical vein of mineralisation in plagioclase matrix containing apatite and intergrown aegirine and iron oxides, fringed by K-feldspar; (b) BM1968 P37 218 vein of mineralisation with aegirine and K-feldspar, but which also contains pyrochlore and various carbonates including bastnäsite, suggesting mobility of Nb and REE extends into outer aureole.



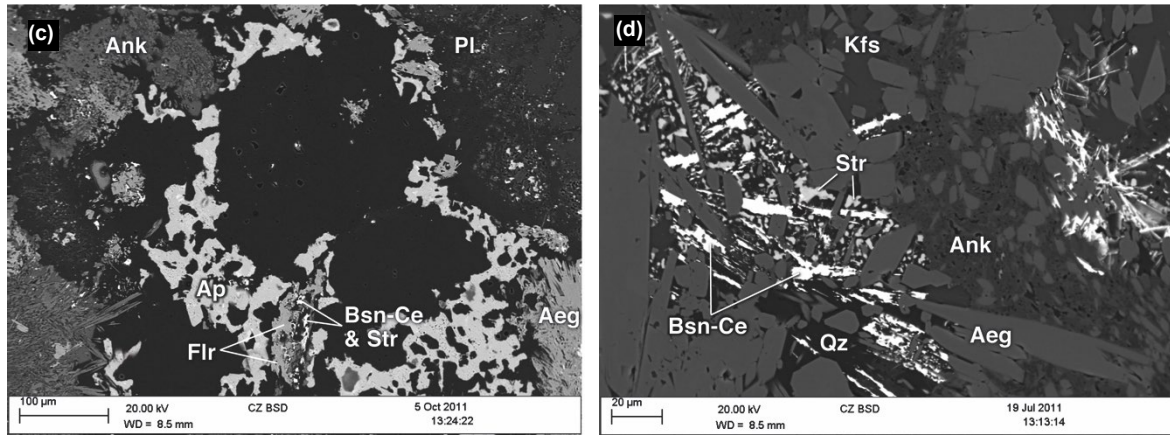
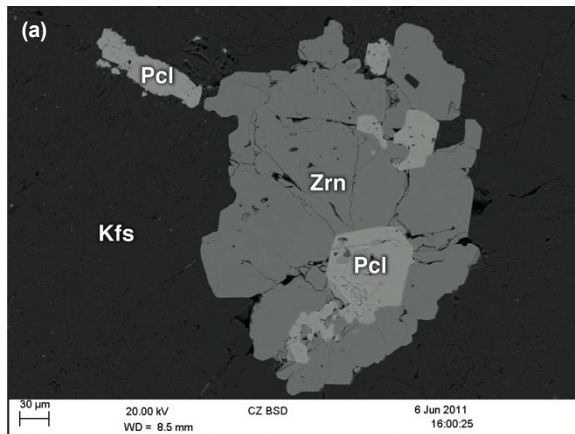


Fig. 4. Back-scattered electron images of mineralogy in medium-grade fenite:

(a) Chilwa Island: BM1968 P37 78 characteristic mineral assemblage of this grade of fenite: zircon, fluorapatite and ilmenite found in veins of aegirine and K-feldspar; (b) Chilwa Island: BM1968 P37 68 fluorapatite in slightly more altered fenite preferentially associates with calcite, aegirine and K-feldspar. Microassemblages of zircon, fluorapatite and ilmenite are now becoming unusual; (c) Kangankunde: BM1968 P37 242 mineralised veins are more diverse than at Chilwa Island and with more RE-minerals than lower-grade fenite. Here skeletal fluorapatite associates with bastnäsite-(Ce), strontianite, fluorite, aegirine and Fe-rich ankerite; (d) Kangankunde: BM1968 P37 198 vein of mineralisation of bastnäsite-(Ce) and strontianite with secondary quartz and Fe-rich ankerite.



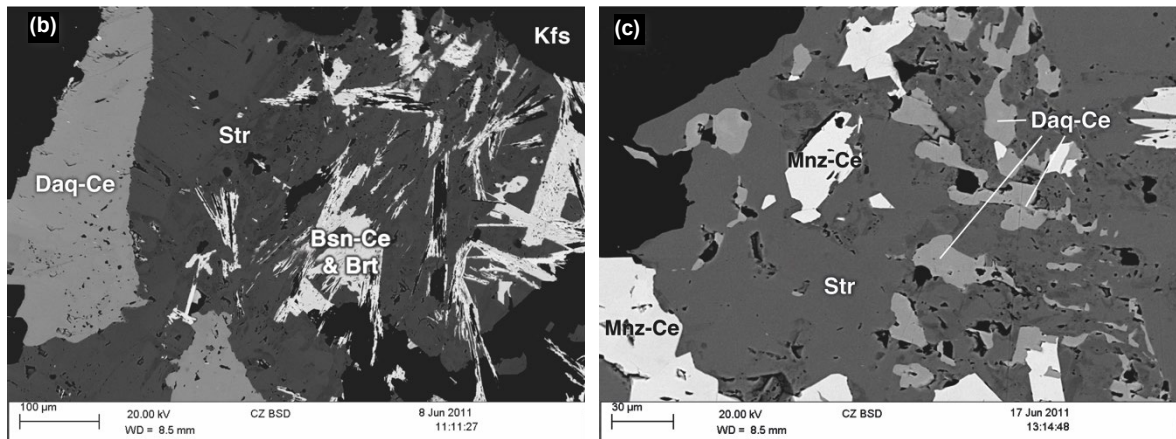


Fig. 5. Back-scattered electron images of mineralogy in brecciated fenite:

(a) Chilwa Island: BM1968 P37 146 breccia predominantly composed of K-feldspar contains occasional associations of zircon and pyrochlore grains; (b) Kangankunde: BM1968 P37 212 highly mineralised breccia containing strontianite and RE-bearing minerals daqingshanite and bastnäsite-(Ce) intricately intergrown with baryte; (c) Kangankunde: BM1968 P37 254 also highly mineralised, with strontianite, daqingshanite present, together with monazite-(Ce).

Summarising briefly similarities in fenite mineralogy, alkaline alteration at both complexes is seen to be widespread and pervasive. Moving from low-grade to medium-grade fenite, this alteration becomes less confined to veins and fractures and spreads increasingly inwards from grain margins, creating the turbidity in feldspar noted by Woolley (1969) where country rock feldspar of oligoclase composition has undergone alteration to albite (Fig. 6a,b).

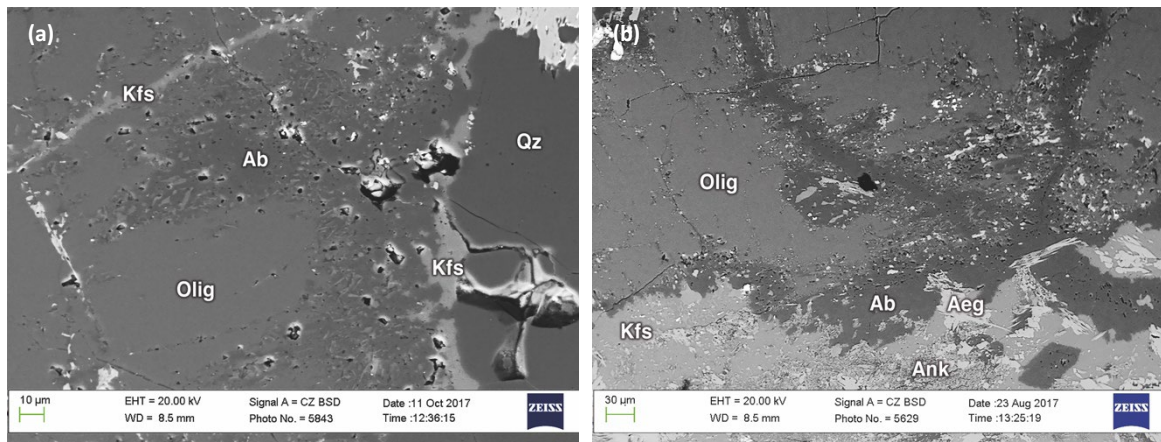


Fig. 6. Back-scattered electron images showing alteration of oligoclase feldspar grains to albite by alkaline fluids in medium-grade fenite: (a) Chilwa Island BM1968 P37 100; (b) Kangankunde BM1968 P37 250. Olig = oligoclase. Albite alteration of oligoclase extends beyond grain boundaries. K-feldspar formation in veins occurs subsequent to plagioclase alteration.

Fluorapatite and rutile at both complexes exhibit zoning and can host inclusions of submicron secondary zircon and monazite. Fluorapatite and rutile become porous in appearance in more altered areas of medium-grade fenite (Figs 7a-d, 8a-d).

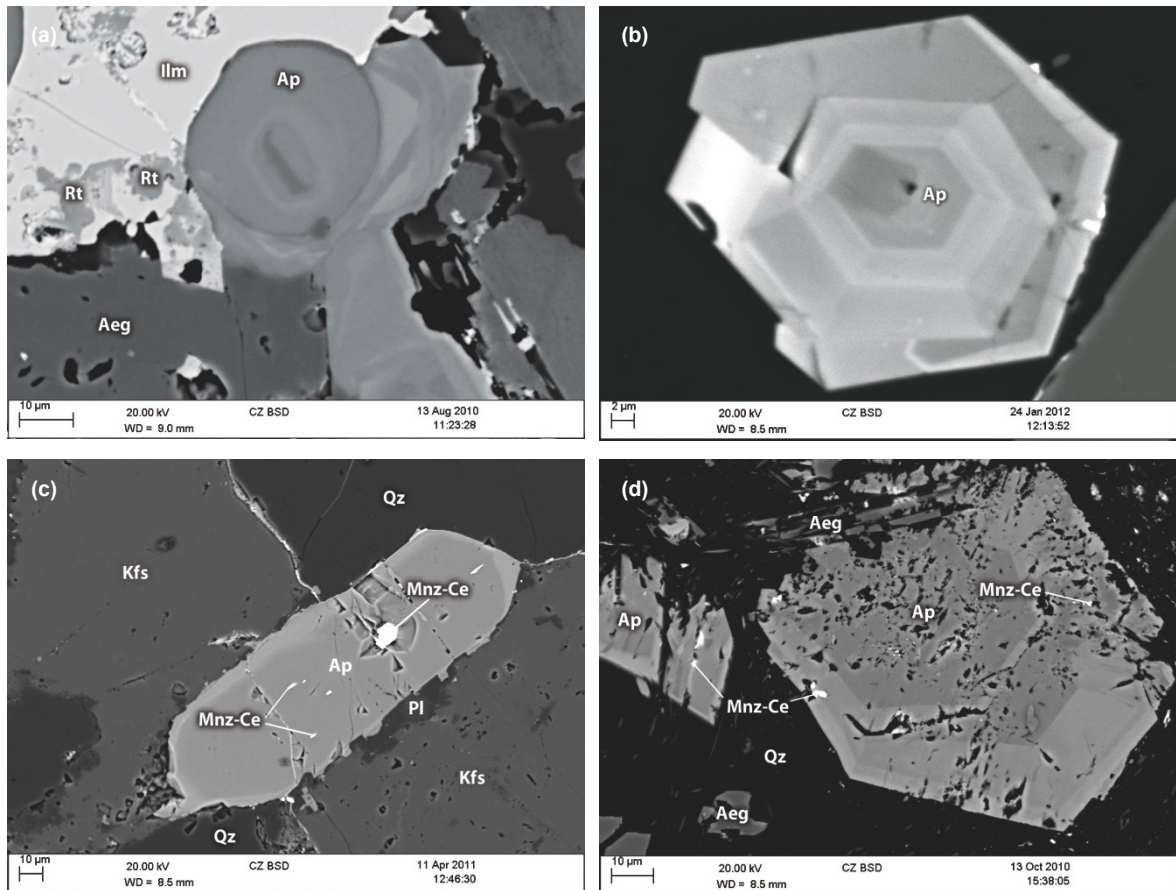
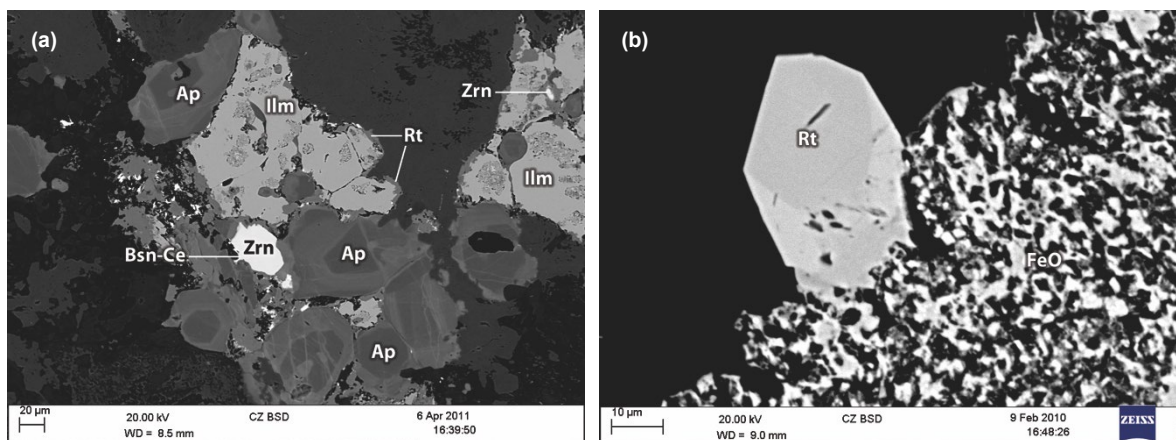


Fig. 7. Back-scattered electron images of fluorapatite in fenite with zoning and/or with inclusions:

(a) Chilwa Island: BM1968 P37 78 fluorapatite in medium-grade fenite showing complex multiple zoning, contiguous ilmenite grain shows areas of dissociation into rutile and magnetite ; (b) Kangankunde: BM1968 P37 193 multiple zones in fluorapatite in low-grade fenite; (c) Chilwa Island: BM1968 P37 126 zoned fluorapatite grain with monazite-(Ce) inclusions of varying size in medium-grade fenite; (d) Kangankunde: BM1968 P37 193 zoned fluorapatite grain exhibiting porosity in low-grade fenite. Bright grains infilling pores are monazite-(Ce).



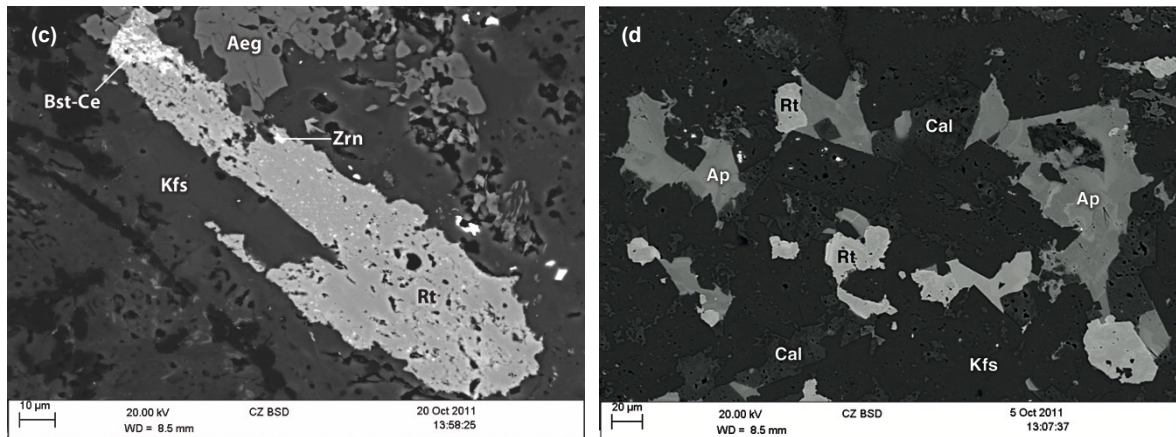
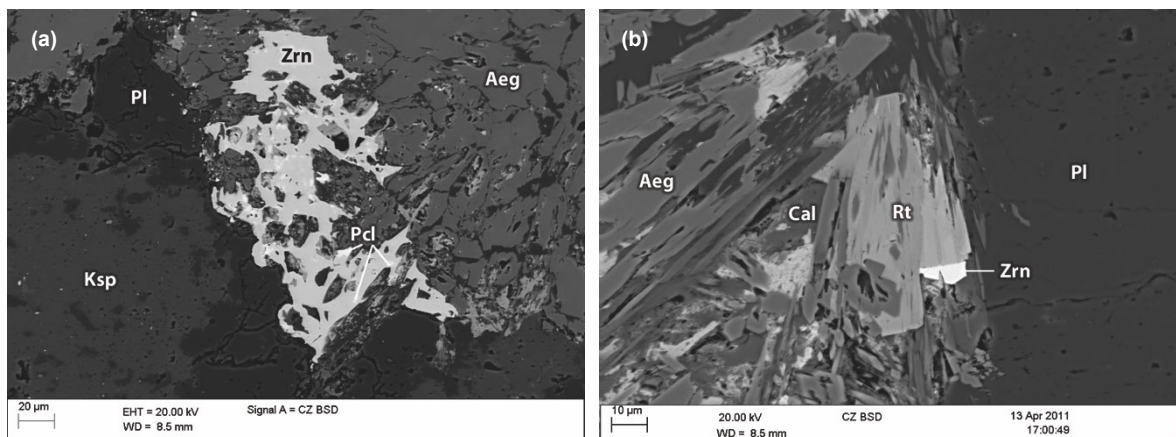


Fig. 8. Back-scattered electron images of rutile in fenite:

(a) Chilwa Island: BM1968 P37 101 assemblage of ilmenite, fluorapatite and zircon in medium-grade fenite. Segregation of rutile and magnetite from ilmenite grains has developed and rutile now forms rims around outside of ilmenite grains. Also note two generations of zircon present: one larger resorbing original grain and secondary grain forming in apatite at top right corner of image; (b) Kangankunde: BM1968 P37 193 zoned rutile segregating out at edge of iron oxide vein in low-grade fenite; (c) Chilwa Island: BM1968 P37 54 porous rutile grain in more altered medium-grade fenite. Bright areas in pores are secondary zircon; (d) Kangankunde: BM1968 P37 242 zoned rutile and fluorapatite grains in medium-grade fenite. Both minerals are becoming porous.

