

Alkaline-Silicate REE-HFSE Systems

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Abstract

Development of renewable energy infrastructure requires critical raw materials, such as the rare earth elements (REEs, including scandium) and niobium, and is driving expansion and diversification in their supply chains. Although alternative sources are being explored, the majority of the world's resources of these elements are found in alkaline-silicate rocks and carbonatites. These magmatic systems also represent major sources of fluorine and phosphorus. Exploration models for critical raw materials are comparatively less well developed than those for major and precious metals, such as iron, copper, and gold, where most of the mineral exploration industry continues to focus. The diversity of lithologic relationships and a complex nomenclature for many alkaline rock types represent further barriers to the exploration and exploitation of REE-high field strength element (HFSE) resources that will facilitate the green revolution. We used a global review of maps, cross sections, and geophysical, geochemical, and petrological observations from alkaline systems to inform our description of the alkaline-silicate REE + HFSE mineral system from continental scale (1,000s km) down to deposit scale (~1 km lateral). Continental-scale targeting criteria include a geodynamic trigger for low-degree mantle melting at high pressure and a mantle source enriched in REEs, volatile elements, and alkalis. At the province and district scales, targeting criteria relate to magmatic-system longevity and the conditions required for extensive fractional crystallization and the residual enrichment of the REEs and HFSEs. A compilation of maps and geophysical data were used to construct an interactive 3-D geologic model (25-km cube) that places mineralization within a depth and horizontal reference frame. It shows typical lithologic relationships surrounding orthomagmatic REE-Nb-Ta-Zr-Hf mineralization in layered apatitic syenites, roof zone REE-Nb-Ta mineralization, and mineralization of REE-Nb-Zr associated with peralkaline granites and pegmatites. The resulting geologic model is presented together with recommended geophysical and geochemical approaches for exploration targeting, as well as mineral processing and environmental factors pertinent for the development of mineral resources hosted by alkaline-silicate magmatic systems.

Introduction

The global push to decarbonize energy production and transport is underpinning rapid growth in the demand for critical raw materials used in a range of new technologies and is driving expansion and diversification in their supply chains (Hodgkinson and Smith, 2018). The rare earth elements (REEs) are recognized as particularly critical due to their importance in the direct-drive generators of wind turbines and the motors of electric vehicles and the dominance of their supply chain by China (Cox and Kynicky, 2018; Goodenough et al., 2018;

European Commission, 2020). Although alternative sources are being explored, the majority of global REE resources are found in alkaline-silicate rocks and carbonatites (Chakhmouradian and Wall, 2012). Alkaline-silicate igneous systems also host deposits of other critical raw materials, including the high field strength elements (HFSEs) such as niobium, zirconium, and hafnium, plus fluorine, phosphate, and scandium (Wall et al., 1999; Mitchell, 2015; Pirajno, 2015; Dostal, 2017; Williams-Jones and Vasyukova, 2018; Broom-Fendley et al., 2020). Demand for the REEs and other critical raw materials is increasing (Hund et al., 2020) and is not likely to be met by recycling alone for some decades (Alonso et al., 2012; Binnemans et al., 2013; Jowitt et al., 2018). Mining of known occurrences and discovery of new deposits will therefore be

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required to secure their future supply (Goodenough et al., 2018).

This article provides an overview of REE + HFSE mineral systems associated with alkaline-silicate magmatism and provides a guide for economic geologists who wish to develop their contained resources. The mineral exploration industry has historically focused, and continues to focus, on major and precious metals, such as iron, copper, and gold (Arndt et al., 2017), the mineral systems of which are better understood (e.g., Hedenquist et al., 2000; Barnes and Lightfoot, 2005; Sillitoe, 2010; McCuaig and Hronsky, 2014; Goldfarb and Groves, 2015; Hagemann et al., 2016). We present a critical review of the literature on alkaline-silicate magmatic systems, with geologic and exploration targeting factors pertinent for the development of critical raw material resources from their contained mineralization. This includes the complex mineralogy and geometallurgy of alkaline-silicate systems, which must be considered in the development of any exploration model, as well as the environmental and social issues that may be associated with rare element mining. Previous reviews have provided highly valuable summaries of alkaline-silicate systems and their associated mineral deposits (e.g., Verplanck et al., 2014; Dostal, 2016, 2017; Morgenstern et al., 2017; Banks et al., 2019; Woolley, 2019). We synthesize these and other observations into a generalized scale-dependent mineral systems model (e.g., Knox-Robinson and Wyborn, 1997; McCuaig et al., 2010; McCuaig and Hronsky, 2014), with recommendations on geophysical, geochemical, and geologic techniques to apply during exploration. Relevant to the continental scale (300–10,000 km), we discuss the temporal distribution of various mineralization types and the influence of tectonic setting. We then present province-scale controls (~300 km) pertaining to translithospheric structures that guide magma ascent, the persistence of magmatism, the importance of depth of emplacement, and the influence of country-rock lithology on mineralization potential and the formation of alteration aureoles. At the district scale (~25 km lateral) we present a schematic interactive 3-D model for an idealized alkaline-silicate system (App. 1). This model illustrates the key lithologic relationships and relative position of various classes of mineralization in alkaline-silicate REE + HFSE systems. Pop-up panels within this model show grade tonnage information and REE profiles for each deposit class, as well as information on ore mineralogy and processing technology status. In the manuscript we discuss associated targeting criteria for mineralization, relevant at the prospect and deposit scale.

Alkaline-Silicate Rocks

Volcanic and plutonic silicate rocks that have an excess of alkalis relative to aluminium ($(\text{Na} + \text{K})/\text{Al} > 1$) on a molar basis and that therefore contain (real or normative) minerals with a similar excess of alkalis (such as alkali-rich amphibole or clinopyroxene) have been termed alkaline or peralkaline by various authors (Sørensen, 1974; Fitton and Upton, 1987; Le Maitre et al., 2005). The presence of feldspathoid minerals warrants classification as alkaline, whereas the term peralkaline is used exclusively for rocks that meet the above chemical definition. Peralkaline rocks are divided into miaskitic and apaitic varieties—the former having the REEs + HFSEs

largely hosted by the minerals zircon and titanite and the latter containing a wealth of complex Na-Ca-HFSE minerals, many of which contain structurally essential halogens (Marks and Markl, 2017). Extreme enrichments in alkalis can form hyperagpaitic assemblages, denoted by the presence of appreciable amounts of water-soluble minerals and the (partial) destabilization of alkali feldspar and feldspathoids (Marks and Markl, 2017). More broadly, the term alkaline-silicate refers to igneous systems that contain alkaline or peralkaline rocks, even if these systems are volumetrically dominated by metamorphous lithologies (Marks et al., 2011).

Alkaline-silicate complexes predominantly occur in continental tectonic settings and are found throughout the geologic record, from the Neoproterozoic to the present day (Woolley and Kjarsgaard, 2008; Figs. 1–3). Alkaline-silicate magmas have a mantle source, although the exact nature of that source varies between and within provinces (Bell and Simonetti, 2010; Hutchison et al., 2019, 2021). They are most commonly associated with lithospheric-scale extension, although some post-collisional alkaline magmatic provinces are associated with transcurrent tectonics (Hou et al., 2009; Banks et al., 2019; Goodenough et al., 2021). Alkaline-silicate complexes commonly occur in provinces, which are regional-scale features (10s to 100s km extent) comprising several individual igneous complexes. Each complex may include both alkaline-silicate rocks and carbonatites, with carbonatite-bearing systems typically associated with more oxidized upper mantle sources (Braunger et al., 2020). Many more alkaline-silicate occurrences are known when compared to carbonatites (>3,000 in compilation of Woolley, 2019, and other books in this series, see <http://alkcarb.myrocks.info/> vs. >600 carbonatites; Walter et al., 2021). Carbonatites represent important sources of REEs and HFSEs and are described in detail elsewhere (Verplanck et al., 2016; Wang et al., 2020); here we focus on the alkaline-silicate components of these igneous systems.

Before focusing on the geology of alkaline-silicate systems, the sections below summarize engineering, social, and environmental factors that are best considered at an early stage of any exploration campaign. We then present the geology and associated exploration approaches for these mineral systems at a range of scales, gradually focusing in from continental to deposit scale.

