Review

Fenites associated with carbonatite complexes: A review

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ABSTRACT

Carbonatites and alkaline-silicate rocks are the most important sources of rare earth elements (REE) and niobium (Nb), both of which are metals imperative to technological advancement and associated with high risks of supply interruption. Cooling and crystallizing carbonatitic and alkaline melts expel multiple pulses of alkali-rich aqueous fluids which metasomatize the surrounding country rocks, forming fenites during a process called fenitization. These alkalis and volatiles are original constituents of the magma that are not recorded in the carbonatite rock, and therefore fenites should not be dismissed during the description of a carbonatite system. This paper reviews the existing literature, focusing on 17 worldwide carbonatite complexes whose attributes are used to discuss the main features and processes of fenitization. Although many attempts have been made in the literature to categorize and name fenites, it is recommended that the IUGS metamorphic nomenclature be used to describe predominant mineralogy and textures. Complexing anions greatly enhance the solubility of REE and Nb in these fenitizing fluids, mobilizing them into the surrounding country rock, and precipitating REE- and Nb-enriched micro-mineral assemblages. As such, fenites have significant potential to be used as an exploration tool to find mineralized intrusions in a similar way alteration patterns are used in other ore systems, such as porphyry copper deposits. Strong trends have been identified between the presence of more complex veining textures, mineralogy and brecciation in fenites with intermediate stage Nb-enriched and later stage REE-enriched magmas. However, compiling this evidence has also highlighted large gaps in the literature relating to fenitization. These need to be addressed before fenite can be used as a comprehensive and effective exploration tool.

1. Introduction

Carbonatites and alkaline-silicate (hereafter referred to as alkaline) rocks are the most important sources of rare earth elements (REE) and niobium (Nb) (Wall, 2014; Goodenough et al., 2016), both high profile raw materials critical to technological advancement. Intrusions of both carbonatite and alkaline rocks are typically found in close spatial relationship with aureoles of high temperature metasomatically altered country rock, termed fenites. These alteration aureoles have great potential as exploration indicators. However, the vast majority of prior research has been focused on the intrusions themselves, with little attention paid to the potential for alteration to inform exploration. This

contribution seeks to explore that potential by reviewing the current knowledge of fenite types, formation and relationship to economic mineralization.

The process of alteration (fenitization) is generally viewed to result from multiple pulses of alkali-rich fluid expelled from cooling and crystallizing carbonatitic or alkaline melt (Morogan, 1994; Le Bas, 2008). Fenites are typically composed of, and characterized by, K-feldspar, albite, alkali pyroxenes and/or alkali amphiboles (Zharikov et al., 2007). However, mineral assemblages are highly variable and dependent on a number of parameters such as protolith mineralogy, permeability and structure, in addition to fluid composition, temperature and pressure (Dawson, 1964; Heinrich, 1966; Le Bas, 1987; Platt,

1996). The secondary mineral assemblages associated with fenitization are often visible in hand sample, whereas other effects such as the formation of turbidity in feldspars (e.g. Woolley, 1969; Heinrich and Moore, 1969; Vartiainen and Woolley, 1976; Garson et al., 1984; Kresten and Morogan, 1986; Morogan and Woolley, 1988; Williams-Jones and Palmer, 2002; Le Bas, 2008) or the modification of primary mafic phases can be more subtle and only visible via optical microscopy. Vein networks often develop early on in the fenitization process, facilitating the passage of fluids expelled from the melt through fractures and joints in the country rock, to form the outer fenite aureole (Woolley, 1969). The scale of fenitization varies greatly from centimeters to several kilometers from the intrusive contact. Fenites are often associated with hydraulic fracturing and brecciation, exhibiting both temporal, spatial, mineralogical and chemical variations, resulting in both horizontal and vertical zoning.

Fluids derived from cooling alkaline magmas or carbonatite intrusions transport high quantities of alkalis and volatiles. These were originally constituents of the magma that are not retained in the carbonatite rock, therefore descriptions of intrusions are incomplete without also characterizing their associated fenite. Fenitizing fluids emanating from evolved and subsequently enriched magmas, form REE and Nb micro-mineral assemblages in the country rock (Elliott et al., 2016; Dowman et al., 2017). These can provide information regarding their source magma and any associated mineral deposits, effectively acting as exploration indicators. Fenites are vertically and horizontally extensive, forming 3D aureoles around these intrusions and are therefore likely to be identified at a variety of different erosion levels, even where source intrusions are not necessarily exposed. However, resource exploration has predominantly focused on intrusive units in alkaline and carbonatite complexes as these are the primary sources and hosts of REE and Nb deposits (Wall, 2014; Goodenough et al., 2016). There is a distinct lack of emphasis in the literature regarding fenites, with only a few recent publications appreciating the importance of fenitizing fluids with regard to element mobility within the system (e.g. Arzamastev et al., 2011; Al Ani and Sarapää, 2013; Trofanenko et al., 2014; Dowman et al., 2017). As such, our comprehension of the relationship between intrusions, fluids and country rock is relatively restricted. This is in complete contrast to other ore systems, such as porphyry copper deposits, where alteration patterns and zones are a standard exploration tool (e.g. Hedenquist et al., 1998; Sillitoe, 2010).

This paper is the product of an expert council workshop as part of the HiTech AlkCarb project, funded by the Horizon 2020 Research and Innovation Programme of the European Union. This project brings together a variety of multi-disciplinary academic and industrial partners from around the world to develop new geomodels to explore for 'high technology elements' in alkaline rocks and carbonatites. Although the locations of many alkaline and carbonatite complexes are well known (e.g. Woolley and Kjarsgaard, 2008), these exploration models are required in order to better target unexposed economic deposits. Fenite enrichment is not typically sufficient to warrant exploitation; however, these rocks do have the potential to be used in the future as exploration tools to target critical metal resources.

1.1. Rare earth elements and critical metals

New technologies are utilizing an increasingly diverse array of elements in their manufacture. Amongst these are a sub-group of 'critical metals' (European Commission, 2017a, b), so defined as they are economically important metals with a significant risk of supply disruption. Carbonatite and alkaline rock-related deposits dominate the supply of REE and Nb, in addition to being sources of phosphate, fluorite, copper, titanium, platinum group elements and dimension stone. Alkaline and ultramafic rocks also provide vermiculite, nepheline and are potential sources of scandium and tantalum (e.g. Woolley and Kjarsgaard, 2008; Wall, 2014; Mitchell, 2015; Goodenough et al., 2016).

The term rare earth elements (REE) is used in this manuscript to represent the lanthanide series elements lanthanum (La) to lutetium (Lu), plus scandium (Sc) and yttrium (Y). Although the division between light and heavy rare earth elements is variably defined, the European Commission (2014) subdivides these into light REE (LREE) consisting of La-Sm, and the heavy REE (HREE) consisting of Eu-Lu including Y. These metals have advantageous paramagnetic, mechanical and spectral properties (Gupta and Krishnamurthy, 2005; British Geological Survey, 2011; Wall, 2014), making them useful in a wide range of industrial processes.

The vast majority of REE production occurs in China ($> 95\%$) (British Geological Survey, 2017; European Commission, 2017a), with only three other major mining operations globally. These consist of a weathered carbonatite at Mt Weld, W. Australia (e.g. Hoatson et al., 2011; Pirajno, 2015); a nepheline syenite at Lovozero, Kola Peninsula, Russia (e.g. Kogarko et al., 2010; Arzamastev et al., 2011; Wall, 2014); and as a by-product of Ti exploitation from mineral sand at Orissa, India (e.g. Gupta and Krishnamurthy, 2005; British Geological Survey, 2011). Currently Nb production is dominated by the carbonatite-related laterite deposits at Araxá and Catalão II, Brazil (e.g. Mitchell, 2015); carbonatite at St Honoré, Canada (Mitchell, 2015); and the nepheline syenite at Lovozero, Russia (Linnen et al., 2014). However, prospective deposits for both REE and Nb exist worldwide (see Fig. 1). Therefore, to develop a reliable and sustainable supply of these critical metals, complexes and deposits within politically stable countries must be explored and developed. Fenites do not contain exploitable quantities of critical metals, but do have great potential to be used as an exploration tool. Of the commodities listed above, only fluorite, vermiculite, phosphate and dimension stone have previously been mined from fenite.

1.2. Classification

Fenites are described as a metasomatic family by the IUGS (Zharikov et al., 2007), formed at high temperatures and characterized by a certain suite of minerals, but no attempt for further subdivision or more detailed nomenclature has been made by the IUGS. Fenite terms originally used by Brögger (1921) to describe the Fen type locality, Norway are listed in the IUGS classification of igneous rocks (Le Maitre et al., 2002). However, names such as tveitåsite and ringite are local, specific to Fen, and not commonly used elsewhere. Within fenites and their associated intrusive rocks, other forms of localized metasomatic processes are also observed, for example: autometasomatism in the peripheral parts of intrusions, contact metasomatism at the intrusion-country rock interface, and near-vein metasomatism forming symmetrical zonation on either side of a vein (Zharikov et al., 2007).

The classic definition of the term fenitization by Brögger (1921), involves the removal of silica from the protolith. However, during the metasomatism of undersaturated igneous rocks (e.g. Nurlybaev, 1973; Viladkar, 2015) there is no loss of silica, and often some gain relative to the protolith. As such, Bardina and Popov (1994) argued that fenitization is marked by an increase in alkali content ($Na_2O + K_2O$), irrespective of silica content or mobility.

Many endeavours have been made in the literature to subdivide fenites further into categories, dating back to von Eckermann (1948). For example, Kresten (1988) classified fenites as contact, aureole or veined depending on their spatial relationship to the source intrusion; Verwoerd (1966) first attempted to use the ratio of Na and K to classify fenites as sodic, potassic or intermediate, terms still used widely in the literature; and Morogan (1994) used a continuous scale of fenitization intensity to classify fenites as low, medium or high-grade. Russian literature names rocks that retain some of the original texture or protolith mineralogy, using the modifier "fenitized" added before the protolith name (e.g. Arzamastev et al., 2011; Kozlov and Arzamastsev, 2015). Additionally, the prefix "apo-" is used to indicate the nature of this protolith following the recommendations of the IUGS for metamorphic

REE mines / **Other REE deposits/ occurrences**

Primary deposits:
- Carbonatite-associated
- Alkaline igneous rock-associated
- Iron-REE deposits
- Hydrothermal deposits exclusive alkaline settings

Secondary deposits:
- Marine placers
- Alluvial placers
- Paleoplacers
- Ion-adsorption clays
- Ash-fall placers
- By-product of tin mining

1 Bokan Mountain, USA
2 Alay, Canada
3 Rock Canyon Creek, Canada
4 Thor Lake, Canada
5 Nisikkatch, Canada
6 Hoidas Lake, Canada
7 Elliot Lake, Canada
8 Saint-Honoré, Canada
9 Strange Lake, Canada
10 Snowbird, USA
11 North Fork, USA
12 Lemhi Pass, USA
13 Bald Mountain, USA
14 Bear Lodge, USA
15 Iron Hill, USA
16 Wet Mountains, USA
17 Pea Ridge, USA
18 Hicks Dome, USA
19 Carolina placers, USA
20 Mountain Pass, USA
21 Mountain Pass, USA
22 Gallinas Mountains, USA
23 Pajarito Mountain, USA
24 Sierra de Tamaulipas, Mexico
25 Morro Dos Seis Lagos, Brazil
26 Catalão I, Brazil
27 Araxá, Brazil
28 Serra Verde, Brazil
29 Pocos de Caldas, Brazil
30 Barra do Itapirapuã, Brazil
31 Sarfartôq, Greenland

32 Motzfeldt, Greenland
33 Ilimaussauq, Greenland
34 Fen, Norway
35 Bastnäs, Sweden
36 Norra Kärr, Sweden
37 Olserum, Sweden
38 Sokli, Finland
39 Lovozero and Khibina complexes, Russia
40 Tomtor, Russia
41 Gornoe Ozero, Russia
42 Khamna, Russia
43 Kizilcaoran, Turkey
44 Aksu Diamas, Turkey
45 Tamazeght complex, Morocco
46 Bou Naga, Mauritania
47 Nile Delta and Rosetta, Egypt
48 Karonge, Burundi
49 Mrima, Kenya
50 Wigu Hill, Tanzania
51 Kangankunde, Malawi
52 Songwe Hill, Malawi
53 Congolone, Mozambique
54 Ambohimirahavavy, Madagascar
55 Etanero, Namibia
56 Okorusu, Namibia
57 Eureka, Namibia
58 Kalkfeld, Namibia
59 Ondurakorume, Namibia
60 Steenkampskraal, South Africa
61 Zandkopsdrift, South Africa

62 Pilanesberg Alkaline Complex, South Africa
63 Naboomspruit, South Africa
64 Phalabowra (Palabora), South Africa
65 Richards Bay, South Afrca
66 Chavara, India
67 Amba Dongar, India
68 Sarnu, India
69 Orrisa, India
70 Wajiertage, China
71 Mushgai Khudag, Mongolia
72 Lugin Gol, Mongolia
73 Bayan Obo, China
74 Weishan, China
75 Maoniuping/Dalucao, China
76 Miayoa, China
77 Xunwu/Longnan, China
78 Dong Pao, Vietnam
79 Thai Peninsula, Thailand
80 Perak, Malaysia
81 Eneabba, Australia
82 Jangardup, Australia
83 Mount Weld, Australia
84 Brockman, Australia
85 Nolans Bore, Australia
86 Mary Kathleen, Australia
87 Olympic Dam, Australia
88 WIM 150, Australia
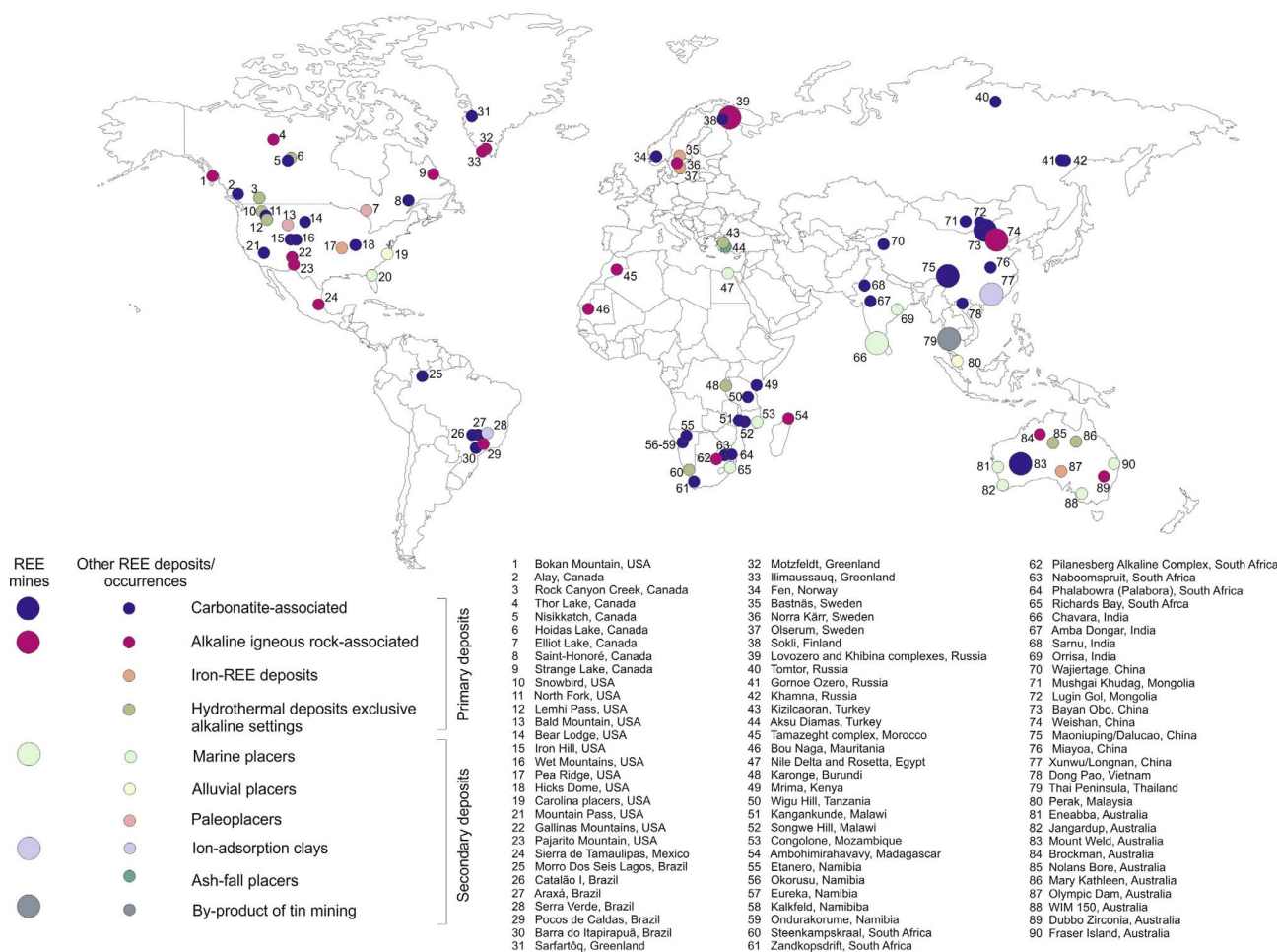89 Dubbo Zirconia, Australia
90 Fraser Island, Australia

Fig. 1. Classification of global REE deposits based on current exploitation status and geological setting. Contains British Geological Survey materials ©NERC [2017].

rocks (Fettes and Desmons, 2007) e.g. apogneiss fenite. However, many of these classification schemes do not provide much information to the reader or have genetic connotations, leading to a history of baffling nomenclature, but reflecting the complexity of the fenitization process. As such, we recommend that a nomenclature classification scheme similar to that used by the IUGS for metamorphic rocks (Fettes and Desmons, 2007) be used to name fenites, by using structural and mineralogical modifiers e.g. veined aegirine-albite fenite; brecciated orthoclase fenite. Here it is worth mentioning the collective term 'alkali metasomatites' used in Russian literature to denote rocks mineralogically similar to fenites, but generated by fluids of unknown provenance. These rocks are named on the basis of their predominant mineral, such as albitite or aegirinite (e.g. Es'kova, 1976; Ugryumov and Dvornik, 1984).