Overgrowths on minerals are present at both locations. These include rutile around ilmenite, pyrochlore on zircon, xenotime on zircon and zircon on rutile (Fig. 9a-d).



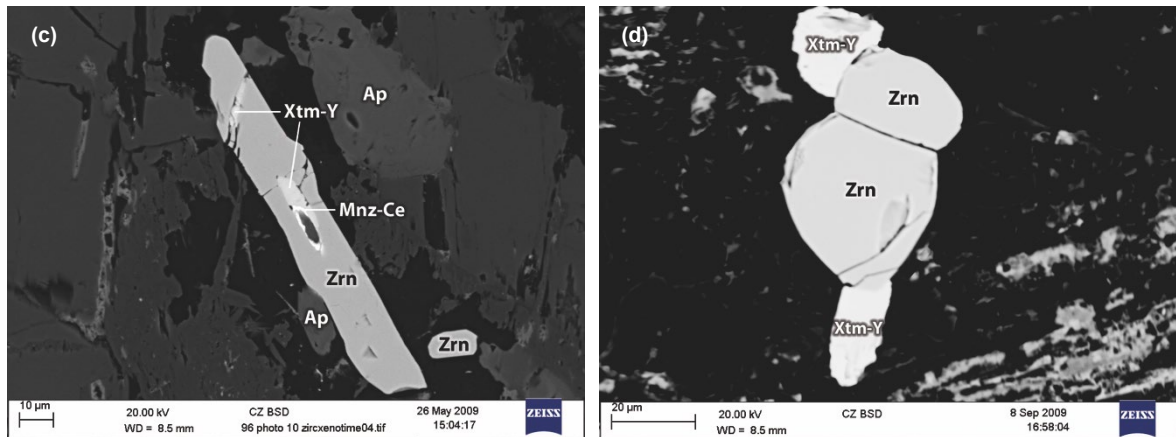
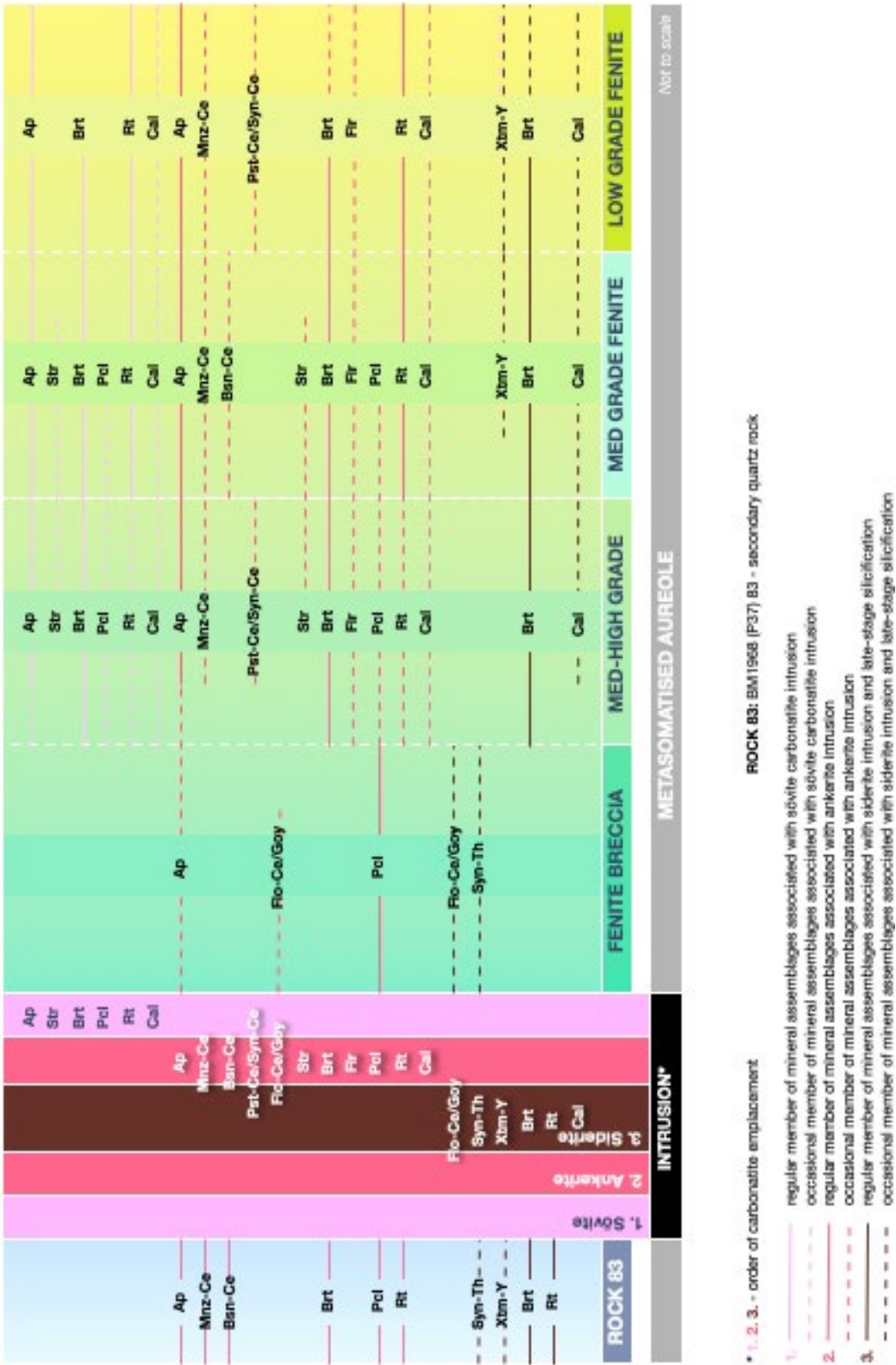


Fig. 9. Back-scattered electron images of mineral overgrowths in fenite:

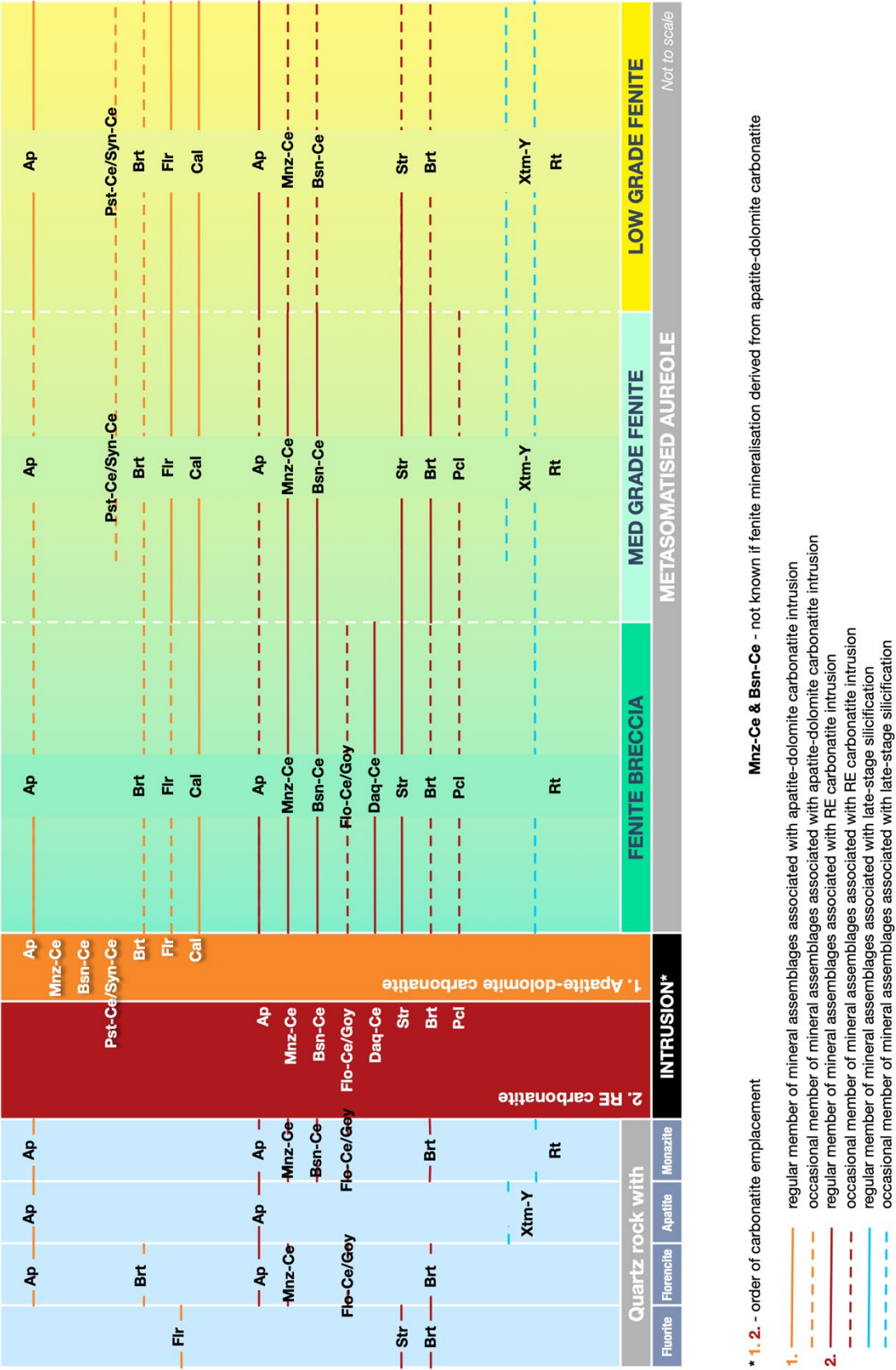
(a) Chilwa Island: BM1968 P37 102 resorbing zircon with developing pyrochlore grains in more altered medium-grade fenite; (b) Kangankunde: BM1968 P37 218 zoned rutile with zircon overgrowth in low-grade fenite; (c) Chilwa Island: BM1968 P37 96 Zircon in medium-grade fenite with xenotime forming in fracture zones in grain, also with monazite-(Ce); (d) Kangankunde: BM1968 P37 201 xenotime grains formed on rims of zircon grains in low-grade fenite.

At each complex, all carbonatitic minerals have a fenite counterpart in their respective metasomatic aureole. The only exception is baddeleyite at Kangankunde, a mineral in the apatite-dolomite carbonatite, which has not been detected in the fenite aureole. The regular and occasional components of alteration-derived mineral assemblages in fenite at each complex are set out in Fig. 10 and Fig. 11. The location of these minerals in the carbonatites of the complex is also shown.

The major differences between the fenites at the two complexes are a more diverse array of minerals at Kangankunde, a contrast that increases with proximity to the carbonatite; in the more altered parts of the aureoles, a greater abundance of RE minerals at Kangankunde than at Chilwa Island; and the identity of the main RE-bearing mineral, which is monazite-(Ce) at Kangankunde and fluorapatite at Chilwa Island.



433 Fig. 10. Alteration-derived mineral assemblages across the carbonatite complex at Chilwa Island (area shown not to
434 scale).



436 Fig. 11. Alteration-derived mineral assemblages across the carbonatite complex at Kangankunde (area shown not to

437 scale). Note complex mineralogy of breccia compared to paucity of minerals in breccia at Chilwa Island.

LREE composition of RE-bearing minerals

Having established the presence of RE-bearing minerals throughout the fenite sequence at both complexes, their LREE profiles were further studied by SEM-EDS analysis.

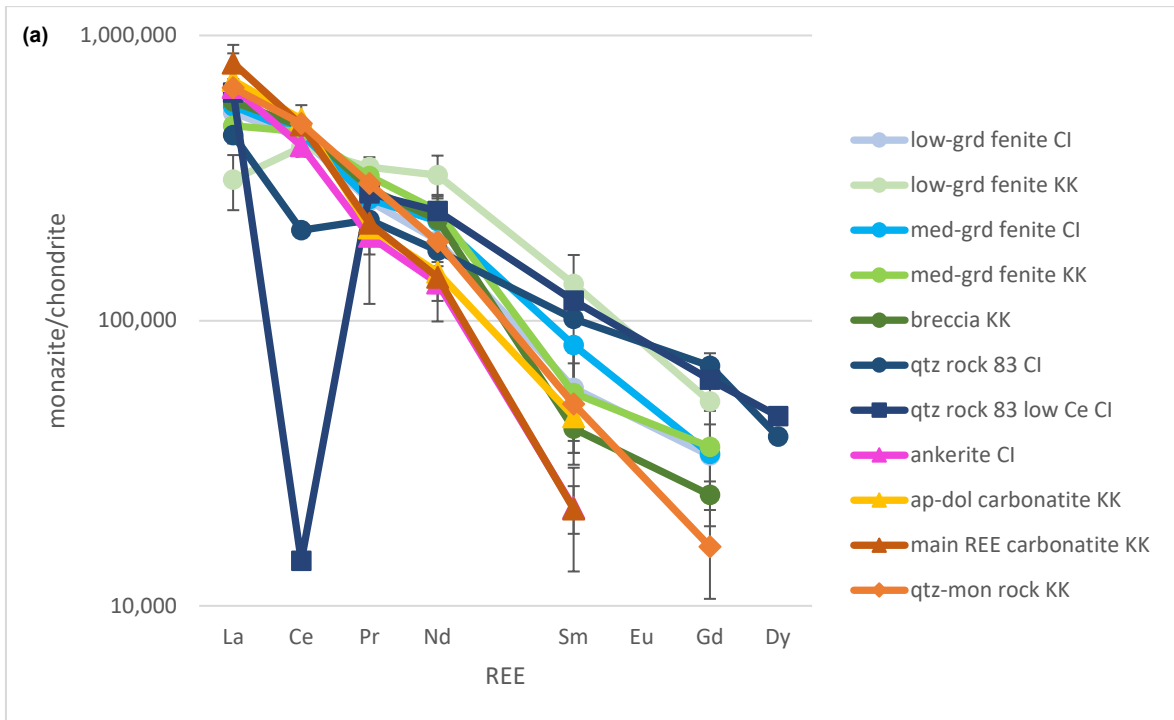
Chondrite-normalised La/Nd ratios in RE-bearing minerals at Chilwa Island and Kangankunde are set out in Table 2. Grains are too small to be analysed by laser ablation.

The fenite profiles of these minerals were then compared to their carbonatitic counterparts (Fig. 12a-d). All non-fenite analyses at Kangankunde are taken from Wall (2000).

Chondrite values used are those of McDonough and Sun (1995).

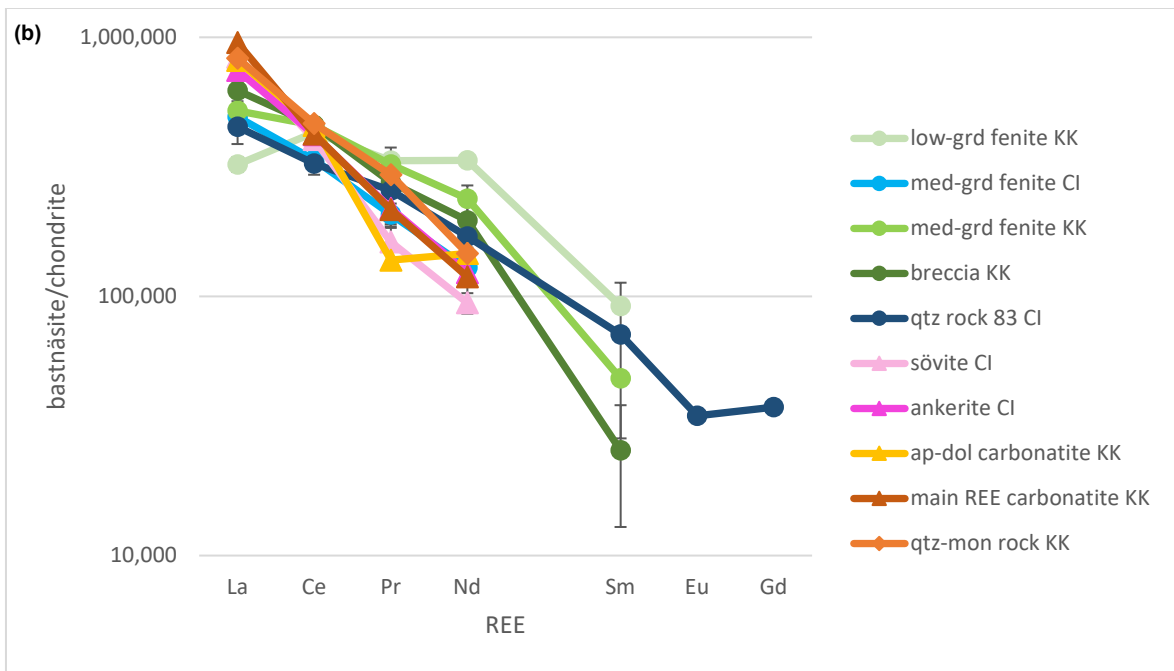
RE-minerals are largely absent from highly altered rock at Chilwa Island except for the areas of secondary quartz, which contain monazite-(Ce) and also monazite-(La). Monazite-(La) has not been detected elsewhere at either complex and hence reference in this paper to monazite, bastnäsite and parisite at the complexes is to the -(Ce) member. Fluorapatite grains at both complexes have variable RE content, and are commonly zoned in low and/or medium-grade fenite. Analyses were taken from RE-enriched zones as REE levels in zones dark under back-scattered electron imaging are below detection by SEM-EDS.