Metallurgical Challenges and the Importance of REE Profiles

The diversity of minerals within alkaline-silicate deposits is much greater than that of most mined base metal or precious metal deposits. Consequently, mineralogy and metallurgy are important considerations during REE + HFSE exploration in alkaline-silicate systems. The mineralogical diversity results because these magmas typically contain dozens of elements at weight percent concentration and crystallize at low temperatures where complex solid solutions stabilized by entropy are thermodynamically unfavorable (Putnis, 1992). Rare earth minerals represent 233 (4%) of the 5,455 species approved by the International Mineralogical Association (Downs, 2006, rruff.info/ima); however, at the time of writing only four are processed commercially for the REEs (bastnäsite-Ce, monazite-Ce, loparite-Ce, xenotime-Y). Apatite associated with alkaline rocks has also been processed commercially for

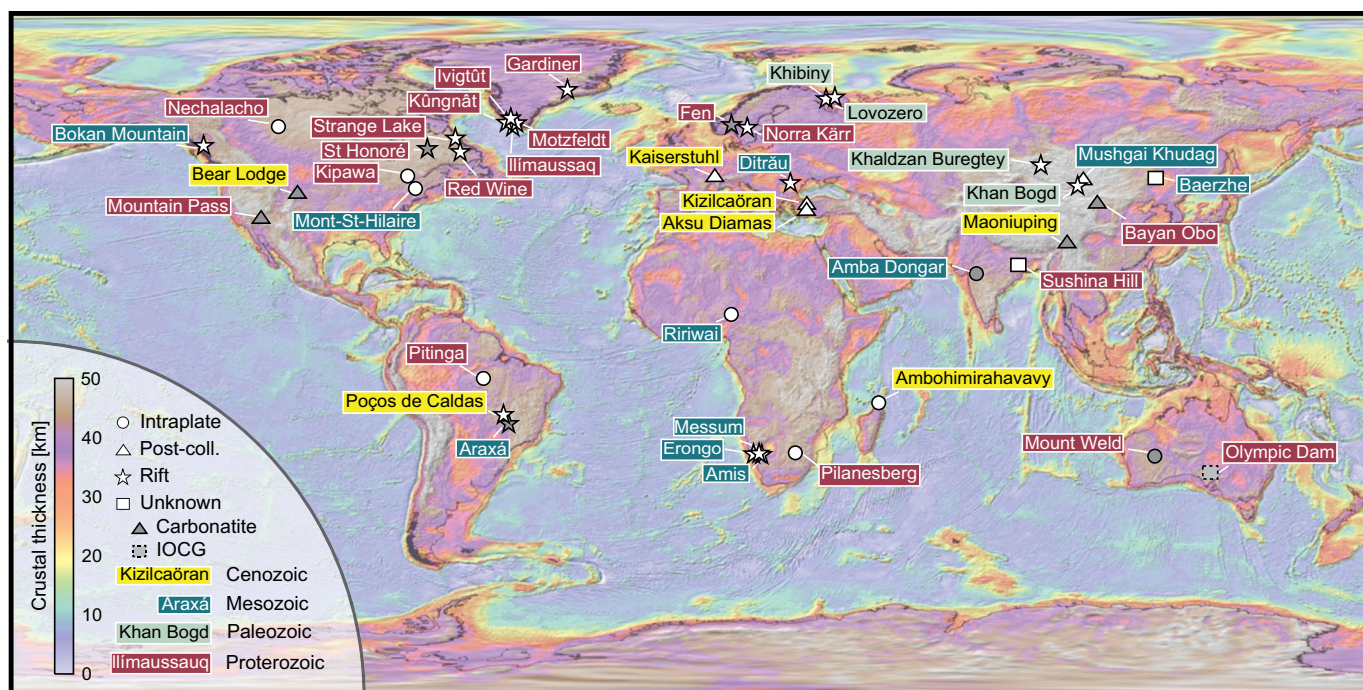


Fig. 1. A world map showing rare earth element-high field strength element (REE-HFSE) deposits and alkaline-silicate complexes mentioned in the main text. Alkaline-silicate complexes with and without carbonatite are shown in white, and systems containing major carbonatite-associated REE deposits are shown in gray. The crustal basement thickness map is an inversion of satellite gravity data (Alvey et al., 2018). IOCG = iron oxide copper-gold.

REEs (Jordens et al., 2013; Suli et al., 2017), and ion adsorption deposits, including those representing weathering products of alkaline-silicate rocks, currently supply the majority of the world's heavy REEs (HREEs; Bao and Zhao, 2008; Weng et al., 2015; Jowitt et al., 2017; Li et al., 2019). Since the REEs are usually dispersed in a number of phases that are not equally processable, grade tonnage diagrams cannot be used to directly assess the economic potential of a deposit. Metallurgical procedures for several other REE minerals are at pilot stage, including eudialyte, steenstrupine, and allanite (see App. 2; Davris et al., 2017; Stark et al., 2017; Voßenkaul et al., 2017; Battsengel et al., 2018; Kursun et al., 2019). Recovery rates and energy usage are improving rapidly as the pertinent metallurgical techniques mature (e.g., Wall et al., 2017; Demol et al., 2019; Marion et al., 2020). Other critical raw materials found in alkaline rocks are commercially extracted from a range of ore minerals, including pyrochlore (niobium), columbite (niobium, tantalum), apatite (phosphate), and zircon (zirconium, hafnium) (Gibson et al., 2015). In addition to mineralogy, the texture of the rocks influences the efficiency of beneficiation, with large grains able to be processed more easily than fine-scale intergrowths (e.g., Hagni, 1999; Neumann and Medeiros, 2015). The economics of REE deposits are further controlled by the relative abundance of elements, which are commonly expressed as a chondrite-normalized “REE pattern” (Chakhmouradian and Wall, 2012; Chakhmouradian and Zaitsev, 2012; Goodenough et al., 2018). Many companies report total rare earth oxide (TREO) grades, which offer an oversimplified view of the potential economics of a deposit. The HREEs are less abundant than light REEs (LREEs) but command a higher price (Binnemans et al., 2018; Goodenough

et al., 2018; Anenburg, 2020, and associated web tool; lambdar.rses.anu.edu.au/alambdar). Neodymium, an LREE that is used in high-strength permanent magnets, is considered the most critical of the REEs for electric vehicle and wind turbine supply chains (Ballinger et al., 2020). Alkaline-silicate associated deposits tend to have flatter REE profiles than carbonatites, so are relatively enriched in the rarer and more valuable middle and heavy REEs (see pop-ups in 3-D model, App. 1).

As highlighted above, metallurgical factors have a major influence on project economics, as they control the potential yield of a commodity that might be liberated during ore processing, the reagent and energy requirements of this processing, and the expected market value of the extracted commodity. Considering metallurgy late in the exploration process risks the spending of significant effort to understand the geology of an uneconomic deposit. Workflows for the analysis of REE minerals and textural information prior to metallurgical test work can be gleaned using relatively inexpensive petrographic techniques, such as optical microscopy and chemical mapping via microanalytical methods (Grammatikopoulos et al., 2013; Smythe et al., 2013; Edahbi et al., 2018).

Environmental and Social Considerations

The most important environmental and social considerations associated with the mining of REE-HFSE deposits in alkaline rocks are different from those of many other ore deposits. Radioactivity is the most high-profile environmental concern (Chakhmouradian and Wall, 2012), whereas acid mine drainage, often a major environmental consideration in mining scenarios, is usually not a problem (Verplanck et al., 2014). There have been only a few published environmental studies of

mines in alkaline-silicate systems and also relatively few long-term studies of REEs and associated minor elements in the environment. As a result, there is a much smaller set of regulatory data to inform environmental and social considerations.

The risks posed by the radionuclides uranium and thorium require special consideration in all alkaline-silicate systems (Chakhmouradian and Wall, 2012). These elements occur in many deposits, either in the REE and Nb minerals or in other associated phases. When sequestered within REE ore minerals, these actinides are not separated from the REEs until the later stages of the beneficiation process, which can result in production of mine waste that is enriched in radionuclides. The issue here is not necessarily the danger of irradiation, but rather the burden and cost of radioactive waste management for the mining company or operator. Measures to address radioactivity will be greater at the processing plant than at the mine site. Although the concentrations of U and Th in alkaline rocks are highly variable, experience so far suggests that the issue is likely to be a social concern even where the actual environmental risk is negligible (Ali, 2014; Jamaludin and Lahiri-Dutt, 2017; Speiser et al., 2019). If addressed poorly during exploration, mining, and extraction activities, this problem can damage public trust and potentially halt operations indefinitely (Phua and Velu, 2012; Ali, 2014). Environmental and safety reporting should follow the well-documented standards developed by the uranium sector (see www.world-nuclear.org). Depending on the cultural tolerance and legislation regarding radiation from mining (Wall, 2013) there is a possibility for extraction of uranium as a by-product (Roberts and Hudson, 1983; Huston et al., 2016). This may increase the economic viability of deposits while simultaneously reducing the radioactivity of the waste products (see www.wise-uranium.org). Thorium poses a greater risk for projects than uranium due to its lower global demand and higher abundance. (Th is not included in British Geological Survey [Brown et al., 2019] or U.S. Geological Survey [2019] global resource compilations.) While some Th can be separated during beneficiation, the REEs and Nb, Ta, Zr minerals usually incorporate some Th into their lattices (e.g., monazite, REE fluorocarbonates, pyrochlore). As a result, the extraction of REEs from these minerals can pose a radiation risk (Phua and Velu, 2012; Wall, 2013).

In general, the toxicity of the REEs is thought to be low; however, few long-term data sets exist (Pagano et al., 2015). The REEs have been used in growth promoters and fertilizers in China and in a variety of medical applications, including drug delivery and magnetic resonance imaging. Health risks associated with prolonged exposure to Ce, and also other REEs, have been noted in some industrial and agricultural settings (see Rim et al., 2013; Wall, 2013). Cerium nanoparticles are toxic (García et al., 2011; Dahle and Arai, 2015), and although REEs have been used in catalytic converters for many cars, there are few environmental studies on this subject. The REEs have been measured in river water (Kulaksiz and Bau, 2011; Brito et al., 2018) but there are few environmental limits and regulations for them.