This manuscript follows the carbonatite nomenclature recommended by the IUGS, as outlined in Le Maitre et al. (2002), using the prefix of most abundant carbonate mineral present e.g. calcite carbonatite, dolomite carbonatite, ankerite carbonatite. Names used in the literature have been converted to this scheme; however, where iron-rich carbonate minerals have not been specifically identified, the term ferrocarbonatite is used.

1.3. Geological setting and models

Carbonatites are an extraordinary group of igneous rocks containing > 50% carbonate minerals (Heinrich, 1966; Le Bas, 1981; Woolley and Kempe, 1989) including calcite, dolomite, ankerite, siderite and magnesite (Woolley and Kempe, 1989). The term alkaline encompasses a wide variety of rock types and mineralogy (Fitton and Upton, 1987; Le Bas, 1987) which cannot all be covered within the scope of this paper. No precise term has been agreed upon to define alkaline rocks, however 'alkaline' implies a deficiency in silica and aluminium relative to the alkali elements (Na and K) (Fitton and Upton, 1987; Leelanandam, 1989; Mitchell, 1996). Although it is recognized that both carbonatites and alkaline-silicate intrusions are capable of forming fenites, the focus of this paper is carbonatite-related fenitization, and therefore alkaline-related fenitization is referred to separately (see Section 5.3).

Intracontinental geological settings and rift valleys often host both alkali and carbonatitic magmatism, however carbonatites are also found in relation to subduction processes (Fitton and Upton, 1987). An in depth discussion of carbonatite magma genesis is beyond the scope of this paper, therefore the reader is recommended the following references for more information. Two opposing theories exist for the origin of carbonatite magmas. The first suggests that carbonatite magmas are produced from parent alkaline magmas via a complex combination of liquid immiscibility and/or crystal fractionation processes (e.g. Le Bas, 1981; Treiman and Essene, 1985; Andersen, 1989; Kjarsgaard and Hamilton, 1989; Ray and Shukla, 2004). This is supported by the fact that 74% of known carbonatite occurrences are associated with alkaline rocks (Heinrich, 1966; Woolley, 2003; Le Bas, 2008; Woolley and Kjarsgaard, 2008), such as nepheline syenites, ijolites and pyroxenites that are considered to have formed from the immiscible silicate magmas (Le Bas, 1987). The second theory indicates that some carbonatites are derived directly from the mantle, and therefore sourced from depths greater than the carbonate solidus at ~70 km, below which dolomite-
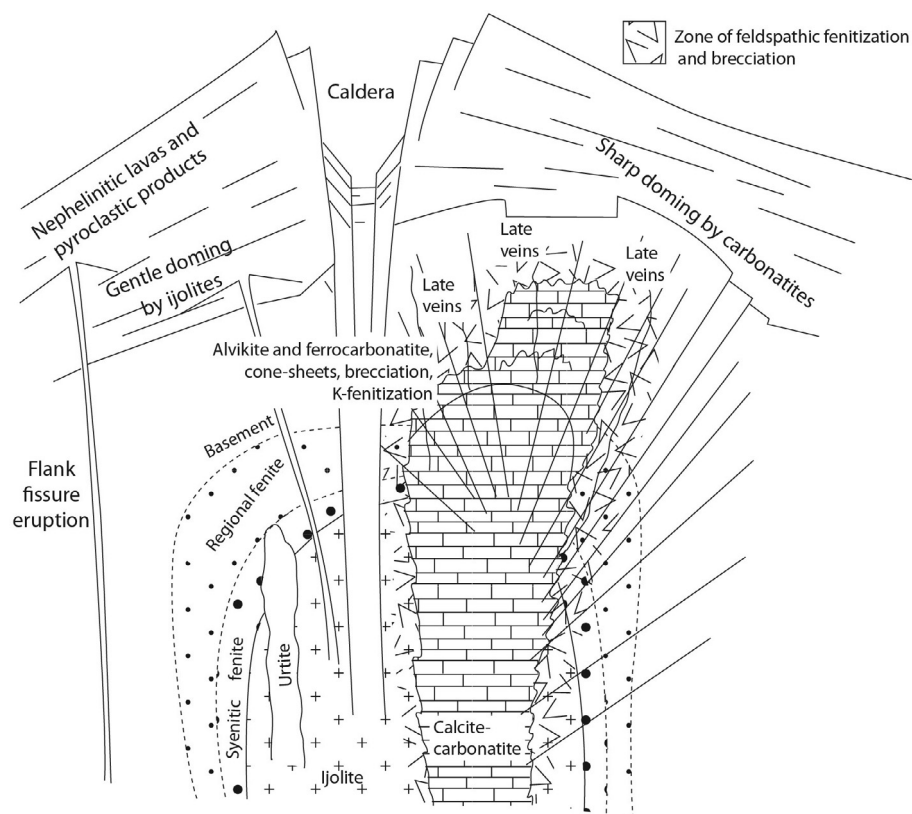
Fig. 2. Conceptual model of fenitization and brecciation associated with alkaline and carbonatitic magmas adapted from Le Bas (1977).

bearing peridotite can melt to produce carbonatitic magmas (e.g. Bailey, 1989; Harmer and Gittins, 1998; Chakhmouradian et al., 2009).

Conceptual models of alkaline and carbonatite magmatic systems have not advanced dramatically since that proposed by Le Bas (1977) (see Fig. 2). Recent research driven by resource exploration has progressed our understanding of these systems and the model is now outdated. The model lacks any emphasis on the formation and location of potential ore deposits; details of fenite formation and characteristics such as brecciation, veining and zonation; in addition to the role of hydrothermal fluids in and around the complex. With very few exceptions (e.g. Arzamastsev et al., 2000; Mikhailova et al., 2016), there is little information on the vertical extent of individual rock series and their association mineralization (Verplanck et al., 2014).

1.4. Fen, Norway: fenite type locality

The type locality of fenitization was first described by Brögger (1921) in his memoir on the Fen carbonatite complex, Norway. Since the initial studies of the 1920s, further investigation of this complex has advanced our understanding of its petrography (Sæther, 1958; Marien et al., 2017), mineral chemistry (Kresten and Morogan, 1986; Andersen, 1989), whole-rock geochemistry (Kresten, 1988), and isotopic signature (Verschure and Maijer, 2005).

The Fen Complex (see Fig. 3) consists of a roughly circular 5 km² central core of Neoproterozoic (578 ± 24 Ma) calcite carbonatite and alkaline intrusions of the melteigite-ijolite-urtite series with subordinate nepheline syenite, that were emplaced into Mesoproterozoic granitic gneiss country rock (Brögger, 1921; Kresten and Morogan, 1986; Andersen, 1989; Dahlgren, 1994; Verschure and Maijer, 2005). The Fen Complex, which has been historically mined for Nb and Fe, lies at the center of a larger area defined as the Fen Province, which incorporates many small satellite intrusions of dolomite and ferrocarbonatite extending over 1500 km² (Dahlgren, 1987; Dahlgren, 1994). Intrusion of these carbonatite magmas and preceding alkaline rocks are associated with at least two brecciation events (Kresten and Morogan,

1986) that facilitated at least two stages of fenitization. The first event created a fenite aureole 700 m wide, and the second > 1.5 km wide (Verschure and Maijer, 2005), much greater than the 200 m previously described by Brögger (1921) which was restricted to a narrow zone along the intrusion-country rock contacts.

Brögger (1921) argued that the fenite at Fen was the product of metasomatism adjacent to the ijolite-melteigite intrusions during a process he named "Fenitisierung" or fenitization. However, further study has shown that fenitization is the product of fluids originating from both the alkaline and carbonatitic intrusions (Kresten and Morogan, 1986). Based on microscope observations of thin sections, Brögger (1921) described the progressive metasomatism from the unaltered granite, through to the ijolite-melteigite contact. This involved the alteration of an original country rock mineral assemblage of quartz, K-feldspar, oligoclase, biotite and hornblende to an albite and aegirine-rich fenite near the contact. The stages involved in this progressive metasomatism are shown in Fig. 4.

2. Fenite types and formation

There are many parameters that control the characteristics of a fenite; therefore it cannot be assumed that a certain protolith will produce a distinct fenite mineral assemblage. The complexity of the process is reflected in the diverse range of nomenclature used in the literature.

Protolith characteristics such as mineralogy, texture, structure, porosity and permeability have a large bearing on the extent of fenitization. Chemical buffering by the country rock determines the intensity and extent of fenitization which can vary greatly from centimeters to several kilometers. Intense fenitization occurs where there is a large chemical gradient between fenitizing fluids and country rock, such as granite, granitic gneisses or meta-sediments. In contrast, country rocks dominated by quartz or carbonate lithologies including sandstone, marbles and limestones, typically display little evidence of fenitization, reflecting their low degree of reactivity. This relationship is reflected by
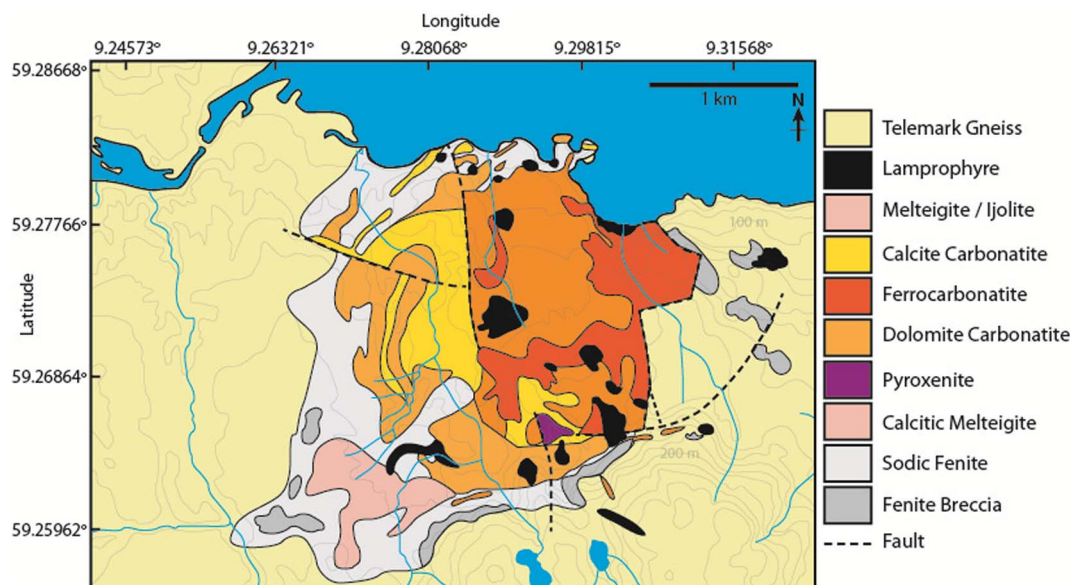
Fig. 3. Geological map of the Fen Complex, Norway as a type site for fenitization. Map adapted from Verschure and Maijer (2005).

the scale of fenitization surrounding carbonatite intruded into proto-liths with varying chemical gradients. For example, fenite in sandstone surrounding the Amba Dongar carbonatite, India, is < 300 m thick (Doroshkevich et al., 2009), compared to fenites of the Shawa and Dorowa complexes, Zimbabwe, both of which extend > 2 km diameter into the granitic gneiss country rock (Johnson, 1966). Feldspar-rich fenites at Bayan Obo, China only extend 2–4 m into Middle Proterozoic meta-sandstones and marbles (Le Bas, 2008).

The fenite mineral assemblage and chemistry is also dependent on the protolith, but additionally affected by the composition, temperature and pressure of the fenitizing fluid (Dawson, 1964; Heinrich, 1966; Le Bas, 1987; Platt, 1996). Pyroxene and amphibole chemistry is particularly sensitive to the fenitizing fluid characteristics (Sutherland, 1969). Mineralogy is also dependent on the intensity of metasomatism; however, this rarely decreases linearly away from the contact. Late-stage intrusions in the fenite aureole, such as the Jammi dykes in the Sokli carbonatite complex, Finland (Al Ani and Sarapää, 2009; Al Ani and Sarapää, 2013; Sarapää et al., 2013; Sarapää et al., 2015), cause high intensity fenitization away from the central intrusion. Additionally, fluids utilize highly permeable planes of weakness (Ortoleva et al., 1987), causing preferential fenitization leading to asymmetrical fenite aureoles (e.g. Fen complex, see Fig. 3).

2.1. Veined vs pervasive fenites

Cross-cutting vein textures and zoned apatite crystals (see Figs. 5A and 5B) observed in fenite aureoles indicate that alkali metasomatism is a multi-phase process (Le Bas, 2008). The distribution of the metasomatic (or fenite) parageneses can form two end member macrotextures, either pervasive throughout the country rock, or localized adjacent to veins that follow pre-existing structural weaknesses, such as fractures

(e.g. Kresten, 1988; Morogan and Woolley, 1988; Sindern and Kramm, 2000; Pirajno et al., 2014). Since fenite mineral assemblages result from the reaction between fenitizing fluids and the surrounding country rock, these macrotextures are a response to the distribution of fluids and the dynamics of fluid flow in the host rock.

Fenitizing fluids can flow either along grain boundaries and mineral cleavage planes (porous flow), and/or within dilated fractures. During porous flow, fluid is able to interact with a larger surface area of rock than fluid confined to fractures. This enables pervasive fenitization, causing metasomatic minerals to be distributed throughout the country-rock (see Figs. 5C and 6A). Pervasive fenites are commonly observed in the immediate vicinity of carbonatite and alkaline intrusions and extend radially away from the fenitizing fluid source (Kresten, 1988). Pervasive fenites are typically divided into zones on the basis of mineralogical and textural changes (e.g. Rubie, 1982; Morogan and Woolley, 1988). The intensity of fenitization typically decreases with distance from the source intrusion. This most likely reflects a reduction in the fluid-rock ratio and changing fluid-rock chemistry gradient with distance. One example of this process is the Okorusu fenite, Namibia, which displays undulating or scalloped alteration fronts that formed during the permeation of fenitizing fluids via porous flow (see Fig. 5E). This fluid forms a reaction front that advances irregularly through the greywacke country-rock due to differences in porosity and fluid-mineral reactions across the front (Ortoleva et al., 1987).