Other RE-bearing minerals such as the thorian-synchysite of Chilwa Island, and florencite-goyazite and daqingshanite at Kangankunde were not analysed because of small grain size and/or low REE content.



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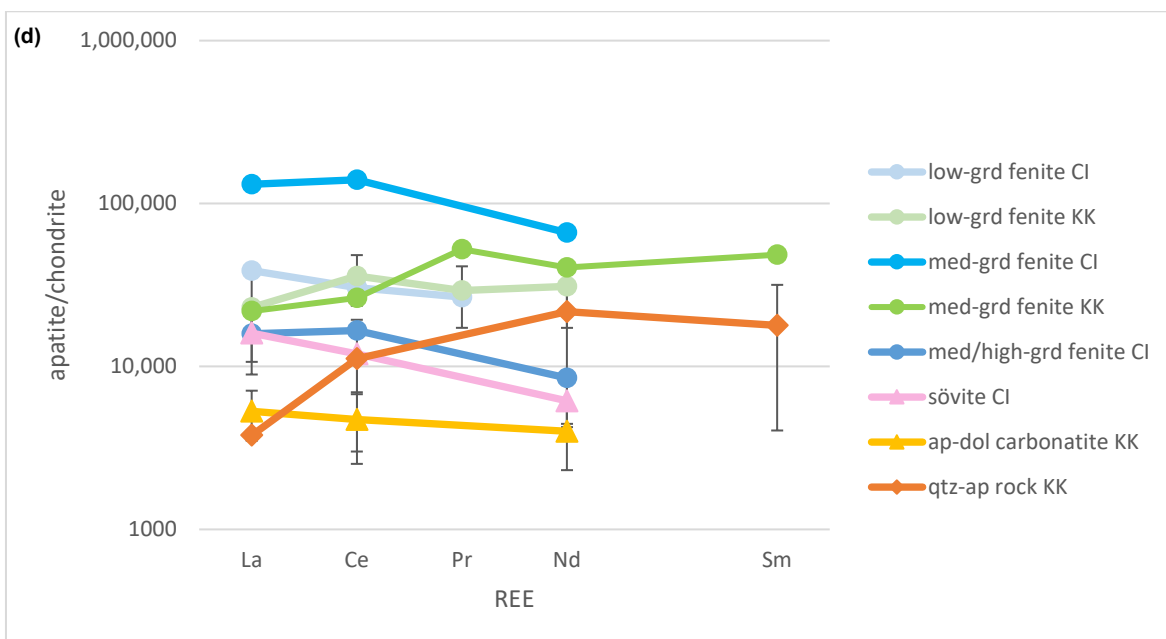
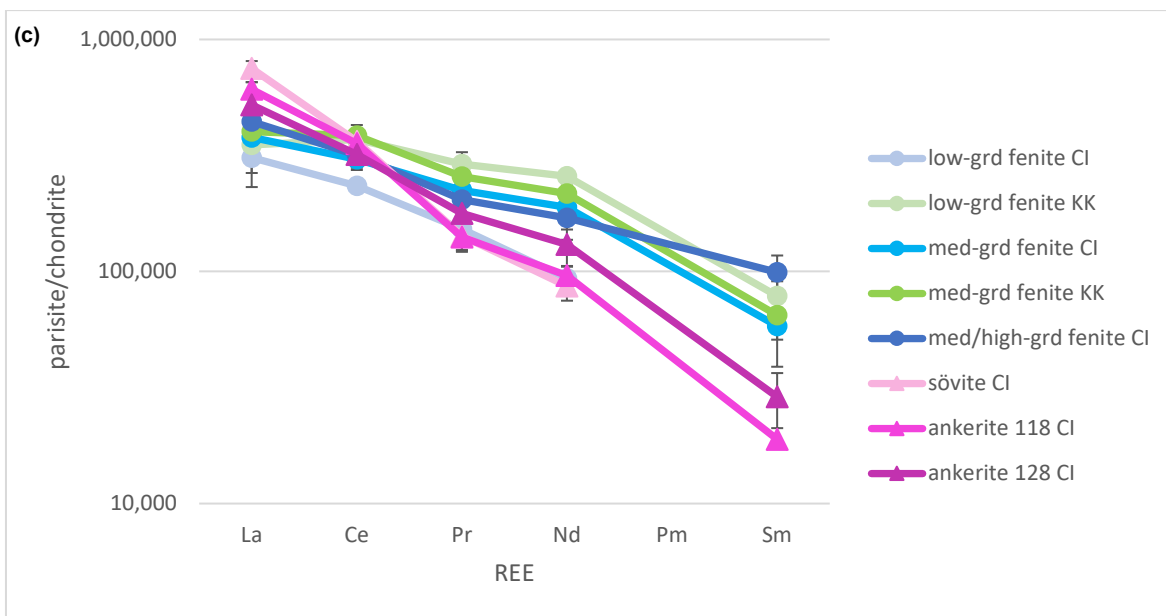


Fig. 12. Chondrite-normalised LREE profiles of RE-bearing minerals at the carbonatite complexes of Chilwa Island (CI) and Kangankunde (KK) (a) monazite; (b) bastnäsite; (c) parisite; (d) fluorapatite. Error bars represent one standard deviation.

Table 2. (La/Nd)_{cn} ratios of RE-minerals at Chilwa Island (CI) and Kangankunde (KK).

Rock type	Monazite-(Ce)		Bastnäsite-(Ce)		Parisite-(Ce)	
	CI	KK	CI	KK	CI	KK
Fenite						

Low-grade fenite	~2.8	~1.0		~1.0	~3.3	~1.4
Medium-grade fenite	~2.5	~2.0	~3.8	~2.2	~2.0-2.6	~1.9
Breccia		~2.6		~3.2		
Carbonatite & quartz rocks						
Ankeritic sövite			~8.9		~8.7	
Ankerite	~2.6		~6.1		~4.0-6.3	
RE-rich carbonatite		~5.6		~8.0		
Apatite-dolomite carbonatite		~3.5		~5.6		
Quartz rock 83	~2.6		~2.6			
Quartz-monazite rock		~4.7		~5.7		

471

472

473 **Summary of RE-mineral profiles at the complexes**

474 RE-bearing minerals across the fenite aureole at both complexes have flatter RE profiles,
475 lower LREE/MREE ratios, and are more enriched in MREE than their carbonatite
476 analogues (Fig. 12).

477

478 Monazite-(Ce) and bastnäsite-(Ce) traces in lower grade fenites differ in that Kangankunde
479 displays a convex pattern between La and Nd that is not apparent in Chilwa Island profiles
480 (Fig. 12a,b).

481

482 Fluorapatite patterns are relatively flat, but La/Nd ratios are lower at Kangankunde than at
483 Chilwa Island. (La/Nd)_{cn} ratios are typically around 2 in medium-grade fenite at Chilwa
484 Island but close to 0.5 in equivalent fenite grade at Kangankunde.

485

486 With the exception of fluorapatite, profiles of RE-bearing minerals from quartz rocks at
487 Kangankunde are flatter than the same minerals from its carbonatites, but are steeper than

those from fenites. At Chilwa Island, minerals from the quartz-rich rock BM1968 P37 83 are the most MREE-enriched in the aureole. Monazite-(Ce) and bastnäsité-(Ce) in this rock are more MREE-enriched than these minerals from the quartz-monazite rock at Kangankunde. However, it is noted that the quartz-rich specimen at Chilwa Island is from the fenite aureole, whereas the quartz-monazite rock at Kangankunde is found within the carbonatite zone.

Whole-rock chemistry of fenites

Tables of results are included in Supplementary Information Table S8.

Similarities

The mineralogical variation across the fenite aureoles into discrete zones comprising breccia, medium-grade fenites and low-grade fenites is reflected in whole-rock chemistry, among major and trace elements, as well as the REE.

Data confirm the pattern of alkaline alteration at both complexes as described above. We note that marked Na depletion occurs in breccia and quartz-rich rock, which are the most highly metasomatised areas in the aureoles (Fig. 13a,b). Depletion of Na and also Si in generally more altered rock reflects progressive metasomatic replacement of primary quartz and plagioclase by carbonate at Kangankunde, and by orthoclase at both complexes, particularly at Chilwa Island.

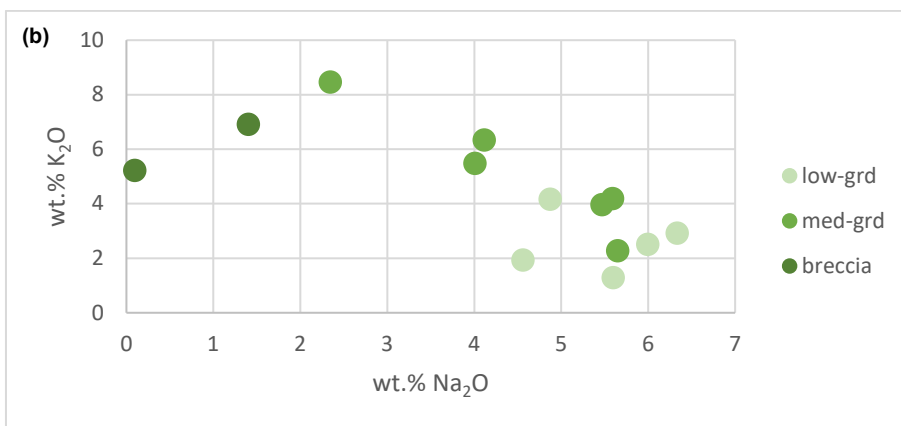
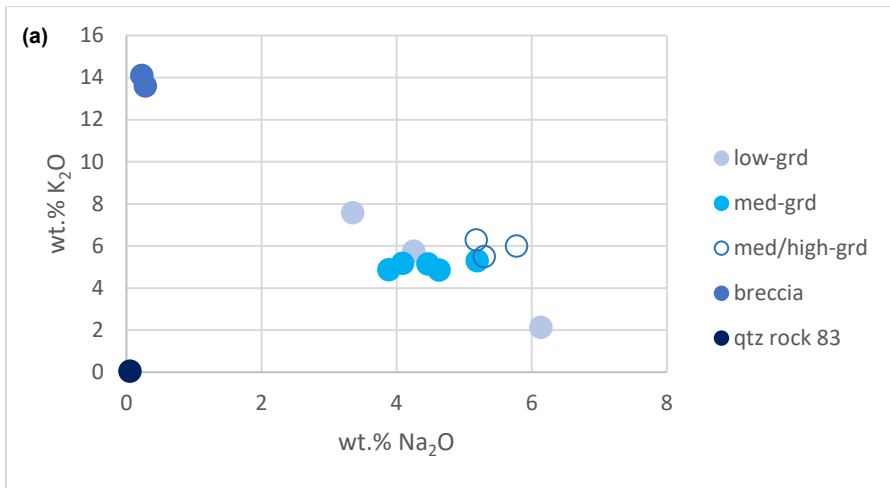


Fig. 13. Plots of wt.% K₂O vs wt.% Na₂O: (a) Chilwa Island; (b) Kangankunde.

Among the trace elements, a carbonatitic-style of enrichment in Ba, Th, Nb, Pb and Sr and depletion in Co, Cr, Ni and V occurs in fenite. As would be expected, this becomes generally more pronounced as fenitisation grade and proximity to the carbonatite increases. Fig. 14 illustrates the similarity in pattern in profiles exhibited by carbonatites and fenites. It also hints at a possible paragenetic relationship between rock 83 and siderite at Chilwa Island.

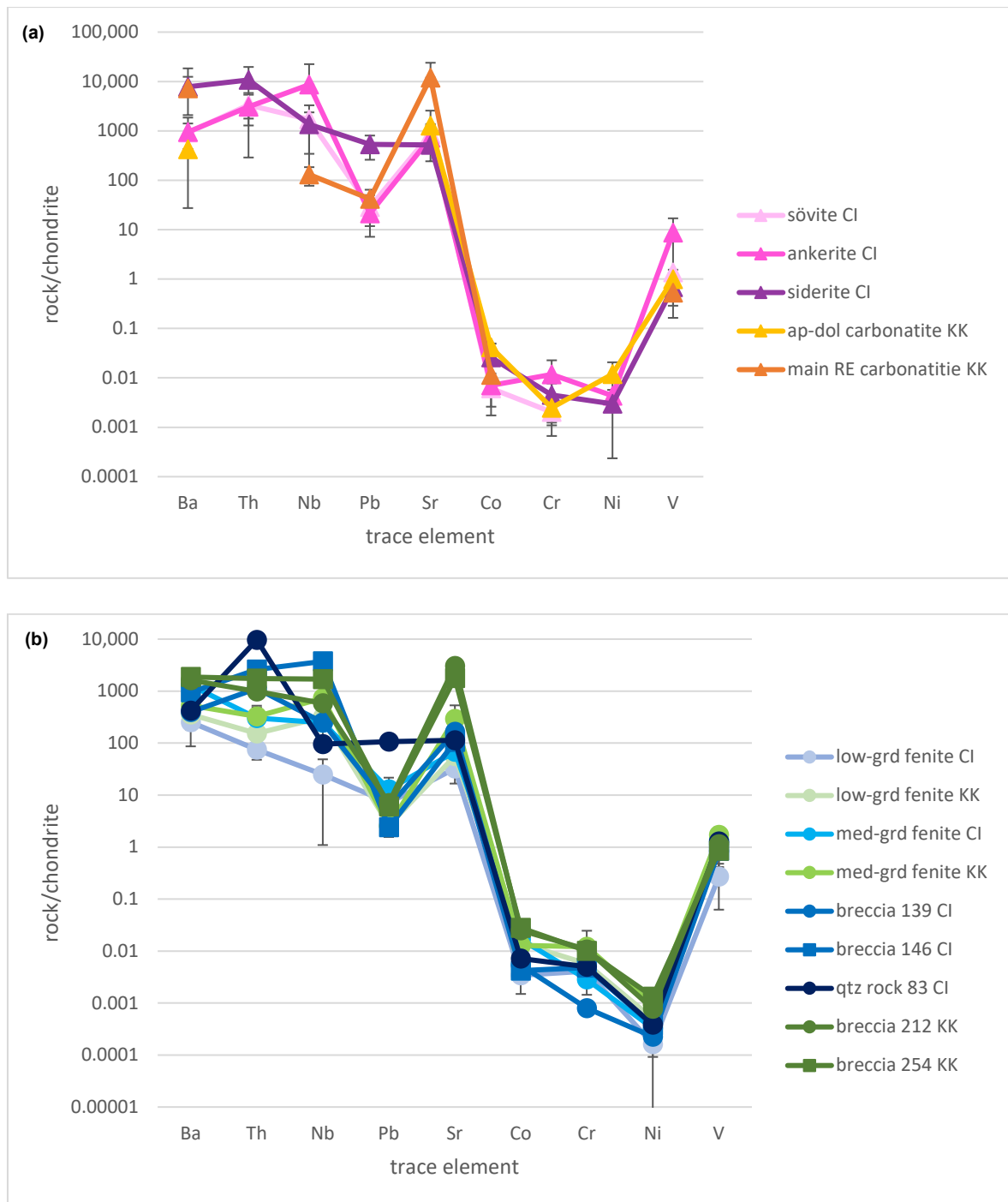
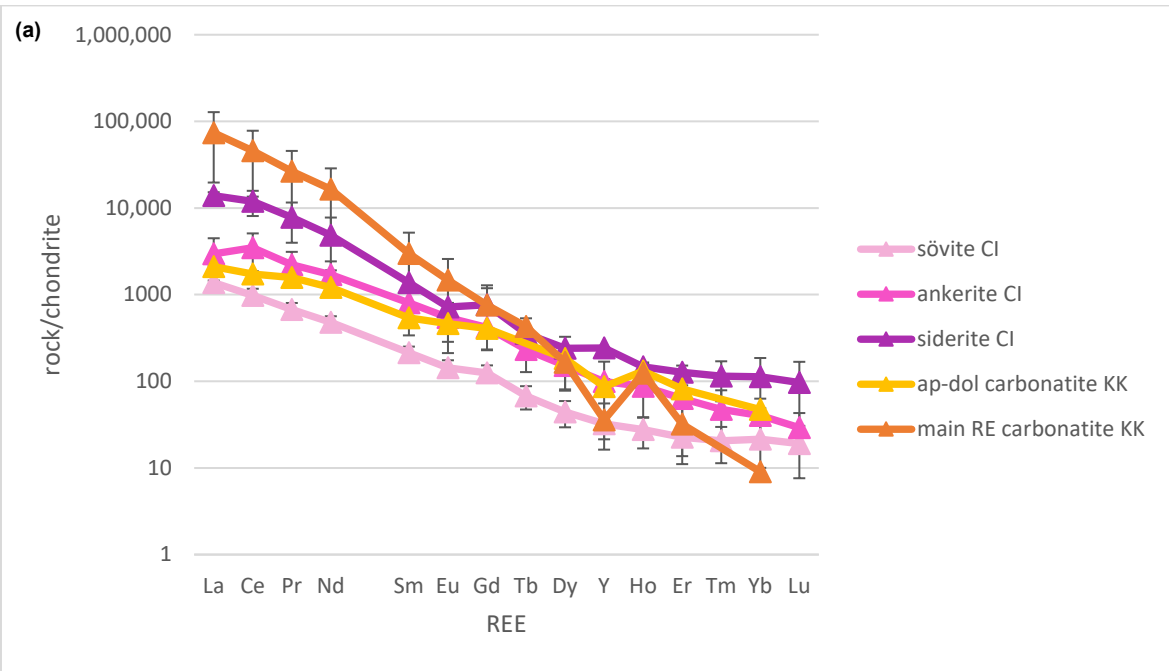


Fig. 14. Chondrite-normalised trace element profiles of whole rocks across the carbonatite complexes at Chilwa Island (CI) and Kangankunde (KK): (a) carbonatite; (b) fenite. Values plotted are averages except for breccia and quartz-rich rock. Error bars represent one standard deviation. Chondrite values used are from McDonough and Sun (1995).