We recommend that the environmental impact of various production options be compared quantitatively with life cycle assessment (LCA) simulations (Wall et al., 2017; Pell et al., 2019, 2021). These can inform decisions about the impact of

various project options—for example, the effect that various reagent source pathways have on emissions and on water use (e.g., CO₂ · eq per kg of commodity produced, particulate generation).

Continental-Scale Characteristics

Within the mineral systems concept (Knox-Robinson and Wyborn, 1997; McCuaig et al., 2010; McCuaig and Hronsky, 2014; Banks et al., 2019) a series of processes occur to mobilize and concentrate a commodity, depositing it downstream at a site of mineralization. At the continental scale (>1,000 km) the main processes that control the potential for ore formation are (1) a source of the commodity, (2) the generation of a medium to carry the commodity, and (3) a geodynamic event that can mobilize the commodity. To form a deposit, all components of a mineral system must be present; therefore, screening at the continental scale can help identify promising search areas at the province scale (~300 km). The mineral systems approach can be used to derisk projects before relatively more expensive and specialist exploration techniques are used at finer spatial scales (Banks et al., 2020). In the case of alkaline-silicate REE-HFSE systems and carbonatite-bearing systems, most of the commodity and its transporting medium (magma) are thought to originate from the mantle. The source composition is therefore influenced by global-scale (bio)geochemical cycles that have evolved throughout geologic time (White, 2015). The mobilization of REEs from the mantle is triggered by tectonic and mantle geodynamic perturbations that generate silicate melt and facilitate their ascent into the continental crust. At the continental and province scales, targeting factors are similar for alkaline-silicate and carbonatite systems, and the topics discussed in the following sections apply to carbonatites as well as to the alkaline-silicate systems that are the main focus of this article.

Alkaline-silicate rocks and carbonatites can be broadly divided into two associations: those in continental rift and intraplate settings and those formed in postcollisional settings (Figs. 1, 2). In the latter, magmatism is generally associated with a change in stress regime from compressional to transcurrent that postdates continental collision by millions to tens of millions of years (Goodenough et al., 2021). Alkaline magmatism also represents a minor but ubiquitous component of oceanic island systems (Fitton and Upton, 1987; Willbold and Stracke, 2006). No economic mineralization, other than construction materials, is known from alkaline-silicate systems from oceanic island settings (Woolley and Kjarsgaard, 2008; Woolley, 2019), perhaps because a thinner lithosphere does not afford the magmas sufficient opportunity to fractionate and residually enrich the incompatible REEs and HFSEs (cf. Wiesmaier et al., 2012). For this reason, the oceanic island setting will not be discussed further.

Screening at the continental scale aims to identify province-scale features that potentially contain REE + HFSE mineralization. Exploration indicators, as with many ore deposit types, are therefore country-scale geologic maps, crustal-scale cross sections, and an understanding of the geodynamic history of a region or craton. Continental-scale geochemical mapping of igneous rocks can also be used to delineate and extend known and favorable regions for mineralization. Such an approach has been applied to Archean nickel sulfide and gold systems

in Western Australia (McCuaig et al., 2010) where a restricted range of Nd isotope depleted mantle model ages of low-Ca granites map the edge of a paleocraton at time of their emplacement. This shows excellent spatial correlation with known nickel and gold mineral systems.

Tectonic settings and triggers for mantle melting

Alkaline-silicate systems are most commonly coincident with continental sutures and the margins of cratons (Burke et al., 2003; Pirajno, 2015; Humphreys-Williams and Zahirovic, 2021; Fig. 1). In continental rift and intraplate settings, alkaline-silicate melts are generated where the plate divergence rate is low (e.g., 12.4 mm yr⁻¹, Basin and Range, Bennett et al., 2003; 5–15 mm yr⁻¹, East African rift, Saria et al., 2014) or along the failed arm of rift triple junctions associated with thermochemical mantle plumes and continental breakup (Dewey and Burke, 1974; Bell and Simonetti, 2010; Ernst and Bell, 2010). In such settings, as seen in the modern East African rift (Mahood, 1984; Hutchison et al., 2016a; Rooney, 2020b), the East Greenland Tertiary province (Brooks and Nielsen, 1982), and the Mesoproterozoic Gardar rift of southwest Greenland (Upton et al., 2003; Upton, 2013) magmas tend to be sodic, rather than potassic, and commonly attain peralkaline compositions (Marks et al., 2011). Though several major mineralized alkaline-silicate and carbonatite systems are known from postcollisional settings, the academic community have thus far focused on the intraplate and rift-related systems, and the literature on postcollisional settings is therefore less comprehensive (Goodenough et al., 2021). Melt compositions in postcollisional settings tend to be potassic, and mantle melting here has been attributed to slab break-off, lithospheric delamination, and adiabatic decompression associated with orogenic collapse (Kay and Mahlburg Kay, 1993; Huw Davies and von Blanckenburg, 1995). In both rift and postcollisional settings, experimental evidence indicates that the alkali-rich, Si-poor nature of the primary silicate melts is best explained by low-degree partial melting of mantle beneath thick continental crust (Massuyeau et al., 2015; Schmidt and Weidendorfer, 2018; Figs. 1, 2). Such high-pressure melting further yields high concentrations of REEs, HFSEs, P, and CO₂ for a given

source composition. Geophysical techniques such as seismic tomography, magnetotellurics, and satellite gravity mapping can be used to infer the present-day structure and thickness of the crust (Fig. 1), providing information on areas where high-pressure mantle melting might have recently occurred (Percival et al., 2006; Clowes, 2010; Alvey et al., 2018). For older terranes, crustal thickness can be inferred where the uplift and erosion history are known, for example via petrochronology and phase-equilibrium modeling of metamorphic assemblages associated with orogens (e.g., Weller et al., 2021).

In most continental rift and intraplate examples, the physical trigger for melting is likely to be a combination of adiabatic decompression associated with crustal thinning and, in some cases, plume-lithosphere interaction (Kieffer et al., 2004; Koptev et al., 2015; Rooney, 2017). Adiabatic decompression associated with crustal thinning can impart a subtle yet persistent influence on the upper mantle that is compatible with five to tens of million years' duration of activity of some alkaline provinces (e.g., East African rift; Macgregor, 2015). For alkaline-silicate and carbonatite complexes peripheral to and roughly contemporaneous with flood basalt volcanism, melt generation likely reflects the influence of a thermochemical mantle plume (Ebinger and Sleep, 1998; Ernst and Bell, 2010; Furman et al., 2016). In these intraplate occurrences, low-degree melting may reflect the destabilization of asthenospheric mantle rocks or metasomes in the subcontinental lithospheric mantle, perhaps via fluxing by deep-derived volatiles or via adiabatic decompression toward the edge of a plume head (Garcia et al., 1993; Haase et al., 2019). Alkaline-silicate and carbonatite systems associated with continental flood basalts tend to slightly predate (<10 m.y.) or overlap with the timing of these flood-volcanic events (Ernst, 2014).

Alkaline magmatism can also be associated with hotspot tracks—the tails of mantle plumes. At the Cretaceous Monteregian Hills province in Quebec, Canada, radiogenic Pb and primitive He isotope compositions indicate major contributions from a mature mantle plume source (Roulet and Stevenson, 2013; Chen and Simonetti, 2015; Méjean et al., 2020). Recent U-Pb zircon geochronology supports the hotspot model, with age dates broadly consistent with the modeled

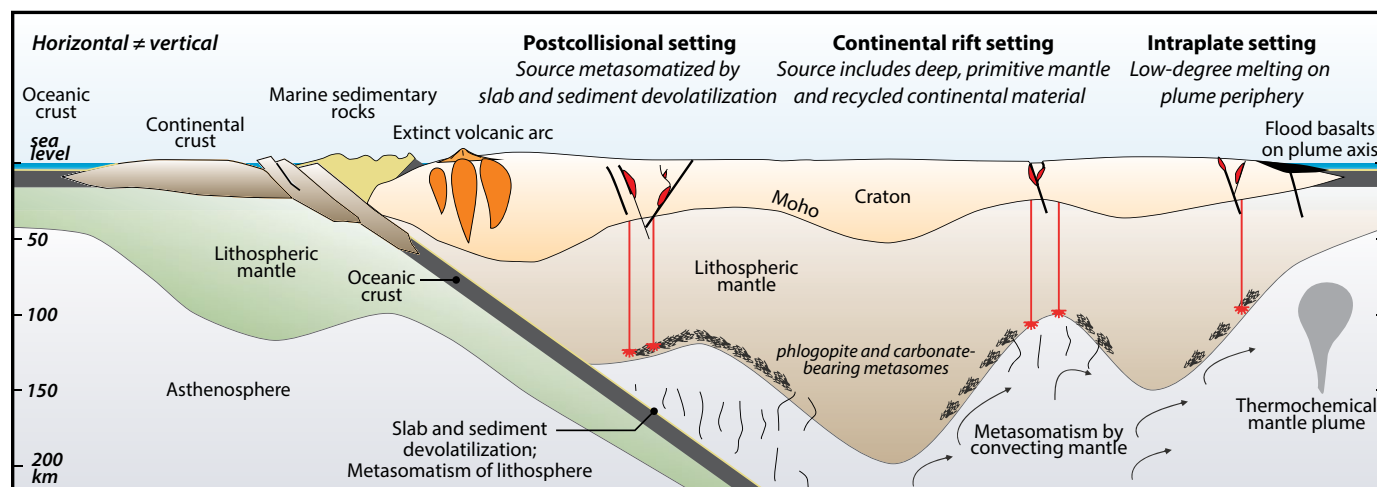


Fig. 2. A schematic cross section at continental scale showing the tectonic settings and melt sources inferred for postcollisional, continental rift, and intraplate alkaline-silicate magmatic systems. Vertical scale follows Condie (2016).

track of the Great Meteor hotspot (Kinney et al., 2021). However, there has been some debate as to whether plume impingement simply introduced material to the lithospheric mantle (cf. Aulbach et al., 2013), and low-degree melting was triggered later via structural reactivation of paleorifts during opening of the North Atlantic Ocean (Rouilleau and Stevenson, 2013).

