Rare earth mobility as a result of multiple phases of fluid activity in fenite around the Chilwa Island Carbonatite, Malawi

Emma Dowman1,2,3 Frances Wall2,3 Peter J. Treloar1 and Andrew H Rankin1
1 Department of Geography and Geology, Kingston University, Kingston-upon-Thames, KT1 2EE, UK
2 Camborne School of Mines, University of Exeter, Penryn Campus, Penryn, TR10 9FE, UK
3 The Natural History Museum, Cromwell Road, London, SW7 5BD, UK
Emma Dowman emma@abdm.co.uk

Keywords: fenite, rare earths, fluid inclusions, apatite

Abstract
Carbonatites are enriched in critical raw materials such as the rare earth elements (REE), niobium, fluorspar and phosphate. A better understanding of their fluid regimes will improve our knowledge of how to target and exploit economic deposits. This study shows that multiple fluid phases penetrated the surrounding fenite aureole during carbonatite emplacement at Chilwa Island, Malawi. The first alkaline fluids formed the main fenite assemblage and later microscopic vein networks contain the minerals of potential economic interest such as pyrochlore in high-grade fenite and RE minerals throughout the aureole. Seventeen samples of fenite rock from the metasomatic aureole around the Chilwa Island carbonatite complex were chosen for study (Natural History Museum, London collection BM1968 P37). In addition to the main fenite assemblage of feldspar and aegirine ± arfvedsonite, riebeckite and richterite, the fenite contains micro-mineral assemblages including apatite, ilmenite, rutile, magnetite, zircon, RE minerals and pyrochlore in vein networks. Petrography using SEM-EDX showed that the RE minerals (monazite, bastnäsite and parisite) formed later than the fenite feldspar, aegirine and apatite and provide evidence of REE mobility into all grades of fenite. Fenite apatite has a distinct negative Eu anomaly (determined by LA-ICP-MS) that is rare in carbonatite-associated rocks and interpreted as related to pre-crystallisation of plagioclase and co-crystallisation with K-feldspar in the fenite. The fenite minerals have consistently higher mid REE/light REE ratios (La/Sm = ~1.3 monazite, ~1.9 bastnäsite, ~1.2 parisite) than their counterparts in the carbonatites (La/Sm = ~2.5 monazite, ~4.2 bastnäsite, ~3.4 parisite). Quartz in the low- and medium-grade fenite hosts fluid inclusions, typically a few µm in diameter, secondary and extremely heterogeneous. Single phase, 2- and 3-phase, single solid and multi solid-bearing examples are present, with 2-phase the most abundant. Calcite, nahcolite, burbankite and barite were found in the inclusions. Decrepitation of inclusions occurred at around 200°C.
before homogenisation but melting temperature data indicate that the inclusions contain relatively pure CO₂. A minimum salinity of around 24 wt.% NaCl equivalent was determined. Among the trace elements in whole rock analyses, enrichment in Ba, Mo, Nb, Pb, Sr, Th and Y and depletion in Co, Hf and V are common to carbonatite and fenite but enrichment in carbonatitic type elements (Ba, Nb, Sr, Th, Y, and REE) generally increases towards the inner parts of the aureole. A schematic model contains multiple fluid events, related to first and second boiling of the magma, accompanying intrusion of the carbonatites at Chilwa Island, each contributing to the mineralogy and chemistry of the fenite. The presence of distinct RE mineral micro-assemblages in fenite at some distance from carbonatite could be developed as an exploration indicator of REE enrichment.

**Introduction**

Carbonatites are the most important economic source of rare earth elements (REE). Most carbonatites are characteristically enriched in REE compared to other rock types (Verplanck and Van Gosen, 2011 and references therein), and some, such as Mount Weld, Australia; Mountain Pass, USA; Bear Lodge, USA; Ngualla, Tanzania; Saint-Honoré, Canada; Songwe Hill, Malawi and Lofdal, Namibia have high enough concentrations to constitute ore deposits. The world’s largest REE mine at Bayan Obo, China is also thought to be a highly altered carbonatite (Smith, 2007). Rare earth ore deposits in carbonatites are reviewed in Mariano, (1989); Lipin and McKay, (1989); and Chakhmouradian and Wall, (2012). The economics of REE ore deposits depend very much on which of the REE are in highest concentrations since the price of the REE varies greatly. Generally light REE (La-Nd) are less valuable than mid (Sm- Gd) and heavy REE (Tb- Lu).

A better understanding of the fluid regimes and transport of light, mid and heavy REE in and around carbonatite complexes is important in order to improve ore deposit models, predict where to explore for the more expensive REE, and help to identify more economically viable deposits.

Fenite is a typical rock around carbonatite and alkaline rock complexes. It forms in aureoles of alkaline metasomatic alteration of the country rock around the carbonatite and alkaline silicate intrusions. During the process of fenitisation, feldspar and alkali pyroxene and/or amphibole usually are produced, at the expense of quartz and original feldspar components. Fenitisation is usually progressive with gradational boundaries between fenite and unaltered country rock and, generally, an increasing intensity of alteration towards the intrusion. Fenite aureoles frequently comprise an outer sodic zone and an inner potassic...
fenite (Le Bas, 2008). Sodic fenitisation is generally considered to precede potassic fenitisation, although the causes of this relatively common pattern have not been fully determined. Both calcitic and ankeritic carbonatites can induce both Na- and K-rich fluids (Le Bas, 2008), which suggests that the composition of the parent magma is not 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 of type of alkaline alteration 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 (Le Bas, 2008; Woolley, 1982; Rubie and Gunter, 1983; Viladkar, 2012). Previous studies of the fenitisation process include Morogan and Woolley, (1988); Morogan, (1989); Verschure and Maijer, (2005); Platt and Woolley, (1990); Woolley, (1969); Garson and Campbell Smith, (1958); Carmody, (2012); Andersen, (1989); McKie, (1966). An improved knowledge of fenitisation processes is key to understanding the exsolution and evolution of the fluids exsolved from the alkaline content of carbonatite magmas.

It is well accepted that REE move from carbonatite magma into the fenite aureole. Martin et al., (1978) made one of the first studies of REE mobility into fenite when they identified mobilisation of rare earths into a barren quartzite rock by magma-derived during the emplacement of the Borralan alkaline/carbonatite complex in Scotland. Bühn and Rankin, (1999) investigated element partitioning at the Kalkfeld carbonatite in Namibia. They remarked on the high capability of H₂O-CO₂-Cl-F fluids to transport the LILE and HFSE at high temperatures, and developed a qualitative retention series of elements in the fluid as follows: Cl>Na>K>(Cs,Rb,Pb,Cu,Zr)>U=Th>Ti=Y=Ba>F=Mg>REE=Sr>Mn=Fe which represents an increasing tendency from right to left to partition into the fluid relative to the crystallising carbonatite melt. The incompatible behaviour of the REE has become generally accepted, although it is acknowledged that the 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 literature on rare-earth-bearing minerals in fenite around carbonatites (Le Bas, 2008; Smith, 2007; Andersen, 1989; Morogan, 1989; Morogan and Woolley, 1988; Kresten and Morogan, 1986). However, increasing interest in REE mineralisation in altered rocks, such as fenites, has led to recent reports of rare-earth (RE) minerals. Cordylite-(La), a new mineral species was found in fenite from the Biraya Fe-REE deposit in Irkutsk, Russia (Mills et al., 2012), associated with
many other RE-minerals, such as daqingshanite-(Ce), monazite-(Ce) and bastnäsite-(Ce). Fenite at the Songwe carbonatite complex in Malawi has also been identified as HREE-enriched, including occasional xenotime-(Y) (Broom-Fendley et al., 2013). At Bandito in the Yukon, a fenite (associated with nepheline syenite rather than carbonatite) is also RE-rich, with up to 3.49% TREO+Y in highly metasomatised syenite, which contains minerals such as monazite, bastnäsite and apatite (Endurance Gold Corporation, 2012, 2013).

Previous studies of fluid inclusions related to fenites have demonstrated that fenitising fluids are generally aqueous-CO$_2$-bearing, alkali-bicarbonate brines of variable salinity, capable of carrying the REE, large-ion-lithophile elements and HFSE (Palmer, 1998; Bühn and Rankin, 1999; Bühn et al., 1999, 2001; Williams-Jones and Palmer, 2002; Carmody, 2012).