Carbonatites are typically LREE-enriched, and the LREE content of fenite increases with alteration. Chondrite-normalisation of carbonatite and fenite (Fig. 15a,b) shows that fenites

of both complexes display flatter profiles, with lower La/Yb ratios, than those of their respective carbonatites (Table 3). The exception is at Kangankunde where breccia is more LREE-enriched than the apatite-dolomite carbonatite. The outcrop of this carbonatite is very small and any influence on breccia appears to be overprinted by the later main RE carbonatite as evidenced by the existence of negative Y anomalies in both these REE profiles.



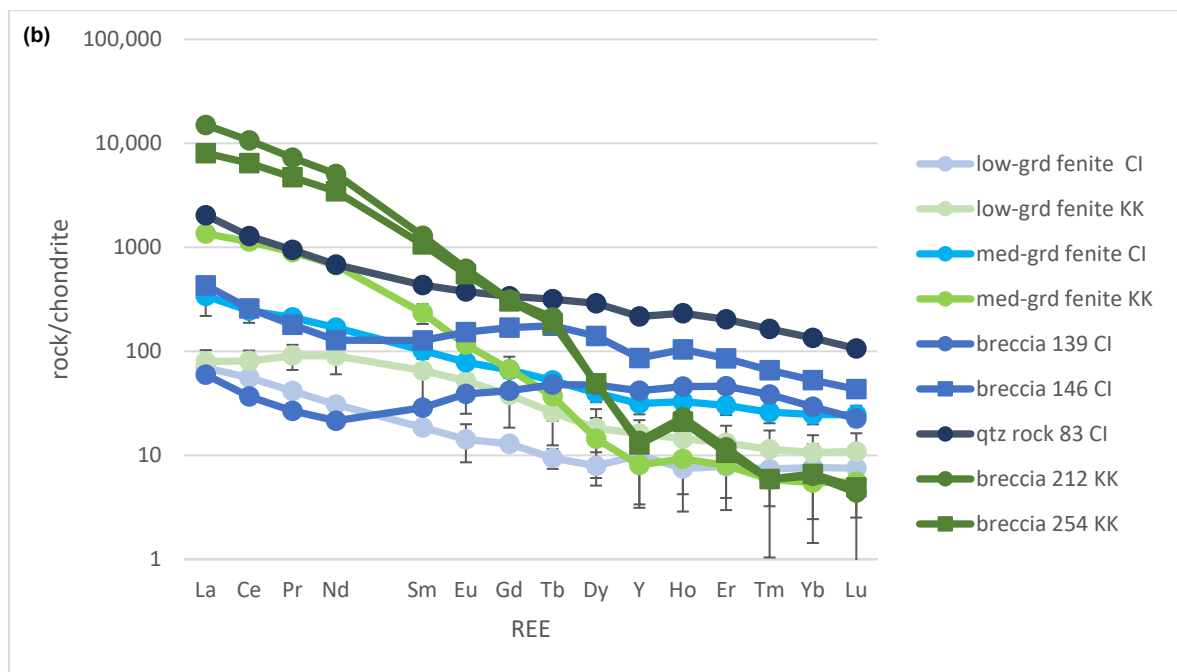


Fig. 15. Chondrite-normalised REE profiles of whole rocks across the carbonatite complexes at Chilwa Island (CI) and Kangankunde (KK): (a) carbonatite; (b) fenite. Values plotted are averages except for breccia and quartz-rich rock. Error bars represent one standard deviation. Chondrite values used are from McDonough and Sun (1995).

Table 3. (La/Yb)_{cn} ratios in whole rock at the Chilwa Island and Kangankunde complexes.

Rock type	Chilwa Island	Kangankunde
Low-grade fenite	9	7
Medium-grade fenite	14	248
Breccia	2 – 8	1200 - 2400
BM1968 P37 83	15	
Sövite	64	
Ankerite	74	
Sideritic carbonatite	123	
Apatite-dolomite carbonatite		45
RE-rich carbonatite		8150

Differences

Kangankunde exhibits a greater continuity of trends in element abundance across the aureole, as indicated in its mineralogy. Of the major elements, passing inwards towards the carbonatite, Fe and Mg (and also Mn) increase as the Na/K ratio decreases. At Chilwa Island, only the high K content of the breccia conforms with either of these trends, and any increase in Fe and Mg from low-grade to medium-grade fenite does not appear to have a strong relationship with Na and K content or ratios (Fig. 16a,b).

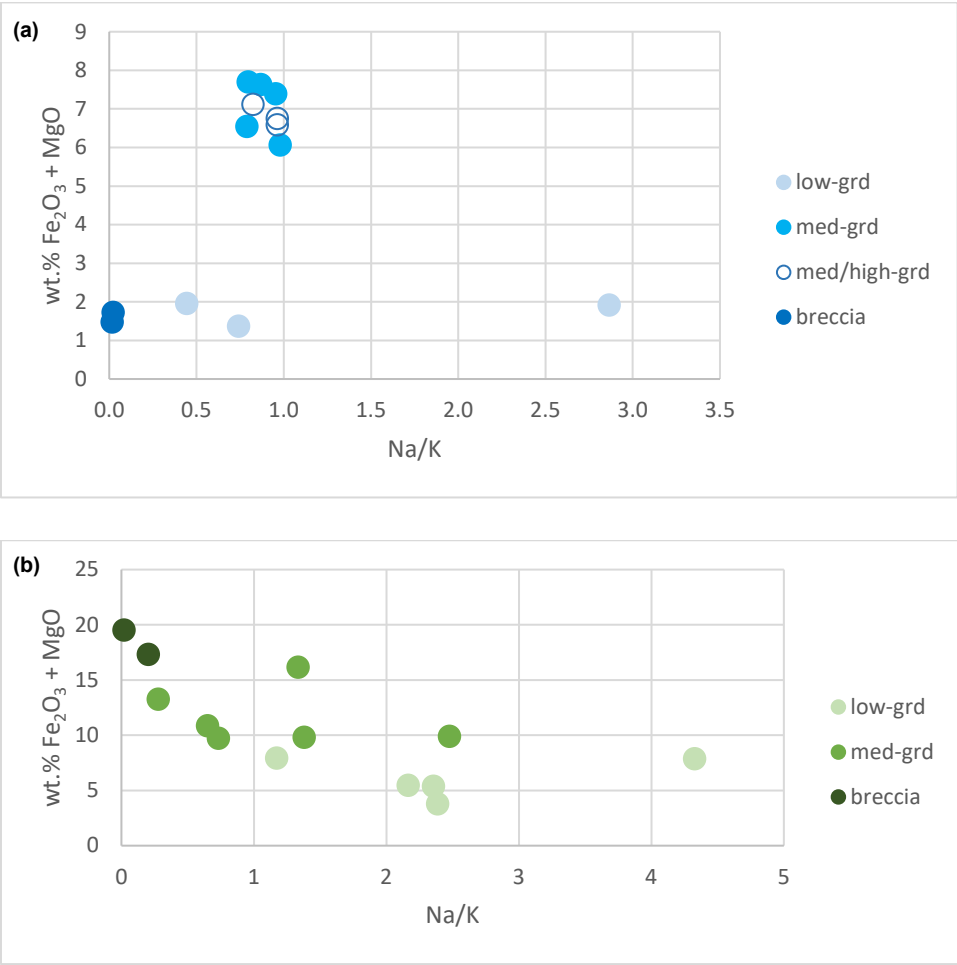


Fig. 16. Plots of wt.% Fe₂O₃ + MgO vs Na/K: (a) Chilwa Island; (b) Kangankunde.

A key difference is the lack of Fe, Mg, Mn and Ca in Chilwa Island breccia, which interrupts increasing trends in these elements from low-grade to medium grade fenites.

Trace elements at Kangankunde show a clear increase in carbonatite-associated elements from the outer aureole inwards to the breccia. At Chilwa Island, this trend is again broken by the breccia, where the Ba and Pb content is below that of medium-grade fenite. The comparatively low level of certain major and trace elements in breccia at Chilwa Island is not surprising given the lack of mineralogical diversity in this part of the aureole. Differences between the complexes are also seen in the detail of trace element enrichment of fenite. In the aureole outside of the breccia, Chilwa Island contains more Ba, Pb and Y than Kangankunde, which can probably be ascribed to the relative enrichment of their respective carbonatites in these elements. However, Nb levels in fenite at Kangankunde are higher than that of its carbonatites and, apart from a pyrochlore-bearing breccia sample, are also greater than the Nb content in fenite at Chilwa Island. This is unexpected because Chilwa Island carbonatites include pyrochlore-bearing sövite, and are more Nb-enriched than Kangankunde carbonatite by a factor of 10. The reason for this difference in fenite Nb content is not known and would require further research. The high migration capacity of Nb (and Ti) has been noted in the fluctuating physical and chemical conditions occurring in the late hydrothermal fluid episodes associated with carbonatite formation (Kozlov *et al.*, 2018), and rutile was found in a fluid inclusion in medium-grade fenite at Kangankunde by Dowman (2014). In addition, Nb-bearing goethite is associated with hydrothermally altered carbonatite in Russia (Chebotarev *et al.*, 2017) and it is possible that goethite in the altered iron oxides of medium-grade fenite at Kangankunde may contain Nb, but this has not been investigated further. Sr is most enriched in the main RE carbonatite at Kangankunde and this is reflected in the higher fenite Sr content throughout the fenite at Kangankunde compared to Chilwa Island, particularly in the breccia (Fig. 14a,b).

585 Chondrite-normalised REE profiles of the carbonatites at the complexes (Fig. 15a)
 586 highlight the two contrasting carbonatites at Kangankunde. The main RE carbonatite is
 587 strongly enriched in the LREE both in absolute abundance and proportionately (Table 3).
 588 The apatite-dolomite carbonatite is more similar in profile to ankerite at Chilwa Island,
 589 except for a negative Y anomaly. This is present in both carbonatites at Kangankunde, but
 590 notably more pronounced in the RE carbonatite. Chilwa Island carbonatites are flatter in
 591 profile than the RE carbonatite at Kangankunde, containing less LREE and more HREE.
 592 They also follow a trend in that magmas in the emplacement sequence at Chilwa Island
 593 become successfully more enriched in REE.
 594
 595 The contrast in carbonatite REE profiles is seen in the profiles of their respective fenites
 596 (Fig. 15b). In medium-grade fenite and more altered areas, chondrite-normalised REE
 597 profiles of Chilwa Island are flatter than those of Kangankunde with $(La/Yb)_{cn}$ ratios of 2-
 598 15 in fenite compared to 248-2400 (Table 3), with each zone containing less LREE than its
 599 Kangankunde equivalent. The reverse is seen with respect to HREE, where higher-grade
 600 fenites at Chilwa Island are enriched in comparison with their Kangankunde counterparts,
 601 both as a proportion and in absolute abundance. This trend may be related to the higher
 602 HREE contents of sideritic carbonatite at Chilwa Island compared to the main REE
 603 carbonatite at Kangankunde.
 604
 605 The Ho and Er content of the quartz rock BM1968 P37 83 from Chilwa Island is the
 606 highest measured anywhere in either complex, and the rock is more HREE-enriched than
 607 most of the ankerite and sövite at Chilwa Island. Whole rock data is not available for
 608 quartz-rich rocks at Kangankunde and it can only be commented that the quartz-monazite

rocks would show marked LREE-enrichment, with quartz-florencite and quartz-apatite rocks being more MREE-HREE-enriched.

REE fractionation further investigated

At both complexes, EDS analyses of the RE-bearing minerals showed that the RE-bearing minerals in fenite have lower $(La/Nd)_{cn}$ ratios than their carbonatite analogues. Mixing of country rock with a dominant RE mineral from the carbonatite or REE fractionation are two possible explanations of this trend.

The first alternative was tested by investigating if mixing a dominant RE-bearing carbonatitic mineral with country rock would produce an approximation to fenite whole rock rare earth profiles. Monazite-(Ce) from Kangankunde was chosen as it is the mineral that exerts the strongest control over REE profiles at either complex.

Monazite-(Ce) REE compositions at Kangankunde vary across the two carbonatites and the quartz-rich rocks. In the model, low percentages of these three different monazite compositions were added to:

a) low-grade fenite whole rock composition, to ascertain whether the results might approximate medium-grade and/or breccia compositions (Fig. 17a-c)

b) medium-grade fenite whole rock composition, to test if the resulting composition could approximate that of breccia (Fig. 18a-c).