The influence of mantle melt source composition on mineralization potential

The xenolith cargo and high concentrations of incompatible elements in alkaline-silicate systems suggest they originate as low-degree partial melts of enriched sources in the lithospheric mantle (Kramm and Kogarko, 1994; Rosatelli et al., 2007; Pilet et al., 2008; Bartels et al., 2015; Foley and Fischer, 2017; Tappe et al., 2017; Fig. 2). Indeed, melting experiments indicate that minor CO₂ and H₂O in the mantle source strongly reduce the silica activity of the produced melts and can depress the peridotite solidus (Massuyeau et al., 2015). Extensive differentiation of these primary melts is required to enrich REEs + HFSEs to economically interesting concentrations (Marks and Markl, 2017).

Direct links between source composition and mineralization potential have not been proven conclusively; however, there is an increasing body of evidence for a link between source composition and mineralization (e.g., Pilet et al., 2008; Hutchison et al., 2019, 2021). The probability of forming a deposit is likely to be elevated where the underlying mantle is enriched in the metals of interest. Sources may also favor mineralization if they can contribute a cocktail of volatiles that promotes the residual enrichment of metals during crystal fractionation in a crustal magmatic system (e.g., fluorine; Guzmics et al., 2012, 2019; Aseri et al., 2015; Beard et al., 2020). Such sources may result from the metasomatism of the lithospheric mantle by fluids or melts derived from subduction of REE-rich marine sediments, including those containing abundant organic phosphorite material or Fe-Mn oxide crusts that accumulate at low rates of sedimentation (Plank, 2013). Marine shale and clay also contain elevated concentrations of REEs and fluorine relative to primitive mantle (4–70 and 30–52× primitive mantle, respectively; Barth et al., 2000; John et al., 2011). In most arcs, the degree of melting is too great, and primitive melts are not associated with notable enrichment of REEs, HFSEs, or alkalis (Elliott et al., 1997; Spandler and Pirard, 2013). Low-degree melting is therefore paramount because the same sediment packages are being subducted below many arc volcanic systems today. Metals and volatile elements may also be introduced to the cratonic lithosphere via the impingement of thermochemical mantle plumes (Aulbach et al., 2013) or via carbonate metasomatism associated with subduction (Tappe et al., 2017).

Xenolith assemblages and geochemical evidence indicate that rift-related alkaline-silicate systems tap sources that contain phlogopite, magnetite, amphibole, apatite, and carbonate minerals and are mostly garnet or spinel lherzolites (Upton and Emeleus, 1987; Köhler et al., 2009; Melluso et al., 2016; Marks and Markl, 2017). Note that melt generation above the garnet stability field may be a factor in the relative enrichment of HREEs, as garnet in the mantle restite would retain the HREEs during melting (Adam and Green, 2006; Bartels et

al., 2015). Primitive volcanic rocks and dikes associated with alkaline-silicate systems suggest that their primary melts are usually reduced alkali-basalt to basanite (feldspar-bearing), or nephelinite in composition (feldspar-free), and are rarely melilititic (Elburg and Cawthorn, 2017; Marks and Markl, 2017; Braunger et al., 2020).

The radiogenic ¹⁴³Nd/¹⁴⁴Nd and ¹⁷⁶Hf/¹⁷⁷Hf isotope systems provide direct information about the source of the metals of interest, rather than a proxy as most geochemical tools do. Many rift-related and intraplate alkaline-silicate rocks have Nd-Hf isotope compositions that overlap with those of high- μ (HIMU) oceanic island basalts (Bell and Simonetti, 2010), indicating that their melt source is mantle dominated and contains a recycled oceanic crust component (Chauvel et al., 1992). Some alkaline-silicate systems, especially in postcollisional settings, have compositions that extend toward enriched mantle 2 and enriched mantle 1 (EM-2 and EM-1) oceanic island basalt compositions (Goodenough et al., 2021), reflecting contributions from continental crustal sources (Willbold and Stracke, 2010). Here, continental material is either introduced to magmas through assimilation during ascent or more likely via incorporation into the mantle source, for example via subduction of sedimentary rocks.

Radiogenic Ar, Xe, and He isotope compositions from intraplate alkaline-silicate rocks and associated carbonatites in Canada, Brazil, and Russia indicate contributions from primordial, deep-seated mantle sources (Sasada et al., 1997; Tolstikhin et al., 2002). The heavy nitrogen isotope composition of alkaline-silicate rocks from the Kola Peninsula further indicates contributions from deep-seated sources, either from recycled oceanic crust or generated via metal-silicate partitioning of nitrogen during formation of our planetary core (Dauphas and Marty, 1999). The $\delta^{11}\text{B}$ isotope composition of carbonatites and their associated alkaline-silicate rocks has become progressively heavier since the Archean (Hulett et al., 2016), consistent with subduction recycling of sedimentary material into their mantle source regions (Smith et al., 2018). Sulfur ($\delta^{34}\text{S}$) isotope compositions are consistent with $\delta^{11}\text{B}$, showing both positive and negative values that extend beyond the range of typical upper mantle melts (mid-ocean ridge basalt; MORB), indicating contributions from recycled surface sources in the lithospheric mantle or in plumes (Hutchison et al., 2019, 2020).

Alkaline-silicate magmas in postcollisional settings tend to be potassic and miaskitic, with common enrichments of LREEs, barium, strontium, and fluorine (Goodenough et al., 2021). The potassic nature and high Rb/Sr of many postcollisional alkaline magmas indicate contributions from a phlogopite-bearing mantle source that has been metasomatized by subduction-related fluids (Couzinié et al., 2016; Tappe et al., 2017; Braunger et al., 2020). Devolatilization reactions in subducting slabs release a host of incompatible elements and can induce metasomatism of the base of the lithosphere (Kerrick and Connelly, 2001; Spandler and Pirard, 2013; Schmidt and Poli, 2014). The negative primitive mantle-normalized Nb-Ta anomalies of postcollisional alkaline rocks (e.g., Liu et al., 2015) are similar to those reported from arc tholeiites and may result from the presence of residual rutile in the slab and the low solubility of Nb-Ta-bearing minerals in subduction zone fluids (Baier et al., 2008; Marschall et al., 2013). The

higher proportion of carbonatite relative to silicate rocks in postcollisional settings may reflect contributions from sources relatively enriched in carbonate (Massuyeau et al., 2015).

The key points for exploration are that mineralized alkaline-silicate rocks are predominantly products of low-degree, high-pressure melting of mantle rocks (crustal thickness ≥ 40 km; Fig. 1) and that the mantle is the dominant source of their REE and HFSE payload. Intraplate and rift occurrences tend to tap deep, plume-influenced sources containing a mixture of recycled oceanic crust and primordial mantle material. Post-collisional complexes have more continental-like geochemical characteristics, potentially reflecting contributions from mantle with more recent subduction-related metasomatism. While source composition is likely to influence mineralization potential, a direct link has yet to be proven.

The temporal distribution of mineralization

Because the composition and dynamics of the Earth's crust and mantle have evolved through geologic time, so has the potential for REE + HFSE mineralization (Fig. 3). As stated above, the controls on REE-HFSE mineralization at the continental scale are similar for alkaline-silicate and carbonatite systems; therefore, statements made in this section apply to both. The oldest known alkaline-silicate and carbonatite

systems formed in the Neoproterozoic and are preserved in cratonic areas of Canada, Finland, and Greenland (Larsen and Rex, 1992; Rukhlov and Bell, 2010; O'Brien et al., 2015; Marks and Markl, 2017). From the Paleoproterozoic onward, alkaline-silicate and carbonatite magmatism is preserved on all continents and has been episodic, with peaks of activity associated with continental rifting and the existence of supercontinents (Rukhlov and Bell, 2010; Woolley and Bailey, 2012; Cawood and Hawkesworth, 2015; Tappe et al., 2017; Fig. 3a).