Chilwa Island contains the whole range of calcite, dolomite and Fe-rich carbonatites (Garson and Campbell Smith, 1958), together with a well-formed fenite aureole containing sodic and potassic fenite. Hence, it is often featured in textbooks. RE minerals are present in the carbonatite, although the complex has not been considered as an important REE source. This study provides new evidence of REE mobility into fenite being a second stage process of mineralisation rather than accompanying the first alkali metasomatism. We present evidence of micromineral assemblages within the main mineral assemblage of the fenite at Chilwa Island. Variable RE signatures of whole rock analyses of fenite and carbonatite and an investigation of the fluid inclusions in fenitic quartz are combined to propose a new model for the metasomatic regime around the carbonatite.

**Approach and methodology**

Our new data, which permit a full interpretation of the Chilwa Island Complex, are presented below. Samples used are from the Natural History Museum, London collection BM1968 P37. Analyses used SEM-EDS, SEM-based CL, LA-ICP-MS and fluid inclusion-based techniques. Full details of analytical techniques are available as supplementary data.
Geological background

The carbonatite complex of Chilwa Island lies in the Cretaceous-aged Chilwa Alkaline Province at the extreme southern end of the East African Rift system. The area has seen repeated emplacement of alkaline and carbonate rocks into amphibolite and granulite facies basement rocks (Bailey, 1977; Kröner et al., 2001). Crustal extension and decompressional melting between 138 and 107 Ma drove alkaline magmatism in the CAP (Eby et al., 1995), producing seventeen carbonatite intrusions, 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 of the eastern chain of carbonatites, in the southwest of Lake Chilwa. The largest of the Malawi carbonatites, it is a ring complex ca. 4 km in diameter, consisting of multiple carbonatite intrusions. Structural relationships indicate sequential emplacement from early outer calcio carbonatites (commonly termed ‘sövite’) inwards to later ankeritic (increasing Mg, Fe) carbonatites and then the youngest central sideritic (Fe, Mn-rich) carbonatite (Garson and Campbell Smith, 1958; Garson, 1965; Le Bas, 1981; Woolley, 2001). Brecciated country rock and fenitised Precambrian granulites surround the carbonatite rocks (Figure 1). The outer margins of alteration of the country rock are hidden beneath the lake and its sediments. No unaltered rock is found on the island, and therefore little is known of the original rocks. A time frame for the complex is provided by K-Ar dating of biotite in the earliest (calcio)carbonatite by Snelling, (1965) at 138 Ma. Eby et al., (1995) used titanite fission-track analysis to date a nepheline-syenite plug intruding carbonatite at 126 Ma, with apatite fission-track dates of 87±9 Ma from the same rock. This accords with fission-track dating of carbonatite-derived apatite in fenite (Dowman, 2014), which yielded an age of 99±4 Ma.
Fig. 1 Geological map of Chilwa Island carbonatite complex [adapted from Garson and Campbell Smith (1958)]. Numbers are approximate locations of fenite samples used in study.
Garson and Campbell Smith, (1958) undertook a comprehensive survey of the mineralogy of the complex. They described sövite carbonatites as varying from almost purely calcite to compositions containing apatite or pyroxene. Minerals found in both sövite and ankeritic carbonatite include pyrochlore, magnetite, feldspar, quartz and barite. Synchysite and florencite are RE-bearing minerals occurring occasionally in these carbonatites. The central sideritic carbonatite is described as being of secondary origin (Woolley, 2001), and is a rock rich in Fe- and Mn-oxides, characterised by numerous druses and veinlets that are lined with minerals such as quartz, calcite and barite. The RE-bearing minerals, florencite and bastnäsite were identified within some of these druses.

The outermost carbonatite, sövite, is surrounded by a collar of potassic feldspathic breccia. The breccias are the end-stage or high-grade fenite, probably broken up during episodes of high pressure in the history of the carbonatite central complex. Outside the breccia lies fenitised country rock, divided by Woolley, (1969) into a less fenitised group of 'quartz fenites' and an inner group of 'syenitic fenites'. The mineralogy of the less altered quartz fenites is inherited primarily from the basement and is dominated by plagioclase and quartz, with minor aegirine also present. In the syenitic fenites, quartz and plagioclase are being replaced by a new mineralogy of orthoclase, aegirine and sodic amphiboles, with magnesioarfvedsonite being identified in syenite fenite, and riebeckite in quartz fenite. No RE-minerals are described in any type of fenite.

Garson and Campbell Smith, (1958) proposed metasomatism of the aureole by several waves of fenitisation. This alteration was through fluids channelled along a network of veins and grain boundaries throughout the rocks. Woolley, (1969) made a distinction between the potassic breccias and the more sodic outer aureole, attributing the cause to fluids that were temporally separated, and probably from different sources. Both Garson and Campbell Smith, (1958) and Woolley, (1969) interpret fenite mineralogy, including the presence of apatite in veins of alteration, as being an indicator that fenitising solutions were probably rich in water and CO2, and that they carried K, Fe and Na cations, and mobilised P2O5.

In addition to the evident metasomatism of the outer parts of the complex, the sideritic carbonatite rocks may also have undergone secondary alteration (Garson and Campbell Smith, 1958) as a result of oxidation, and areas of sövite may have been replaced by more ankeritic carbonatite. A late-stage hydrothermal and silicification event, associated with the final waning of carbonatite activity, probably affected all parts of the complex in a selective manner, with some rocks being replaced, and others remaining unchanged.
probably mobilised from the country rocks, and alteration introduced secondary minerals, such as quartz, calcite and barite, as described in druses in the core sideritic carbonatite, as well as quartz and quartz-fluorite veins in both carbonatite and fenite rocks.

Mineralogy of the fenite aureole

For this paper, a straightforward scheme to distinguish the fenite rocks is required. Although not ideal, because alteration can often form a continuum, the terminology of low-grade and medium-grade fenite as used here reflects relative intensity of metasomatism, and approximately matches the earlier petrographic descriptions of Garson and Campbell Smith, (1958) and Woolley, (1969) of ‘quartz fenite’ and ‘syenite fenite’. Low-grade fenite at Chilwa Island generally comprises less than 10% veins of aegirine/iron oxide alteration, and high-grade fenite refers to rocks with a monophase matrix of either orthoclase or secondary quartz.

Low-grade fenite has a matrix of quartz and plagioclase. Feldspar exhibits both perthitic and antiperthitic textures. Samples from this fenite grade provide a few examples of magnetite containing a trelliswork of ilmenite (Figure 2a) but veins are scarce, and where present, are usually of aegirine and K-feldspar. Some apatite, rutile and ilmenite assemblages are present in which minerals show porosity, but rarely any zoning. Monazite, although not common, is the only RE-mineral that occurs regularly, usually in association with apatite. Parisite, xenotime and pyrochlore appear to be very rare in this part of the aureole, only being found in one sample.

The medium-grade fenite group contains several samples that appear more strongly altered, and they are treated here as a subgroup of medium/high-grade rocks. The matrix of the majority of medium-grade fenites is still feldspar and quartz, but the feldspar is increasingly turbid, rarely exhibiting perthitic textures, and quartz is a less important phase than in the low-grade fenite. Some evidence of secondary quartz is indicated adjacent to areas of aegirine alteration. Aegirine mineralisation is more extensive, being concentrated in veins often fringed by K-feldspar, which is now a more common mineral. The main characteristic of this grade of fenite is seen within these veins, especially the presence of micro-assemblages of ilmenite, fluorapatite and zircon, which were found in every medium-grade sample (Figure 2b). Ilmenite grains frequently show areas of Fe-rich and Ti-rich separation, and are often associated with magnetite grains and occasionally with Nb-bearing rutile grains (Figures 2c and 2d). Apatite is now rarely porous, and displays strong zoning. Amphibole (magnesioarfvedsonite, richterite) was detected in some sections, invariably associated with aegirine. Rare earth minerals occur regularly in the areas of mineralisation.
Monazite is the most common of these, often in the form of rim grains in apatite. Bastnäsite, typically shard-like in form, is also present, but is rarer than monazite. Parisite and xenotime are scarce and only noted in a few sections, as was carbonate, which usually has a composition of calcium, or more rarely, ankeritic carbonate.

The more altered subgroup within the medium-grade fenites is dominated by a mineralogy of aegirine and K-feldspar (orthoclase), with an increasing presence of recrystallised quartz. Only vestiges of the ilmenite-apatite-zircon microassemblages remain. Apatite is now much scarcer, and exhibits no zoning or any association with monazite. Sodic amphiboles (magnesioarfvedsonite, richterite) are found together with aegirine, but in no greater abundance than in the less fenitised members of this group. Zircon, usually located in aegirine, appears ragged in shape with signs of resorption (Figure 2e). A greater variety of trace phases is seen, such as barite, pyrite, carbonates (a few examples of both calcium carbonate and ankeritic carbonate) and also the Ca-bearing RE fluorcarbonate parisite-(Ce) (Figure 4a), although the RE minerals monazite and bastnäsite are absent.