Fenitizing fluids may exploit pre-existing structural weaknesses in the host rock or cause the propagation of new fractures by fluid over-pressure or volume changes related to metasomatic mineral reactions (Skelton et al., 2007; Sachau et al., 2015). During fracture-hosted flow, only a small fraction of the fenitizing fluids can metasomatize the country rock adjacent to the host fractures (see Figs. 5D and 6B), forming veined fenites. The volume of country rock affected by fluid-
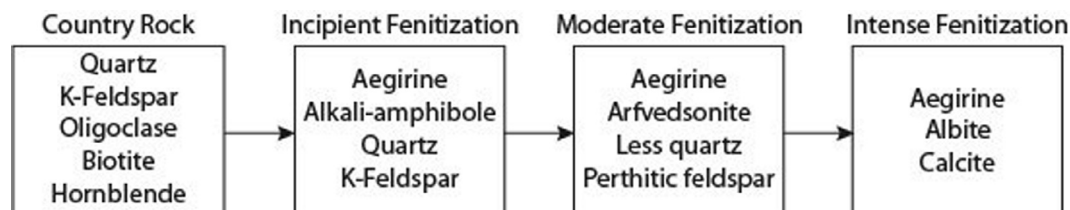

Fig. 4. Progressive stages of fenitization and mineral assemblages at Fen, Norway as described by Brögger (1921). Intense fenitization is proximal to intrusion and unfenitized country rock, distal.
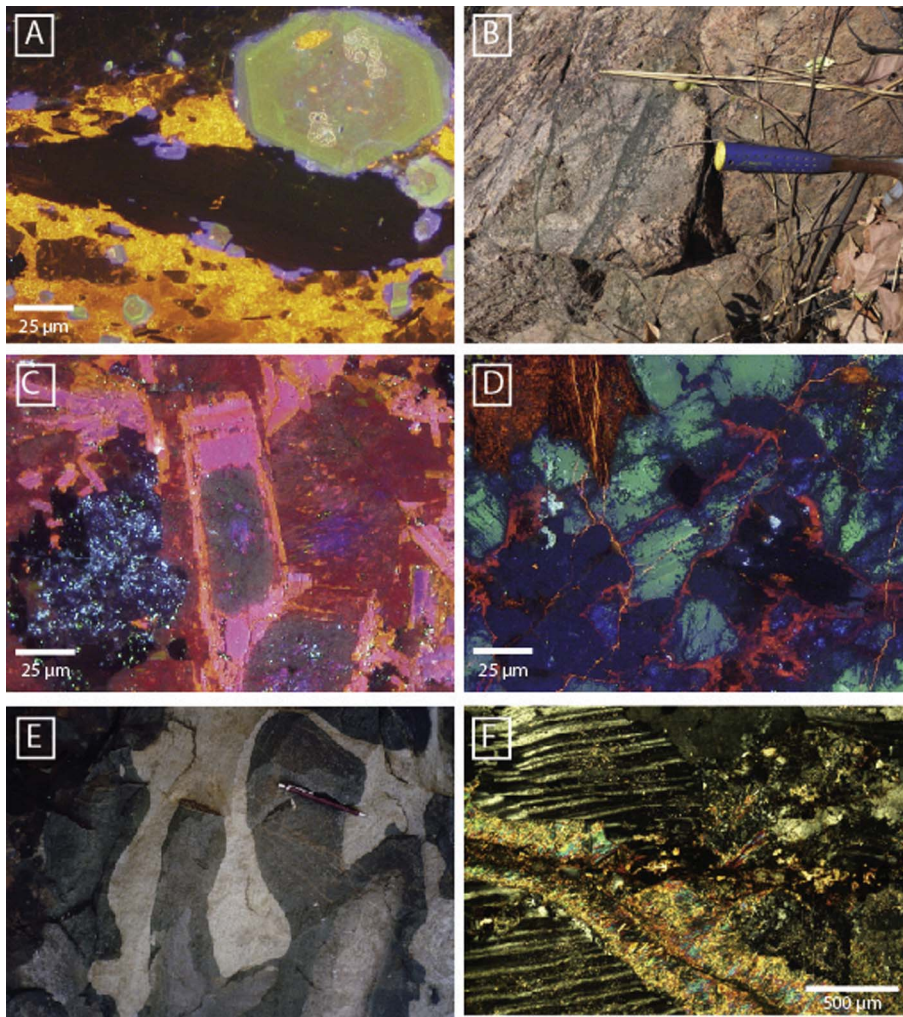
Fig. 5. A: Cathodoluminescence (CL) image showing zoned euhedral apatite (green-purple) with adjacent pyroxene vein (black) and calcite (yellow-orange). **B:** Veined fenite at Nkalonje, Malawi with hammer for scale. **C:** CL image showing growth of new feldspar (pink-red) during fenitization at Chenga, Malawi around a pre-existing feldspar core (grey) **D:** CL image of incipiently fenitized gneiss at Kangankunde, Malawi. Introduction of ferric iron along fractures by fenitizing fluids luminesces red in non-luminescent amphiboles and green unaltered feldspars. Fe-rich carbonate luminesces orange. **E:** Progressive pervasive sodic fenitization front metasomatizing greywackes at Okorusu, Namibia with pen for scale. **F:** XPL image of fracture used by multiple pulses of fenitizing fluid at Sokli, Finland forming a vein with multiple layers of minerals mirrored either side of vein. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
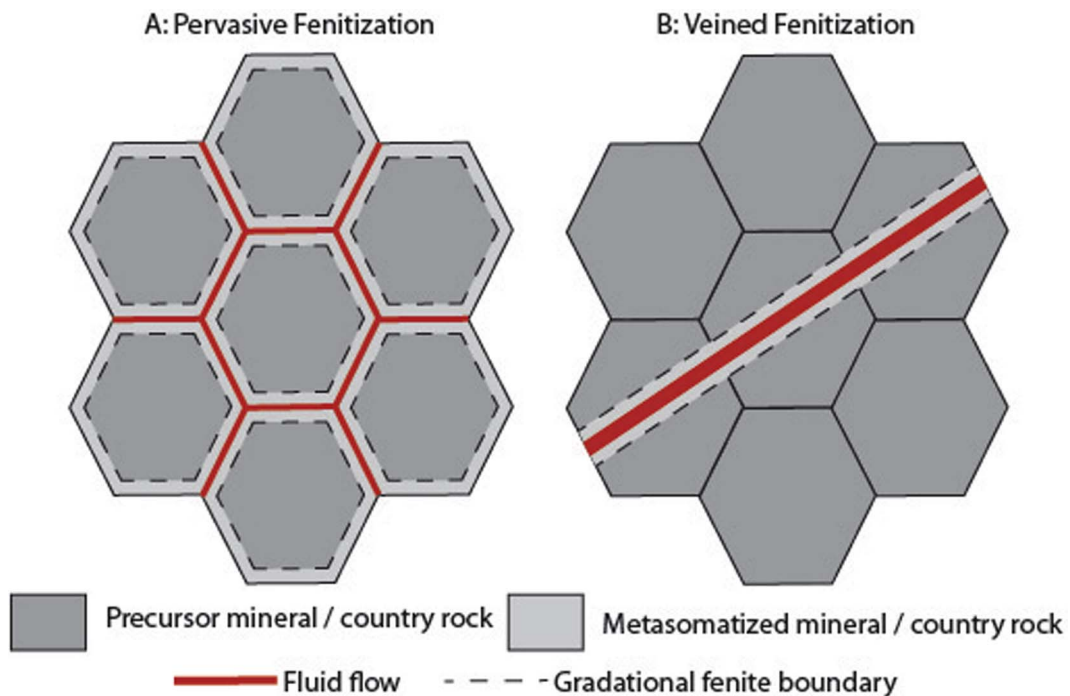
Fig. 6. Schematic diagram illustrating the difference between pervasive fenitization (A) and veined fenitization (B). Fluid interacts with a larger volume of country rock during diffuse porous flow than fluid flowing through fracture.

rock interaction during fracture-confined fluid flow is limited relative to diffuse porous flow (see Fig. 6). Fluid hosted in fractures are essentially chemically isolated from the surrounding country rock and will therefore retain their alkali-rich chemistry over greater distances. Fractures act as effective conduits, efficiently facilitating transport of fluids to the outer fenite aureole. The formation of zoning during metasomatic processes is common, and can result from changes in the chemistry of a single fluid infiltrating the country rock (e.g. Korzhinskii, 1968; Brady, 1977; Meinert, 1998; Winter, 2001). However, individual fenite veins can show multiple zones of differing minerals with clearly defined contacts, mirrored either side of a fracture. These patterns suggest precipitation from different generations of successive fluids, that repeatedly utilized the same fracture system during the course of fenitization (see Fig. 5F).

Fenites of greater complexity display a combination of veined and pervasive fenitization, indicating that they have experienced both porous and channelised fluid flow at various times during evolution of the complex. Shifts in the importance of flow mechanism most likely reflect adjustments to fenitizing fluid pressure, confining pressure and porosity/permeability characteristics of the fenite. Subtle changes to these parameters may result from rock-fluid chemical reactions or mechanical failures such as fracturing.

The dynamics of fluid flow during fenitization are poorly understood. However, analogies with other fluid-rich geological systems, such as metasomatized porphyry stockworks (e.g. Ortoleva et al., 1987; Robb, 2005), can be drawn to demonstrate that the passage and pathways of fluid flow have fundamental consequences for element mobilization and deposition. One example is the intrusion of the Cornubian granite batholith, England, which was accompanied by the formation of vein networks channelling hot aqueous fluids and vapours expelled from an overpressurized magma reservoir. The resulting tin-tungsten mineral veins are bound by greisen wall-rock alteration (e.g. Jackson et al., 1989; Dominy et al., 1995) during a process broadly similar to metasomatism adjacent to fenite veins. Greisenization is a post-emplacement metasomatic process leading to remobilization of Si and Al within the granitoid, which can be preceded or followed by potassic or sodic alteration (Stemprok, 1987). Alteration in the Cornubian Orefield is categorized into pervasive and joint-controlled greisens (Stemprok, 1987), forming similar alteration patterns to those observed in fenites (see Fig. 6). Pervasive greisenization is observed at Cameron Quarry, St. Agnes, where it caused complete alteration of the granite porphyry (Hosking and Camm, 1985). Other sites display limited alteration adjacent to joint-greisens such as Wheal Prosper, St Austell (Bennett et al., 1981), analogous to veined fenites.

The formation of skarns is another analogy for metasomatism in fenites. Skarns are metasomatic rocks that typically form at the contact between a silicate intrusion and a carbonate country rock, forming zones of differing modal mineralogy extending away from the contact, similar to a fenite. Typical mineralogy consists of Ca-Mg-Fe-Mn silicates such as forsterite, diopside, phlogopite and garnet (Kwak, 1987; Meinert, 1992; Zharikov et al., 2007). Veins are a common feature of both fenite aureoles and skarns, resulting from metasomatic fluids confined in bodies or pipes cross-cutting the intrusion or country rock (Zharikov et al., 2007), the size of which is dependent on country rock reactivity and fracture permeability (Bussell et al., 1990).

2.2. Breccias

Carbonatite emplacement is often accompanied by widespread brecciation and fracturing of the basement rock (Heinrich, 1966; Tuttle and Gittins, 1966; Le Bas, 1977; Rubie and Gunter, 1983). Swinden and Hall (2012) identified two predominant types based upon their study of Songwe Hill, Malawi. The first type is a feldspathic breccia (see Fig. 7A) consisting of alkali feldspar-rich fragments ± carbonatite clasts in a matrix of alkali feldspar, carbonate and oxides with varying proportions of quartz due to fenite comminution during brecciation. The second is a

carbonatite-rich breccia consisting of carbonatite and subordinate fenite clasts in a carbonate-rich matrix. The majority of breccias directly related to carbonatite complexes can be fitted into either of these two categories with varying proportions of clast types and protoliths. Brecciation is most commonly seen at the carbonatite-country rock contact, typically consisting of feldspathic breccias intruded by later carbonatitic dykes or veins (see Fig. 7B). Examples include Sokli (Vartiainen and Woolley, 1976; Notholt, 1979); Fen (Verschure and Maijer, 2005); Kangankunde and Chilwa Island, Malawi (Woolley, 1969); Homa Mountain, Kenya (Clarke and Roberts, 1986); Dicker Willem, Namibia (Reid and Cooper, 1992); Toror Hills, Uganda (Sutherland, 1965b) and Okorusu, Namibia (Bhn et al., 2002). The brecciated transition zone between fenite and carbonatite at Sokli is highlighted by a reduction in gravity and low seismic velocities on geophysical surveys (Vartiainen and Paarma, 1979).

The presence of breccias at many carbonatite complexes attests to the explosive release of fluids and volatiles from an evolving magma below (Verplanck et al., 2014; Croll et al., 2015). At higher fluid pressures, masses of comminuted fenite and/or carbonatitic material can explosively breach the surface to form extrusive tuffs (Le Bas, 2008), which was experimentally demonstrated by Lorenz et al. (1991). Explosive release of these fluids may explain observations of tuffs and lapilli tuffs at Kruidfontein, South Africa and Rangwa, Kenya (Le Bas, 2008). Alternatively, Kresten (1988) interpreted brecciation surrounding carbonatites as the result of volume increase during the fenitization process. The latter mechanism may also be responsible for the dilation of numerous fractures which host quartz veins.

The timing of brecciation around carbonatite complexes is more subjective and possibly site-specific. Where fully fenitized breccia clasts are entrained in carbonatite, it can be hard to determine whether fenitization occurred prior to, or during their incorporation. Previous sections have presented evidence that carbonatite emplacement and the release of fluids/volatiles is a multi-stage process. Evidence indicating multiple stages of brecciation and feldspathization between intrusion events includes, for example, feldspathized breccia blocks incorporated in carbonatite intrusions at Chilwa Island (Woolley, 1969) and Sokli (Vartiainen and Woolley, 1976) (see Fig. 7C). Brecciation often occurs prior to late-stage carbonatite intrusions (see Fig. 7B), as manifested by the *in situ* injection of carbonatite into previously shattered country rock at Mountain Pass, USA (Castor, 2008); the intrusion of carbonatite dykes and veins into intensely brecciated and fractured fenites at Sokli (Vartiainen and Paarma, 1979); and the intrusion of a feldspathic breccia vent by later carbonatite sheets at Songwe Hill (Garson, 1965).

Brecciation accompanying igneous activity is not exclusive to carbonatites, and breccias often occur surrounding alkaline complexes. These breccias are often interpreted as hydrothermal products resulting from the escape of volatiles from magma during boiling stages, leading to intense hydraulic fracturing (Burnham, 1985; Pirajno, 2015). Diatremes are often filled with highly permeable and porous vent breccias and tuffs (Afanasyev et al., 2014; Elliott et al., 2015) that provide efficient intrusive pathways and hosts for later carbonatite magmas. This process can form REE-enriched (up to ~3 wt% TREO) carbonatite stockworks such as the Bull Hill phonolitic diatreme at Bear Lodge, USA (Moore et al., 2015) and diatreme breccias at Kaiserstuhl, Germany (Hornig-Kjarsgaard, 1998).