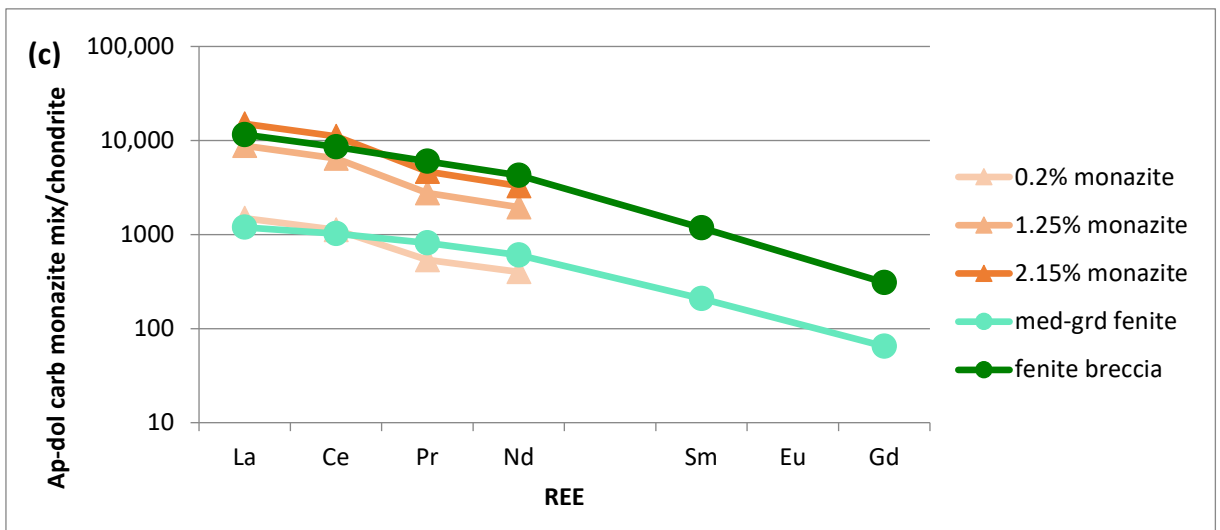
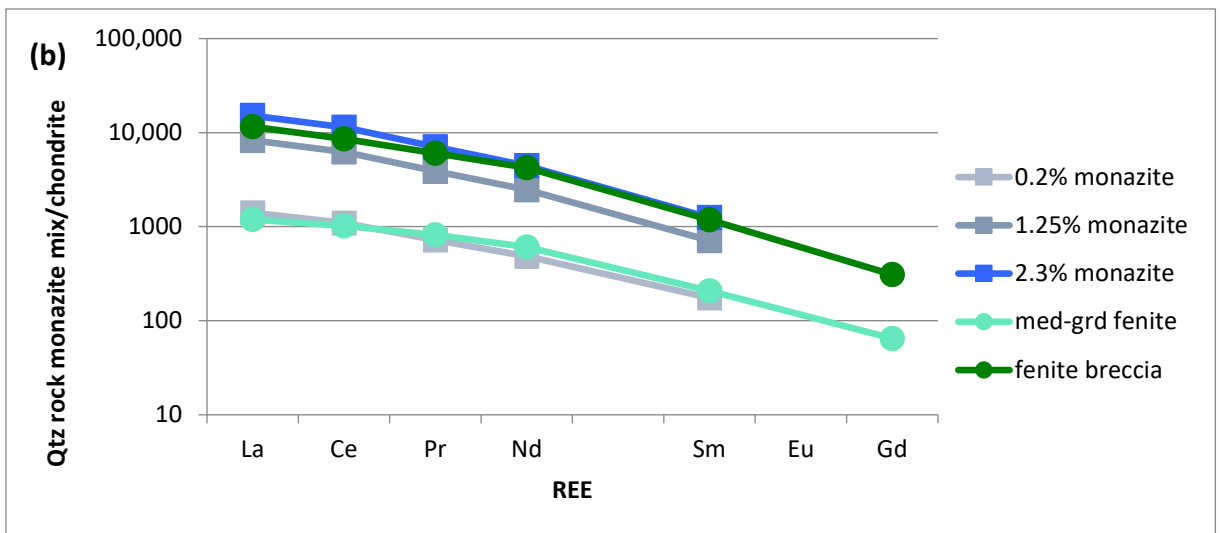
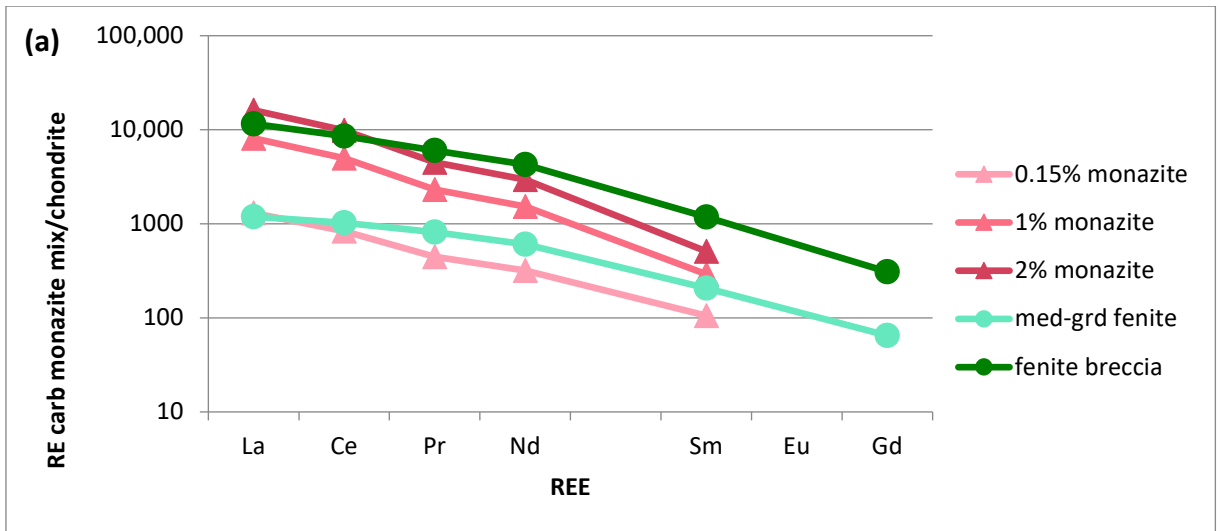


Fig. 17. Chondrite-normalised REE profiles generated by addition of monazite-(Ce) percentages to low-grade fenite at Kangankunde: (a) addition of monazite from RE-rich carbonatite to low-grade fenite whole rock composition;

(b) addition of monazite from quartz-monazite rock to low-grade fenite whole rock composition; (c) addition of monazite from apatite-dolomite carbonatite to low-grade fenite whole rock composition.

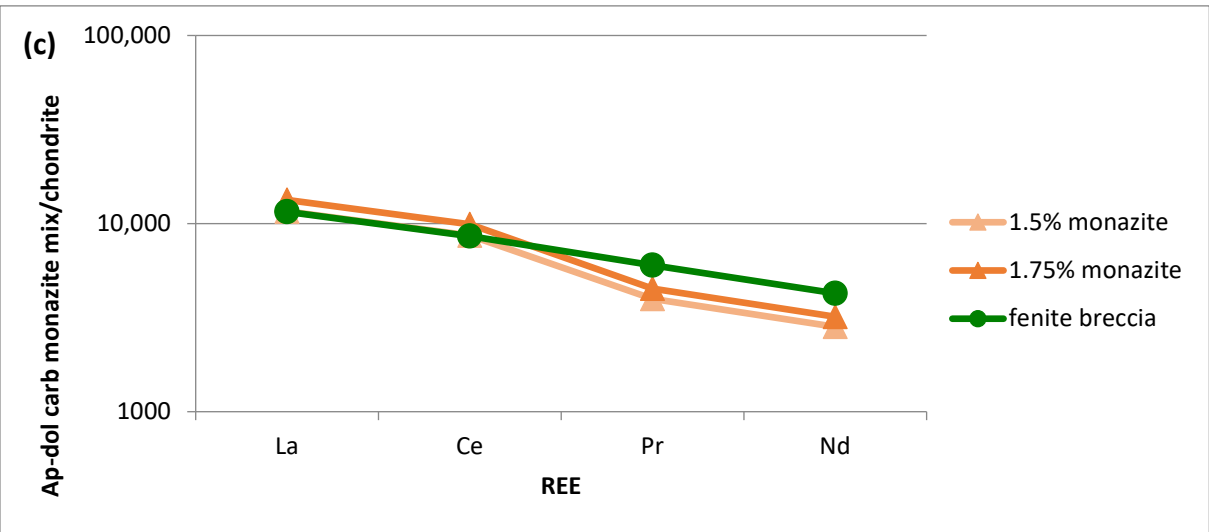
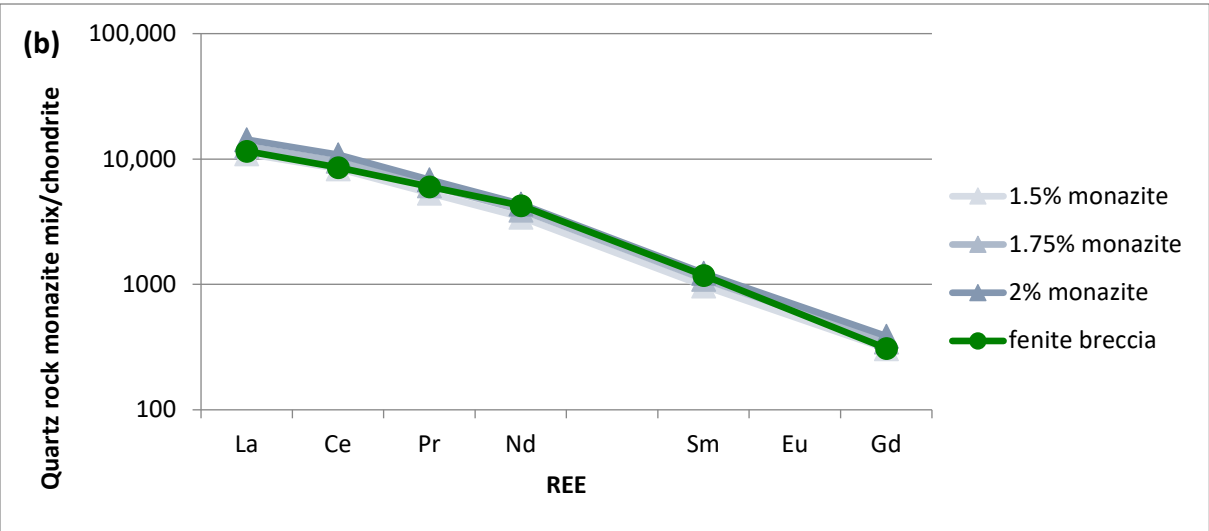
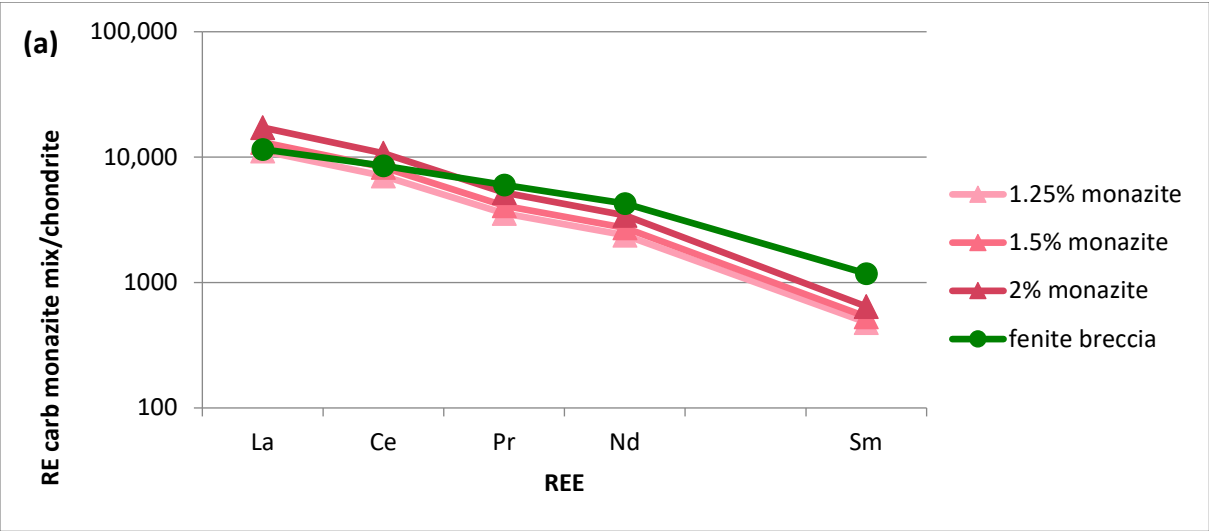


Fig. 18. Chondrite-normalised REE profiles generated by addition of monazite-(Ce) to medium-grade fenite at Kangankunde: (a) addition of monazite from RE-rich carbonatite to medium-grade fenite whole rock composition; (b) addition of monazite from quartz-monazite rock to medium-grade fenite whole rock composition; (c) addition of monazite from apatite-dolomite carbonatite to medium-grade fenite whole rock composition.

Mixes of country rock with monazite-(Ce) from the carbonatites, particularly from the RE-rich carbonatite, do not resemble the profiles of more altered fenite (Figs 17, 18). The REE profiles generated are too steep and La/Nd ratios are too high. The mixes with monazite-(Ce) from the quartz-monazite rock result in better matches, particularly the close approximation to breccia composition produced by adding this monazite to medium-grade fenite.

We therefore suggest that REE fractionation may be a better explanation for the lower $(\text{La/Nd})_{\text{cn}}$ ratios of fenite, particularly noting that the best mixing results came from quartz rock monazite-(Ce), which is of non-primary magmatic origin, and may itself have formed from RE-fractionating fluids. This accords with the view of Broom-Fendley, Elliott, *et al.* (2021); and Broom-Fendley, Siegfried, *et al.* (2021) who suggested that, subsequent to precipitation of LREE minerals in carbonatite, the more incompatible HREE are expelled in residual hydrothermal fluids, and that REE fractionation occurs in most cases of fenitisation.

The carbonatites at Chilwa Island and Kangankunde were not the focus of this study but some support for these authors' suggestions regarding early precipitation of LREE-rich minerals in carbonatite may be provided at Chilwa Island by the abundance of apatite, the main REE-bearing mineral at this complex, in sövite and sövitic ankerite, which are early carbonatites in the emplacement sequence. Apatite in early sövite is more LREE-enriched

than the MREE-rich apatite in later ankerite (Dowman, 2014). Back-scattered electron images of two ankerite carbonatites suggest that after apatite deposition, later mineralisation occurred that involved the HREE and HFSE, taking the form of overgrowths of minerals such as xenotime-(Y), zircon and pyrochlore (Fig. 19a-d), as is seen in fenite (Fig. 9a-d). Metasomatic alteration of these carbonatites also includes the formation of K-feldspar and secondary quartz. At Kangankunde, it is not known whether or how the REE content of minerals evolved during the emplacement of the small apatite-dolomite carbonatite. However, the RE-carbonatite appears to have initially crystallised burbankite before the main phase of RE mineralisation of monazite-(Ce) and bastnäsite-(Ce). Xenotime, florencite-goyazite and apatite appeared later in the paragenetic sequence (Wall, 2000).

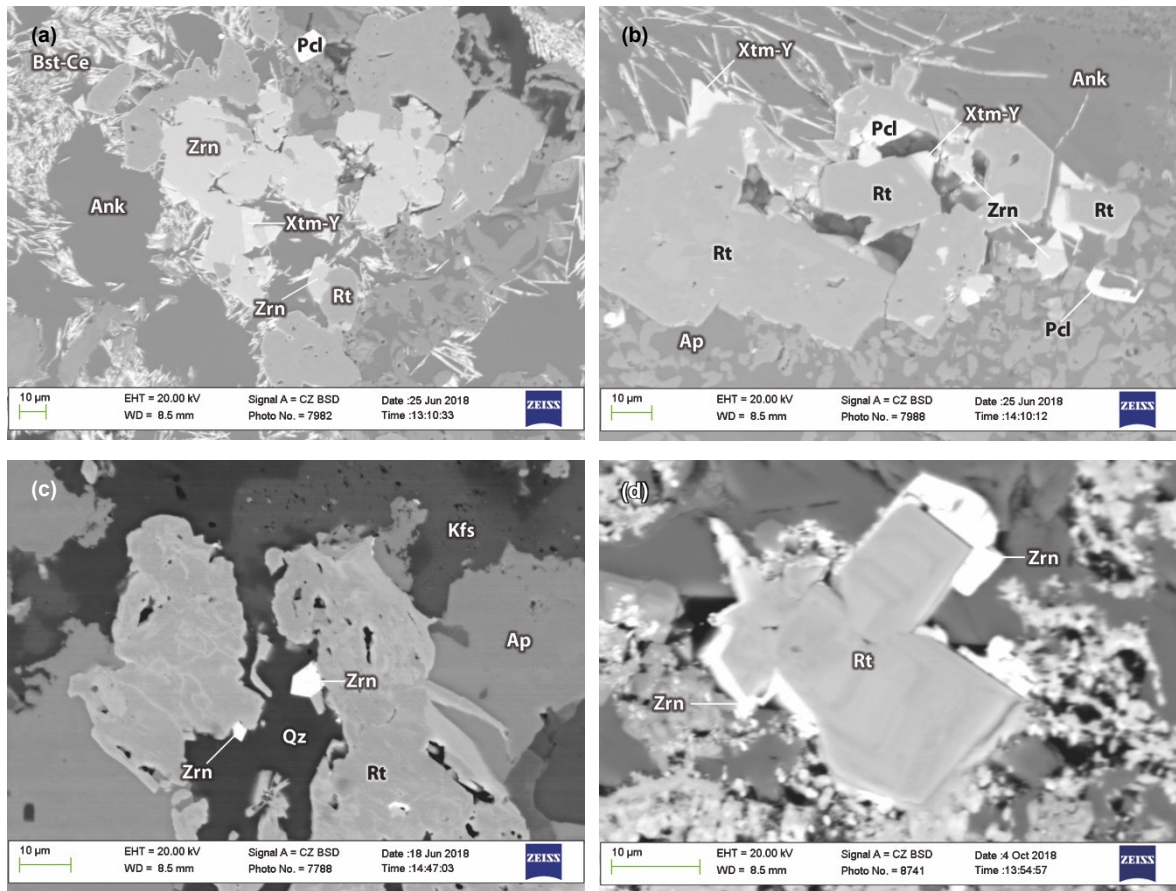


Fig. 19. Back-scattered electron images of HREE and HFSE mineralisation in carbonatite at Chilwa Island:
 (a) BM1957 1056 102 ankeritic fluorapatite-rich carbonatite with area of late-stage zircon with xenotime-(Y) overgrowths; (b) BM1957 1056 102 ankeritic fluorapatite-rich carbonatite with patchily-zoned rutile with xenotime-(Y) and pyrochlore overgrowths, zircon also present; (c) BM1957 1056 128 ankeritic carbonatite with irregularly zoned rutile with zircon overgrowths. Metasomatic alteration of carbonatite is also evidenced by presence of quartz and K-feldspar; (d) BM1957 1056 113 'sideritic' carbonatite with xenotime overgrowths on zoned rutile.

Discussion

Common characteristics

Alkali alteration

Alkaline alteration at both complexes occurs both in veins and fractures and also spreads inwards from grain margins, indicating that crystal boundaries formed additional channels for fluid migration. The existence of interconnected micropores forming fine-scale channels for fluids is common in alkaline feldspars (David and Walker, 1990; Finch and Walker, 1991 and citations therein; Plümper *et al.*, 2017; Yuan *et al.*, 2019; Yuguchi *et al.*, 2019).