The pink colour of the breccia (high-grade fenite) reflects its almost monophasic K-feldspar composition. The microassemblages and aegirine of the medium-grade fenite are absent, although secondary quartz is still found. Pyrochlore is now present, usually associated with increasingly ragged zircon grains (Figure 2f), and goyazite was detected in thread-like veins. An unidentified Th-rich RE mineral was found, but no carbonate was present.

The highest-grade fenite is represented by sample BM1968 P37 83. This is also an almost monophasic rock, but, in contrast to the breccia, is composed of secondary quartz. No feldspar of any variety was seen in this section. Other minerals in the section are assemblages of apatite and pyrochlore, the latter often rich in Pb. The apatite is often associated with RE minerals, such as monazite-(Ce),(La), xenotime and an unidentified Th-MREE phase (Figure 4b). Bastnäsite-(Ce) and zoned goyazite were seen in areas of pyrochlore mineralisation.
Fig. 2 Back-scattered electron images of fenites from Chilwa Island

a) magnetite with ilmenite in low-grade fenite BM1968 P37 130
b) typical mineral assemblage of apatite, zircon and ilmenite in medium-grade fenite BM1968 P37 78
c) Ilmenite showing rutile-magnetite separation in medium-grade fenite BM1968 P37 96
d) Ilmenite associated with magnetite, also apatite and zircon in medium-grade fenite BM1968 P37 101
e) Zircon resorbing in aegirine in medium/high-grade fenite BM1968 P37 54
f) Pyrochlore and zircon association in breccia BM1968 P37 146
The mineralogical data are summarised in Table 1 and Figure 3a. Figure 3a illustrates in a qualitative way the relative abundance of different minerals across the fenite aureole. Figures 3b and 3c (from whole-rock analyses) indicate the quantitative variation of major elements (by wt. %) and selected trace elements (chondrite-normalised) in the composition of each fenite zone.

**Table 1** Summary of mineralogy in fenite zones at Chilwa Island

<table>
<thead>
<tr>
<th>Fenite grade</th>
<th>Matrix</th>
<th>Fenite mineral assemblages</th>
<th>Apatite habit</th>
<th>Carbonates, sulfides</th>
<th>RE minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low-grade</strong></td>
<td>Plagioclase with minor orthoclase. Perthite common. Quartz 25-30%.</td>
<td>A few veins of aegirine (&lt;10%), occasionally accompanied by apatite, zircon, ilmenite, rutile and amphibole. Magnetite grains, some with 'ilmenite treillis'.</td>
<td>Absent, or a few grains per section. Some porous, but zoning rare. Occasionally contain monazite inclusions.</td>
<td>Rare carbonate veins, variable Ca, Fe, Mn content. Small grains of barite common to absent. One section contained a few grains of pyrite and a single galena.</td>
<td>Monazite-(Ce) with Th found in each section. Rare parisite-(Ce), and one xenotime grain in one section.</td>
</tr>
<tr>
<td><strong>Medium-grade</strong></td>
<td>Plagioclase is dominant, orthoclase forming around mineralised areas. Perthite rarely seen. Quartz typically 20-25%.</td>
<td>Veins of aegirine form 15-20% of section, associated with microassemblages of ilmenite/apatite/zircon, often also Nb-bearing rutile. Ilmenite separation into Fe and Ti phases. Magnetite grains in most sections, sometimes with 'ilmenite treillis'. Na-amphibole found amongst aegirine grains.</td>
<td>Common part of micro-assemblages. Typically zoned and with RE minerals (mostly monazite) inclusions. Rare submicron zircon inclusions.</td>
<td>Most sections contain common small barite grains and occasional pyrite. Carbonate rare, may be of calcite or ankerite.</td>
<td>Monazite-(Ce) is most common, more abundant than in low-grade fenite. Bastnäsite-(Ce) also occurs. One example of xenotime-(Y) seen, also one unidentified REE-Th-Sr carbonate phase.</td>
</tr>
<tr>
<td><strong>Medium/high grade</strong></td>
<td>Feldspar dominated by orthoclase. No perthite. Primary quartz rare.</td>
<td>Aegirine mineralisation typically 45-60%. Amphibole and Nb-rutile are present but microassemblages of ilmenite/apatite/zircon are rare or absent. Secondary quartz forms up to 10% of section. A few pyrochlore grains now present.</td>
<td>Less frequent as fenite grade increases. When present, rarely zoned, and without RE mineral inclusions.</td>
<td>Frequent small barite grains. A few pyrite grains. Carbonate (mostly calcite, but also ankerite) may occur with recrystallised quartz.</td>
<td>Monazite and bastnäsite rare or absent. Parisite-(Ce) present in most sections.</td>
</tr>
<tr>
<td>Breccia</td>
<td>Orthoclase</td>
<td>No aegirine. Small areas of recrystallised quartz. Occasional assemblages of zircon and pyrochlore. Pyrochlore may be Pb-U-bearing.</td>
<td>Absent.</td>
<td>None found.</td>
<td>Unidentified REE-Th phosphate phase, also goyazite.</td>
</tr>
</tbody>
</table>
Fig. 3  
a) Qualitative distribution of minerals in fenite zones at Chilwa Island  
b) Distribution of major elements by wt. % in fenite zones at Chilwa Island  
c) Concentration/chondrite abundance of selected trace elements in fenite zones at Chilwa Island
a) Line thickness indicates relative mineral abundance.
Chilwa Island major elements wt. %

<table>
<thead>
<tr>
<th></th>
<th>Low - grade fenite</th>
<th>Medium - grade fenite</th>
<th>Breccia</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃ (t)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>MgO</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CaO</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
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<tr>
<td>P₂O₅</td>
<td></td>
<td></td>
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</tbody>
</table>

**INCREASING INTENSITY OF ALTERATION**

**SiO₂ wt. %**

- 56 - 60
- 61 - 65
- 66 - 70
- 71 - 75
- 76 - 80
- 81 - 85
- 86 +

(Note different scale)
Carbonatite mineralogy

Four carbonatite samples have been studied and their mineralogy is summarised in Table 3. Ankerite with Mg>Fe and calcite are the dominant minerals together with one or more of apatite, pyrochlore and quartz. Parisite-(Ce), bastnäsite-(Ce), monazite-(Ce), and florencite-goyazite are all present as accessory phases (Figures 4c-4f).

Table 2 Summary of mineralogy of carbonatite sections from Chilwa Island

<table>
<thead>
<tr>
<th>Carbonatite</th>
<th>Matrix minerals</th>
<th>Accessory minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ankeritic sövite 1957 1056 102</td>
<td>Calcium carbonate</td>
<td>Parisite-(Ce), contains Th</td>
</tr>
<tr>
<td></td>
<td>Apatite</td>
<td>Goyazite-florenceite</td>
</tr>
<tr>
<td></td>
<td>Ankeritic carbonate Ca&gt; Mg&gt;Fe&gt;Mn</td>
<td>Pyrochlore, contains Ce, Pb and Th</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Xenotime</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nb-bearing rutile</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Barite</td>
</tr>
<tr>
<td>Pyrochlore-bearing ankeritic</td>
<td>Ankeritic carbonate Ca&gt; Mg&gt;Fe&gt;Mn</td>
<td>Quartz</td>
</tr>
<tr>
<td>carbonatite 1957 1056 118</td>
<td>Apatite</td>
<td>Calcium carbonate</td>
</tr>
<tr>
<td></td>
<td>Pyrochlore (with Ce, Y, Th)</td>
<td>Parisite-(Ce), contains Th</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Strontianite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Barite</td>
</tr>
<tr>
<td>Ankeritic carbonatite 1957 1056</td>
<td>Ankeritic carbonate Ca&gt; Fe&gt; Mg&gt;Mn</td>
<td>Strontianite</td>
</tr>
<tr>
<td>128</td>
<td>Quartz</td>
<td>Nb-bearing rutile</td>
</tr>
<tr>
<td></td>
<td>K-feldspar</td>
<td>Apatite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bastnäsite-(Ce) contains Th</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Monazite-(Ce), contains Th</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Parisite-(Ce), contains Th</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Goyazite-florenceite</td>
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<tr>
<td></td>
<td></td>
<td>Pyrite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Barite</td>
</tr>
<tr>
<td>Sideritic carbonatite 1957 1056</td>
<td>Fe-Mn oxides</td>
<td>Th-RE carbonate</td>
</tr>
<tr>
<td>113</td>
<td>Calcium carbonate</td>
<td>Goyazite-florenceite</td>
</tr>
<tr>
<td></td>
<td>Quartz</td>
<td>Synchysite-(Ce), contains Th</td>
</tr>
</tbody>
</table>
Fig. 4 Back-scattered electron images of REE-bearing minerals at Chilwa Island

a) Vein of quartz and calcite containing parisite and barite in medium/high-grade fenite
BM1968 P37 54

b) Apatite with associated monazite, xenotime and unidentified Th-MREE phase in high-grade fenite
BM1968 P37 83

c) Strontianite with bastnäsite inclusions, and goyazite and rutile grains in ankeritic carbonatite
1957 1056 128

d) Parisite and pyrochlore in sövite and ankeritic carbonate 1957 1056 102

e) Mineralisation in ‘sideritic’ carbonatite 1957 1056 113

f) Detail of unidentified Th-rich REE phase in ‘sideritic’ carbonatite 1957 1056 113
**Apatite**

Apatite is an important mineral at Chilwa Island where it is found in both fenites and carbonatites.