2.3. Sodic vs potassic fenites

The whole-rock ratio of Na to K is used to classify fenites as sodic, intermediate or potassic (Verwoerd, 1966). Historically, sodic fenites were attributed to alkali magmatism such as the formation of ijolites, and carbonatite-related fenitization was thought to be potassic (Morogan, 1994). However, this is no longer thought to be the case as many carbonatites are associated with both potassic and sodic fenites (Woolley, 1982; Le Bas, 2008). The type of fenite formed is not dependent on carbonatite composition, with sodic and potassic fenites
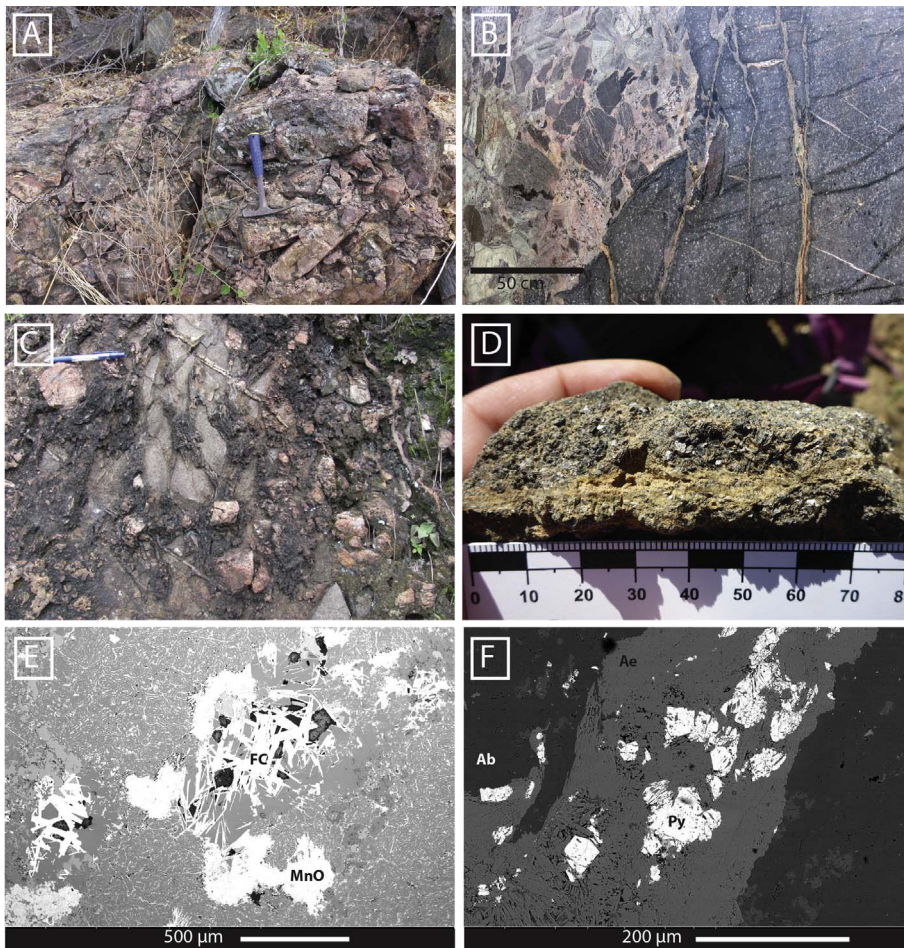
Fig. 7. **A:** Fenite breccia consisting of K-feldspar rich clasts at Chenga, peripheral to Songwe Hill, Malawi. **B:** Carbonatite dyke intruding sodic fenite breccia at Lofdal, Namibia. **C:** K-feldspar rich fenite clasts incorporated within carbonatite intrusion at Songwe Hill, Malawi. **D:** Hand sample of glimmerite fenite adjacent to carbonatite intrusion at Bayan Khushu, Mongolia. **E:** SEM backscatter electron image of fenite sample from Songwe Hill, Malawi showing REE-fluorcarbonates (FC) and manganese oxides (MnO) in a matrix of Fe-rich carbonates and exsolved iron oxide (intergrown grey and white). **F:** SEM backscatter electron image of fenite sample from Sokli, Finland showing pyrochlore (Py) in an aegirine vein (Ae) intruding albite (Ab).

being found adjacent to intrusions of either calcite or dolomite carbonatite (Le Bas, 2008).

The spatial variation between potassic and sodic fenites is distinct at a number of carbonatite complexes globally. Le Bas (1981) and Woolley (1982) proposed a vertical zonation in fenite chemistry, with more sodic compositions hypothesized to occur at depth and potassic fenites at shallower crustal levels. This model could explain the presence of sodic fenites around older complexes due to deeper cross sections being exposed by prolonged erosion (Le Bas, 2008). Very few carbonatite complexes are sufficiently well-exposed to display this vertical zonation pattern (e.g. Amba Dongar, India: Doroshkevich et al., 2009), but the majority of carbonatite complexes show horizontal variations in fenite chemistry. Carbonatites of the Chilwa Province, Malawi, typically exhibit an outer sodic fenite and inner potassic aureole associated with intense brecciation (Woolley, 1982), also reported at Wicheeda, Canada (Trofanenko et al., 2014). In addition to spatial controls on fenitization, observations such as cross-cutting relationships at many complexes such as Bayan Obo (Le Bas, 2008); Chilwa Province (Woolley, 1969; Woolley, 1982); and Chipman Lake, Canada (Platt and Woolley, 1990), suggest there is also a temporal control on fenitization with an early sodic phase typically overprinted by later potassic fenitization.

The alkali content in a carbonatite-derived fluid varies dramatically, which is reflected in the extreme geochemical variations among published fenite compositions (see Fig. 8). The few available estimates range from up to 3 wt% dissolved Na_2CO_3 in expelled hydrothermal fluids at Oldoinyo Lengai, Tanzania (Carmody, 2012) to up to 30 wt% $Na_2O + K_2O$ in bulk fluids from inclusions at the Okorusu and Kalkfeld carbonatites, Namibia (Bhn et al., 2002). This variation in alkali concentration may result from a difference in the depth of carbonatite magma generation and complexity of magma evolution. Woolley and Church (2005) suggest that carbonatite magmas generated by high-level fractionation and immiscibility processes in a peralkaline crustal magma chamber will have a higher alkali content than those that move rapidly from a mantle source to the shallow crust.

Fenitization is traditionally considered to involve the removal of silica (Brögger, 1921) and the addition of alkalis ($Na_2O + K_2O$) (Bardina and Popov, 1994), which can clearly be seen illustrated by the general fenitization trends in Fig. 8. The majority of complexes show a substantial increase in alkalis between 0.5 and 10 wt% and a decrease in silica between 0.5 and 29 wt%. This trend is most clearly demonstrated in fenites of the type locality (Fen) (Fig. 8B); Sokli, Finland (Fig. 8C); Silai Patti, Pakistan (Fig. 5D); and Newania, India (Fig. 8F), all of which replaced protoliths of granite or geochemically similar metamorphic rocks such as gneiss or schist. In the majority of fenites, alkalis are enriched in the country rock during fenitization due to a large compositional gradient between fluids and protolith. Protoliths with a low initial silica content can experience enrichment in silica during fenitization, such as the 23 wt% increase observed in the marble at Lac a la Perdrix, Canada (Fig. 8E). However, this is not the case where country rock has an initially high alkali content. For example, aplitic granite, consisting solely of feldspar and quartz (Le Maitre et al., 2002), loses up to 2.3 wt% alkalis during fenitization at Meech Lake, Canada (Fig. 8D). Fenitization of nephelinite can cause minor alkali enrichment or depletion (up to 2.3 wt%) such as that seen at Amba Dongar (Fig. 8D) and Koga, Pakistan (Fig. 8F).

Spatial and temporal fenite variations are thought to be dependent on the temperature, pressure and CO_2 content of the fenitizing fluid (Rubie and Gunter, 1983). Potassium is considered to be more mobile than Na at lower temperatures and therefore transported by fluids to shallower depths, to form shallower potassic fenites at lower
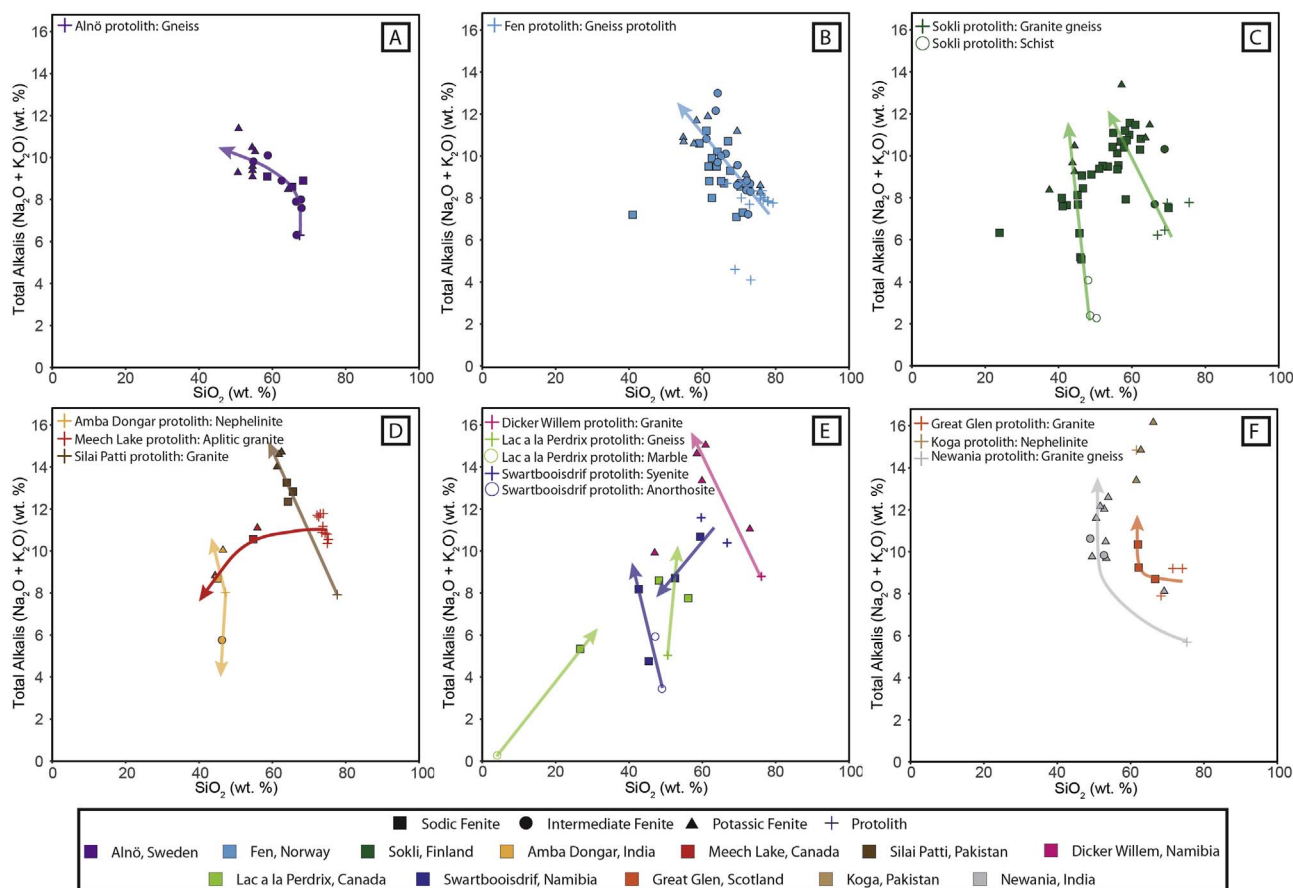
Fig. 8. Concentration of silica and total alkalis in fenites and their protoliths surrounding carbonatite complexes around the world. Fenites are divided into sodic, intermediate or potassic categories and arrows indicate general fenitization trends. All data available in Supplementary Table 1. **A:** Fenitization of gneiss protolith at Alnö, Sweden (Morogan, 1989). **B:** Fenitization of granitic gneiss at Fen, Norway (Kresten, 1988; Verschure and Maijer, 2005). **C:** Fenitization of gneiss and schist at Sokli, Finland (Vartiainen and Woolley, 1976; Al Ani and Sarapää, 2013). **D:** Fenitization of nephelinite at Amba Dongar, India (Viladkar, 2015); aplitic granite at Meech Lake, Canada (Hogarth, 2016); and granite at Silai Patti, Pakistan (Le Bas, 2008). **E:** Fenitization of granite at Dicker Willem, Namibia (Cooper and Reid, 2000); gneiss and marble at Lac a la Perdrix, Canada (Hogarth and van, 1996); and syenite and anorthosite at Swartbooisdrif, Namibia (Drüppel et al., 2005). **F:** Fenitization of granite at Great Glen, Scotland (Garson et al., 1984); nephelinite at Koga, Pakistan (Le Bas, 2008); and granite gneiss at Newania, India (Viladkar and Wimmenauer, 1986).

temperatures. Na is preferentially lost from fluids at deeper crustal levels whilst temperatures are still > 600 °C, forming an earlier, deeper sodic fenite (Heinrich and Moore, 1969; Le Bas, 1981; Rubie and Gunter, 1983). This is supported by the common association of brecciation and potassic fenitization, suggesting that the latter occurred during volatile release and hydraulic fracturing. These processes indicate shallow depth, such as the roof of a magma chamber, and account for vertical chemical zonation of the fenite aureole (Le Bas, 2008). Another model, proposed by Woolley (1982), involves a high initial $Na_2O:K_2O$ ratio in the carbonatite intrusion, causing initial expulsion of Na to form an early sodic fenite. Continued release of Na-rich fluids subsequently enriches the melt in K, causing later potassic fenitization favored at lower temperatures of < 450 °C determined by Rubie and Gunter (1983).

Processes that cause spatial and temporal segregation of Na and K-rich fluids are unlikely to conform to the same model at every alkali complex, and many fenites do not fit the patterns discussed above at all ("there are infinite variations on a fenite theme" – Heinrich, 1985). Carbonatites surrounded by exclusively sodic or potassic fenites could be explained by different depths of erosion; for example, exclusively sodic fenitization is observed at the Newania complex (Viladkar and Pawaskar, 1989), whereas carbonatites at Rufunsa, Zambia (Woolley, 1969) and Bukusu, Uganda (Vartiainen and Woolley, 1976) lack sodic fenitization. However, the presence of K-feldspar crystals rimmed by albite at the Ruri Hills carbonatite, Kenya, and Koga, as well as K-feldspar rich fenite cut by late albite veins at Bayan Obo (Le Bas, 2008),

suggest that sodic fenitization does not always occur prior to potassic.

2.3.1. Sodic fenites

One of the most conspicuous features of sodic fenites are the abundant green veins and veinlets of sodic pyroxenes and amphiboles cross-cutting alkali feldspar (see. Fig. 7B and F). Quartz and minor minerals such as calcite, fluorite and apatite are also observed in small quantities (Le Bas, 2008; Doroshkevich et al., 2009). Pyroxene and amphibole chemistry is highly dependent on the fenitizing fluid composition, pressure and temperature (PT), in addition to the composition of their precursor minerals in the protolith (Sutherland, 1969). Magnesioarfvedsonite coexisting with aegirine is the most common mineral assemblage in sodic fenite veins reported in the literature (e.g. Sutherland, 1969; Hogarth and Lapointe, 1984; Le Bas, 2008). However, classification of amphiboles from nine carbonatite-related fenites (Fig. 9) shows sodic–calcic amphiboles such as richterite to be far more common. In rare cases, the activity of F^- in the fenitizing fluid is sufficiently high to facilitate crystallization of F-dominant amphiboles, such as fluororicherite and fluoromagnesio-arfvedsonite (Bazhenov et al., 1993; Bazhenov et al., 2000). Nedosekova (2007) noted that the F content of amphiboles decreases outwards in fenites of the Il'mensky-Vishnevogorsky complex, Russia. Hogarth and Lapointe (1984) observed at Cantley, Canada, that during early stages of fenitization, pyroxene typically replaces quartz, whereas feldspar is replaced by amphibole.