Resource tonnage data as a function of age reveal several major pulses of REE mineralization (Smith et al., 2016; Fig. 3b). The earliest two are associated with relatively small discrete deposits (3.3 and 4.2 Mt TREO) that formed during the Paleoproterozoic in intraplate settings. Through the Mesoproterozoic, the thickness of juvenile continental crust increased to >35 km (Dhuime et al., 2015), and major REE deposits were formed on multiple paleocontinents. These include iron oxide copper-gold-related REE mineralization at Olympic Dam, Australia (6.6 Mt TREO; Oreskes and Einaudi, 1990), a major portion of the mineralization at the Bayan Obo deposit, China (30.8 Mt TREO; Song et al., 2018), the Sulphide Queen deposit at Mountain Pass, USA (1.6 Mt TREO; Castor, 2008), and the Kvanefjeld and Kringlerne deposits of the Ilímaussaq Complex, Greenland (11.1 and 28.0 Mt TREO; Upton, 2013).

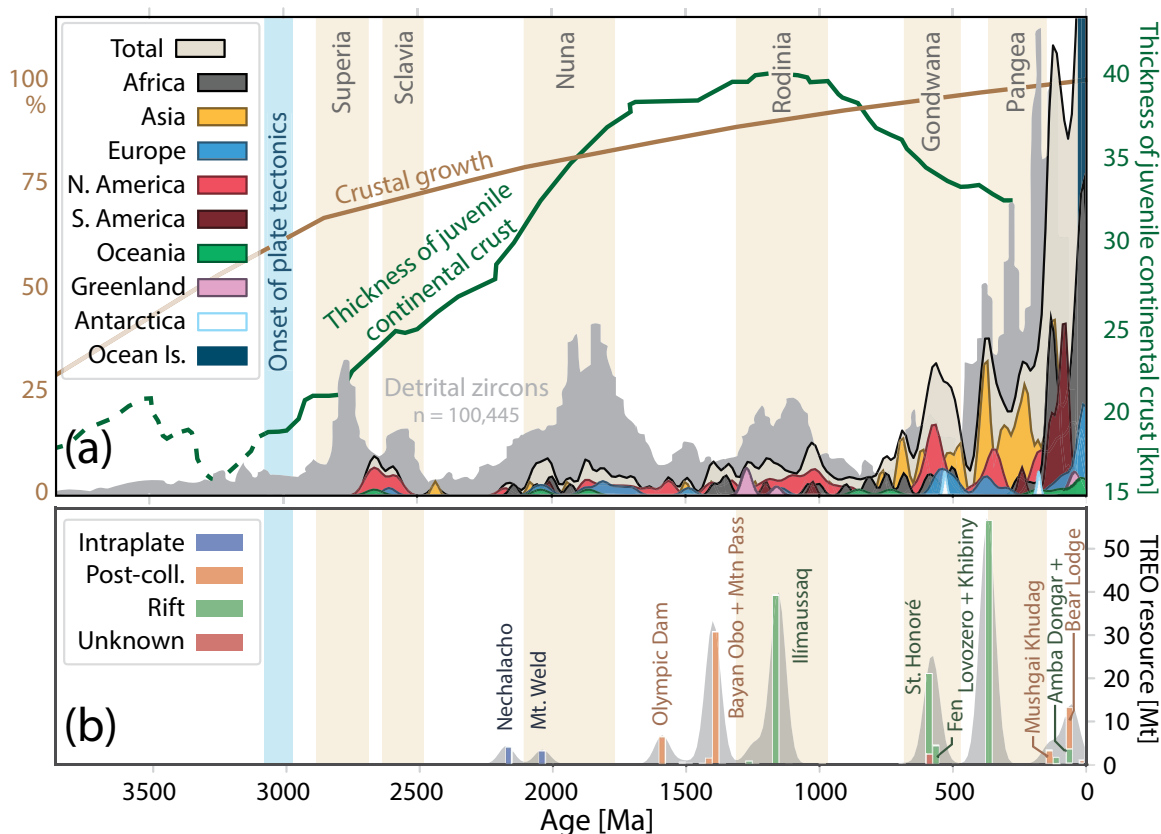


Fig. 3. Age distribution diagram for alkaline-silicate and carbonatite systems. (a) Kernel density curves for occurrences based on data from Woolley and Kjarsgaard (2008) and Marks and Markl (2017) ($n = 377$). Vertical bars indicate the existence of supercontinents after Cawood and Hawkesworth (2015). Global detrital zircon abundances after Voice et al. (2011) are a proxy for the rate of growth of the continental crust (cf. Arndt and Davaille, 2013). The volume percentage of continental crustal growth is after Dhuime et al. (2012), and the emergence of plate tectonics and thickness of juvenile continental crust are after Dhuime et al. (2015). (b) Histogram of total rare earth oxide (TREO) resources (measured + inferred, $n = 107$), with bin width set at 25 m.y. Resource data are also shown in a grade-tonnage diagram in Figure 7.

The sum total of Mesoproterozoic-age REE mineral systems represents ~30% of current global REE resources by tonnage (Smith et al., 2016). The Proterozoic saw the assembly of two supercontinents named Nuna (Columbia) and Rodinia (Fig. 3a) and their subsequent breakup by the emplacement of the Keweenaw (1115–1085 Ma) and Mackenzie (1267 Ma) large igneous provinces (Ernst and Bleeker, 2010) and the Gardar alkaline province (1325–1144 Ma; Upton, 2013; Stockmann et al., 2018). This period was also notable for the development of extensive base and precious metal mineralization (Huston et al., 2010). The late Proterozoic saw emplacement of the St Honoré alkaline-silicate and carbonatite complex, Canada, with mantle melting likely triggered by movement on the St. Lawrence rift and opening of the Iapetus Ocean (O'Brien and van der Pluijm, 2012; Tremblay et al., 2013; Néron et al., 2018).

In the Paleozoic, rifting and alkaline magmatism developed across the Baltic Shield of northern Europe (Goodenough et al., 2016). The world's largest alkaline complexes, Khibiny and Lovozero, were emplaced as part of the Kola alkaline province in Russia, an area that shows repeated alkaline magmatism throughout the Proterozoic (Downes et al., 2005; Kalashnikov et al., 2016a).

A somewhat smaller pulse of REE mineralization is preserved from the most recent 200 m.y. (Smith et al., 2016). This REE resource peak is small, considering the abundance of alkaline-silicate and carbonatite systems known from the same time period (Fig. 3). It is dominated by deposits with a comparatively shallow depth of emplacement (e.g., Mianning-Dechang belt, China, Hou et al., 2009; Liu and Hou 2017; Chilwa province, Malawi; Broom-Fendley et al., 2017; Baerzhe, China, Wu et al., 2021).

The apparent lack of REE mineralization in the Archean might have resulted from high mantle temperatures and consequently greater degrees of partial melting relative to more recent times (Herzberg et al., 2010; Weller et al., 2019). Thin, nascent continental crust (Dhuime et al., 2015), or potentially a vertical tectonic regime (Bédard et al., 2013), was apparently not conducive to alkaline magmatism or REE mineralization.

The largest known REE deposits formed in the Proterozoic and Paleozoic and likely reflect an availability of enriched mantle source material, with a geodynamic environment conducive to persistent or repeated generation of high-pressure, low-degree mantle melting over long geologic timescales. The advent of plate tectonics began the subduction recycling of continentally derived sediments into the mantle (Delavault et al., 2016), locally enriching REEs and other incompatible elements relative to primitive mantle (e.g., Willbold and Stracke, 2010). In the Proterozoic, the thickness of juvenile continental crust increased from ~20 to 35 km (Fig. 3), as recorded by a compilation of Nd isotope model ages, Si contents, and Rb/Sr ratios (Dhuime et al., 2015). A thicker lid of continental crust would have promoted higher-pressure mantle melting, with experimental data indicating that the resultant melts would have been Si poor and alkali rich (Massuyeau et al., 2015). In some alkaline-silicate REE-HFSE systems, reactivation of continental sutures may be important for mineralization. Indeed, nearly 90% of deformed alkaline rocks and carbonatites on the African continent occur within known or inferred Proterozoic suture zones, and isotopic evidence suggests that

melting of these deformed rocks may contribute to later magmatism (Burke et al., 2003; Rooney, 2020b). Multiple periods of reactivation are recorded in REE ores of the giant Bayan Obo carbonatite deposit where Sm-Nd ages of mineralization span 1.0 b.y. (e.g., Song et al., 2018).

The mechanisms responsible for the small peak of the Mesozoic to Cenozoic (≤ 200 Ma) REE tonnage remain to be determined. The reduced tonnage could reflect mineralization of REEs at depths not yet explored. Indeed, the influence of confining pressure on mineralization potential in alkaline-silicate systems is not currently well constrained (see "Volcanic connections and the depth of emplacement" section below). Additionally, a shift in the dominant tectonic style may have reduced the potential for REE mineralization. The temporal reduction in global REE tonnage correlates with a shift from Mesoproterozoic, single-lid-like tectonics, as recorded by abundant A-type granites and anorthosites, toward a Cenozoic subduction-dominated tectonic style, as indicated by the presence of ophiolites and blueschists (Stern, 2020).