**Apatite in fenite**

In low-grade and medium-grade fenite, apatite is characteristically a vein-hosted mineral. Apatite-bearing veins are scarce in low-grade fenite, where apatite is typically unzoned and porous (Figure 5a), sometimes with monazite inclusions. Under cathodoluminescence, it luminesces in shades of purple, and is often associated with scarlet-luminescing K-feldspar (Dowman, 2014). The red luminescence of the feldspar is characteristic of fenitisation processes, and is attributed to the incorporation into the mineral of the activator, Fe\(^{3+}\), which is contained in fenitising fluids of high alkalinity and of moderate to high temperature. In non-alkaline rocks, K-feldspar luminesces bright blue (Mariano et al., 1973; Mariano, 1978; 1988).

The porous appearance of apatite both in this low-grade fenite, and in the high-grade fenite BM1968 P37 83 (Figure 4b), may be the result of incipient dissolution or resorption of grains. Apatite is a much more common phase in medium-grade fenite, where it is typically found in fine-grained assemblages together with zircon, ilmenite, magnetite and rutile. Monazite inclusions and multiple concentric zones are characteristic of apatite in this zone (Figure 5b). Zones vary in number, thickness and sequence, but the most common BSE signature has a dark centre, surrounded by very bright zones, with a rim of intermediate brightness. CL images show the zones as different shades of purple and highlight the location of this mineral in areas of metasomatic alteration, as evidenced by the ubiquitous presence of K-feldspar (Dowman, 2014). Chemical mapping of a strongly zoned grain shows that the bright zones are REE-rich and relatively Ca- and P-impoverished (Figure 6).

Apatite persists into the medium/high-grade fenites, where the fine-grained assemblages of the medium-grade zone disappear. Here, apatite commonly occurs together with calcium carbonate, and continues to be a relatively common phase, but displays neither zoning nor porosity, and does not contain monazite inclusions (Figure 5c). However, apatite is absent where a higher intensity of metasomatism has produced rocks dominated by either aegirine and K-feldspar, such as in the most fenitised medium/high-grade fenite, BM1968 P37 137, or as in the high-grade breccia, by K-feldspar alone.

The unusual sample, BM1968 P37 83, is also strongly metasomatised, but alteration has created a mineralogy of drusy recrystallised quartz instead of K-feldspar. Apatite is present as a minor phase in this rock, and is found most commonly in association with pyrochlore.
(Figure 5d). Grains typically display a porous, inclusion-rich outer zone and a clean inner zone, but zoning caused by variation of REE content, typical of apatite in medium-grade fenite, is absent.

Apatite is a common phase in all carbonatite sections apart from the sideritic sample (1957 1056 113), where it is completely absent. The ankeritic sövite 1957 1056 102 contains apatite that is intricately intergrown with calcium carbonate and is associated with pyrochlore and parisite (Figures 4d and 5e). In sample 1957 1056 118, apatite is abundant, and also appears with pyrochlore, and ankeritic carbonate (Figure 5f).

Zoning in apatite in carbonatite is not common and was only seen in a small number of separated grains from sövite 1957 1056 59, where concentric zoning was generally of a less complex nature than that seen in apatite in medium-grade fenite. CL imaging reveals a bluer hue than that seen in apatite in fenite, but the association of apatite with K-feldspar was again apparent (Dowman, 2014). Carbonatitic apatite appears to lack a strong association with monazite, and inclusions found in apatite grains from 1957 1056 59 were of calcite. A few inclusions of barite and strontianite were seen in apatite of the pyrochlore-rich carbonatite, 1957 1056 118.
Fig. 5 Back-scattered electron images of apatite in fenite and carbonatite at Chilwa Island

a) Porous, unzoned apatite in low-grade fenite BM1968 P37 72
b) Zoned apatite in medium-grade fenite BM1968 P37 78
c) Unzoned apatite in medium/high-grade fenite BM1968 P37 68
d) Apatite associated with pyrochlore in high-grade quartz-rich rock BM1968 P37 83
e) Apatite associated with calcite in ankeritic sövite 1957 1056 102
f) Apatite associated with pyrochlore in ankeritic carbonatite 1957 1056 118
Fig. 6 Element maps of strongly zoned apatite in medium-grade fenite BM1968 P37 78.

a) BSE image  b) Si  c) P  d) Ca  e) Ce  f) Y  (Na not shown as no zoning evident)
REE patterns in apatite in medium-grade fenite and in carbonatite

Laser ablation analysis of apatite (Table 3) was undertaken to enable a comparison of the REE chemistry of apatite in medium-grade fenite with that of apatite from sövite and ankeritic carbonatite. Mean chondrite-normalised laser ablation data are shown in Figure 7.

Apatite zoning and changes in fluid composition

Apatite zoning, visible under both back-scattered electron imaging and under cathodoluminescence imaging, is most developed in medium-grade fenite, but also occurs occasionally in carbonatite. Zoning in apatite is common, and is thought to result from temporal changes in the environment during crystal growth (Waychunas, 2002) in pulses of metasomatic fluids (Rae et al., 1996; Coulson and Chambers, 1996).

Zoning in apatite at Chilwa Island reflects varying REE content, with zones enriched in the REE being depleted in Ca and P, suggesting an exchange between these elements. Metasomatic alteration of minerals occurs in the majority of cases by coupled dissolution-reprecipitation (Hetherington et al., 2010). The structure and chemistry of apatite allow for numerous substitutions (Hughes and Rakovan, 2002), but Harlov and Förster, and references therein, (2003) note that the two main coupled cation substitutions involving the REE are:

\[
\text{Si}^{4+} + (Y+\text{REE})^{3+} = \text{P}^{5+} + \text{Ca}^{2+}
\]

\[
\text{Na}^{+} + (Y+\text{REE})^{3+} = 2\text{Ca}^{2+}
\]

The element maps (Figure 6) indicate that, despite the sodic alteration of the fenite, the more likely substitution in Chilwa Island fenitic apatite involves Si rather than Na. Monazite inclusions as rim grains in apatite are also likely to have been formed by this process (Harlov and Förster, 2003), and postdate apatite. In BM1968 P37 83, monazite is formed where apatite has become porous.

Fenite apatite contains a distinct negative Eu anomaly, which persists on normalisation to the host rock (Figure 7, Table 4). However, several factors combine to make an inheritance of the anomaly from a possible basement origin of apatite unlikely. Sövite at Chilwa Island contains abundant apatite, and thus the surrounding metasomatic environment is favourable for apatite formation. The apatite geochemical data can be interpreted using the classification and regression trees (CART) of Belousova et al., (2002) to assign the host rock from which the apatite derived. Results suggested a larvikite (syenitic) or jacupirangite (pyroxenitic) rather than a granitic host. The cathodoluminescence colour of granitic apatite is typically yellow to orange (Kempe and Götze, 2002) rather than the violets seen in fenite.
apatite. At Chilwa Island, the presence of apatite in assemblages of other metasomatic minerals in fenite, its RE-zoning and monazite inclusions all indicate a carbonatite association.