The chemical composition, temperature and pressure of fenitizing
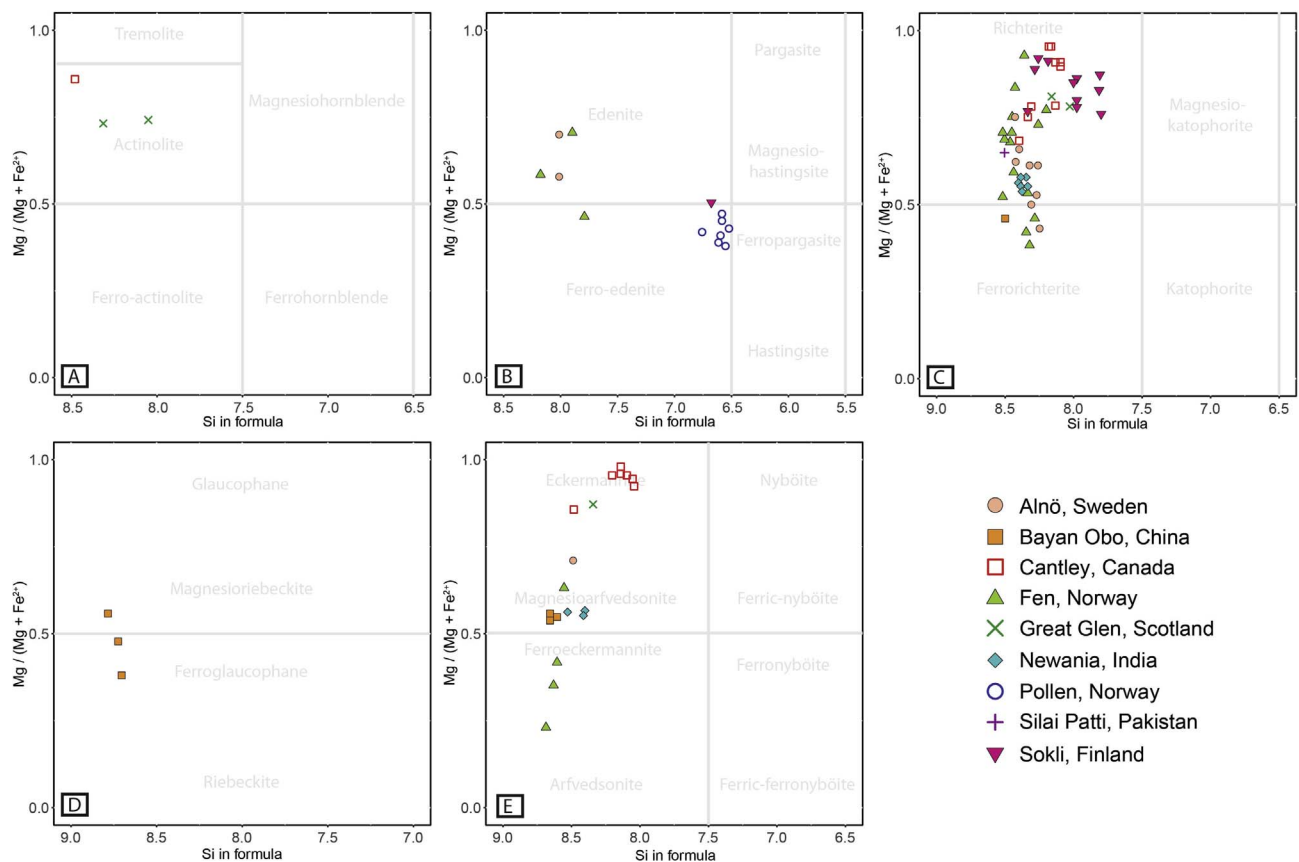
Fig. 9. Classification of amphiboles plotted on graphs of Mg:Fe^{3+} ratio and Si calculated in tetrahedral position of formula using the scheme outlined in Leake et al. (1997) and Leake et al. (2004). **A:** Calcic amphiboles with $Ca_B \geqslant 1.50$, $(Na + K)_A < 0.50$. **B:** Classification of calcic amphiboles with $Ca_B \geqslant 1.50$, $(Na + K)_A \geqslant 0.50$. **C:** Classification of sodic–calcic amphiboles with $(Na + K)_A \geqslant 0.50$. **D:** Classification of sodic amphiboles with $(Na + K)_A < 0.50$. **E:** Classification of sodic amphiboles with $(Na + K)_A \geqslant 0.50$. All data available in Supplementary Table 2. Data sources: Alnö, Sweden (Morogan and Woolley, 1988); Bayan Obo, China (Le Bas, 2008); Cantley, Canada (Hogarth and Lapointe, 1984); Fen, Norway (Kresten and Morogan, 1986; Andersen, 1989); Great Glen, Scotland (Garson et al., 1984); Newania, India (Viladkar and Wimmenauer, 1986); Pollen, Norway (Robins and Tysseland, 1983); Silai Patti, Pakistan (Le Bas, 2008); and Sokli, Finland (Vartiainen and Woolley, 1976).

fluids changes over time as the source magma cools and evolves. Therefore, sodic fenites represent the end product of a series of complicated fluid-mineral reactions resulting from pulses of fenitizing fluids of differing chemical composition and temperature. During fenitization, alkalis are typically exchanged for silica in an open system, and mineral chemistry is continuously adjusted as fluid-rock interactions strive toward equilibrium (Hogarth and Lapointe, 1984). As a result, early-stage fenite mineral assemblages are often replaced, partially replaced or rimmed by late stage minerals with a composition reflecting this fluid evolution. For example, at Cantley, pyroxenes with an augite-rich core and aegirine-rich rim occur in addition to zoned amphiboles with a Ca-poor rim. These minerals record the change from an early Ca-rich and alkali-poor fluid to a late Ca-poor and alkali-rich fluid which may have resulted from decreasing temperature (Hogarth and Lapointe, 1984). Similarly, aegirine-augite at Fen display erratic core-rim zoning (Andersen, 1989) and fenite at Silai Patti contains aegirine-augite crystals rimmed by magnesio-arfvedsonite (Le Bas, 2008). Hogarth and Lapointe (1984) suggested that amphiboles and pyroxenes formed in an open system that allowed adjustment of mineral composition to reflect fluid chemistry and PT conditions, would exhibit a curved chemical trend. This evolution of mineral chemistry can be observed at Fen and Alnö, Sweden (see Figs. 9C and 10). Those formed in a closed system with no exchange of mass, tend to show little geochemical variation and be clustered on a graph, similar to those from Cantley (see Figs. 9E and 10).

Mineral composition also varies within a fenite aureole depending on proximity to the source intrusion, and therefore grade of fenitization. In the Fen Complex, amphiboles proximal to intrusions have

richterite and magnesio-arfvedsonite, alkali-rich compositions. Distally, the amphibole is dominated by arfvedsonite and riebeckite compositions with lower alkali content (Andersen, 1989). A similar trend is observed in pyroxenes at Fen, Alnö and Oldoinyo Lengai. At these complexes, Na-rich aegirine is prevalent in high grade fenite proximal to the contact, while distal pyroxene in lower grade fenite trends toward diopside and hedenbergite (see Fig. 10) (Morogan and Woolley, 1988; Andersen, 1989; Carmody, 2012). This trend is thought to be enhanced at Fen, due to compositional difference between multiple successive carbonatite intrusions expelling fluids with variable chemistry (Andersen, 1989).

With relatively few exceptions, a feature common to fenitic pyroxenes and amphiboles, including those displayed in Fig. 9, is the high and apparently non-stoichiometric silica content. The majority of amphibole analyses show excess Si relative to the tetrahedral position, leading to Si_T values > 8 (see Fig. 9).This phenomenon has previously been identified by Vartiainen and Woolley (1976, 1986, 1988) and is typically accompanied by low Al contents. The Ti content has also been observed to decrease in amphiboles and pyroxenes with increasing fenite grade (Kresten and Morogan, 1986; Morogan and Woolley, 1988). One explanation for apparently high Si content in these minerals could be the presence of significant light trace element substitutions such as Li, hosted in the amphibole C-site (Pfaff et al., 2008). Laser ICP-MS analysis of silicate minerals from the Gardar Province, South Greenland, has shown high Li concentrations up to 2895 ppm in amphiboles and 278 ppm in pyroxenes (Marks et al., 2004). These minerals are typically analysed by microprobe, which is unable to detect Li, leading to disproportionately high Si contents during formula calculations
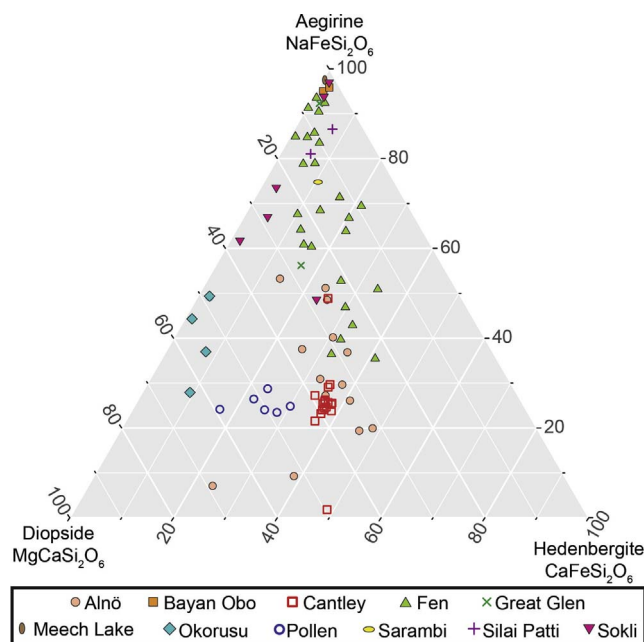
Fig. 10. Ternary diagram showing the proportions of end members analysed in pyroxenes from fenites surround carbonatite complexes around the world. All data available in Supplementary Table 3. Data sources: Alnö, Sweden (Morogan and Woolley, 1988); Bayan Obo, China (Le Bas, 2008); Cantley, Canada (Hogarth and Lapointe, 1984); Fen, Norway (Kresten and Morogan, 1986; Andersen, 1989); Great Glen, Scotland (Garson et al., 1984); Meech Lake, Canada (Hogarth, 2016); Okorusu, Namibia (Shivdasan, 2003); Pollen, Norway (Robins and Tysseland, 1983); Sarambi, Brazil (Haggerty and Mariano, 1983); Silai Patti, Pakistan (Le Bas, 2008); and Sokli, Finland (Vartiainen and Woolley, 1976).

(Pfaff et al., 2008).

2.3.2. Potassic fenites

Potassic fenites can contain up to 90% K-feldspar in addition to albite, relict quartz and a minor mineral assemblage including apatite, pyroxene and rutile (Le Bas, 2008; Doroshkevich et al., 2009). Alternatively, the addition of Mg to a potassic fenite can cause the phlogo-pitization of K-feldspar, forming widespread or localized accumulations of phlogopite such as those observed in the Sokli fenite (Vartiainen and Woolley, 1976). Intense fenitization can ultimately lead to a rock containing high proportions of feldspar, assuming that the original protolith is Si-bearing. This process has been called convergent fenitization and is common in potassic fenite, but uncommon in sodic fenite (Heinrich, 1966). As discussed in Section 2.2, potassic fenites are typically brecciated (see Table 1) and intruded by later stage magmatic events or sodic fenite veins.

2.3.3. Glimmerites

Although not as common as orthoclase-rich fenites, a substantial proportion of carbonatites (~20%, see Table 1) are associated with micaceous metasomatic rocks (Rosatelli et al., 2003), which have not been well-documented or explained. Rocks consisting almost entirely of mica (see Fig. 7D) are conventionally labelled glimmerite and traditionally refer to ultramafic intrusive units (Khamrabayev et al., 1992; Le Maitre et al., 2002). Therefore many glimmerites associated with carbonatites have also been interpreted as igneous (e.g. Hornig-Kjarsgaard, 1998; O'Brien et al., 2015; Sarapää et al., 2015). However, observations at complexes such as Mt Weld, Australia suggest this viewpoint requires revision. This carbonatite complex is surrounded by a 500 m wide fenite aureole, which gradually transitions from a po-tassium-rich phlogopite rock into a country rock of mafic volcanics (Hoatson et al., 2011), indicating that the glimmerite is not a primary igneous rock. Carbonatite veins and bodies at Bull Hill in the Bear

Lodge Mountains, USA, Aley and Upper Fir, Canada (Chakhmouradian et al., 2015; Mitchell, 2015; Moore et al., 2015) are all surrounded by halos of phlogopite glimmerite at the country rock contact. Phlogopite is also widespread in fenites at Sokli, forming along veins or widely disseminated throughout the fenite and thought to be the result of feldspar replacement due to potassic metasomatism (Vartiainen and Woolley, 1976). Khamrabayev et al. (1992) observe that micas found in association with carbonatites are often devoid of any accessory inclusions such as apatite and zircon that are typical of igneous mica. Textural evidence and alteration patterns therefore suggest that at least some glimmerites associated with carbonatites are the result of meta-somatic alteration of Mg-rich country rocks and are not igneous in origin (Khamrabayev et al., 1992; Rosatelli et al., 2003; Jones et al., 2013; Chakhmouradian et al., 2015).

2.4. Rheomorphic fenites

Melting of fenites may occur if volatiles, such as CO_2 and H_2O, and alkalis are introduced into the country rock by fluids exsolved from carbonatite or alkali-silicate magmas. Continued fluxing of volatiles could sufficiently depress the solidus to cause partial melting and in-jection of fenites into both the carbonatite and surrounding country rock (King and Sutherland, 1966; Evdokimov, 1982; Haggerty and Mariano, 1983; Cooper and Reid, 2000). Heinrich (1966) suggests that mobilization occurs to such a degree that the fenite behaves as a magma, however, this does not necessarily imply that the fenite has melted completely. Partial fenite melting to produce a crystal mush can occur at temperatures of ~700 °C, forming magmatic textures observed in rheomorphic fenites. The addition of volatiles from CO_2 and H_2O-rich fenitizing fluids could therefore depress the solidus of particular country rocks such as metasediments or ultra-mafics, below the esti-mated fenitization temperature of 400–500 °C (von Eckermann, 1966; Currie and Ferguson, 1971; Le Bas, 1981; Haggerty and Mariano, 1983; Morogan and Martin, 1985; Rosatelli et al., 2003). Rheomorphism of fenites is very difficult to prove or disprove on the basis of field or petrographic evidence alone, which may explain the skepticism and controversy that surrounds the subject and consequent lack of research.

Isotopically, fenites display a continuous evolution from initial country rock to the magmatic source of the fenitizing fluids. Ijolites at Iivaara, Finland are observed to grade into metasomatized country rock, suggesting that the ijolites were formed, at least in part, by rheomorphism of the high grade fenite (Kramm, 1994). Differences in Sr and Nd isotopic signatures and trace element abundances are used to support a different genetic source between recrystallized and primary magmatic ijolites. Rheomorphic fenites in the Salitre I complex, Brazil were described by Haggerty and Mariano (1983) as dykes consisting of aegirine, nepheline and sanidine. They are interpreted to be of non-igneous origin due to their highly oxidized nature, a common feature of fenite, and the paucity of alkaline pyroxene and magnetite observed in the local igneous suite. Isotopic methods were used by Kramm and Sindern (1998) to differentiate between texturally and petrographically similar magmatic syenite and syenitic fenites at Oldoinyo Lengai, Tanzania. The latter are high grade fenites with a magmatic texture thought to originate by partial melting.

The term pseudotrachyte was first introduced by Sutherland (1965a) to describe trachytes that were not intrusive, but appeared to have formed *in situ*. The term was used to describe trachyte-like rocks from Toror, Alnö and Kaiserstuhl. Described as being derived from brecciated feldspathic fenites that had become locally mobilized (Sutherland, 1965b; Le Bas, 1981), these rocks had all the character-istics of a primary magmatic trachyte: sheeted, porphyritic, aphanitic groundmass and flow textures (Sutherland, 1965b). Pseudotrachytes were also described by Cooper and Reid (2000) at Dicker Willem, alongside Sr, Nd and Pb isotope data that resembled those of the high grade potassic fenites, not the magmatic suite of rocks. The transition of a recrystallized feldspathic rock to feldspathic breccia, and then

Table 1
Summary of fenite characteristics for key carbonatite complexes used in this manuscript. Fenite size describes distance from carbonatite to outer detected limit of fenite.