In summary, the continental-scale features that may indicate the likelihood of alkaline-silicate associated REE-HFSE mineralization include the following: (1) a tectonic history that resulted in the metasomatic enrichment of the mantle, e.g., at suture zones between cratonic blocks, and (2) a trigger for low-degree mantle melting, e.g., an episode of continental rifting, a thermochemical mantle plume, or a hotspot track. Country-wide geochemical, geophysical, and geologic mapping data sets will typically provide information to guide exploration at the continental scale.

Clusters and Alignments of Deposits at the Province Scale

Once promising province-scale (~300 km) search regions have been identified, these may be mapped in finer detail, searching for promising districts at the scale of individual intrusive or volcanic systems (~25 km; Fig. 4). Province-scale exploration should map crustal-scale structures that can focus magma ascent from the mantle (Black et al., 1985; Hutton, 1988; Petford et al., 2000; Magee et al., 2018). Within alkaline-silicate and carbonatite provinces, magmas have been focused toward intersections of crustal lineaments (Sørensen, 1970; Acocella et al., 2003; Pirajno, 2010; Decrée et al., 2015; Robertson et al., 2016; Banks et al., 2019), and intrusions may be nested to the point that they overlap (e.g., Gardar province, Greenland; Fig. 4b; Upton, 2013; Finch et al., 2019) or alternatively may be strung out along crustal lineaments (e.g., Montereigian Hills, Canada, Eby, 1987; Damaraland alkaline province, Namibia; Fig. 4c; Marsh, 1973; Miller, 2008).

In continental rift settings, intrusions are commonly located within a 60- to 100-km-wide zone bounded by and containing translithospheric faults that may show transcurrent and vertical offset (Sørensen, 1970). In the Gardar province, Greenland, the largest intrusive bodies (Igdlerfigsalik, Ílímaussaq, Nunarsuit, Motzfeldt) straddle these long-lived faults and are crosscut by them (Upton, 2013; Finch et al., 2019). The importance of fault-bounded zones for magma focusing is also apparent in the Chilwa province, Malawi (Garson, 1965; Nyalugwe et al., 2019) and the modern East African rift (Bastow et al., 2008). Many continental rifts are asymmetric (Brune et al., 2014), with a lower plate characterized by

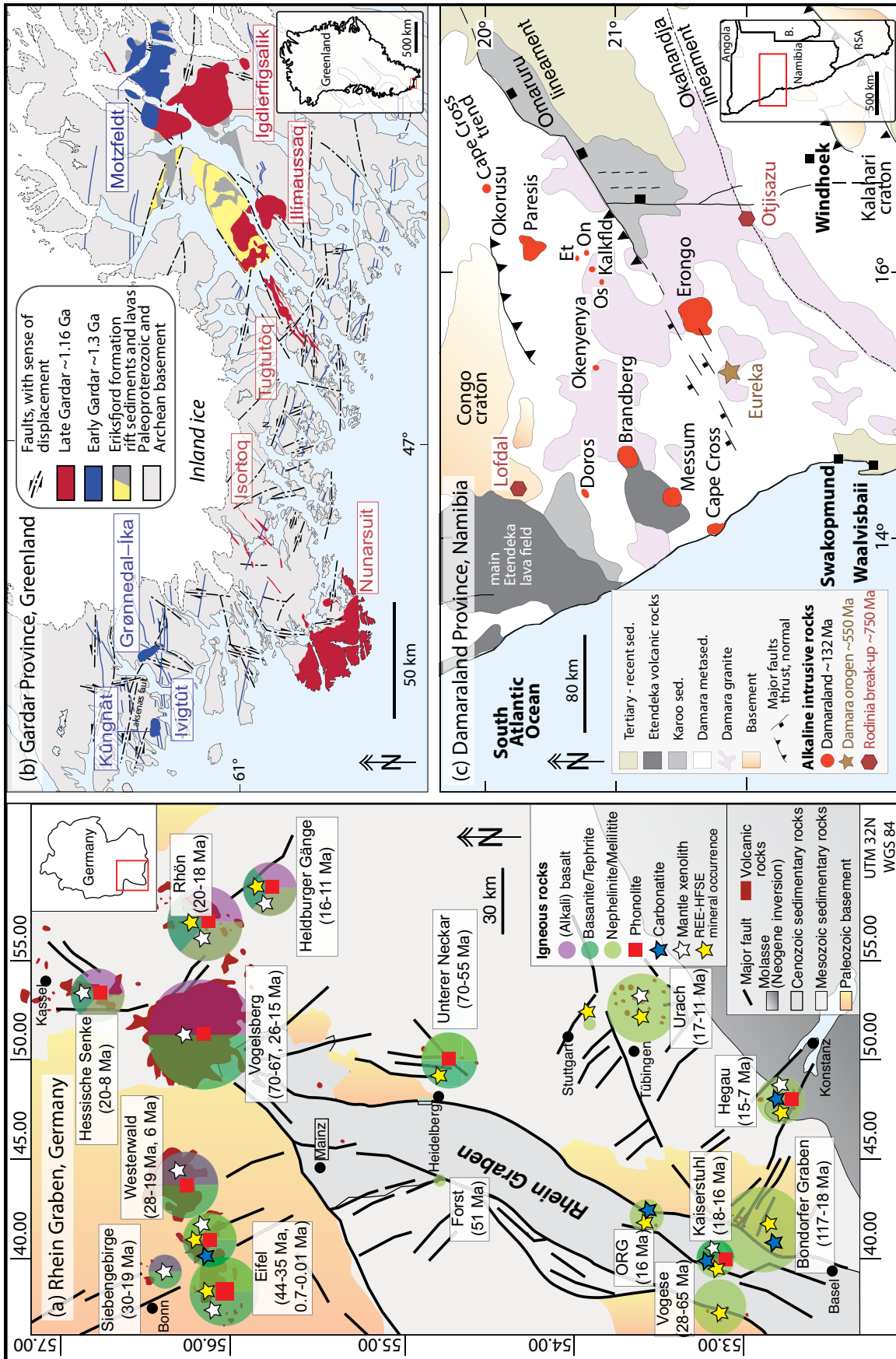


Fig. 4. Province-scale maps of alkaline-silicate rare earth element-high field strength element (REE-HFSE) systems showing major crustal structures that control the location of intrusive and volcanic complexes at the district scale (~25 km). (a) The Variscan-Miocene Rhine Graben system in southwest Germany after Banks et al. (2019), emplaced in a postcollisional setting. (b) The Mesoproterozoic Gardar province in southwest Greenland after Sørensen (2006) and Upton (2013), emplaced in a continental rift setting. Here, large, inferred NE-SW-trending structures follow faults that are parallel to the Ketilidian margin. The Paatusoq Complex (not shown, east of the Greenland ice cap) is situated on the intersection of major east-west faults and Jokum's shear, a major terrain boundary. (c) The Cretaceous Damaraland province of Namibia, associated with the Etendeka-Paraná large igneous province and the opening of the South Atlantic Ocean, after Brown et al. (2014). The Cape Cross trend follows an inferred, rift-perpendicular structure that runs parallel to the Omaruru lineament. Note that scale varies among the three maps.

marked thinning and extension and an upper plate, commonly with steeper normal faults and alkalic magmatism (Şengör and Natal'in, 2001; Lund, 2008). While the effect of rift asymmetry on REE-HFSE mineralization potential has not been examined in detail, the greater thickness of the upper plate and lower degree of mantle melting beneath it probably favor REE-HFSE mineralization on the upper margin of asymmetric rift systems.

In postcollisional alkaline-silicate and carbonatite provinces, the intrusions are commonly aligned along crustal-scale transcurrent shear zones (Hutton and Reavy, 1992; e.g., Mianing-Dechang belt, China, Hou et al., 2009; Kaiserstuhl and related Miocene complexes, southwest Germany, Banks et al., 2019). These structures trace relict, potentially ephemeral, permeability through which mantle melts traversed thickened continental crust (Sylvester, 1989; Bonin, 2004).

Magnetic surveys represent an effective tool for mapping structural lineaments that represent potential crustal permeability (Riedel et al., 2013). Additionally, they are effective in the search for intrusive systems under cover, of particular exploration interest in partially covered provinces that host proven mineralization. To resolve features on the scale of individual intrusive or volcanic systems (~25 km) a maximum flight line spacing of 400 m should be used. At this scale of investigation, surveys must be conducted using airborne techniques and are typically implemented by governments or international development organizations (e.g., World Bank Mining Governance and Growth Support project; Nyalugwe et al., 2019). Magnetometers are most often flown together with gamma-ray spectrometers.