Rather than being inherited, the Eu anomaly suggests the presence of Eu$^{2+}$ and therefore a more reducing environment either at, or before, the time of apatite crystallisation, with Eu$^{2+}$ being preferentially partitioned into an alternative mineral. Under oxidising conditions, because Eu$^{3+}$ would be expected to behave in a similar way to Sm and Gd, REE fractionation would not occur. However, this explanation needs to be compatible with the evidence for the existence of oxidising conditions at Chilwa Island. This evidence includes firstly, the purple cathodoluminescence of fenite apatite, which is attributed to Eu$^{3+}$ activation compared to the blue luminescence seen in apatite from carbonatite, which is related to Eu$^{2+}$ (Mariano and Ring, 1975; Hayward and Jones, 1991; Portnov and Gorobets, 1969; Voron’ko et al., 1992). Secondly the redox effect of the alkali content of liquids (Markl et al., 2010) does not appear to be applicable to Chilwa Island. This is associated with closed systems of predominantly sodic nature in quartz-absent rocks, where crystallisation of minerals incorporating ferric iron, such as aegirine or arfvedsonite, leads to reduction of the residual fluid. At Chilwa Island, rocks are not quartz-poor, and aegirine formation was followed by ferric amphiboles, and we thus infer that oxidised fluids continued to enter the aureole via the open system pertaining at the complex. Thirdly, Eu is thought to be predominantly in the trivalent state in relatively low temperature hydrothermal fluids below 250˚C (Sverjensky, 1984), which may be typical of the fenite environment in the less intensely metasomatised parts of the aureole.

At Chilwa Island, the sequence of fluids is thought to have become increasingly oxidised over time. The favoured explanation for the negative Eu anomaly is that apatite formed relatively early in this sequence. Eu$^{2+}$ was partitioned into earlier, and probably also contemporaneous, minerals. Plagioclase and K-feldspar take up Eu more readily than other REEs, leading to negative Eu anomalies in co-existing phases (Leeman and Phelps, 1981). It is believed that at Chilwa Island, early alkaline fluids generated from sövite magma would have precipitated plagioclase and limited amounts of K-feldspar, with a possible later expulsion of potassic fluids producing further K-feldspar. The attribution of the apatite negative anomaly to mineral crystallisation sequence was tested by plotting Eu/Eu* against Sr in apatite (Dowman, 2014). Sr also partitions preferentially in feldspar, and apatite plots would be expected to demonstrate a relationship between decreasing Sr and a deepening negative Eu anomaly if crystallisation sequence effects were dominant. However, although no clear relationship emerged, both plagioclase and orthoclase at Chilwa Island are known...
to have pronounced positive Eu anomalies (David Banks personal communication). The precipitation order of minerals is therefore considered the most likely cause of the negative Eu anomaly in apatite.

Apatite in fenite is equally enriched in LREE, and is more enriched in the HREE than apatite in carbonatite (Figure 7, Table 3). Fenite apatite is also more enriched in all REE than the ankeritic carbonatitic apatite. The trend of relative MREE/HREE fenite enrichment is also seen in other RE-bearing minerals.

Table 3 LA-ICP-MS REE in apatite at Chilwa Island (ppm)

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Y</td>
<td>1625 894</td>
<td>1553 492</td>
<td>2761 1572</td>
<td>219 27</td>
<td>1367 221</td>
</tr>
<tr>
<td>La</td>
<td>2687 1107</td>
<td>3520 1050</td>
<td>1902 939</td>
<td>2592 301</td>
<td>168 56</td>
</tr>
<tr>
<td>Ce</td>
<td>5370 2378</td>
<td>6877 1559</td>
<td>4476 1953</td>
<td>5191 565</td>
<td>606 154</td>
</tr>
<tr>
<td>Pr</td>
<td>640 301</td>
<td>913 283</td>
<td>708 297</td>
<td>620 66</td>
<td>94 22</td>
</tr>
<tr>
<td>Nd</td>
<td>2606 1300</td>
<td>3473 925</td>
<td>3336 1447</td>
<td>2276 242</td>
<td>512 121</td>
</tr>
<tr>
<td>Sm</td>
<td>460 250</td>
<td>560 159</td>
<td>726 343</td>
<td>292 33</td>
<td>191 40</td>
</tr>
<tr>
<td>Eu</td>
<td>34 16</td>
<td>59 22</td>
<td>71 46</td>
<td>68 7</td>
<td>78 14</td>
</tr>
<tr>
<td>Gd</td>
<td>417 234</td>
<td>456 129</td>
<td>687 347</td>
<td>168 19</td>
<td>256 49</td>
</tr>
<tr>
<td>Tb</td>
<td>53 30</td>
<td>55 16</td>
<td>91 49</td>
<td>14 1</td>
<td>41 7</td>
</tr>
<tr>
<td>Dy</td>
<td>313 175</td>
<td>307 90</td>
<td>543 315</td>
<td>56 6</td>
<td>259 45</td>
</tr>
<tr>
<td>Ho</td>
<td>58 32</td>
<td>57 16</td>
<td>102 59</td>
<td>7 1</td>
<td>46 7</td>
</tr>
<tr>
<td>Er</td>
<td>147 82</td>
<td>141 41</td>
<td>260 157</td>
<td>12 1</td>
<td>113 19</td>
</tr>
<tr>
<td>Tm</td>
<td>18 9</td>
<td>18 6</td>
<td>34 22</td>
<td>1 &lt;1</td>
<td>13 2</td>
</tr>
<tr>
<td>Yb</td>
<td>99 53</td>
<td>99 30</td>
<td>198 132</td>
<td>6 1</td>
<td>64 11</td>
</tr>
<tr>
<td>Lu</td>
<td>13 6</td>
<td>14 4</td>
<td>27 18</td>
<td>1 &lt;1</td>
<td>7 1</td>
</tr>
</tbody>
</table>

* n = 3 for BM1968 P37 78

Fig. 7 Chondrite-normalised average REEY for apatite in fenite (green) and carbonatite (red/pink) at Chilwa Island. Ank carb = ankeritic carbonatite. Data from LA-ICP-MS. Error bars represent one standard deviation.
Table 4 Eu/Eu* anomaly at Chilwa Island
a) in whole-rock fenite and carbonatite

<table>
<thead>
<tr>
<th>Low-grade fenite</th>
<th>Medium-grade fenite</th>
<th>Breccia</th>
<th>BM1968 P37 83</th>
<th>Sövite</th>
<th>Ankeritic carbonatite</th>
<th>Sideritic carbonatite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.03±0.22</td>
<td>0.95±0.05</td>
<td>1.07±0.03</td>
<td>0.97</td>
<td>0.84±0.02</td>
<td>0.88±0.06</td>
<td>0.66±0.02</td>
</tr>
</tbody>
</table>

b) in apatite in medium-grade fenite, sövite and ankeritic carbonatite

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25±0.03</td>
<td>0.29±0.04</td>
<td>0.35±0.10</td>
<td>0.86±0.01</td>
<td>1.08±0.01</td>
</tr>
</tbody>
</table>

LREE-MREE patterns in monazite, bastnäsite and parisite

EDS analyses of LREE to MREE patterns of monazite, bastnäsite and parisite are shown in Figure. 8. The fenite minerals all show higher MREE/LREE ratios compared to their carbonatitic counterparts. This is particularly notable in the mid REE-enrichment in minerals of the high-grade, quartz-rich rock, BM1968 P37 83.

REE variation in minerals in carbonatite and in fenite

In general, the LREE enrichment of carbonatites is reflected in the composition of their RE-bearing minerals, although considerable variation in REE distribution in minerals occurs at many complexes (Smith et al., 2000; Zaitsev et al., 1998, Bühn et al., 2001; Cooper and Paterson, 2008). At Chilwa Island, the RE-bearing minerals in fenite all have lower La/Nd ratios than their carbonatitic equivalents. This is also true for the RE-rich carbonatite complex of Kangankunde in Malawi (Dowman, 2014).

Variations in REE profiles may result from a number of factors. Firstly, carbonatite fractionation from Ca-rich to more Fe/Mg- and fluid-rich compositions may drive down La/Nd ratios in minerals (Bühn et al., 2001; Cooper and Paterson and citations therein. 2008; Drüppel et al., 2005). The carbonatite sequence at Chilwa Island indicates this could be a relevant factor.

Another factor to be considered is that the precipitation order of minerals is intricately linked to carbonatite fractionation (Hogarth, 1989; Woolley and Kempe, 1989; Le Bas, 1999; Bühn, 2008). Early LREE-rich crystallising phases such as allanite and monazite may cause a flatter REE profile in later minerals such as apatite (Hoskin et al., 2000; Miles et al., 2013). This factor is discounted at Chilwa Island as no allanite was identified in any section, and the expected Nd anomalies are not present in monazite. Furthermore, it is thought that monazite crystallised later than apatite and would therefore have played no role in determining apatite composition.
A third factor is that hotter, CO₂-rich fluids may promote La-enrichment of minerals, with lower La/Nd mineral ratios resulting from dominantly aqueous fluids of lower temperature (Smith et al., 1999; 2000; Zaitsev et al., 1998). Evidence from fluid inclusions at Chilwa Island was insufficient to establish the existence of this relationship.