Complex	Country	Location	Carbonatite Types	Age	Country Rock	Fenite Size	Fenite Characteristics	Fenite Mineralogy	References
Alnö	Sweden	62.4500, 17.1833	Calcite, dolomite: diatreme, sheet dykes	Cambrian: 585 Ma	Gneisses	500–600 m	Sodic, intermediate, potassic, pseudotrachytes, 6% volume loss	Albite, K-feldspar, arfvedsonite, aegirine-augite	Morogan (1989), Skelton et al. (2007)
Amba Dongar	India	21.9875, 74.0617	Calcite, ankerite, siderite: diatreme, ring dykes	Cretaceous: 66–62 Ma	Quartzitic sandstone	< 300 m	Deeper sodic, shallower potassic	Sodic: aegirine-augite, alkali feldspar, quartz. Potassic: K-feldspar, quartz, albite	Doroshkevich et al. (2009)
Araxá	Brazil	−19.6333, −46.9333	Dolomite, calcite: intrusions, veins	Cretaceous: 90–80 Ma	Quartzites, schists	2.5 km	Glimmerite from fenitization of pyroxenites		Traversa et al. (2001), Mitchell (2015)
Bayan Obo	China	41.80194, 109.9900	Dolomite: intrusions	Meso-proterozoic: 1656–1223 Ma	Meta-sandstones, dolomite marbles	2–4 m	Early sodic, later potassic	Sodic: amphibole, albite, iron oxides, microcline. Potassic: K-feldspar cut by albite veins	Le Bas (2008), Xu et al (2008), Wall (2014)
Bear Lodge	USA	44.4833, −104.4500	Calcite: veins and intrusions in diatremes	Eocene: 45 Ma	Granite		Glimmerite, potassic		Moore et al. (2015)
Chipman Lake	Canada	49.9667, −86.2000	Dolomite, ankerite: intrusions in stockwork	Proterozoic: 1022 Ma	Granites, metavolcanic greenstones	Broad	Early sodic, later potassic	Sodic: alkali feldspar, alkali-amphiboles, carbonate. Potassic: phlogopite, alkali-amphiboles	Platt and Woolley (1990)
Dicker Willem	Namibia	−26.4667, 16.0167	Calcite: cone sheets, intrusions, plugs, breccia pipes	Eocene: 49 Ma	Granitoids, granite gneisses		Breccia, pseudotrachytes, potassic	Orthoclase, albite, hematite, calcite	Reid and Cooper (1992), Cooper and Reid (2000)
Fen	Norway	59.2716,9.3066	Calcite, dolomite, siderite: ring complex, intrusions, veins, intrusions in diatreme	Neoproterozoic: 578 Ma	Granitic gneiss	> 1.5 km	Breccia, potassic, sodic. At least 2 stages	Potassic: mica, amphibole, calcite, apatite. Sodic: alkali feldspar, aegirine-augite, sodic-amphiboles (Magnesio-arfvedsonite, riebeckite, ferro-richterite)	Kresten and Morogan (1986), Andersen (1989), Dahlgren (1994), Verschure and Maijer (2005)
Kangun-kunde	Malawi	−15.1240, 34.9103	Dolomite, ankerite: vent, veins	Cretaceous: 136–123 Ma	Amphibolites, quartz reefs, granitic pegmatites	> 1 km	Breccia, potassic, sodic	Orthoclase, plagioclase, alkali-amphiboles (riebeckite, magnesio-arfvedsonite, crossite, soda-tremolite), aegirine, calcite, ilmenite, phlogopite	Woolley (1969)
Lofdal	Namibia	−20.3500, 14.7500	Calcite, dolomite, ankerite: plutonic, dyke swarm, diatremes	Proterozoic: 765 Ma	Gneisses, schists	> 3 m	Breccia, potassic, sodic	K-feldspar, albite, calcite	Wall et al. (2008), Bodeving et al. (2017)
Mountain Pass	USA	35.4833, −115.5333	Calcite, dolomite, ankerite: intrusions	Proterozoic: 1375 Ma	Schists, gneisses	> 200 m	Breccia, potassic	K-feldspar, phlogopite, carbonate, magnesio-riebeckite	Castor (2008)
Mt Weld	Australia	−28.8635, 122.5475	Calcite, dolomite: vent, stocks, intrusions	Proterozoic: 2025 Ma	Sedimentary-volcanic sequences	500 m	Breccia, glimmerite	Phlogopite-rich	Hoatson et al. (2011)
Okorusu	Namibia	−20.0331, 16.7667	Calcite: plutonic, intrusions	Cretaceous: 137–124 Ma	Greywackes, quartzites, schists, limestones	> 1 km	Breccia, potassic, sodic, pyroxenite	Potassic: K-feldspar. Sodic: aegirine-augite, calcite, biotite, sodic-amphiboles, albite	Bühn et al. (2001, 2002)
Sokli	Finland	67.7973, 29.3221	Calcite, dolomite: pipe, intrusions, veins in stockwork	Devonian: 370–360 Ma	Gneisses, amphibolites, schists, ultramafics	1–2 km, >30 km²	Breccia, potassic, sodic	Amphibole, phlogopite, carbonate	Appleyard and Woolley (1979), Vartiainen and Paarma (1979), Al Ani and Sarapää (2009), Sarapää et al. (2013)
Songwe Hill	Malawi	−15.6897, 35.8153	Calcite, ankerite: vent, intrusions		Granulites, gneisses	> 1 km	Breccia, potassic, sodic (Chenga)	Potassic: K-feldspar. Sodic: aegirine-augite, sodic-amphiboles, albite	Croll et al. (2015)
Tundulu	Malawi	−15.5391, 35.8069	Calcite, ankerite, siderite: pluton, intrusions, vents, possible diatreme	Cretaceous: 133 Ma	Granulties, gneisses, granites	2.3 km	Breccia, potassic, sodic	Potassic: orthoclase, microcline. Sodic: aegirine, sodic-amphiboles, albite, orthoclase, calcite	Garson (1965), Ngwenya (1994), Woolley (2001), Broom-Fendley et al. (2016)
Wasaki Peninsula	Kenya	−0.4667, 34.3833	Calcite, siderite: intrusions, veins, diatreme	Miocene: 16–13 Ma	Granodiorite	200–300 m	Breccia, potassic	Potassic: orthoclase, albite, aegirine-augite	Woolley (2001), Le Bas (2008)

Table 2
Summary of critical metal enrichment in carbonatite and fenite at complex examples used in manuscript.

Complex	Commodity	Carbonatite Enrichment	Fenite Enrichment	Fenite Characteristics	Fluid chemistry	Notes	References
Alnö	REE	< 1463 ppm	Potassic: 102–499 ppm TREE	Sodic, intermediate, potassic, pseudotrachytes, 6% vol. loss	PO_4^{3-}, CO_3^{2-}, HCO_3^-, F^- rich, 640 °C	Increasing REE fractionation with decreasing fenite intensity	Morgan (1989), Hornig-Kjarsgaard (1998), Skelton et al. (2007)
Amba Dongar	REE, F	15 wt% TREE	HREE, 11.6 Mt at 30 wt% CaF_2	Deeper sodic, shallower potassic	F-rich, 600–700 °C	Fenite Nd/La ratio > carbonatite ratio	Deans et al. (1972), Mariano (1989), Palmer and Williams-Jones (1996), Doroshkevich et al. (2009)
Araxá	Nb	1.6 wt% Nb_2O_5, 1737–16906 ppm TREE	Laterite: 462 Mt at 2.5 wt% Nb_2O_5. Glimmerite: 200–7316 ppm TREE	Glimmerite		Supergene laterite enrichment of Nb	Traversa et al. (2001), Mitchell (2015)
Bayan Obo	REE	750 Mt at 4.1 wt% REO		Early sodic, later potassic	Fenite amphiboles and biotites enriched in F		Smith (2007), Le Bas (2008), Xu et al. (2008), Wall (2014)
Bear Lodge	REE, Gold	13.3 Mt at 3.2 wt% TREO (Bull Hill Diatreme)	LREE	Glimmerite, potassic	F^-, SO_4^{2-}, MREE rich		Andersen et al. (2013), Moore et al. (2015)
Chipman Lake	REE	1–17% REE in early burbankite		Early sodic, later potassic	Early Na and F-rich fluid		Platt and Woolley (1990)
Dicker Willem		32–352ppm Nb, 168–515 ppm TREE		Breccia, potassic, pseudotrachytes	HCO_3^-	Low temperature hydrothermal overprint	Reid and Cooper (1992), Cooper and Reid (2000)
Fen	REE, Nb	1.03–4 wt% TREO, 0.35–0.45 wt% Nb_2O_5	385–585 ppm TREE	Breccia, potassic, sodic. At least 2 stages.	CO_3^{2-}, PO_4^{3-}, F^- rich	Increasing REE fractionation with decreasing fenite intensity	Andersen (1986), Lie and Østergaard (2011), Mitchell (2015)
Kangun-kunde	REE	0.37–10 wt% TREO		Breccia, potassic, sodic	f^-, PO_4^{3-}, Cl^- rich		Woolley (1969), Woolley and Kempe (1989), Wall et al. (2008), Dowman (2014)
Lofdal	REE	0.43–0.64 wt% TREE, HREE enriched	10–25% HREO + Y, 1393 ppm Nb	Breccia, potassic, sodic	Early F^- rich fluid contains LREE, later HREE	Enrichment by late-stage hydrothermal activity	Wall et al. (2008), Bodeving et al. (2017)
Mountain Pass	REE	20 Mt at 8.9 wt% TREO		Breccia, potassic			Castor (2008)
Mt Weld	REE, Nb, P	17.5 Mt at 8.1 wt% TREO; 37.7 Mt at 1.07 wt% Nb_2O_5; 77 Mt at 13.5 wt% P_2O_5	< 9 wt% TREO	Breccia, glimmerite		Supergene laterite enrichment	Hoatson et al. (2011)
Okorusu	F, REE, P	0.2 wt% TREO; 1–3 wt% P_2O_5	80–285 ppm REE in fluorite; 2.9 Mt at 61% CaF_2; 2.7 Mt at 49% CaF_2	Breccia, potassic, sodic, pyroxenite	Up to 3 wt% REE and 3 wt% F. Late stage fluids HCO_3^-	Late stage mineralization HREE enriched, sodic fenite may be related to nepheline syenite	Bühn et al. (2001, 2002)
Sokli	REE, P	0.1–1.83 wt% TREE	1–2 wt% TREE	Breccia, potassic, sodic		Late stage dykes have highest REE potential	Al Ani and Sarapää (2013)
Songwe Hill	REE	8.4 Mt at 1.6 wt% TREO	1.37Mt at 1.61 wt% TREO	Breccia, potassic, sodic		Late stage black carbonatite av. 3.7% TREO	Croll et al. (2015)
Tundulu	REE, P	2.3 Mt at 12.5 wt% P_2O_5; 3.27 Mt at 2.4 wt% TREE (Nathace Hill)		Breccia, potassic, sodic (Chenga)	Acidic, containing F, P, Cl	Late stage HREE enrichment	Ngwenya (1994), Broom-Fendley et al. (2016), Kruger (2016)
Wasaki Peninsula		322 ppm La, 957 ppm Ce		Breccia, potassic			Bowden (1985), Woolley (2001), Le Bas (2008)

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mobilized pseudotrachyte that intruded the country rock at Tundulu, was traced by Garson (1962). These rocks consist of small fragments of feldspar, recrystallized to form clear K-rich feldspar laths in a microcrystalline matrix (Le Bas, 2008).

3. Fenites related to economic deposits

Alkaline and carbonatite complexes are often associated with high concentrations of economically important minerals, enriched in REE, Nb and phosphate (Wall, 2014; Goodenough et al., 2016). These rocks also host many non-critical resources such as iron, copper, titanium, fluorite, uranium, thorium and vermiculite, some of which have been mined since 770 AD (Heinrich, 1966; Mariano, 1989; Pell, 1996).

Localities described and discussed in this section have been defined as 'of economic importance', either as a past producer, an active mine or a deposit (i.e. those with a quantified mineral resource) by Woolley and Kjarsgaard (2008).

3.1. Fenites at REE-rich deposits

Drawing similarities between fenites surrounding REE-rich carbonatites is problematic due to the majority of deposits lacking detailed descriptions, including attributes or mineralogy, of any fenite present. Additionally, fenites are zoned, both horizontally and vertically, and therefore differing levels of erosion can remove important features or not reveal fenites adjacent to intrusions, causing difficulties when attempting to model an integrated system.

Fractional crystallization processes cause magmas to evolve (Thompson et al., 2002; Ray and Shukla, 2004), typically in a plutonic environment, to form a typical sequence of multiple carbonatite generations. These generations may not all be observed at a given site, but typically evolve from a calcite to dolomite and then a later ferrocarbonatite phase (Heinrich, 1966; Le Bas, 1981). Magma evolution is associated with increasing Fe, Ba, Mn and decreasing Sr (Le Bas, 1981), and REE tend to be concentrated in the later or last carbonatite differentiates (Heinrich, 1966; Le Bas, 1981; Wall, 2014). Each phase of carbonatitic magmatism is associated with the release of fenitizing fluids, leading to multiple stages of fenitization which are represented as different assemblages or vein generations in the country rocks. As such, the complexity of a fenite could potentially reflect magma evolution, and therefore the likelihood of REE-enrichment in the source intrusions.

The Fen Complex is one such site that displays all three of these carbonatite species, with the last differentiate (ankerite carbonatite) enriched in Th and REE up to 1.5 wt% (Andersen, 1986; Lie and Østergaard, 2011; Marien et al., 2017). This is reflected in fenite surrounding the complex which increases in total rare earths (TREE) and HREE with increasing intensity of fenitization (Andersen, 1986; Lie and Østergaard, 2011). Several stages of carbonatite intrusions can also be observed at Mountain Pass, including calcite, dolomite and a stage with composition intermediate between these two which contains the most economic REE grades. Fenitized gneisses can contain up to 9% rare earth oxides (REO) hosted by allanite. These fenites contain magnesio-riebeckite that replaces earlier amphibole and pyroxene (Castor, 2008).

Fenites surrounding REE-enriched intrusions typically display both sodic and potassic metasomatism, suggesting fenitization resulted from multiple fluid pulses. Amba Dongar is a clear example of this association, displaying vertical zonation of sodic and potassic fenites (see Section 2.1) related to calcite, ankerite and siderite carbonatite intrusions. Sodic fenites at this site contain mineral assemblages of aegirine-augite, alkali feldspar and quartz whereas the potassic fenite consists predominantly of K-feldspar, quartz and albite with only minor pyroxene. These florencite-bearing potassic fenites display higher Nd/La ratios than the carbonatite intrusions, indicating HREE enrichment in the fenites (Doroshkevich et al., 2009). Late-stage carbonatite dykes cross-cut both sodic and potassic fenites in the Jammi area of the Sokli

Complex, and host the highest REE content, enriching the surrounding fenites up to 2% TREE (Sarapää et al., 2013). Intensely brecciated potassic fenites have been recorded at the Lofdal carbonatite-nepheline syenite complex, extending up to several metres from carbonatite intrusions and consisting predominantly of K-feldspar (Bodeving et al., 2017). Calcite carbonatite at Lofdal contains on average 1300 ppm TREE compared to 356 ppm TREE in the potassic fenite. Brecciated and intensely metasomatized early sodic fenites several tens of metres wide, consist almost entirely of albite and quartz and host aggregates of later HREE-rich xenotime (Swinden and Siegfried, 2011; Dodd et al., 2014).

As discussed in Section 2.2, brecciation events often accompany carbonatite emplacement (Heinrich, 1966; Tuttle and Gittins, 1966; Le Bas, 1977; Rubie and Gunter, 1983). Although incidents of brecciation have not been reported at every REE-rich carbonatite complex, there is a strong correlation between the presence of breccia and mineralization. Table 2 shows that 70% of REE-enriched fenites have brecciation reported in their associated literature. Lack of observation does not necessarily mean lack of brecciation, due to the literature focus, bias of observations and level of erosion. Widespread brecciation associated with carbonatite emplacement indicates some pulses of fluids and volatiles sourced from the evolving magma are released explosively (Verplanck et al., 2014). The presence of these fluids and volatiles attests to the evolution and crystallization of the carbonatite magma, the same processes that concentrate incompatible REEs in the residual carbonatite melt (Heinrich, 1966; Le Bas, 1981; Wall, 2014), therefore it is logical that an association between brecciation and mineralization would exist.

The Chilwa Alkaline Province comprises at least 14 carbonatite and 15 alkaline intrusions (Woolley, 2001). Exposures of breccia can be found at six of these intrusive complexes, the majority of which consist of feldspathic breccia (see Fig. 7A) in close proximity to the intrusion-fenite contact. The Kangunkunde carbonatite is surrounded by a feldspathic breccia which grades into an intermediate to sodic fenite with distance from the intrusion. However, the Chilwa Island breccia exhibits a sharp contact and much higher concentrations of potassium (Woolley, 1969; Dowman, 2014). Breccias at Songwe Hill, Malawi can be divided into carbonatite and fenite breccias, the latter of which can contain metasomatized clasts several metres in diameter and hosting up to 1.37 Mt of mineralized material at a grade of 1.61% TREO (Croll et al., 2015). Brecciation is not restricted to complexes in Malawi, but is observed surrounding carbonatites worldwide. Intensity of brecciation often decreases with distance from the intrusion-fenite contact such as the multi-stage brecciation at Fen (Verschure and Maijer, 2005; Lie and Østergaard, 2011), Sokli (Vartiainen and Paarma, 1979) and Lofdal. Quarrying within the Lofdal complex has exposed breccias containing clasts fenitized to varying degrees, thought to represent multi-phase gaseous release events preceding the intrusion of a large body of carbonatitic magma and numerous vein systems (see Fig. 7B).

The role of ligands in the transportation of REEs into the fenite is discussed in greater detail in Section 4. Fenitizing fluids are often carried away in vein networks and dissipate, providing little evidence beyond rare fluid inclusions to support their theoretical composition. However, some complexes contain minerals directly precipitated from the fenitizing fluids that provide clues as to their chemical composition. One example is the presence of minerals such as fluorapatite in the fenites of Lofdal, Namibia that attests to the presence of F^- and PO_4^{3-} (Wall et al., 2008) in the fenitizing fluids. Late stage HREE-enriched fluorite at Okorusu, Namibia is thought to result from the growing dominance of carbonate over fluoride ligand complexing with time (Bhn et al., 2002), resulting in overprinting of the fenite near the carbonatite-country rock boundary with 7–10 Mt of 35 wt% CaF_2 (Deans et al., 1972; Mariano, 1989). Enrichment of PO_4^{-3}, CO_3^{-2}, HCO_3^- and F^- in the fenitizing fluids of the Alnö Complex, facilitated the mobilization of REE out of the carbonatite intrusion and into the surrounding fenite aureole, enriching the adjacent potassic fenite by 102–499 ppm TREE (Morogan, 1989). The Amba Dongar carbonatite complex has

been actively mined for fluorite since 1972. The 11.6 Mt deposit at 30 wt% CaF_2 is hosted in fenite veins and fractures formed by the interaction of carbonatite-derived fluids and surrounding Cretaceous sandstones (Deans et al., 1972; Mariano, 1989; Palmer and Williams-Jones, 1996). This florencite-bearing fenite was enriched in REE before late stage fluorite precipitation (Doroshkevich et al., 2009) resulting from the interaction of F-bearing carbonatite-derived fluids and low temperature Ca-bearing meteoric fluids (Palmer and Williams-Jones, 1996).