Alkaline alteration may have resulted from fenitising fluids generated from the carbonatite magma either coevally or prior to emplacement, and possibly related to a first boiling episode caused by decompression during magma ascent (Candela, 1997). At both Chilwa Island and Kangankunde, early alkaline fluids are more sodic, and later fluids are more potassic, as evidenced by overprinting of sodic fenitisation by potassic fenitisation (Woolley, 1969). This sequence is not uncommon, but not wholly understood. Woolley (1982) suggested that early sodium loss from magma at depth would cause the alkali fraction of the ascending magma to become increasingly potassic. Both Woolley (1982) and Le Bas (2008) observed that this is consistent with field relationships, where potassium fenitisation is generally more important at higher structural levels. This idea of

magma evolution is supported by Koster van Gross (1990) whose experimental evidence indicated that alkali-rich CO₂-H₂O fluids become increasingly K-rich and Na-poor with decreasing pressures. In both complexes this suggests that a transition from sodic to a more potassic alteration may accompany the emplacement of the later, more Mg- and Fe-rich magmas at higher levels in the intrusion.

Magma evolution and the plurality of carbonatites would probably have generated repeated episodes of alkaline metasomatism. Carbonatite at both complexes contains orthoclase but not sodic feldspar. Potassic fluids may have introduced some Al and Si as well as K into carbonatite. Questions arise about the mechanism responsible, and also about the lack of evidence for carbonatite autometasomatism by sodic fluids. One potential answer is that rather than simple expulsion of magmatic fluids outwards into country rock, a circulation of fluids within the complex may have periodically occurred, during which time any earlier sodic alteration of the carbonatite could have been overprinted by later potassic fluids.

Mineralisation and its pattern

In contrast to the pervasive alkaline alteration of the aureoles, mineralisation is mostly confined to discrete veins (Figs 3b, 4a,c,d). This could result from a partial separation in timing of alkaline and mineralising fluid expulsions. Each carbonatite emplacement may be associated with pulses of mineralisation from a second, possibly episodic, boiling event driven by stages of crystallisation of anhydrous phases which increase vapour pressure in the magma (Candela and Bevin, 1995; Candela, 1997). Rutile and fluorapatite at both complexes exhibit zoning, attributable to differences in Nb and REE content respectively, suggesting that these minerals were formed from pulses of fluids of varying composition (Figs 7,8). Certain of these fluids may have been aqueous and solute-rich which fenitised

the country rock and autometasomatised carbonatite itself (Walter *et al.*, 2021). Primary alkali REE-carbonates are absent in both fenites and it is suggested that these are rarely preserved at carbonatite complexes, being dissolved by later fluids and then replaced by monazite-(Ce) and alkali-free REE-(fluor)carbonates (Anenburg *et al.*, 2022). The presence of cross-cutting trails of heterogeneous fluid inclusions in quartz, with daughter minerals that include nahcolite, burbankite and rutile, provides further evidence that country rocks were metasomatised by a series of alkaline and mineralising fluid expulsions.

Late-stage fluids and silicification

The periodic recirculation of fluids within the aureole suggested above with respect to alkaline alteration could also explain the presence of areas of rocks of secondary quartz and mineral overgrowths at both complexes. The rocks of secondary quartz are located in both fenite and carbonatite, and are indicative of selective silicification across the complexes. No overprint by any later alkaline fluids is seen, thus silicification would apparently postdate alkaline alteration. In carbonatite and fenite, these quartz rocks are REE-enriched, implying further mobilisation and concentration of the REE (and HFSE) at the complex, this time under Si-rich conditions. This may also have promoted the overgrowths of xenotime, zircon and pyrochlore in both fenite and carbonatite (Figs 9,19). It could have been driven by a combination of hydrothermal fluids with Si derived from the country rocks and REE from the magmatic fluids (von Eckermann, 1948; Garson and Campbell Smith, 1958), rather than any late-stage silicic component of magma. Simandl and Paradis (2018) proposed that silica removed from country rock during fenitisation will migrate inwards towards the intrusion, which could explain the presence of quartz rocks within the carbonatite. Woolley (1969) considered quartz in sideritic carbonatite at Chilwa

Island to be the result of secondary processes, suggesting that silicic fluids could be drawn inwards and upwards towards the intrusion. This is interpreted as fluid recirculation, and is supported by the mineralogy of this carbonatite which is composed largely of secondary calcite and iron and manganese oxides, with quartz lining the druses. Silica saturation at Chilwa Island could therefore have arisen from late-stage interaction between cooling fluids from the carbonatite melt and groundwater in country rock (Simonetti and Bell, 1994). At Kangankunde, Wall (2000) described ground water interacting with fluid systems, while Broom-Fendley *et al.* (2017) indicated a role for meteoric water in the formation of quartz rocks in more distal parts of the aureole. Furthermore, at both complexes, the crystallisation of rutile adjacent to magnetite in fenite is similar to that described by Southwick (1968) in an investigation of rutile-bearing ultramafic rock in Maryland, USA. He considered this association to be indicative of oxidising events following the laboratory experiments of Lindsley (1963) where a simple oxidation of ilmenite could have rutile and magnetite as stable end products. Oxidation is also invoked by Tan *et al.* (2015) to explain the intergrowth of magnetite and rutile in a Fe-Ti oxide-bearing gabbro in Xinjie in China. Cooling of the geothermal system may have drawn in oxidised surface waters, as suggested by Garson and Campbell Smith (1958) at Chilwa Island and by Wall *et al.* (1994) at Kangankunde, with the resulting oxidising fluid events affecting large parts of the aureoles.

There is nothing in our work here that disagrees with the probable role of meteoric fluids in constraining the late-stage mineralogical evolution of both complexes.

Mineral REE ratios

The carbonatite RE-minerals investigated here have REE chemistries with higher (La/Nd)_{cn} ratios than their fenite analogues. Changes in REE ratios have been reported by Chakhmouradian *et al.* (2017), who noted that where apatite is present in carbonatite, (La/Yb)_{cn} ratios fall from between 30 and 500 in igneous apatite to ≤25 in hydrothermal varieties.

The small size and fragility of fluid inclusions hosted in the complexes limits full characterisation of the fluids that promoted REE fractionation beyond noting that CO₂-bearing and aqueous fluid inclusions are present in both aureoles, and that Cl was not detected at either aureole. CO₂-bearing potassic fluids are implicated in the formation of breccia (Rubie and Gunter, 1983), and CO₂ fluids may play a more important role than aqueous fluids within higher temperature zones in the carbonatite complexes (Smith *et al.*, 2000). These authors also linked increasing solubility of the MREE and HREE over time to fluids with falling temperature and a change from CO₂ to H₂O dominance, which may have promoted (re)mobilisation of the MREE and HREE (Andrade *et al.*, 1999; Broom-Fendley *et al.*, 2013). This was possibly via a dissolution-reprecipitation process (Broom-Fendley *et al.*, 2021a; b) as evidenced by the presence of porous fluorapatite containing submicron zircon in medium-grade fenite and breccia at Kangankunde, and skeletal zircon in breccia at Chilwa Island.

Contrasting characteristics

Breccia composition and mineralogy

A more extensive survey of carbonatite complexes is required to determine whether intense potassic breccia is a common feature of complexes lacking RE-rich carbonatite.

The reason for the contrast in breccias at the two complexes may be associated with CO₂-

rich potassic fluids undergoing a first boiling where magma pulses fracture rock causing a rapid reduction in pressure (Rubie and Gunter, 1983). As described above, the breccias at Kangankunde and Chilwa Island differ in that Chilwa Island breccia is more K-rich and more shattered. Most minerals are absent from Chilwa Island breccia, with even zircon being altered to a skeletal appearance. This event could therefore have been more intense or concentrated at Chilwa Island than at Kangankunde. The sequence of metasomatising fluids at each complex may also be a key factor, particularly with respect to the relative timing of the expulsion of potassic fluids and of the main mineralising episode (Table 4).

Carbonate abundance in fenite

The outer fenite and the breccia at Kangankunde both contain calcite as well as more ankeritic carbonates, despite the lack of a calcite carbonatite at Kangankunde. Conversely, despite the presence of substantial calcite carbonatite at Chilwa Island, little calcite, or carbonate in general, is seen in the fenite. Conclusions regarding carbonate mobility in metasomatic fluids are limited here to commenting that the greater mobility at Kangankunde may be attributed to the more fractured country rock outside its breccia, which provided conduits for carbonate transport. It is not clear whether the evolution of a RE-rich carbonate is associated with greater carbonate mobility, or whether any relationship exists between the degree of RE-enrichment of carbonatite and the extent of fracturing of country rock. No theoretical foundation exists for either proposition and it can only be commented that the shallower erosion level at Kangankunde compared to Chilwa Island may imply that magma was not constrained in a pipe network, thus permitting greater magma/fluid mobility and a more pervasive distribution of carbonate in the aureole.

A mineralogical explanation of the differing amount of carbonate in fenite at the two complexes is that Ca at Chilwa Island was taken up in the growth of fluorapatite, which is less common at Kangankunde, perhaps because P was preferentially taken up in monazite. To our knowledge, no relationship between carbonate in fenite and RE-rich monazite-bearing carbonatite has ever been established.

Niobium in fenite

It is unclear why fenite at Kangankunde is richer in Nb than that at Chilwa Island, whose complex hosts pyrochlore-bearing carbonatite. The data suggest that Nb in fenite does not provide a reliable indicator of the Nb enrichment of the associated carbonatite. This could be because the principal Nb-bearing mineral, pyrochlore, precipitates from carbonatite magma rather than crystallising during the later hydrothermal stages. However, Nb may be more mobile in fluids generated at Kangankunde but it is again unclear whether this is characteristic of fenites associated with RE-rich carbonatites.

Main RE-bearing mineral

The dominant RE-bearing mineral in fenite in the two complexes is fluorapatite at Chilwa Island and monazite-(Ce) at Kangankunde. These are also the key RE-bearing minerals in their respective carbonatites. Identifying these minerals in metasomatic aureoles may therefore provide an indicator of the probable style of RE mineral enrichment in their carbonatites. This is considered important as carbonatite deposits that have produced REE on a commercial scale contain monazite as the principal phosphate mineral (Wu *et al.*, 1996; Castor, 2008; Chakhmouradian *et al.*, 2017).

Ligands at Chilwa Island and Kangankunde

857 **REE mobility**

858 A detailed investigation into the ligands that could have complexed the REEs is beyond the
859 scope of this paper, but a brief summary is included here regarding which ligands may
860 have been dominant at each complex, indicating whether any differences exist between the
861 RE-rich Kangankunde and the RE-poor complex of Chilwa Island.

862

863 Fluorine is common in the fenite mineralogy at both locations, but particularly at
864 Kangankunde, where fluorite, fluorapatite and fluorcarbonates are all present. Fluorine
865 appears to be important, commonly in combination with other ligands, at other carbonatite
866 complexes. Activity of F^- and PO_4^{3-} in hydrothermal fluids was associated with fluorapatite
867 formation in fenite at Lofdal in Namibia (Wall *et al.*, 2008) and with HREE mineralisation
868 and evolved ferrocarnatitic magmatism at the REE-Nb Abitibi carbonatite in Canada
869 (Nadeau *et al.*, 2015). Morogan (1989), writing about fenitisation at Alnö in Sweden, cited
870 Humphris (1984), suggesting that the ligands able to mobilise REE into fluids and
871 transport them out to the potassic fenite would include F^- , PO_4^{3-} , CO_3^{2-} and HCO_3^- .

872

873 Broom-Fendley *et al.* (2016) reported transport of REE complexes by both F- and Cl-
874 bearing fluids at Kangankunde and also at Tundulu, another carbonatite complex in
875 Malawi. In following Migdisov and Williams-Jones (2014) and Williams-Jones and
876 Migdisov (2014) they considered that Cl is the most probable complexing agent in REE-
877 bearing hydrothermal systems although its presence at Kangankunde and Tundulu is only
878 inferred, as Cl was not detected in apatite structure or in fluid inclusions. Furthermore, Cl
879 was not present in the fluid inclusions investigated from the outer parts of the aureoles at
880 Chilwa Island and Kangankunde (Dowman, 2014), and is not found in the composition of
881 apatite in fenite.

The laboratory-based cooling experiments of REE-bearing carbonatites carried out by Anenburg *et al.* (2020) indicated that Na-REE and K-REE are the dominant complexes stable in REE-mobilising hydrothermal fluids. The authors did not identify the anion(s) that would charge balance these cationic complexes although they commented that Na facilitates solubility of P and F, which could help explain the presence of apatite daughter minerals in fluid inclusions at Chilwa Island (Dowman, 2014). The experiments also noted LREE-HREE decoupling in the presence of alkalis, particularly K, with increased solubility of HREE, which would accord with the low LREE/HREE whole rock ratios of the potassic breccia at Chilwa Island and help account for $(La/Yb)_{cn}$ ratios of fenite REE-minerals being lower than those in carbonatite. The key role that alkaline fluids may play in the mineralisation of hydrothermal REE-fluorcarbonates by promoting the simultaneous transport of REE, fluoride and carbonate is further underlined by an investigation of the solubility and speciation of REE in alkaline fluids via *in situ* X-ray absorption spectroscopy (Louvel *et al.*, 2022). This provided evidence that alkaline fluids rich in F and CO_3^{2-} enhance hydrothermal mobilisation of LREE at temperatures ≥ 400 °C and HREE at temperatures ≤ 200 °C. On the basis that F is widely recorded in the fenite assemblages and Cl is not, we would suggest that, contrary to Broom-Fendley *et al.* (2016), F was the dominant ligand in transporting key elements in both complexes described here.

Nb mobility

Nb has clearly been transported and precipitated into the fenite at both complexes, especially at Kangankunde.

Experimental studies by Zraisky, Korzhinskaya and Kotova (2010) of Ta and Nb solubility in fluoride solutions at 300-550° concluded that hydrothermal transport of Nb and Ta was only possible if the solutions were of concentrated fluoride, especially HF-rich. Timofeev, Migdisov and Williams-Jones (2015) investigated the solubility of Nb in fluoride-bearing aqueous solutions at temperatures of 150-250°C, finding that solubility increased markedly at higher HF concentrations, and that precipitation of Nb-solids and fluorite could occur on an increase in pH if an acidic country rock fluid reacted with carbonate rocks. The presence of F-rich minerals such as fluorcarbonates and F-rich pyrochlores (as found at both Chilwa Island and Kangankunde) at the Bailundo Carbonatite Complex in Angola was taken to indicate fenitising fluids enriched in F-, with high HF activity (Roseiro, 2017; Roseiro *et al.*, 2019). Chebotarev *et al.* (2017) also invoked F and low pH to explain the evolution of Nb mineralisation in the Chuktukon carbonatite massif in Russia, commenting that during hydrothermal alteration, fluids were able to dissolve fluorapatite in carbonatite. The idea of low pH is problematic, as although the pH of the metasomatic fluids at Chilwa Island and Kangankunde is not known, it is not thought to have been low in all fluid events, as calcite is present in fluid inclusions at both locations. However, it is noted that fluorapatite at Kangankunde is porous or replaced in the Nb-rich more altered fenite.

Alternative suggestions include that of Tanis *et al.* (2015) who investigated the mobility of Nb in rutile-saturated NaCl- and NaF-bearing aqueous fluids under metamorphic conditions, and found a greater solubility of rutile in Na-F-bearing fluids. In addition, Kozlov *et al.* (2018), in their study of Ti-Nb mineralisation in the late stage Petyayan-Vara rare earth carbonatites of the Vuoriyarvi Massif in Russia, reported that Nb and Ti migrated together in metasomatic fluids, in which the ligands were F, and to a lesser

extent, PO_4^{3-} and CO_3^{2-} . The significance of an alkaline component of fluids has previously been described in relation to REE transportation and fractionation (Anenburg *et al.*, 2020; Louvel *et al.*, 2022). Together with higher levels of F at Kangankunde compared to Chilwa Island, this may have facilitated Nb-enrichment of Kangankunde medium-grade fenite. In our view, this suggests that F-rich alkaline fluids were key to REE transportation at both Kangankunde and Chilwa Island.

The role of fluid sequence and fluid composition

Here we outline how different sequences of metasomatising fluids at Kangankunde and Chilwa Island can help explain their respective fenite rock composition and mineral assemblages.

Differences in the size, number and composition of the host carbonatites at each location would have affected both the aggregate fluid events and the detailed fluid components. Some fluid events probably caused only minor alteration, and/or may have been overprinted by later fluids. However, we conjecture that the overall sequence of key fluid expulsions at the complexes could have been broadly similar, as set out in Table 4. Each carbonatite expelled sodic-dominated alkaline fluids preceding mineralisation, which may itself have been interspersed or accompanied by further alkaline fluids. Potassic alteration became dominant over sodic alteration in subsequent alkali influxes, and is associated with further mineralisation. In the inner aureoles of both complexes, it appears to have overprinted earlier sodic episodes. The intensity and timing of the potassic alteration in relation to the main mineralising event may exert a strong control on the spatial distribution of RE-bearing minerals in the inner aureole at each complex. The transition from sodic to potassic flux is thought to be concurrent with fractionation of carbonatite

from Ca-rich compositions to more Mg- and Fe-rich phases, emplaced at successively higher levels in the intrusion.

In addition, at Chilwa Island, the predominantly orthoclase mineralogy of the breccia may result from an incursion of a highly potassic late-stage fluid, such as that described by Rubie and Gunter (1983). In this scenario, potassic metasomatism may take place at high temperatures if the fluid is either CO₂-rich or boiling as a result of a rapid reduction of pressure, such as by rock fracturing. This fluid episode occurred after the main mineralising events derived from ankerite, and to a lesser extent, sövite. In effect, the hot potassic fluid leached nearly all the prior mineralisation derived from the earlier fluids from the inner aureole, as well as most residual components from the country rock. This potassic fluid was, however, limited in spatial extent. It appears to have been followed by a minor expulsion of mineralising fluids from the central sideritic carbonatite. The higher HREE content of the sideritic carbonatite may have produced the relatively high HREE/LREE ratios of the breccia.