A brief examination of the role of ligands notes that the transportation of the REE in fluids is thought to be facilitated by their binding to a variety of ligands to form co-ordination complexes of different stability (Gieré, 1996). Suggested ligands include Br⁻, Cl⁻, NO₃⁻, OH⁻ and F⁻, as well as P₂O₅²⁻, SO₄²⁻ and CO₃²⁻. The stability of the REE with these ligands is contentious and is a continuing area of active research. F is common at Chilwa Island as evidence by the presence of fluorapatite and F-rich RE-carbonate minerals, and was previously thought likely to be a key ligand operating to complex the REE and Th (Keppler and Wyllie, 1990; Finch, 1995; Goodenough et al., 2000; McCreath et al., 2012). The effectiveness of fluoride complexes, compared to chloride and sulphate complexes, as agents of REE transport is now being questioned (Migdisov and Williams-Jones, 2014), and F may act more as a binding ligand that promotes REE deposition, particularly where fluid interacts with host rocks of a higher pH. At Chilwa Island, this could have occurred when feldspar-bearing rocks buffered the hydrothermal fluids expelled from the carbonatite. However, at Chilwa Island, sulphate complexes are not important, and the role of Cl is undetermined, but Cl was not detected in fluid inclusions analysed by laser ablation ICP-MS (David Banks, personal communication).
Fig. 8 Chondrite-normalised LREE in minerals in fenite (green) and carbonatite (red/pink) at Chilwa Island
a) monazite  b) bastnäsite  c) parisite
Data from EDS. Error bars represent one standard deviation. Fenite 83 monazites are individual analyses
Whole-rock chemistry

Tables of results are included in supplementary information.

Major elements

As expected from the mineralogical variations across the fenite aureole, the major element data also indicate that the fenite samples fall into discrete groups, although without any obvious subdivision of the medium-grade group. Some unexpected similarities exist between the low-grade fenites and breccia, which given the spatial separation of these groups in the aureole, might have been expected to exhibit the strongest contrasts. Both groups have a low Fe, Mg, Mn and Ti content compared to the medium-group fenite (Figure 3b).

Apart from the quartz rock BM1968 P37 83, which is devoid of alkalis, total alkali content is similar across fenite grades, but this masks a change from the strongly potassic breccia adjacent to the carbonatite to the outer fenite zones where levels of Na and K are similar (Figure 3b).

Trace elements

Among the trace elements, a similarity of pattern of enrichment and depletion exists between carbonatite and fenite, with enrichment in Ba, Mo, Nb, Pb, Sr, Th and Y and depletion in Co, Hf and V. Enrichment in carbonatitic type elements generally increases towards the inner parts of the aureole (Figure 3c). Fenite normalisations to the series sövite, ankeritic carbonatite and sideritic carbonatite revealed a sequence of increasing differences in element concentration between fenite and carbonatite (Dowman, 2014).

REE

Normalisation of the REE to average lower continental crust, which is taken as a proxy for country rock, shows the fenite profiles to be flatter than those of the carbonatites (Figure 9, also see chondrite normalisations in Table 5). Carbonatites are relatively LREE-enriched, and the HREE content of breccia and the main (medium-grade) fenite group is higher than that of sövite, and similar to that of ankerite. The most altered rocks display distinctive profiles. BM1968 P37 83 has higher levels of the REE from Dy to Lu than any of the averaged results for carbonatite in the complex, and the highest level of Ho and Er of any of the rocks analysed. The unusual profiles of the two breccia samples show a rising trend from Nd to Tb, with relatively high levels of the HREE. Fenite Eu anomalies are generally smaller than those of carbonatites, and may be either mildly positive or negative. No clear difference in anomalies exists between fenite groups, but carbonatites show increasing negative anomalies in the sequence sövite-ankeritic carbonatite-sideritic carbonatite (Table 4a).
Fig. 9 Lower continental crust-normalised rare earth elements for average fenite grades (green) and carbonatites (red/pink) at Chilwa Island. Error bars represent one standard deviation.
Table 5 Chondrite-normalised La/Yb ratio for fenites and carbonatites at Chilwa Island

<table>
<thead>
<tr>
<th>Rock</th>
<th>Low-grade fenite</th>
<th>Medium-grade fenite</th>
<th>Breccia</th>
<th>BM1968 P37</th>
<th>Sövite</th>
<th>Ankerite</th>
<th>Siderite</th>
</tr>
</thead>
<tbody>
<tr>
<td>La/Yb</td>
<td>6.7-15.0</td>
<td>8.5-26.9</td>
<td>2.0-8.2</td>
<td>15.1</td>
<td>48-220</td>
<td>27-164</td>
<td>78-240</td>
</tr>
</tbody>
</table>

Fluid inclusion data

Examination under the optical microscope showed that quartz is the most important host for inclusions. Feldspar is also a common matrix mineral, but is highly altered and does not contain easily identifiable inclusions. Quartz is not common in more altered fenite, and when present, is generally recrystallised and without fluid inclusions. The investigation was therefore restricted to lower-grade fenite. The inclusions found in the low- and medium-grade fenite are typically a few µm in diameter, secondary in nature and extremely heterogeneous. Among the larger inclusions, single phase, 2- and 3-phase, single solid and multi solid-bearing examples are present, with 2-phase being the most abundant, and single phase also common (Figure 10). Little change in the proportions of different inclusion types was found between low- and medium-grade fenite beyond a small increase in the number of solid-bearing inclusions found in medium-grade fenite. Inclusions are often found in crosscutting trails, but were too small to allow characteristics of particular trails to be distinguished. CL imaging of quartz grains revealed a low-luminescent network of fractures coinciding spatially with the inclusion trails (Dowman, 2014).
Based on Raman analyses, these fluid inclusion assemblages comprise: i) CO$_2$-rich aqueous fluids with little or no methane and nitrogen, ii) monophase aqueous inclusions, iii) liquid and vapour aqueous inclusions and iv) multiphase carbonate-bearing inclusions containing nahcolite and burbankite daughter phases indicative of REE-Ca-H$_2$O-CO$_2$ compositions. These fluids seem to have followed the same pathways in the quartz as indicated by the CL which could indicate either several pulses of different fluids at different times or heterogeneous trapping of mixed or unmixed pulses of fluid. A combination of both seems most likely.

Microthermometric measurements were hampered by decrepitation of inclusions at around 200°C before total homogenisation occurred, but data relating to the melting temperature of CO$_2$ clustered close to the triple point of -56.6°C, indicating the inclusions contain...
relatively pure CO\textsubscript{2} and little of other volatiles such as CH\textsubscript{4} and N\textsubscript{2}, which depress melting points. Partial homogenisation of the CO\textsubscript{2} phase was always to the liquid phase at temperatures between 0.3 and 30.2°C, corresponding to CO\textsubscript{2} densities of ~0.9 to 0.6g/cm\textsuperscript{3}. No systematic relationship could be determined between homogenisation temperature and CO\textsubscript{2} fill. Whether these fluids were also chloride-rich is unresolved because halite (NaCl), though tentatively identified optically, if present, is Raman inactive. Also, although Cl was not detected by ICP-MS analysis of the fluid inclusions (David Banks, personal communication), this is at variance with microthermometric data for frozen inclusions. These showed first melting temperatures of frozen inclusions commonly occurred at around -24°C, which is close to the eutectic temperatures for both NaCl-H\textsubscript{2}O and NaHCO\textsubscript{3}-H\textsubscript{2}O systems (Shepherd et al., 1985). Unfortunately, final melting temperatures could not be recorded with any degree of accuracy to determine total salinities.
Towards a model for metasomatism in fenite at Chilwa Island

The main purpose of this paper is to develop a model to enable characterisation of the metasomatic fluids that caused wall rock fenitisation at Chilwa Island. In order to do this, certain aspects of magmatic fluids need to be briefly addressed.

Firstly, fluid expulsion from magma is unlikely to constitute a single event (Verschure and Maijer, 2005). At Chilwa Island, it is highly likely that multiple fluids were generated. The complex is thus the result of a number of episodes of magma emplacement, each of different composition, each of which would have produced associated fluids.

Secondly, two processes can lead to oversaturation of the key volatiles, water and carbon dioxide, with subsequent magma boiling and the expulsion of fluids. A ‘first boiling’ can result from a decrease in pressure during magma ascent (Candela, 1997). Fluids lost by a carbonatite in this way may be predominantly alkaline, and thus be responsible for fenitisation (Wall, 2000). ‘Second boilings’ occur isobarically when crystallisation of anhydrous phases concentrates volatiles in the remaining melt. The fluids subsequently expelled may be more mineralising in nature, carrying and precipitating elements such as Ca, Fe, Zn and the REE (Drüppel et al., 2005; Gieré, 1996; Brimhall and Crerar, 1987). As melts may also undergo a series of crystallisation episodes, volatile saturation would therefore be a ‘quasi-periodic process’ (Candela and Brevin, 1995), resulting in multiple associated fluid expulsions from each magma.