The country rock into which the carbonatite intrudes and size of the resulting fenite show no apparent correlation with REE enrichment in the source intrusion or the fenite. Carbonatites can intrude a wide variety of country rock types which have no bearing on the degree of REE-enrichment in the intrusion or resulting fenite (e.g. sandstone, Amba Dongar – Doroshkevich et al. (2009); granite gneisses, Sokli - Appleyard and Woolley (1979), Vartiainen and Paarma (1979), Sarapää et al. (2013); and sedimentary sequences, Bayan Obo – Le Bas (2008) and Mianning, China – Xie et al. (2014)). The degree of REE enrichment in the source intrusion is not proportional to the radius of subsequent fenitization. Carbonatite at Dorowa, Zimbabwe contain < 160 ppm TREE, and are surrounded by > 1 km of fenitization (Johnson, 1966; Harmer et al., 1998). In contrast, the ankerite carbonatites at Amba Dongar locally contain > 15 wt% TREE and are associated with < 300 m of fenitization (Doroshkevich et al., 2009).

3.2. Fenites at niobium-rich deposits

Carbonatites and alkaline rocks are the world's largest source of niobium (Mariano, 1989), hosting all currently and formerly operating niobium mines. Niobium tends to be found in the intermediate stages of carbonatite differentiation, in contrast to REE which tend to be found in the later, more evolved magmas (Mariano, 1989). Primary carbonatite-hosted niobium deposits typically contain between 3000 and 5000 ppm Nb, however, secondary and supergene processes can further enrich niobium concentration by more than a factor of 10 (Mitchell, 2015). Intense weathering of the Araxá Complex, Brazil has produced a lateritic residue containing 462 Mt of ore at 2.5 wt% Nb_2O_5 with a thickness of > 120 m (Mitchell, 2015).

The high charge to ionic radius ratio of niobium makes it insoluble in fluids other than silicate melts, therefore ligands must be present to enhance its mobility (Linnen et al., 2014). Experimental study of the solubility of Nb in aqueous solutions indicates an increase in solubility with an increased concentration of HF, indicating ligand complexing to form $NbF_2(OH)_3$ (Timofeev et al., 2015). As such, niobium should be mobilized by fenitizing fluids into the metasomatized country rock (Le Bas, 2008). Evidence of this process has been reported at Kangunkunde in the form of fenites enriched in Nb to concentrations higher than those of the source carbonatite, facilitated by the presence of F^- in the fenitizing fluids (Dowman, 2014). Amphiboles and biotites associated with niobium mineralization in the Bayan Obo Complex are enriched in fluorine relative to the rest of the fenite, indicating high HF activity in the fenitizing fluids (Smith, 2007). Mitchell (2015) also states that pyrochlore can be found in significant quantities (50 vol%) in fenite veins associated with Nb-rich carbonatite complexes such as Sarfartôq, Greenland and Prairie Lake, Canada. Therefore, Nb is being mobilized in fenitizing fluids in these complexes. Pyrochlore group minerals are major constituents in the carbonatites, phoscorites and metasomatic fenite aureoles of the Sokli alkaline-carbonatite complex (see Fig. 7F) (Lee et al., 2006).

4. Fenite as an exploration indicator

Fenitizing fluids contain ligands such as chloride-, fluoride-, sulfate-, phosphate- and/or carbonate anions, which can form complexes with REE and Nb, substantially enhancing their solubility (Andersen, 1986; Haas et al., 1995; Williams-Jones et al., 2012; Tsay et al., 2014)

and allowing transport of these elements into the surrounding fenite aureoles (see Table 2). Here they precipitate to form mineral assemblages of REE, Nb and fenite minerals (see Fig. 7E) (Hogarth, 2016; Bodeving et al., 2017; Dowman et al., 2017).

The strength of different REE and Nb complexes in aqueous solution can vary, depending on the ligand. Research into this speciation indicates that Cl^- ligands increase LREE solubility, whereas F^- and CO_3^{2-} ligands form stronger complexes with MREE and HREE (Williams-Jones et al., 2012; Tsay et al., 2014). The composition of the fenitizing fluid can therefore lead to LREE/HREE fractionation. Harlov et al. (2002) indicates that Cl-rich and F-rich fluids could have responsible for the depletion of Y, REE, Na and Si from apatites at Kiirunavaara, Sweden, and Broom-Fendley et al. (2016) observed a similar LREE depletion in apatites from the Kangankunde carbonatite. Dolomitic melts at the Seligdar complex, Russia, evolved brines containing 38–42 wt% NaCl-eq which likely removed LREE and Th from apatites, and redistributed these elements into monazite-(Ce) and xenotime-(Y) (Prokopyev et al., 2017). Calcite carbonatite ring dykes on Chilwa Island were depleted in HREE relative to high grade fenites and breccias which have higher HREE:LREE ratios. This fractionation most likely resulted from F^- in late-stage fenitizing fluids preferentially mobilizing HREE, as evidenced by fluorite, quartz and barite veining (Dowman et al., 2017). Similar trends have been observed at Fen and Alnö, both of which display increasing REE fractionation with decreasing intensity of fenitization (Morogan, 1989; Verschure and Maijer, 2005). Sodic fenites at Alnö display greater HREE enrichment, with La/Lu ratios increasing from low to high intensity fenitization, proximal to the carbonatite (Morogan, 1989).

Micro-mineral assemblages enriched in REE and Nb have been recorded in fenites globally (see Fig. 7E and F, Table 2). Locations of many carbonatite complexes have already been well documented (Woolley and Kjarsgaard, 2008), however drilling is often the most costly stage of exploration. Thus, the features, mineralogy and geochemistry of a fenite aureole may act as an exploration indicator to determine the level of REE or Nb enrichment in the source intrusion. In addition, fenits have a large footprint, sometimes up to several kilometres diameter and extensive in depth. The distinctive characteristics of the concentric fenite aureole pattern, easily distinguished in the field, could act as a vector toward unexposed carbonatite intrusions and ore-deposits. Recognition of potassic feldspar-pyrite alteration related to gold mineralization in alkaline igneous rocks has already been used as a key to successful exploration at Bear Lodge (Noble et al., 2009). Broad zones of similar, pervasively-altered country rock accompany vein-hosted gold mineralization at Cripple Creek, USA, which have also been noted for their REE enrichment and the presence of bastnäsite and monazite (Noble et al., 2009). Alkali metasomatism associated with potassic syenites has also been used to focus gold exploration in Russia (Dvornik, 2015).

5. Discussion

5.1. Stages of fenitization and their timing

Fenitization is described as a polyphase process, resulting from multiple pulses of fluid released from a cooling and crystallizing intrusion (Morogan, 1994; Le Bas, 2008). These fluids form inner potassic and outer sodic fenite aureoles, however there is still much debate about how they form. Many theories exist as to whether each aureole relates to a discrete fenitization event involving fenitizing fluids of different composition, or whether each fluid pulse evolves with distance from the source intrusion.

The elemental exchange that occurs between the fluid and rock during metasomatism can cause the fluid to evolve spatially and temporally (Harlov and Austrheim, 2012; Kusebauch et al., 2013). As such, intense fenitization near the intrusion-country rock boundary could theoretically change the fluid chemistry, forming a fenite of differing

chemical composition distal to the source intrusion. This process could potentially explain the pattern of inner potassic and outer sodic fenite aureoles observed at many carbonatite complexes (see Section 2.3). However, the change in fluid composition would likely be gradual as fenitization reactions progressed. A gradational boundary between aureoles would therefore be expected, which is not recorded in the literature or observed by the authors.

In contrast, many carbonatite complexes display cross-cutting relationships between early sodic fenites cut by later potassic stages (Woolley, 1969; Woolley, 1982). A number of explanations have been proposed for the expulsion of fluids with different chemistry, including falling temperatures or increasing CO_2 levels (Rubie and Gunter, 1983), or an initial Na-rich intrusion which gradually loses Na to fenitization until K becomes the dominant alkali (Woolley, 1982). Fluid inclusion studies of the Amba Dongar fenites indicate that Na-rich fluids were expelled first at a depth of > 10 km followed by later expulsion of K-rich fluids upon the magma reaching shallower crustal levels (Doroshkevich et al., 2009). The presence of multiple cross-cutting vein generations (Le Bas, 2008) and zoned apatites also provide evidence to support fenite formation by multiple fluid pulses as opposed to a single evolving fluid.

The process of fenitization is often considered to involve the metasomatic addition of alkalis and removal of silica from the country rock (e.g. Brögger, 1921; von Eckermann, 1948; McKie, 1966). The metasomatic replacement of K-feldspar with plagioclase also releases excess silica, often causing intergrown plagioclase-quartz textures such as myrmekite (Becke, 1908). However, the fate of this silica in the carbonatite-fenite system has been an ongoing conundrum for geologists.

Upon studying the Alnö carbonatite complex, von Eckermann (1948) hypothesized that silica removed during metasomatic processes migrated into the carbonatite intrusion. Woolley (1969) expanded on this idea and suggested that silica was driven inward and upward, carried either up a central pipe incorporated within the magmatic intrusion, or carried to the surface as a brine. This hypothesis is supported by Skelton et al. (2007) and Vartiainen and Woolley (1976). The latter suggested that high level extensively silicified carbonatites in Rufunsa Valley, Zambia may have acted as a sink for fenite-derived silica. The presence of wollastonite in the outer zone of the carbonatite at Alnö, Sweden is thought to have formed via the metasomatic reaction of calcite with quartz (Skelton et al., 2007; Putnis and Austrheim, 2010), also indicating an ingress of silica down gradient into the carbonatite. Silica in the Melteig fenites of the Fen Complex, Norway appears to have a different destination however. Observations by Kresten and Morogan (1986) indicate that low grade fenites in this area contain more quartz than the initial gneissic granite protolith and quartz veins are common, indicating a degree of silicification. Late stage silica-rich veins are common in many carbonatite complexes including Sokli, Finland (Vartiainen and Woolley, 1976) and the Wasaki Peninsula, Kenya (Le Bas, 2008), suggesting that fenitizing fluids which have exchanged alkalis for silica during metasomatic reactions, may then transfer and precipitate quartz in the outer aureole. The common factor between these complexes is that silicification appears to be the last stage of fenitization.

5.2. Implications of veining and brecciation

Brecciation has significant implications for fenitization and mineralization in carbonatite complexes, creating efficient fluid pathways and facilitating fluid movement (Verschure and Maijer, 2005; Lie and Østergaard, 2011) toward the outer fenite aureole (see Graphical Abstract). The importance of breccias in relation to fluid movement is demonstrated by feldspar-rich fenites at the Wasaki Peninsula, Kenya. These contain fractures filled with a mix of iron oxides, aegirine-augite, feldspars, carbonate and quartz that grade into a feldspathic breccia proximal to the intrusion (Le Bas, 2008). Brecciation also often preceedes mineralization such as F, Ba and U-Th mineralization (Le Bas,

1987) and is found to occur prior to REE-fluorcarbonate precipitation at Tundulu, Malawi (Broom-Fendley et al., 2016).

Formation of fine-grained mineral phases during fenitization may effectively act as a seal, retaining fluid in the immediate vicinity of the intrusion. This process is analogous to the kimberlite alteration model proposed by Afanasyev et al. (2014), in which fluids flowing through the pipe are proposed to reduce breccia porosity and permeability by alteration to fine hydrous minerals. This process suppresses fluid flow and effectively seals off unaltered sections, very applicable to fenites which display highly heterogenous intensities of metasomatism. Sealing of magmatic and hydrothermal fluids in the inner complex, by the formation of early fenites may lead to pressure build up exceeding lithostatic pressure, resulting in hydraulic fracturing and the formation of shock breccias. Rapid decompression following the failure of country rock can lead to boiling and separation of H_2O and CO_2 phases, causing destabilization of complexing ligands and subsequent mineral precipitation (Robb, 2005). Multiple pulses of these fluids form veins of varying composition throughout the lifetime of the complex (see Graphical Abstract). Early stage sodic fenite veins containing pyroxenes and amphiboles are superseded by intermediate stage Nb-bearing veins followed by late stage REE-bearing veins. The micro-mineral assemblages precipitated from these fenitizing fluids can provide information regarding element enrichment in the source intrusion.

The style of fenitization could also be used to determine the approximate extent of erosion and relative depth in a volcanic system. High pressures prevalent at deeper crustal levels resist the pervasive migration of fluid through the rock, and therefore favour flow in structural conduits such as veins (Robb, 2005). Deep crustal vein systems indicate that fluid is channelized on a coarse scale, although a small degree of pervasive diffusive scale can occur between veins (Newton, 1989). Intrusion of magma into very shallow crust, and the subsequent release of fluids, is typically accompanied by intense fracturing of the host rock (Meinert, 1992). Therefore the presence of breccia in a fenite aureole is likely to be indicative of very shallow crustal levels. Knowledge regarding the relative depth of erosion and position of the fenites in the volcanic system is important to determine where the source intrusion lies relative to the current surface, and whether there is potential for the presence of an associated mineral deposit. However, these fluid pathways are not mutually exclusive and veining can be spatially extensive and form throughout the intrusion's cooling history (Misra, 2000).

The fenite fluid flow pathways and the resulting fluid-rock interaction has important consequences for the morphology of reaction fronts and the distance over which elements can be transported, as demonstrated by skarn and porphyry stockwork systems (Ortoleva et al., 1987; Kelemen et al., 1995; Robb, 2005). Migration of fluids in fracture or vein networks limits the volume of country rock interacting with the fluid (Cartwright and Barnicoat, 1999), therefore maintaining chemical gradients over larger distances. Better understanding of the fluid flow mechanism and dynamics in fenites has important implications for understanding element redistribution from source intrusions into surrounding fenites. The presence of a fenite vein network could transport fluids further from the source, enriching the outer aureoles in elements such as REE and Nb. This geochemical signature and resulting indicative mineral assemblages could be used during exploration to find the source intrusion.

5.3. Properties and chemistry of fenitizing fluids

There have been a number of studies attempting to provide a chemical and thermodynamic framework for fenitization processes. Understanding the chemical and physical properties of the fenitizing fluids can assist in determining the nature of the magmatic source and any associated element enrichments, potentially indicating the presence of an economic mineral deposit. The multiple pulses of fluid associated with fenitization cause differences in the distribution and abundance of

REE in sodic, intermediate and potassic fenites (Morogan, 1989; Dowman, 2014) relating to evolution of the source melt.

Experimental work undertaken by Zaraiskii (1989) (summarized by Bardina and Popov (1994), Zharikov and Rusinov (1998)) indicates a lower fenitization temperature limit of 500 ± 30 °C at 1 kbar, defined by the stability of the aegirine-augite-microcline-perthite paragenesis. The upper limit of fenitization is not as well constrained, but probably approaches 700 °C, based on consensus of measured temperatures between 600 and 700 °C at Amba Dongar (> 700 °C, Williams-Jones and Palmer, 2002); Iivaara, Finland (660 °C, Sindern and Kramm, 2000); and Alnö (640 °C – Skelton et al., 2007). This temperature is supported by the stability of alkali amphiboles such as riebeckite and arfvedsonite, which are constrained between 650 and 800 °C (Kovalenko et al., 1977).

Fluids are considered to be highly oxidizing, causing significant quantities of Fe^{3+} to be incorporated into the fenite mineral assemblage, including feldspar, pyroxene and hematite crystals (Haggerty and Mariano, 1983). This trait is easily recognized using cathodoluminescence, due to ferric iron substituting in the tetrahedral sites of feldspar crystals, functioning as an activator for bright red cathodoluminescence (see Figs. 5C and D) (Mariano, 1983; Finch and Klein, 1999; Mariano and Mariano, 2014) - this is termed the "alkali ferric iron effect" (Carmichael and Nicolls, 1967).