In contrast, at Kangankunde, the effect of late-stage potassic-dominated fluids was less intense but still apparently overprinted sodic alteration associated with the emplacement of the RE carbonatite. Potassic breccia preceded the main RE mineralisation event which was the result of the action of deuteritic fluids between 250°C and 400°C (Broom-Fendley *et al.*, 2017).

Table 4 is a speculative summary of possible fluid characteristics of the major metasomatic episodes at each complex, and highlights differences in the fluids and their local effects.

981 **Table 4.** Proposed sequence of key metasomatic fluids at Chilwa island and Kangankunde.

1 Alkaline fluids, sodic-dominated			
Fluid source	Extent of fluid	Element mobility and mineralogical expression in aureole	Difference between complexes and suggested cause or comments
Chilwa Island: sövite	Pervasive and spatially extensive	Na alteration across aureole	Less K in this fluid at Kangankunde – reason not known
Kangankunde: apatite-dolomite carbonatite			
2 Mineralising, multiple event possibly interspersed with further minor alkaline fluid expulsions			
Fluid source	Extent of fluid	Element mobility and mineralogical expression in aureole	Difference between complexes and suggested cause or comments
Chilwa Island: sövite and ankerite	Mostly restricted to structurally-controlled veins and fractures, possibly reactivated earlier pathways	Zoned fluorapatite formed by multiple fluid events. Ca, P and REE brought into aureole	Main mineralising event at Chilwa Island mainly from ankerite
		Chilwa Island: Nb, Ti, Fe, Ba incorporated into micro mineral assemblages including fluorapatite, zoned Nb-rich rutile, ilmenite, baryte, magnetite. Aegirine and amphibole formed	
Kangankunde: apatite-dolomite carbonatite		Kangankunde: Y, Zr, Fe, Ti, Mg expelled into aureole. Early aegirine formed	Lesser mineralising event at Kangankunde from small carbonatite. Greater MREE-enrichment at Kangankunde results from relative enrichment of apatite-dolomite carbonatite in MREE compared to Chilwa Island sövite and early ankerite
3 Alkaline fluids, potassic-dominated			
Fluid source	Extent of fluid	Element mobility and mineralogical expression in aureole	Difference between complexes and suggested cause or comments
Chilwa Island: later ankerite or sideritic carbonatite	Chilwa Island: probably altered outer carbonatites and is pervasive in breccia but was restricted in spatial extent with relatively little effect on lower-grade fenite	Chilwa Island: removal of most prior mineralisation in breccia. Partial to complete dissolution of country rock zircon. Possible mobilisation of Zr to promote micro zircon inclusions in fluorapatite further out in aureole	More intense but spatially limited event at Chilwa Island compared to Kangankunde – reason not known. Kangankunde RE carbonatite probably expelled early more sodic fluids
Kangankunde: Main RE carbonatite	Kangankunde: probably altered apatite-dolomite carbonatite and is pervasive in breccia. Limited alteration of lower-grade fenite.	May have created fluorapatite porosity at Kangankunde	
4 Mineralising, multiple fluid event possibly interspersed with further minor alkaline fluid expulsions			
Fluid source	Extent of fluid	Element mobility and mineralogical expression in aureole	Difference between complexes and suggested cause or comments
Chilwa Island: late ankerite and/or sideritic carbonatite	Chilwa Island: very limited event, expressed as thin veins across aureole	Chilwa Island: Th, Y, Pb, Mo, Ba and REE (including HREE) mobilised into aureole to enrich breccia and quartz rock in MREE and HREE and form RE-bearing fluorcarbonates and thorian synchysite. Carbonate found in thin veins	Chilwa Island: minor mineralising event from smallest carbonatite in complex. Paucity of carbonate possibly caused by preferential uptake of Ca by fluorapatite, or because carbonate retained in conduits at greater depth
Kangankunde: main REE carbonatite	Kangankunde: main mineralising event, pervasive in breccia becoming increasingly vein-focused with distance from carbonatite	Kangankunde: Mn, Ba, Nb, Sr, LREE influx into aureole plus further mobilisation of Fe, Mg, Ca. Formation of carbonates, aegirine, rutile, iron oxides, strontianite, fluorite, amphibole and RE-bearing minerals, particularly monazite	Kangankunde: major mineralising event from main carbonatite. Carbonate abundance may be related to shallower depth of carbonatite emplacement or possibly to more mobile fluids/magma
5 Fluids, progressively oxidised, promoting silicification - probably contemporaneous with end stages of fluid 4 event			
Fluid source	Extent of fluid	Element mobility and mineralogical expression in aureole	Difference between complexes and suggested cause or comments
Si mobilised from country rocks by hydrothermal fluid and/or interaction with groundwater	Secondary quartz found in veins and patches from carbonatite out to medium-grade fenite	Rocks of secondary quartz associated with RE-bearing minerals at both complexes. HFSE, HREE mobility to form overgrowths	Kangankunde has a greater variety of secondary quartz rocks documented. Data at Chilwa Island is scarce
		(Re)precipitation of calcite with quartz in sideritic carbonatite at Chilwa Island (Re)precipitation of calcite with quartz in main RE carbonatite at Kangankunde. Low temperature fluids may be associated with precipitation of fluorite at Kangankunde	

982

	Chilwa Island
	Kangankunde
	Both complexes

Conclusion

We report here the mineralogy and whole rock compositions across metasomatised aureoles associated with two carbonatites of contrasting RE-enrichment. The two carbonatites are the Chilwa Island and Kangankunde bodies in southern Malawi. Our data show that, at both complexes, mineralisation and alkaline alteration during carbonatite emplacement occurred in pulses. K/Na ratios increased in later alkaline fluids. This change to potassic dominance appears to be associated with carbonatite differentiation to Mg- and Fe-bearing phases, with these evolved later magmas being emplaced at higher levels within the intrusion. A common feature of both complexes is fluid circulation within the aureoles, as evidenced by the potassic metasomatism of carbonatites and by silicification across the aureoles, together with further mobilisation of REEs by late meteoric fluids. These characteristics may apply to most carbonatite complexes with well-developed fenite aureoles.

However, the contrasts between the two complexes revealed by the study are more intriguing. The fenite mineral assemblages differ distinctly at each complex. The components of these fenite assemblages match those minerals present within their respective host carbonatites. Furthermore, the main RE-bearing mineral found within fenite – fluorapatite at Chilwa Island and monazite at Kangankunde – is also the key RE-bearing mineral of the carbonatite. Knowing which minerals are present in fenite should thus constitute a general guide to minerals expected to occur in the carbonatite. A particular emphasis should be placed on identifying the main RE-bearing mineral in fenite. This is important as it could predict the style of RE-enrichment of the associated

1008 carbonatite, and therefore the likelihood of it being a potential economic resource. It
1009 should also be noted that fenite RE-bearing minerals typically have lower La/Nd ratios
1010 than their equivalents in carbonatite.

1011

1012 A strong contrast in breccia mineral diversity was found between the two carbonatites.
1013 Breccia mineralogy may serve as an indicator of the style and level of RE-enrichment of
1014 the host carbonatite, with greater mineral diversity being associated with RE-rich
1015 carbonatites. The presence or absence of a diverse breccia mineralogy can also provide
1016 information about the sequence of fluid events that occurred at the complex. The key here
1017 appears to be the relative timing and explosivity of potassic fluid expulsion and the main
1018 mineralisation event. At Kangankunde, the mineralisation event post-dated potassic
1019 alteration, thus preserving a mineral-rich breccia. At Chilwa Island, potassic fluids, which
1020 may have been at higher temperatures and more explosive than those at Kangankunde,
1021 removed prior mineralisation of the breccia, and subsequent mineralisation events were
1022 minor.

1023

1024 The differences outlined above offer a tantalising prospect for predicting whether a fenite
1025 is associated with a RE-rich carbonatite. To establish whether these contrasts are
1026 significant and/or reliable, a detailed study of further complexes would be recommended.
1027 Clarification of certain other aspects touched on in this study would increase our
1028 knowledge of carbonatitic systems. Two questions are relevant here. The first question is
1029 whether fenite associated with RE-rich carbonatites contains more carbonate and Nb than
1030 those fenites surrounding a RE-poor carbonatite and possible reasons for this. The second
1031 question is whether breccia fracturing and barren breccias are typically found at apatite-
1032 bearing carbonatites, and the extent to which this might be controlled by erosion levels and

magma plumbing structure. A further question involves determining which key ligand or ligand combination operates at carbonatite complexes. All of these questions should build on existing research.

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Andersen, T. (1989) Carbonatite-related contact metasomatism in the Fen complex, Norway: effects and petrogenetic implications. *Mineralogical Magazine*, **53**, 395–414.

Andrade, F.R.D., Möller, P., Lüders, V., Dulski, P. and Gilg, H.A. (1999) Hydrothermal rare earth elements mineralization in the Barra do Itapirapua carbonatite, southern Brazil: Behaviour of selected trace elements and stable isotopes (C, O). *Chemical Geology*.

Anenburg, M., Mavrogenes, J.A., Frigo, C. and Wall, F. (2020) Rare earth element mobility in and around carbonatites controlled by sodium, potassium, and silica. *Science Advances*, **6**.

Anenburg, M., Broom-Fendley, S. and Chen, W. (2022) Formation of Rare Earth Deposits in Carbonatites. *Elements*, **17**, 327–332.

Arzamastev, A., Arzmasteva, L. and Zarskii, G. (2011) Contact interaction of agnatic

1058 magmas with basement gneisses: an example of the Khibina and Lovozero massifs.
1059 *Petrology*, **19**, 115–139.

1060 Bailey, D. (1977) Lithospheric control of continental rift magmatism. *Geological Society*
1061 *of London Journal*, **133 SRC-**, 103–106.

1062 Bardina, N. and Popov, V. (1994) Fenites: systematics, formation conditions and
1063 significance for crustal magma genesis. *Zapiski Vseross. Mineral. Obshcheswa*, **113**,
1064 485–497.

1065 Le Bas, M. (1981) Carbonatite magmas. *Mineralogical Magazine*, **44 SRC-**, 133–140.

1066 Le Bas, M. (2008) Fenites associated with carbonatites. *The Canadian Mineralogist*, **46**
1067 **SRC-**, 915–932.

1068 Broom-Fendley, S., Wall, F., Brady, A., Gunn, A., Chenery, S. and Dawes, W. (2013)
1069 Carbonatite-hosted, late-stage apatite as a potential source of heavy rare earth
1070 elements? P. in: *Mineral Deposit Research for a High-Tech World*,. *Proceedings of*
1071 *the 12th Biennial SGA Meeting*. Uppsala.

1072 Broom-Fendley, S., Styles, M.T., Appleton, J.D., Gunn, G. and Wall, F. (2016) Evidence
1073 for dissolution-reprecipitation of apatite and preferential LREE mobility in
1074 carbonatite-derived late-stage hydrothermal processes. *American Mineralogist*, **101**,
1075 596–611.

1076 Broom-Fendley, S., Wall, F., Spiro, B. and Ullmann, C. V. (2017) Deducing the source
1077 and composition of rare earth mineralising fluids in carbonatites: insights from
1078 isotopic (C, O, $^{87}\text{Sr}/^{86}\text{Sr}$) data from Kangankunde, Malawi. *Contributions to*
1079 *Mineralogy and Petrology*, **172**, 96. Springer Berlin Heidelberg.

1080 Broom-Fendley, S., Elliott, H.A.L., Beard, C., Wall, F., Armitage, P., Brady, A., Deady, E.
1081 and Dawes, W. (2021a) Enrichment of heavy REE and Th in carbonatite-derived
1082 fenite breccia. *Geological Magazine*.

1083 Broom-Fendley, S., Siegfried, P.R., Wall, F., O'Neill, M., Brooker, R., Fallon, E., Pickles,
1084 J. and Banks, D. (2021b) The origin and composition of carbonatite-derived
1085 carbonate-bearing fluorapatite deposits. *Mineralium Deposita*, **56**, 863–884.

1086 Brown, T.J., Idoine, N.E., Raycraft, R.E., Shaw, A.R., Deady, A.E., Hobbs, S.F. and Bide,
1087 T. (2017) *World mineral production 2011-2015*. P. in: *British Geological Survey*.

1088 Buckley, H.A. and Woolley, A.R. (1990) Carbonates of the magnesite–siderite series from
1089 four carbonatite complexes. *Mineralogical Magazine*, **54**.

1090 Bühn, B. and Rankin, A. (1999) Composition of natural, volatile-rich Na-Ca-REE-Sr
1091 carbonatitic fluids trapped in fluid inclusions. *Geochimica et Cosmochimica Acta*, **63**,
1092 3781–3797.

1093 Bühn, B., Rankin, A.H., Radtke, M., Haller, M. and Knoechel, A. (1999) Burbankite, a (Sr,
1094 REE, Na, Ca)-carbonate in fluid inclusions from carbonatite-derived fluids;
1095 identification and characterization using laser Raman spectroscopy, SEM-EDX, and
1096 synchrotron micro-XRF analysis. *American Mineralogist*, **84**, 1117–1125.

1097 Bühn, B., Wall, F. and Le Bas, M.J. (2001) Rare-earth systematics of carbonatitic
1098 fluorapatites, and their significance for carbonatite magma evolution. *Contributions to*
1099 *Mineralogy and Petrology, Volume 141, Issue 5, pp. 572-591 (2001).*, **141**, 572–591.
1100 Springer-Verlag.

1101 do Cabo, V.N., Wall, F., Sitnikova, M.A., Ellmies, R., Henjes-Kunst, F., Gerdes, A. and
1102 Downes, H. (2011) Mid and heavy REE in carbonatites at Lofdal , Namibia. P. in:
1103 *Goldschmidt Conference Abstracts*.

1104 Cahen, L. and Snelling, N. (1966) *The geochronology of equatorial Africa*. P. in.: North-
1105 Holland Publishing Company, Amsterdam.

1106 Candela, P. and Bevin, P. (1995) Physical and chemical magmatic controls on the size of
1107 magmatic-hydrothermal ore deposits. Pp. 2–37 in: *Giant Ore Deposits-II* (A. Clark,

1108 editor). QMinEx Associates and Queen's University, Kingston.

1109 Candela, P.A. (1997) A review of shallow, ore-related granites: Textures, volatiles, and ore
1110 metals. *Journal of Petrology*. .

1111 Carmody, L. (2012) *Geochemical characteristics of carbonatite-related volcanism and*
1112 *sub-volcanic metasomatism at Oldoinyo Lengai, Tanzania*.

1113 Castor, S.B. (2008) The Mountain Pass rare-earth carbonatite and associated ultrapotassic
1114 rocks, California. *Canadian Mineralogist*, **46**, 779–806.

1115 Chakhmouradian, A. and Reguir, E. (2013) REE partitioning between crystals and melts:
1116 beyond the test tube. P. in: *125th Anniversary of GSA*. Denver.

1117 Chakhmouradian, A.R. and Wall, F. (2012) Rare earth elements: Minerals, mines, magnets
1118 (and more). *Elements*, **8**, 333–340.

1119 Chakhmouradian, A.R., Reguir, E.P., Zaitsev, A.N., Couëslan, C., Xu, C., Kynický, J.,
1120 Mumin, A.H. and Yang, P. (2017) Apatite in carbonatitic rocks: Compositional
1121 variation, zoning, element partitioning and petrogenetic significance. *Lithos*, **274**,
1122 188–213.

1123 Chebotarev, D., Doroshkevich, A., Klemd, R. and Karmanov, N. (2017) Evolution of Nb-
1124 mineralization in the Chuktukon carbonatite massif, Chadobets upland (Krasnoyarsk
1125 Territory, Russia). *Periodico di Mineralogia*, **86**, 99–118.

1126 David, F. and Walker, L. (1990) Ion microprobe study of intragrain micropermeability in
1127 alkali feldspars. *Contributions to Mineralogy and Petrology*.

1128 Dowman, E. (2014) Mineralisation and fluid processes in the alteration zone around the
1129 Chilwa Island and Kangankunde carbonatite complexes, Malawi. Kingston
1130 University, UK.