Thirdly, with reference to the relative importance of the role played by the two key volatiles in magma saturation, it is recognised that carbonatite-derived fluids can have very variable CO₂/H₂O ratios, with CO₂ not always dominant (Drüppel et al., 2005). CO₂ saturation may also occur independently of H₂O fluid saturation (Robb, 2009; Keppler, 2003). However, as discussed above in relation to REE ratios, hotter fluids (proximal to the carbonatite) may be CO₂-rich compared to cooler, and more aqueous, distal fluids. In the outer parts of the aureole at Chilwa Island, the fluid inclusion evidence shows that both volatiles are present, but because there is no clear pattern or trend in their distribution, their relative importance here is not determined.

On the basis of the field and laboratory data outlined above, it is possible to propose a robust model for fenitisation at Chilwa Island that involves a sequence of magmatically derived fluids (Figure 11). This data supporting the presence of multiple fluids include the presence of a sequence of carbonatites, each likely to have generated fluids, as well as evidence of the variation in spatial distribution of mineral assemblages, the zonation in
apatite, the contrasts in zircon habit, the existence of high-grade fenites with differing 
monophase matrices, and the heterogeneity of fluid inclusions. Thus, in the model, these 
fluids are related to a succession of magma emplacement events starting with sövite, then 
ankerite and finally siderite. Figure 12 provides a suggested paragenetic sequence for the 
formation of minerals associated with carbonatite emplacement and the fenitisation process.
a) Sövite growth/emplacement
Pervasive sodic-dominant fenitisation either contemporaneous with or pre intrusion emplacement

b) Ankerite growth/emplacement
Intrusion of carbonatite associated with multiple episodes of mineralisation along veins and fractures Increasing oxidisation of fluids, and fractionation of REEs

c) Late ankerite growth/emplacement to pre siderite growth/emplacement
Potassic fluid of limited extent, associated with further brecciation, pervasive in nature proximal to carbonatite and directed along vein and fracture network more distally.
Zr mobilisation?

d) Siderite growth/emplacement
Limited mineralisation along veins and fractures Late-stage hydrothermal circulation remobilises silica

e) Complex after cessation of magmatic and hydrothermal activity
Fig. 11 Schematic model for fluid sequence affecting fenite rocks at Chilwa Island

KEY:
- L: Low-grade fenite
- M: Medium-grade fenite
- MH: Medium/high-grade fenite
- FB: Feldspathic breccia
- C: Carbonatite
a) Early fluids, associated with sövite

The first fenitising fluids were predominantly sodic, and were expelled before or during intrusion of the sövite, probably as a result of decompression-driven first magma boiling (Figure 11a). This is consistent with field data that show plagioclase is present as a matrix material in all low- and medium-grade fenite samples. It also concurs with previous research indicating that sodic fluids are often expelled at an early stage of emplacement of carbonatite complexes (Le Bas, 1977; 2008; Drüppel et al., 2005; McKie, 1966; Vartiainen and Woolley, 1976; Woolley, 1982). This fluid event was spatially more extensive than later events and its extent was probably facilitated by the brecciation, widespread at Chilwa Island, which typically accompanies carbonatite emplacement (Le Bas, 1987). Similar levels of Na in the aureole from medium-grade fenite outwards suggest a pervasive fluid, which altered country rock across the island. On a micro-scale, the inward-spreading turbidity in feldspar grain margins, as described above in the mineralogy of medium-grade fenite, indicates that crystal boundaries formed channels for fluid migration, similar to that seen in quartz under CL imaging (Dowman, 2014). Further migration of fluids may have been facilitated by microporosity of mineral grains (Finch and Walker, 1991).

The sövitic magma may also have experienced a second boiling linked to isobaric crystallisation. However, compared to the ankeritic and sideritic carbonatites, the composition of the sövite is low in Fe, the REE and other typical carbonatitic elements such as Ba, Nb and Y. Therefore, if a second boiling did occur, and these elements were mobilised into the expelled fluids, they would have been at concentrations too low to form the source of the ilmenite and aegirine mineralisation seen in the fenite rocks. The vestiges of any second boiling event would have been largely lost due to subsequent overprinting by fluids from the younger carbonatites. The apatite in the fenite provides the strongest evidence for the existence of this second stage fluid. Sövite at Chilwa Island contains apatite, and is the carbonatite richest in Ca and P. Apatite growth in fenite has been dated (Dowman, 2014) as contemporaneous with carbonatite emplacement, and any fluid arising from a second boiling would have mobilised these elements out into the fenite rocks, where they were precipitated to form the RE-poor cores (Figure 6) of the apatite grains commonly seen in medium-grade fenite.

b) Fluids associated with ankeritic carbonatites

The emplacement of this carbonatite may have been accompanied by an early expulsion of alkali fluids. However, any evidence of a first boiling has been lost among the effects on the aureole from the preceding sövite-related alkali-rich fluid event.
Mineralogical data reported here suggest that a punctuated second boiling event occurred (Figure 11b). This was probably caused by periodic recharge of the magma body as part of an open system (Norton and Pinkerton, 1997). Anhydrous minerals, such as apatite, probably crystallised in successive stages, resulting in the expulsion of fluids as a series of pulses.

Although this fluid event appears to have been more restricted in extent that that associated with the expulsion of the alkaline sövitic fluids, it was probably the main mineralising event as fluids predominantly transported the REE, together with Nb, Ti, Fe, Ba, P and Ca, rather than the alkalis, into the aureole. The RE-bearing mineral, burbankite, identified in fluid inclusions (Dowman, 2014), provides direct evidence that REE were mobilised in fluids from the carbonatite at this stage. The extensive aegirine mineralisation of the aureole is also associated with this episode, and is most likely the result of precipitation of Fe carried in the fluids, together with remobilisation of Na from plagioclase.

Mineralisation is focused chiefly into veins and fractures, suggesting possible structural control along pre-existing lines of weakness. This is supported by the spatial distribution of zircons of Pan African age in these veins (Dowman, 2014) that appear to have acted as nuclei for the characteristic micro-mineral assemblages of Nb-bearing ilmenite and fluorapatite with monazite inclusions that are present in medium-grade fenite rocks. The inference is that carbonatite emplacement may have reactivated earlier tectonic fluid pathways.

Evidence of multiple fluid ingress, with a changing fluid composition, is reflected in REE zoning in apatite in medium-grade fenite (Figure 5b), and perhaps also in the zoning in the outer parts of some apatite grains in the earlier sövite (Dowman, 2014). Fission-track dating of apatite in fenite (Dowman, 2014) established that it is contemporaneous with apatite found in a nepheline-syenite plug of carbonatite age at Chilwa Island (Eby et al., 1995).

c) Late-stage ankerite emplacement to pre-siderite emplacement

A strongly potassic fluid event is associated with a possible first boiling of fluids enriched in CO₂ (Rubie and Gunter, 1983) during the phase of late ankerite/pre-siderite emplacement. This caused a further brecciation episode as well as fracturing of the high-grade fenite of the inner aureole (Figure 11c). Potassic fenite may be produced from magma at higher levels in carbonatite complexes (Le Bas, 2008; Viladkar, 2012) and associating K-fenitisation with relatively late-stage magma here would be compatible with the evolution of the Chilwa Island complex, where the carbonatite emplacement sequence of sövite,
ankerite and siderite is believed to have occurred at successively higher levels (Garson and Campbell Smith, 1958).

Compared to the earlier sodic alkaline fluids, this fluid was spatially restricted in its effect. However, it pervasively altered the breccia, and caused K-feldspar enrichment of the high/medium-grade fenite. Dissolution of zircon in both these zones probably occurred after reaction with this caustic potassic fluid. Zr can become highly mobile in F-rich alkaline fluids (Rubin et al., 1993), and at Chilwa Island, evidence of this can be seen in the reprecipitation of Zr as nano-sized zircon grains occasionally found in apatite (Dowman, 2014). Further out in the aureole, the potassic fluid caused limited alteration along mineral veins. CL imaging revealed potassic feldspar surrounding etched apatite grains (Dowman, 2014). Within the carbonatites, metasomatism by this fluid formed the K-feldspar found in both ankeritic carbonatite and in sövite.