Fenitizing fluids expelled from carbonatites are highly variable. Fluids are predominantly aqueous with relatively low activities of subordinate CO_2, but CO_2/H_2O ratios can vary greatly (Drüppel et al., 2005; Le Bas, 2008). Fluid inclusions of carbonatite-derived fluid at Kalkfeld, Namibia, analysed by Bühn and Rankin (1999), display a wide range in composition from CO_2-rich to Cl^- and HCO_3^--bearing aqueous fluids. However, they are typically thought to be enriched in alkalis, halogens, CaO, MgO and FeO, with varying proportions of Sr, Ba, Nb and REE (Morogan, 1989; Sindern and Kramm, 2000; Drüppel et al., 2005; Skelton et al., 2007). These fluids are also thought to be deficient in SiO_2 and Al_2O_3, thereby removing these elements from the country rock with subsequent redistribution in the fenite aureole (Morogan, 1989; Sindern and Kramm, 2000; Skelton et al., 2007).

Mass balance calculations of element transfer during fenitization have indicated a substantial volume loss during the process, calculated as a 6% volume loss in the highest grade fenite at Alnö (Morogan, 1989) and a 20% volume loss at Iivaara (Sindern and Kramm, 2000). This loss in volume is problematic when determining the true elemental gains/losses during fenitization, as observed changes may solely be due to loss of mass. To remedy this issue, Gresens (1967) developed an equation to determine the mass transfer during metasomatism, accounting for both volume and compositional changes. Grant (1986) later adapted this concept into the isochron diagram which uses elements with no apparent gain/loss during metasomatism as a reference to determine changes in volume and elemental concentrations.

Fluids related to the vertically zoned fenites of Amba Dongar have been extensively studied and modelled by Williams-Jones and Palmer (2002) based on fluid inclusion data. The first fluid to exsolve from the calcite carbonatite is thought to be at > 4 kb and > 700 °C, the same temperature as the carbonatite solidus, representing expulsion at a depth of > 10 km to form the lower sodic fenites. Upon reaching shallower crustal levels of 3–5 km depth, the last fractions of fluid exsolved. These fluids were solute-rich, displayed an intermediate K/Na ratio and were enriched in CaO, Al_2O_3 and SiO_2, forming the upper potassic fenite. Fenitization described at Alnö by Skelton et al. (2007) indicates an original mineral assemblage of biotite, quartz and oligoclase that was metasomatized to a secondary mineral assemblage of albite, K-feldspar, arfvedsonite and aegirine-augite by the addition of K_2O, Na_2O, ± CaO, MgO, FeO causing the release of SiO_2 and H_2O.

The genesis of nepheline resulting from metasomatic alteration of a silicate mineral assemblage, via nephelinization, has caused controversy since von Eckermann (1948) published his memoir regarding Alnö. Revisiting this problem, Tilley (1957) discovered feldspar

textures, such as rounded cores surrounded by nepheline rims and vermicular nepheline growths, that suggested a metasomatic origin. In contrast, Vartiainen and Woolley (1976) state that no nephelinization has been observed in fenites related to carbonatite intrusions. The albite-orthoclase join of the quartz-albite-orthoclase ternary diagram most likely represents the most extreme extent of de-silicification of which carbonatite-derived fenitizing fluids are capable. Although the metasomatic origin of the mineral is still debated, observations of nepheline in fenite aureoles have been recorded at many carbonatite complexes e.g. fenitization of granite at Oldoinyo Lengai (Morogan, 1994); fenitization of gneisses at Oka, Canada (Samson et al., 1995); in rheomorphic fenites surrounding the Paraná Basin carbonatites, South America (Haggerty and Mariano, 1983); and fenitization of granite gneisses at Gifford Creek, Australia (Pirajno, 2015).

5.4. Timescales of fenitization

Very little is understood in relation to the timescale over which fenitization occurs. The duration of fluid-rock interaction at Alnö has been calculated by Skelton et al. (2007) using the disparity between metasomatic reaction and isotope fronts, taking into account permeability enhancement by metasomatic reactions. An estimated timescale of 10^2–10^4 years has been proposed, based on the calculation that fluid diffusivity was $10^{-7} m^2 s^{-1}$ at 600 °C.

No other studies have been undertaken as a comparison, however analogies can be drawn between fenitization and metamorphism in the presence of a fluid phase. Thermodynamic modelling undertaken by Wood and Walther (1983) indicates that a prograde dehydration metamorphic reaction at 700 °C of 2 mm crystals, would reach completion in 70 years, with the H_2O/CO_2 ratio of the hydrothermal fluid having no effect on timescales. This large discrepancy between estimated timescales reflects the lack of understanding relating to fenitization processes, and identifies new research avenues to further our understanding of fluid-related mineralization.

5.5. Why do fenites associated with alkaline and carbonatite intrusions differ?

A detailed discussion of fenitization related to alkaline intrusions goes beyond the scope of this paper, however the extensive mineralization associated with large complexes such as those of the Kola Peninsula, Russia and Gardar Province, Greenland, emphasizes their importance in understanding these systems. Little research has been dedicated to the comparison of alkaline and carbonatite-related fenitization, mostly likely due to the ambiguity of fluid sources created by the close temporal and spatial association of these intrusions (Woolley, 2003; Le Bas, 2008).

Among the different magmas capable of generating fenitizing fluids, melteigite-ijolites and carbonatites appear to be associated with the most voluminous metasomatic overprint. However, peralkaline intrusions produce comparatively small fenites. For example, fenitization extends 1–2 km from the central Sokli carbonatite intrusion (Al Ani and Sarapää, 2009), whereas fenitization surrounding large, highly evolved, agpaitic nepheline-syenite intrusions such as Khibiny and Lovozero, Kola Peninsula, and Ilímaussaq, Greenland, does not typically exceed 100 m from the intrusion (Ferguson, 1964; Gorstka, 1971; Arzamastev et al., 2011).

This striking disparity was interpreted to result from a greater solubility of H_2O in peralkaline melts (Kogarko, 1977; Burnham, 1979; Giehl et al., 2013; Giehl et al., 2014), leading to the effective retention of volatiles in small batches of evolved residual melts enriched in alkalis, ligands, high field strength elements (HFSE) and other incompatible elements such as REE (Marks et al., 2003; Arzamastev et al., 2011; Giehl et al., 2014; Kozlov and Arzamastsev, 2015; Marks and Markl, 2015). These are hypothesized to cause limited fenitization, due to fluids exsolving after the bulk of the intrusion has already solidified
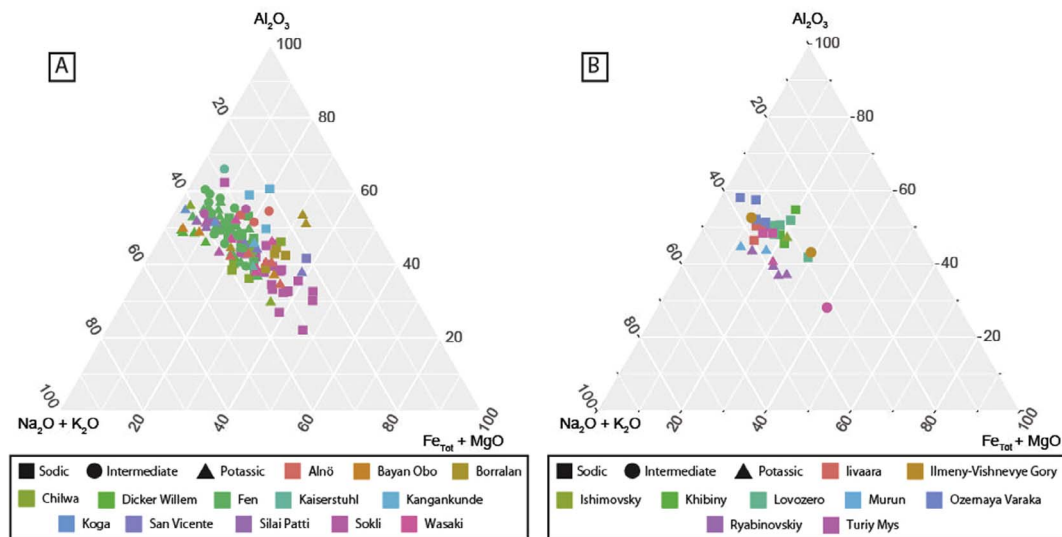
Fig. 11. A: Ternary diagram plotting Al_2O_3–Na_2O + K_2O–Fe_{Tot} + MgO concentrations of fenites related to carbonatite complexes around the world, categorized based on sodic, intermediate or potassic fenitization. B: Ternary diagram plotting Al_2O_3–Na_2O + K_2O–Fe_{Tot} + MgO concentrations of fenites related to alkaline complexes around the world, categorized based on sodic, intermediate or potassic fenitization. All data available in Supplementary Tables 1 and 4. Data sources: Alnö, Sweden, (Morogan, 1989); Bayan Obo, China (Le Bas, 2008); Borralan, Scotland (Woolley et al., 1972; Martin et al., 1978); Chilwa, Malawi (Woolley, 1969); Dicker Willem, Namibia (Cooper and Reid, 2000); Fen, Norway (Kresten, 1988; Verschure and Maijer, 2005); Kaiserstuhl, Germany (Wimmenauer et al., 1977); Iivaara, Finland (Kramm et al., 1993; Sindern and Kramm, 2000); Ilmeny-Vishnevye Gory, Russia (Dvornik, 2015 – unpublished data); Ishimovsky, Russia (Dvornik, 2015 – unpublished data); Kangunkunde, Malawi (Woolley, 1969); Khibiny, Kola Peninsula (Arzamastev et al., 2011); Koga, Pakistan (Le Bas, 2008); Lovozero, Kola Peninsula (Arzamastev et al., 2011); Murun, Russia (Dvornik, 2015 – unpublished data); Ozernaya Varaka, Kola Peninsula (Kozlov and Arzamastsev, 2015); San Vicente, Cape Verde Islands (Le Bas, 2008); Silai Patti, Pakistan (Le Bas, 2008); Sokli, Finland (Vartiainen and Woolley, 1976; Al Ani and Sarapää, 2013); Ryabinovskiy, Russia (Dvornik, 2015 – unpublished data); Turiy Mys, Kola Peninsula (Evdokimov, 1982); Wasaki, Kenya (Le Bas, 2008).

(Arzamastev et al., 2011). Fluids expelled from these melts contain variable amounts of CH_4 or CO_2, but are typically aqueous and Na-rich, often with high salinities up to 30 wt% NaCl equivilent (Konnerup-Madsen, 2001; Krumrei et al., 2007; Graser and Markl, 2008). Fig. 11 indicates no difference in the ratios of Al–Na + K–Fe + Mg between carbonatite-derived and alkaline-derived fenites, and as in carbonatite systems, these fluids have the capacity to mobilize HFSE and REE (Migdisov et al., 2009; Timofeev et al., 2015).

Fluids released from the magma migrate through the periphery of crystallized intrusions, often causing intense metasomatic reactions and hydrothermal alteration. Secondary assemblages of minerals are formed at the expense of primary magmatic minerals (see Fig. 12) (Mariano, 1983; Chakhmouradian and Mitchell, 2002; Marks et al., 2003; Graser and Markl, 2008; Schilling et al., 2009; Borst et al., 2016), often causing mobilization of REE and Nb-rich phases (Chakhmouradian and Mitchell, 2002). This is the same process termed 'internal fenitization' by Mariano (1983). Autometasomatisc reactions and subsequent decrease in volume of fluid released, could therefore explain the limited fenitization observed around nepheline syenites (Arzamastev et al., 2011). The Ilímaussaq nepheline syenite complex, Greenland displays plenty of evidence for these autometasomatic processes acting in and along the complex margins, but with limited effect on the surrounding country rock. Within the intrusion, autometasomatism can be seen as hundreds of square meters of albitized, analcimized and hematitized zones (Ferguson, 1964; Marks and Markl, 2015); mineralogically diverse hydrothermal veins (Engell et al., 1971; Markl, 2001; Markl and Baumgartner, 2002); and secondary mineral assemblages of albite, aegirine, fluorite, analcime, pectolite, cataplelite, gittingsite and other HFSE and REE phases. These features result from the release of aqueous fluids variably enriched in Na, Cl^-, F^-, Ca and Sr during the later stages of crystallization (Markl and Baumgartner, 2002; Graser and Markl, 2008; Borst et al., 2016). Fenitization of the granitic country rock itself is limited however, extending no further than 120 m from the intrusion-country rock contact (Ferguson, 1964).
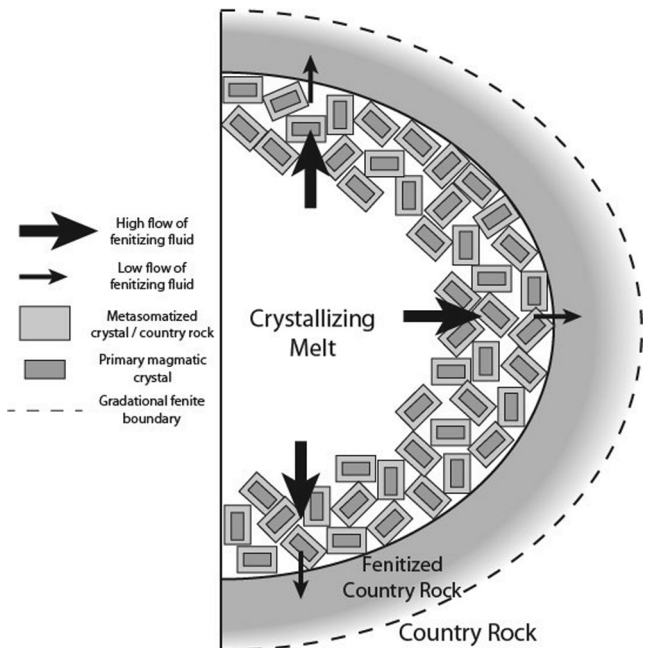
Fig. 12. Schematic diagram illustrating the process of autometasomatism. Crystallizing melt within the magma chamber or intrusion expels alkali-rich fluid that migrates through the periphery of already crystallized alkaline rock, autometasomatizing primary magmatic crystals. As a result, fenitization of country rock is limited due to restricted flow out of intrusion.

6. Conclusions

Recognizing similarities between fenites related to mineralized intrusions is problematic due to the lack of detail reported. However, there is evidence of strong trends between the complexity of fenite textures, such as multiple stages of veining and mineral assemblages, and associated mineralization. This is due to Nb and REE enrichment

Table 3

Summary of some key highlighted gaps in knowledge and literature in regards to fenites and the process of fenitization.

Number	Question
1	Why do carbonatites release Na-rich and K-rich fluids at different times?
2	How long does it take for a carbonatite to cool, and how does this affect fenitization?
3	How does the fenitization style i.e. pervasive / veined, affect the timescale of metasomatism?
4	Can we use diffusion modelling on rimmed crystals e.g. feldspars and aegirine-augites to better define fenitization timescales?
5	How do fluids evolve during progressive fluid-rock interactions, and what implications does this have for fenitization further from the intrusion?
6	What spatial variations can be seen within fenites? E.g. vein composition proximal vs distal, ratio of LREE:HREE with distance?
7	Are carbonate-rich veins in fenites true carbonatite veins or precipitation from hydrothermal fluids? How can the difference be identified and where is the line drawn?
8	Where do we find REE and Nb mineralization within the fenites? Within veins, adjacent to veins or within pervasive fenites?
9	Does fenitization occur at a lava-country rock contact?
10	Can we estimate the amount of REE or Nb present in the carbonatite, based upon their concentrations in the associated fenite?
11	Does K and Na fenite separation occur at each stage of carbonatite or alkaline magmatism?
12	Can a magmatic syenite be distinguished from a syenite formed by fenitization?

typically being discovered in intermediate and late stage carbonatite magma generations, that each exsolve multiple pulses of fenitizing fluids. The presence of brecciation in a carbonatite or alkaline complex also indicates the explosive release of fluids and volatiles which exsolve during evolution, cooling and crystallization of the magma. Therefore, brecciation indicates the presence of more evolved magma generations and therefore an increased likelihood of Nb and REE enrichment in the source intrusion.

Although this manuscript compiles and reviews our current knowledge of fenites and associated metasomatic processes, it also highlights gaps in the literature. Many previous attempts have been made to categorize and name fenites, however it is recommended that the IUGS metamorphic terminology be used to described predominant mineralogy and textures. Alteration patterns and zones have been successfully used as exploration tools to explore for mineralized systems such as porphyry copper deposits in the past. Although fenites have large potential to be used as exploration indicators to find new REE and Nb prospects, there are many areas of research that still need to be addressed (Table 3) before fenites can be used as an integrated and effective exploration tool.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.oregeorev.2017.12.003.

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