Gamma-ray spectrometry is used to determine the U, Th, and K concentration in rocks and soils. This technique is typically sensitive to a penetration depth of 30 cm (Shives, 2015) and has been used to map lithologies and to identify potential zones of mineralization (e.g., McCafferty et al., 2014). Uranium and thorium can be associated with, or contained within, REE-bearing minerals, and gamma-ray spectrometry can therefore be used as an indirect indicator of REE mineralization (Steenfelt, 1991; Bedini and Rasmussen, 2018). One should note, however, that Th and especially U are mobile during low-temperature alteration (Timofeev et al., 2018; Nisbet et al., 2019); therefore, use of gamma-ray spectrometry alone may miss U-Th-poor, REE-HFSE-rich portions of a deposit (Finch et al., 2019), the very parts that would produce the lowest fraction of radioactive by-product (see “Environmental and social considerations” section). It is therefore crucial to use mineralogical information when interpreting radiometric measurements at the district and especially the deposit scale.

District-Scale Characteristics

The district scale focuses on individual intrusive and volcanic complexes that typically spread over 10–40 km in lateral extent (Fig. 5). These complexes tend to comprise several stages of magmatism, only some of which may be associated with REE-HFSE mineralization. We used the spatial relationship between lithologies, structural features, and the location of various types of REE-HFSE mineralization to build an interactive 3-D geologic model for an idealized system at the district scale (25-km cube, Fig. 6; 3-D geomodel in App.

1). The 3-D model is based primarily on observations from the HiTech AlkCarb project's natural laboratories, particularly intrusions of the Gardar province in Greenland and the Damaraland province in Namibia. We have also drawn on literature for many other alkaline complexes (Fig. 5). Below, we discuss the geologic observations used to construct the model. These include the typical relationship between intrusive units, the impacts of volcanism and depth of emplacement, the processes by which wall rocks can influence mineralization, and characteristics of the alteration aureole surrounding intrusive systems. Additional details on the construction of the 3-D model are in Appendix 1.

Within the mineral system framework (Knox-Robinson and Wyborn, 1997; McCuaig and Hronsky, 2014; Banks et al., 2019), focused transport, concentration, and trapping of the commodity are the processes that are critical at the district scale. The preservation of mineralization is of additional concern, especially in rapidly eroding regions with steep topography.

Exploration at the district scale introduces higher-resolution airborne magnetic and radiometric surveys. The typical line spacing for such surveys is 70–100 m in order to resolve distinct volcanic and intrusive phases within the system (Brauch et al., 2018). Geochemical proxies in soil, stream sediment, or surface grab samples may also be used to vector toward mineralization (Steenfelt, 2012; see “Wall-rock influences and fenite alteration halos” section). Such techniques have been applied effectively in diamond and porphyry Cu exploration projects globally (e.g., Schulze, 2003; Grütter et al., 2004; Sillitoe, 2010; Williamson et al., 2016). Hyperspectral imaging techniques are under development and have the potential to directly map the REE content of mineralized rocks exposed at surface (Boesche et al., 2015; Neave et al., 2016; Bedini and Rasmussen, 2018; Möller and Williams-Jones, 2018; Booysen et al., 2020). Such techniques will be best applied in arid environments, such as hot deserts and the Arctic.

Plutonic relationships, magmatic system evolution, and the timescales of alkaline magmatism

A variety of intrusion morphologies are known from continental rift settings (Fig. 5). Large, layered silica-undersaturated examples (diam 18–40 km; blue, brown in 3-D geomodel) include the Devonian Lovozero and Khibiny Complexes in Russia (Kalashnikov et al., 2016a), the Mesoproterozoic Ilímaussaq Complex in southwest Greenland (Ferguson, 1964; Larsen and Sorensen, 1987; Marks and Markl, 2015; Borst et al., 2018), and the Mesoproterozoic Pilanesberg Complex in South Africa (Andersen et al., 2017; Elburg and Cawthorn, 2017). Typically smaller silica-saturated examples (diam 0.3–6 km; dark pink in 3-D geomodel) include the Mesoproterozoic Strange Lake Complex in Canada (Vasyukova and Williams-Jones, 2019a), the Cretaceous Baerzhe Complex in China (Wu et al., 2021), and the Cretaceous Brandberg-Amis Complex in Namibia (Schmitt et al., 2002). Subvolcanic levels (2–5 km) of these alkaline-silicate magmatic systems can host REE mineralization, commonly with higher HREE/LREE than carbonatite REE deposits, as well as zirconium, niobium, tantalum, uranium, and thorium (Dostal, 2017; Goodenough et al., 2018).

Mineralized alkaline-silicate magmatic systems are commonly polyphase, their intrusions preserving a general

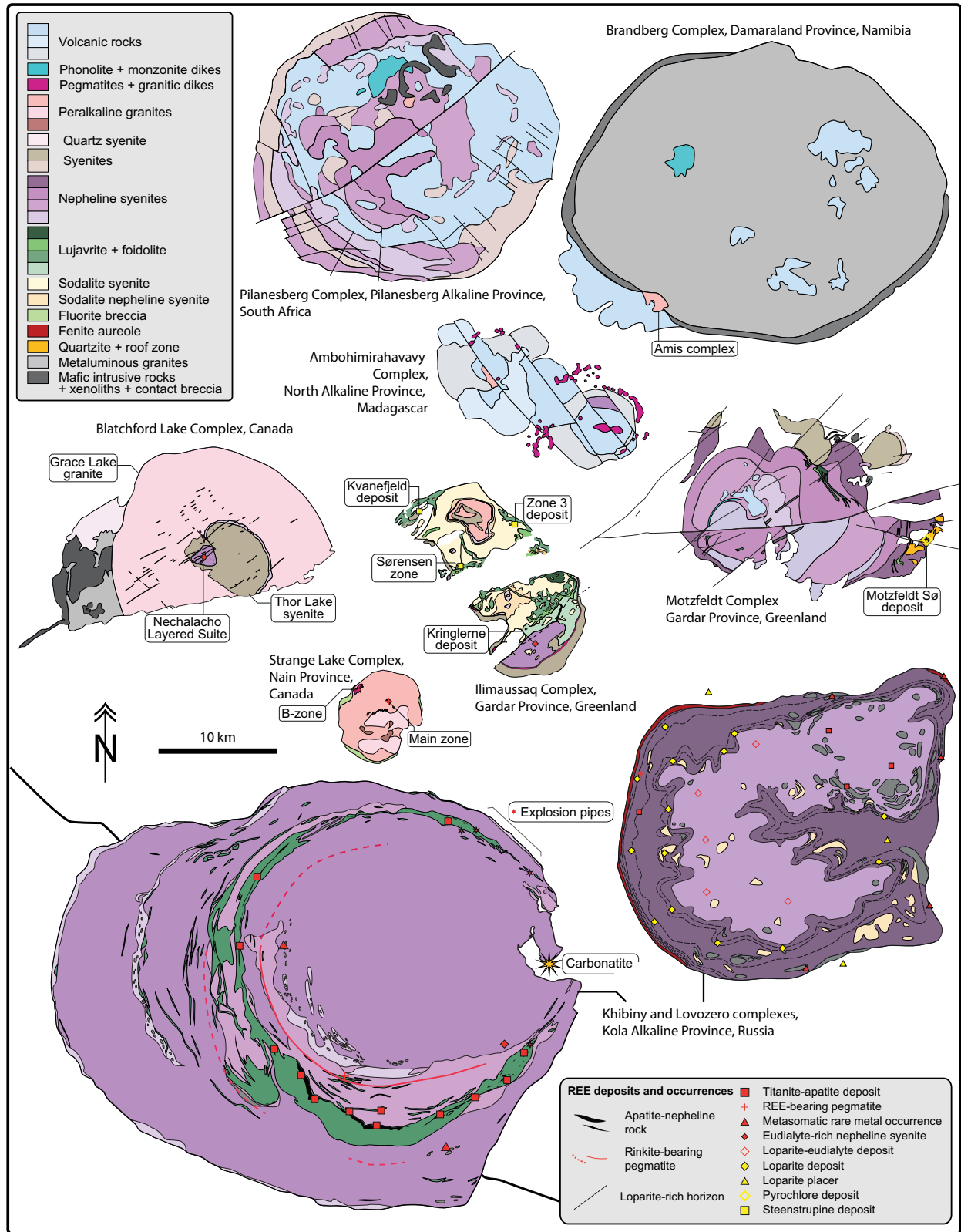


Fig. 5. A compilation of district-scale geologic maps from alkali silicate systems associated with rare earth element-high field strength element (REE-HFSE) mineralization. Scale is consistent between maps. Pilanesberg after Cawthorn (2015), Brandberg after Schmitt et al. (2000), Ambohimirahavavy after Estrade et al. (2019), Blatchford Lake after Williams-Jones (2016a), Ilimaussaq after Upton (2013), Motzfeldt after Finch et al. (2019), Strange Lake after Siegel et al. (2018), and Khibiny and Lovozero after Kalashnikov et al. (2016a). Multiple colors per lithology reflect divisions between similar units in the original maps.