1131 Dowman, E., Wall, F., Jeffries, T., Treloar, P., Carter, A. and Rankin, A. (2017a) Granitoid
1132 zircon forms the nucleus for minerals precipitated by carbonatite-derived metasomatic

- 1133 fluids at Chilwa Island, Malawi. *Gondwana Research*, **51**.
- 1134 Dowman, E., Wall, F., Treloar, P.J. and Rankin, A.H. (2017b) Rare-earth mobility as a
 1135 result of multiple phases of fluid activity in fenite around the Chilwa Island
 1136 Carbonatite, Malawi. *Mineralogical Magazine*, **81**, 1367–1395.
- 1137 Eby, G., Roden-Tice, M., Krueger, H., Ewing, W., Faxon, E. and Woolley, A. (1995)
 1138 Geochronology and cooling history of the northern part of the Chilwa Alkaline
 1139 Province, Malawi. *Journal of African Earth Sciences*, **20**, 275–288.
- 1140 von Eckermann, H. (1948) *The alkaline district of Alnö Island*. P. in.: Sveriges Geologiska
 1141 Undersökning , Stockholm.
- 1142 Elliott, H.A.L., Wall, F., Chakhmouradian, A.R., Siegfried, P.R., Dahlgren, S.,
 1143 Weatherley, S., Finch, A.A., Marks, M.A.W., Dowman, E. and Deady, E. (2018)
 1144 Fenites associated with carbonatite complexes: A review. *Ore Geology Reviews*. .
 1145 Endurance Gold Corporation. (2013) Bandito REE-Niobium Project, Yukon.
 1146 <[http://www.endurancegold.com/s/Bandito.asp?ReportID=566818&_Type=Bandito-](http://www.endurancegold.com/s/Bandito.asp?ReportID=566818&_Type=Bandito-REE-Niobium-Project-Yukon&_Title=Overview)
 1147 REE-Niobium-Project-Yukon&_Title=Overview>.
- 1148 European Commission. (2017) *2017 list of Critical Raw Materials for the EU:*
 1149 *Communication from the European Commission to the European Parliament, The*
 1150 *Council, The European Economic and Social Committee and the Committee of the*
 1151 *Regions COM(2017) 490 final*. Brussels.
- 1152 Finch, A.A. and Walker, F.D.L. (1991) Cathodoluminescence and Microporosity in Alkali
 1153 Feldspars from the Bla Mane So Perthosite, South Greenland. *Mineralogical*
 1154 *Magazine*.
- 1155 Garson, M. (1965) *Carbonatites in Southern Malawi*. P. in.: The Government Printer,
 1156 Zomba, Malawi.
- 1157 Garson, M. and Campbell Smith, W. (1958) *Chilwa Island*. P. in.: The Government

- 1158 Printer, Zomba, Malawi.
- 1159 Goodenough, K.M., Schilling, J., Jonsson, E., Kalvig, P., Charles, N., Tuduri, J., Deady,
 1160 E.A., Sadeghi, M., Schiellerup, H., Müller, A., Bertrand, G., Arvanitidis, N.,
 1161 Eliopoulos, D.G., Shaw, R.A., Thrane, K. and Keulen, N. (2016) Europe's rare earth
 1162 element resource potential: An overview of REE metallogenetic provinces and their
 1163 geodynamic setting. *Ore Geology Reviews*, **72**, 838–856. Elsevier.
- 1164 Goodenough, K.M., Wall, F. and Merriman, D. (2018) The Rare Earth Elements: Demand,
 1165 Global Resources, and Challenges for Resourcing Future Generations. *Natural*
 1166 *Resources Research*, **27**, 201–216.
- 1167 Heinrich, E. (1966) *The Geology of Carbonatites*. P. in.: Rand McNally, Chicago.
- 1168 Humphris, S. (1984) The mobility of the rare earth elements in the crust. Pp. 317–342 in:
 1169 *Rare Earth Geochemistry* (P. Henderson, editor). Elsevier, Amsterdam.
- 1170 Koster van Gross, A. (1990) High-pressure DTA study of the upper three-phase region in
 1171 the system Na₂CO₃-H₂O. *American Mineralogist*, **75**, 667–675.
- 1172 Kozlov, E. and Arzamastsev, A. (2015) Petrogenesis of metasomatic rocks in the fenitized
 1173 zones of the Ozemaya Varaka alkaline ultrabasic complex, Kola Peninsula. *Petrology*,
 1174 **23**, 45–67.
- 1175 Kozlov, E., Fomina, E., Sidorov, M. and Shilovskikh, V. (2018) Ti-Nb Mineralization of
 1176 Late Carbonatites and Role of Fluids in Its Formation: Petyayan-Vara Rare-Earth
 1177 Carbonatites (Vuoriyarvi Massif, Russia). *Geosciences*, **8**.
- 1178 Kresten, P. (1988) The chemistry of fenitization: Examples from Fen, Norway. *Chemical*
 1179 *Geology*.
- 1180 Kresten, P. and Morogan, V. (1986) Fenitisation at the Fen complex, southern Norway.
 1181 *Lithos*, **19**, 27–42. Elsevier Science Pub. Co.
- 1182 Kröner, A., Collins, A., Hegner, E., Muhongo, S., Willner, A. and Kehelpannala, K. (2001)

1183 Has the East African Orogen Played Any Role in the Formation and Breakup of the
 1184 Supercontinent Rodinia and the Amalgamation of Gondwana? New Evidence from
 1185 Field Relationship and Isotopic Data. *Gondwana Research*, 669–671.
 1186 Lindsley, D. (1963) Fe---Ti oxides in rocks as thermometers and oxygen barometers:
 1187 Equilibrium relations of coexisting pairs of Fe---Ti oxides. *Carnegie Institute*
 1188 *Washington Yearbook*, **1962–1963**, 100–106.
 1189 Louvel, M., Etschmann, B., Guan, Q., Testemale, D. and Brugger, J. (2022) Carbonate
 1190 complexation enhances hydrothermal transport of rare earth elements in alkaline
 1191 fluids. *Nature Communications*, **13**, 1456.
 1192 Loye, E. (2014) The geological controls on the heavy rare earth element enriched alteration
 1193 zone of Area 4, Lofdal, Khorixas, Namibia. University of Exeter.
 1194 Martin, R.F., Whitley, J.E. and Woolley, A.R. (1978) An investigation of rare-earth
 1195 mobility: Fenitized quartzites, Borralan complex, N.W. Scotland. *Contributions to*
 1196 *Mineralogy and Petrology*, **66**, 69–73. Springer-Verlag.
 1197 McDonough, W. and Sun, S. (1995) The composition of the Earth. *Chemical Geology*, **120**
 1198 **SRC-**, 223–253.
 1199 McKie, D. (1966) Fenitisation. Pp. 261–294 in: *Carbonatites* (O. Tuttle and J. Getting,
 1200 editors). Interscience Publishers.
 1201 Migdisov, A.A. and Williams-Jones, A.E. (2014) Hydrothermal transport and deposition of
 1202 the rare earth elements by fluorine-bearing aqueous liquids. *Mineralium Deposita*, **49**,
 1203 987–997.
 1204 Mills, S.J., Kartashov, P.M., Kampf, A.R., Konev, A.A., Koneva, A.A. and Raudsepp, M.
 1205 (2012) Cordylite-(La), a new mineral species in fenite from the Biraya Fe-REE
 1206 deposit, Irkutsk, Russia. *The Canadian Mineralogist*, **50**, 1281–1290.
 1207 GeoScienceWorld.

- 1208 Mitchell, R.H. (2015) Primary and secondary niobium mineral deposits associated with
1209 carbonatites. *Ore Geology Reviews*.
- 1210 Morogan, V. (1989) Mass transfer and REE mobility during fenitization at Alnö, Sweden.
1211 *Contributions to Mineralogy and Petrology*.
- 1212 Morogan, V. (1994) Ijolite versus carbonatite as sources of fenitization. *Terra Nova*, **6**,
1213 166–176.
- 1214 Morogan, V. and Woolley, A.R. (1988) Fenitization at the Alnö carbonatite complex,
1215 Sweden; distribution, mineralogy and genesis. *Contributions to Mineralogy and*
1216 *Petrology*.
- 1217 Nadeau, O., Cayer, A., Pelletier, M., Stevenson, R. and Jébrak, M. (2015) The
1218 Paleoproterozoic Montviel carbonatite-hosted REE-Nb deposit, Abitibi, Canada:
1219 Geology, mineralogy, geochemistry and genesis. *Ore Geology Reviews*, **67**, 314–335.
- 1220 Palmer, D.A.S. (1998) The evolution of carbonatite melts and their aqueous fluids :
1221 evidence from Amba Dongar, India, and Phalaborwa, South Africa.
1222 <<http://digitool.library.mcgill.ca/R/?func=dbin-jump->
1223 [full&object_id=35474&local_base=GEN01-MCG02](http://digitool.library.mcgill.ca/R/?func=dbin-jump-full&object_id=35474&local_base=GEN01-MCG02)> (19 December 2018).
- 1224 Platt, R. and Woolley, A. (1990) The carbonatites and fenites of Chipman Lake, Ontario.
1225 *The Canadian Mineralogist*, **28**, 241–250. Mineralogical Association of Canada.
- 1226 Plümper, O., Botan, A., Los, C., Liu, Y., Malthe-Sørenssen, A. and Jamtveit, B. (2017)
1227 Fluid-driven metamorphism of the continental crust governed by nanoscale fluid flow.
1228 *Nature Geoscience*, **10**, 685–690.
- 1229 Roseiro, J. (2017) Química-mineral de pirocloros associados a formações carbonatíticas do
1230 Bailando (Angola): sua utilização como possíveis indicadores petrogenéticos e
1231 metalogenéticos. Universidade de Lisboa, 71 pp.
- 1232 Roseiro, J., Ribeiro da Costa, I., Figueiras, J., Rodrigues, P. and Mateus, A. (2019) Nb-

- 1233 bearing mineral phases in the Bailundo Carbonatitic Complex (Angola):
 1234 metallogensis and implications for mineral exploitation. Pp. 301–304 in: *XII*
 1235 *Congresso Ibérico de Geoquímica/XX Semana Da Geoquímica*. Évora.
- 1236 Rubie, D. and Gunter, W. (1983) The Role of Speciation in Alkaline Igneous Fluids during
 1237 Fenite Metasomatism. *Contributions to Mineralogy and Petrology*, **82** SRC-, 165–
 1238 175.
- 1239 Simandl, G. and Paradis, S. (2018) Carbonatites: related ore deposits, resources, footprint,
 1240 and exploration methods. *Applied Earth Science*, 123–152.
- 1241 Simonetti, A. and Bell, K. (1994) Isotopic and geochemical investigation of the Chilwa
 1242 Island carbonatite complex, Malawi: Evidence for a depleted mantle source region,
 1243 liquid immiscibility, and open-system behaviour. *Journal of Petrology*.
- 1244 Smith, M., Henderson, P. and Campbell, L. (2000) Fractionation of the REE during
 1245 hydrothermal processes: Constraints from the Bayan Obo Fe-REE-Nb deposit, Inner
 1246 Mongolia, China. *Geochimica et Cosmochimica Acta*, **64**, 3141–3160.
- 1247 Smith, M.P. (2007) Metasomatic silicate chemistry at the Bayan Obo Fe–REE–Nb deposit,
 1248 Inner Mongolia, China: Contrasting chemistry and evolution of fenitising and
 1249 mineralising fluids. *Lithos*, **93**, 126–148. Elsevier.
- 1250 Snelling, N. (1965) Age determinations on three African carbonatites. *Nature*, **205** SRC-,
 1251 491.
- 1252 Southwick, D. (1968) Mineralogy of a rutile--- and apatite---bearing ultramafic chlorite
 1253 rock, Harford County, Maryland. *Geological Survey Research*, **600**–C, C38---C44.
- 1254 Tan, W., Wang, C.Y., He, H., Xing, C., Liang, X. and Dong, H. (2015) Magnetite-rutile
 1255 symplectite derived from ilmenite-hematite solid solution in the Xinjie Fe-Ti oxide-
 1256 bearing, mafic-ultramafic layered intrusion (SW China). *American Mineralogist*, **100**.
- 1257 Tanis, E.A., Simon, A., Tschauner, O., Chow, P., Xiao, Y., Burnley, P., Cline, C.J.,

- 1258 Hanchar, J.M., Pettke, T., Shen, G. and Zhao, Y. (2015) The mobility of Nb in rutile-
1259 saturated NaCl-and NaF-bearing aqueous fluids from 1-6.5 GPa and 300-800 °C.
1260 *American Mineralogist*, **100**, 1600–1609.
- 1261 Timofeev, A., Migdisov, A. and Williams-Jones, A. (2015) An experimental study of the
1262 solubility and speciation of niobium in fluorite-bearing aqueous solutions at elevated
1263 temperature. *Geochimica et Cosmochimica Acta*, **158**, 103–111.
- 1264 Verplanck, P., Mariano, A. and Mariano, A. (2016) Rare earth element ore geology of
1265 carbonatites. Pp. 5–32 in: *Rare Earth and Critical Elements in Ore Deposits*. Society
1266 of Economic Geologists Inc.
- 1267 Verschure, R. and Maijer, C. (2005) *Bulletin*. P. in: *NGU Bulletin*. Universitetsforlaget,
1268 45–71 pp.
- 1269 Verwoerd, W. (1966) South African carbonatites and their probable mode of origin. *Ann.*
1270 *Univ. Stellenbosch*, **41**, 121–233.
- 1271 Viladkar, S.G. and Ramesh, R. (2014) Stable Isotope geochemistry of some Indian
1272 Carbonatites: Implications for magmatic processes and post-emplacement
1273 hydrothermal alteration. *Comunicacoes Geologicas t. 101*.
- 1274 Wall, F. (2000) Mineral chemistry and petrogenesis of rare earth-rich carbonatites with
1275 particular reference to the Kangankunde carbonatite, Malawi. University of London.
- 1276 Wall, F. (2013) Rare earth elements. Pp. 312–339 in: *Critical Metals Handbook*. John
1277 Wiley & Sons, Oxford.
- 1278 Wall, F. and Mariano, A. (1996) Rare earth minerals in carbonatites: a discussion centred
1279 on the Kangankunde Carbonatite, Malawi. Pp. 193–225 in: *Rare Earth Minerals:*
1280 *Chemistry, Origin and Ore Deposit* (A. Jones, F. Wall and C. Williams, editors).
1281 Chapman & Hall, London.
- 1282 Wall, F., Barreiro, B. and Spiro, B. (1994) Isotopic evidence for late-stage processes in

1283 carbonatites: rare earth mineralisation in carbonatites and quartz rocks at
 1284 Kangankunde, Malawi. *Mineralogical Magazine*, **58**, 951–952.

1285 Wall, F., Niku-Paavola, V.S., Müller, A. and Jeffries, T. (2008) Xenotime-(Y) from
 1286 carbonatite dykes at Lofdal, Namibia: unusually low LREE:HREE ratio in
 1287 carbonatite, and the first dating of xenotime overgrowths on zircon. *The Canadian*
 1288 *Mineralogist*, **46** SRC-, 861–877.

1289 Walter, B., Giebel, R.J., Steele-MacInnis, M., Marks, M.A.W., Kolb, J. and Markl, G.
 1290 (2021) Fluid release in carbonatitic systems and its implication for carbonatite magma
 1291 ascent, compositional evolution and REE-mineralization.

1292 Weng, Z., Jowitt, S. and Mudd, G. (2015) A Detailed Assessment of Global Rare Earth
 1293 Element Resources: Opportunities and Challenges. *Economic Geology*, **110**, 1925–
 1294 1952.

1295 Williams-Jones, A. and Migdisov, A. (2014) Rare Earth Element Transport and Deposition
 1296 by Hydrothermal Fluids. *Acta Geologica Sinica - English Edition*, **88**, 472–474.

1297 Williams-Jones, A.E. and Palmer, D.A.S. (2002) The evolution of aqueous–carbonic fluids
 1298 in the Amba Dongar carbonatite, India: implications for fenitisation. *Chemical*
 1299 *Geology*, **185**, 283–301. Elsevier.

1300 Woolley, A. (1969) Some aspects of fenitisation with particular reference to Chilwa Island
 1301 and Kangankunde, Malawi. *Bulletin of British Museum of Natural History*
 1302 *(Mineralogy)*, **2**, 191–219 SRC-GoogleScholar FG-0.

1303 Woolley, A. (2001) *Alkaline Rocks and Carbonatites of the World Part 3: Africa*. P. in.:
 1304 The Geological Society, London.

1305 Woolley, A.R. (1982) *A discussion of carbonatite evolution and nomenclature, and the*
 1306 *generation of sodic and potassic fenites*. 13–17 pp.

1307 Wu, C., Yuan, Z. and Bai, G. (1996) Rare-earth Deposits in China. Pp. 281–310 in: *Rare*

1308 *Earth Minerals: Chemistry, Origin and Ore Deposits* (A. Jones, F. Wall and C.
1309 Williams, editors). Chapman and Hall, London.

1310 Yuan, G., Cao, Y., Schulz, H., Hao, F., Gluyas, J., Liu, K., Yang, T., Wang, Y., Xi, K. and
1311 Li, F. (2019) A review of feldspar alteration and its geological significance in
1312 sedimentary basins: From shallow aquifers to deep hydrocarbon reservoirs. *Earth-*
1313 *Science Reviews*, **191**, 114–140.

1314 Yuguchi, T., Shoubuzawa, K., Ogita, Y., Yagi, K., Ishibashi, M., Sasao, E. and Nishiyama,
1315 T. (2019) Role of micropores, mass transfer, and reaction rate in the hydrothermal
1316 alteration process of plagioclase in a granitic pluton. *American Mineralogist*, **104**,
1317 536–556.

1318 Zarsky, G.P., Korzhinskaya, V. and Kotova, N. (2010) Experimental studies of Ta₂O₅
1319 and columbite-tantalite solubility in fluoride solutions from 300 to 550°C and 50 to
1320 100 MPa. *Mineralogy and Petrology*.

1321 Zharikov, V.A., Pertsev, N.N., Rusinov, V.L., Callegari, E. and Fettes, D.J. (2007)
1322 *Metasomatism and metasomatic rocks*.

1323

1324