Mineralisation effects from any second magma boiling associated with late ankeritic emplacement cannot be distinguished from that caused by fluids derived from the sideritic carbonatite.

d) Late-stage fluids associated with siderite emplacement

Two contrasting late-stage fluids are interpreted here as controlling the final stages of metasomatism at the Chilwa Island complex. The first of these was responsible for significant mineralisation; the second was a silicification event (Figure 11d).

d.1 Mineralising fluid

The last mineralising fluid is probably related to the intrusion of sideritic carbonatite (possibly also a late-stage ankerite), and a second magma boiling. This fluid appears to represent a limited expulsion of carbonate-bearing, and possibly CO₂-rich fluid, documented predominantly as thin veins containing carbonate in all fenite grades and which also carry occasional goyazite and an unidentified Th-rich RE mineral in the breccia. The range of elements carried by the fluid points to the sideritic carbonatite as being the source, as only this carbonatite has a composition sufficiently enriched in elements such as Th, Y, Sr, Pb, Mo, Ba and the REE (including the HREE) to explain the presence of minerals in the fenite such as xenotime and barite.

Chemical data from Chilwa Island suggest that the mobilisation and precipitation of the MREE and HREE became more important in fluids exsolved from the later carbonatitites, as the aqueous component of the fluids increased and their temperature decreased (Smith et
al., 2000; Andrade et al., 1999). The hydrothermal origin of barite is in accord with Garson and Campbell Smith's view (1958) when he noted the association of barite with late-stage veinlets. Barite is also present in each carbonatite examined in this study. Xenotime was seen in one carbonatite, the high-grade fenite rock BM1968 P37 83, and as a scarce phase across the fenite aureole out to low-grade fenite. Xenotime is also considered to be a late-stage hydrothermal mineral, possibly being formed at low temperature, via a dissolution-reprecipitation process during fluid-induced alteration of apatite (Harlov, 2011). Cooler temperatures during the waning, more aqueous phase of mineralising fluid episodes may be linked to the formation of the low temperature amphibole, riebeckite. Fractionation of the REE in these siderite-ankerite-derived fluids is suggested by the fall in Nd/Ho ratios from 170-370 in siderite at Chilwa Island to those found in fenite. The high-grade fenite areas (breccia and the quartz-rich rock), most affected by late-stage carbonatitic fluids, have Nd/Ho ratios of between 4 and 24, substantially lower than the ratios of 30-60 for fenite little influenced by this type of fluid. These ratios provide evidence that fractionated carbonatites can lose HREE into fluids driven off from the magma, and thus become relatively depleted in the HREE compared to the LREE, and may explain the MREE-HREE enrichment of fenite RE-bearing minerals compared to their carbonatitic equivalents (Figures 7 and 8). Bühn (2008) proposed a similar process.

Certain parts of the more distal regions of the aureole, as represented by rock BM1968 P37 83, appear particularly enriched in the HREE and Th. In fact, this sample contains more Ho and Er than any other rock analysed, carbonatites included (Figure 9). This may indicate that high-grade quartz-rich areas escaped the purging effects of the earlier, highly potassic fluid, which stripped the breccia in the inner aureole of any pre-existing more LREE-enriched minerals. This pattern of fluid distribution would explain the unusual whole-rock REE composition of the breccia (metasomatised by both potassic and mineralising fluids) and in the quartz-rich rock BM1968 P37 83 (metasomatised by mineralising fluids, but not by the potassic fluid).

That fluids from ankeritic and sideritic carbonatite were probably oxidising in nature can also help to explain, ilmenite mineral separation and the presence of two monazite phases.

Firstly, fluids expelled from siderite carbonatite at Chilwa Island are derived from a rock that is thought likely to have formed during a period of oxidation (Garson and Campbell Smith, 1958). Woolley, (2001) described it as secondary in nature, being almost entirely replaced by iron and manganese oxides, and the brief examination of the siderite carbonatite in this study confirmed the presence of these oxides.
Secondly, the separation out of magnetite and rutile within the ilmenite grains of the micromineral assemblages of medium-grade fenite (Figure 2b and Figure 2c) may be caused by a simple oxidation of ilmenite that produces either these phases as stable end products (Lindsley, 1963) or rutile together with a more Fe-rich ilmenite (Southwick, 1968). Likewise, the magnetite grains with ilmenite lamellae found in low-grade fenite at Chilwa Island (Figure 2a), may be formed by an ‘oxyexsolution mechanism’ (Wang et al., 2012; Haggerty, 1991).

Lastly, in sample BM1968 P37 83, both monazite-(La) and monazite-(Ce) are present (Figure 8a). Monazite may have formed in two phases. Analogously to monazite being more common in reduced S-type granites than in oxidised I-granites, the more common monazite-(Ce) may have crystallised first, with monazite-(La) forming later, when more oxidising conditions led to Ce being in the $4^+$ state, and therefore not able to be accommodated in monazite. Alternative scenarios, such as Ce being taken up by allanite, or Ce$^{4+}$ being taken into cerianite, a mineral that may be formed as a late-stage weathering product, probably did not operate at Chilwa Island, as neither of these minerals was identified. It is thought more likely that Ce$^{4+}$ did not participate in mineral formation, and was flushed out of the system.

d.2 Fluids associated with silicification
Fenitisation is generally associated with the elimination of free quartz (Pirajno, 2009), and in general, quartz in the matrix of the fenites of this study decreases with degree of alteration. However, secondary (recrystallised) quartz is present throughout medium-grade fenite and breccia, with the high-grade sample BM1968 P37 83, wholly composed of this mineral, representing an extreme example. Secondary quartz is also present in three of the four carbonatites examined in this study, suggesting a role for autometasomatism and carbonate replacement. Silicification is probably induced by the introduction of ground water (Garson and Campbell Smith, 1958), with Si being dissolved and mobilised from country rock during magma emplacement, and subsequently reprecipitated by fluids circulating in the complex. It is therefore proposed that a Si-bearing fluid was the last metasomatizing fluid event at Chilwa Island, and occurred during waning carbonatite activity (Garson and Campbell Smith, 1958). Its action is often selective in nature and is commonly associated with REE mineralisation at carbonatite complexes (Garson and Campbell Smith, 1958). The relationship of silicification with carbonatite activity is supported by the high REE content of the quartz high-grade fenite, the presence of quartz in carbonatite, and the association of RE-minerals in veins of secondary quartz in medium/high-grade fenite samples. It is
recognised that silicification can be a weathering process, but this commonly results in the formation of chalcedony rather than clean crystalline quartz. Furthermore, silicification by weathering can have a diffuse effect, and create a cap to the carbonatite. The field relations and mineralogical associations found at Chilwa Island would thus support hydrothermal quartz.

**Fig. 12** Paragenetic sequence of fenite mineral formation associated with carbonatite emplacement and metasomatism at Chilwa Island
### EMPLACEMENT SEQUENCE

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- **Mineral precipitation**
- **Possible mineral precipitation**
Conclusions and implications

All three main carbonatites at the Chilwa Island complex are thought to have undergone magma boiling, leading to the expulsion of fluids that metasomatised the surrounding country rocks.

The nature of the fluid events produced by magma boiling is dependent on whether they derive from a first or second boiling. First magma boilings are associated with alkaline fluids and the pervasive formation of feldspar. Second boilings produce mineralising fluids that create microassemblages of minerals in veins.

During second boiling events, the REE were mobilised, transported and precipitated in the fluids that mineralised the fenites. REE fractionation took place, resulting in the formation of fenitic RE-bearing minerals with lower La/Nd ratios than their carbonatitic equivalents.

A suggested schematic model of the sequence of metasomatising fluids at Chilwa Island assigns elements mobilised in each event. Alkaline alteration of the whole aureole by fluids expelled from sövite was followed by mineralisation derived from ankerite carbonatite. A later alkaline event was more limited and strongly potassic, and occurred before further mineralisation associated with the ‘sideritic’ carbonatite. The aureole underwent later-stage silicification. The main features of this model regarding the nature of the multiple fluid events should be applicable to all alkaline-carbonatite complexes.

The presence of mineral assemblages in fenite at some distance from carbonatite could be developed as an exploration indicator of REE enrichment.

Acknowledgements The authors gratefully acknowledge the Natural History Museum, London for allowing access to its Chilwa Island rock collection, for the whole rock analyses and for the assistance of Teresa Jeffries (deceased) in obtaining laser ablation analyses of apatite. We also thank Kingston University for supporting E. Dowman’s PhD studentship and for the assistance of Richard Giddens in using the scanning electron microscope. We are grateful to Jens Andersen of Camborne School of Mines for assistance with electron microprobe element maps of apatite. We also acknowledge the helpful comments from two anonymous reviewers, whose contributions have improved this manuscript.

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