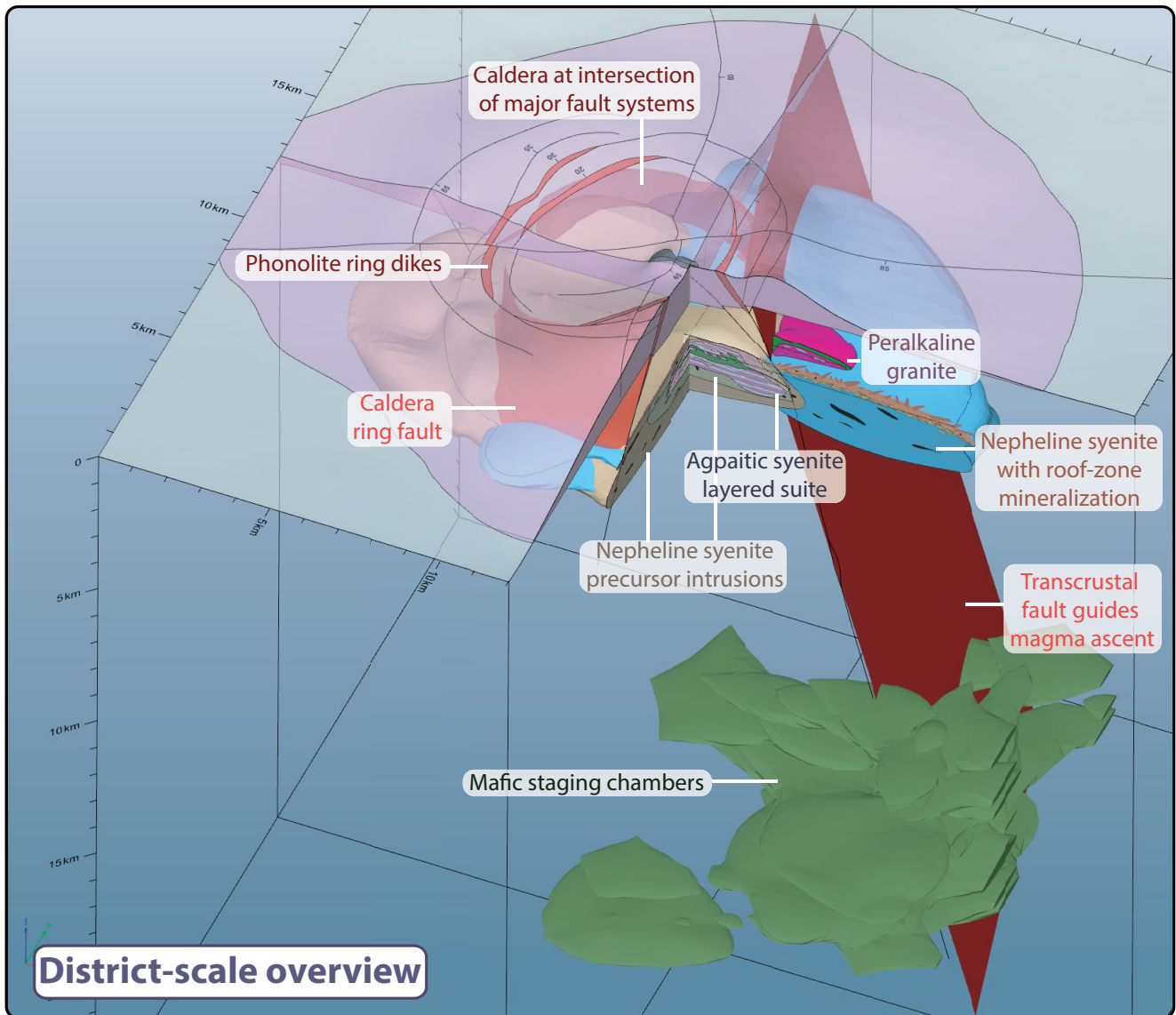


Fig. 6. Overview of the 3-D alkaline-silicate geomodel showing a surface caldera (geometry after Coumans and Stix, 2016) and a series of mafic staging chambers (green) that are inferred from gravity and magnetotelluric surveys (Blundell, 1978; Samrock et al., 2018). Many alkaline-silicate complexes occur on intersections of major fault systems, and magma ascent is thought to be guided by transcrustal fault systems (Banks et al., 2019). At a depth of ~2–3 km is a nested system of intrusions (blue, brown, pale pink). These have undergone a variety of levels of fractionation and of assimilation of country rocks (black, yellow), resulting in the formation of several types of rare earth element-high field strength element (REE-HFSE) mineralization. Detailed views of the mineralization are in Figures 8 and 9. The interactive 3-D model is in Appendix 1.

decrease in silica with time (e.g., Messum, Namibia, Harris et al., 1999; Erongo, Namibia, Trumbull et al., 2003; Blatchford Lake Complex, Canada, Mumford et al., 2014; Möller and Williams-Jones, 2016a; Fig. 5). This is expressed as a succession of intrusive phases that may include granites or quartz syenites toward the exterior, with later nepheline syenites toward the center. The alkali content of polyphase systems displays a similar general increase with time, tracking an increase in the degree of fractional crystallization relative to a primary mantle melt (e.g., Ilímaussaq, Greenland, Marks and Markl, 2015; Motzfeldt, Greenland, Jones, 1984; Finch et al., 2019). It is expressed as a succession from alkali gabbro, through miaskitic toward agpaitic syenite compositions.

The most evolved agpaitic units (purple in the 3-D geomodel) range in size from small sill-like bodies within an otherwise miaskitic intrusive suite (Motzfeldt, Jones, 1984) to layered intrusive bodies that represent the volumetrically dominant lithology (e.g., Lovozero, Khibiny, Kalashnikov et al., 2016a). In particularly large silica-undersaturated systems, carbonatite may occur as minor late plugs or dikes emplaced into the cores or margins of alkaline-silicate intrusions (Fig. 5) (Kalashnikov et al., 2016a).

The systematics of the silica content of alkaline-silicate magmatic systems can be explained using an analogy from continental flood basalt systems (Cox and Hawkesworth, 1985; Arndt et al., 1993; Beard et al., 2017). The first phase

of a magmatic system is intruded into fresh country rocks that may contain minerals stable only at low temperature. Intrusion of this magma establishes a strong chemical potential gradient, and the most mobile components of the country rock are destabilized and assimilated into the magmatic plumbing system. As the magmatic system becomes established, altered country rocks, crystal mushes, and related igneous rocks create a physicochemical barrier between the silicate melt and the fresh country rocks, resulting in a decrease in crustal assimilation with time (Harris et al., 1999; Riisshuus et al., 2008). This effect is captured in the 3-D geomodel via systematic changes to the character of intrusive phases: the first and outermost intrusive phase (blue in Fig. 6; based on Motzfeldt Sø and Grace Lake granite, Blatchford Lake Complex, Fig. 5) is characterized by common xenoliths and a silica-saturated roof zone (orange, see “Silicate roof zone deposits” section below), formed via extensive interaction between the silica-undersaturated intrusive body and its silica-rich country rocks. Later intrusive phases emplaced toward the center of the complex show a progressive decrease in silica content, brought about by a decrease in interaction between their melts and the country rocks (Precursor intrusion i, ii; pale brown, pale green in Fig. 6; e.g., Thor Lake syenite, Blatchford Lake Complex, Fig. 5). This intrusive sequence is characterized by an inward decrease in the number of xenoliths and an increase in autoliths.

Producing the extreme alkali enrichments seen in agpaite systems requires high fractions of crystallization relative to a primary melt composition derived from mantle (>90%; Spandler and Morris, 2016). Direct fractionation of a single package of mantle-derived liquid provides a simple mechanism by which to explain the formation of peralkaline igneous rocks (Ablay et al., 1998). However, recent trace element and radiogenic isotope measurements from pyroclastic volcanic deposits suggest that rejuvenation of magmatic systems partially remelts early formed cumulates or associated igneous rocks to produce silicate melts with more evolved compositions (Wiesmaier et al., 2012; Wolff et al., 2020). A progressive remelting and crystal fractionation model is further supported by the common occurrence of autoliths in layered alkaline intrusions (e.g., Upton, 2013). Whether crystal fractionation results in residual enrichment of the REEs and HFSEs is a delicate balance controlled largely by melt composition and by the mineralogy of the crystallizing assemblage. Dry crystallization (low $\alpha_{\text{H}_2\text{O}}$) produces a mineral assemblage rich in alkali feldspar and poor in clinopyroxene and amphibole (Giehl et al., 2013), which effectively enriches REEs in the residual melts (Beard et al., 2019). The high fluorine content of some mineralized alkaline systems (Andersen et al., 2010; Vasyukova and Williams-Jones, 2016) may further promote residual enrichment as it decreases the activity of REEs in the melt, reducing their uptake into minerals (Beard et al., 2020), and depresses HFSE mineral solubility (Marr et al., 1998; Aseri et al., 2015). Other minor elements, such as chlorine (Marr et al., 1998) and sulfur (Zheng et al., 2021), may also play important roles in the behavior of REEs and HFSEs in alkaline magmatic systems, but their influence is not yet well characterized. In the 3-D geomodel, the degree of fractionation increases inward between intrusive phases, culminating with an agpaite layered intrusion (purple; e.g., Nechalacho

Layered Suite, Blatchford Lake Complex, and Ilímaussaq Complex; Fig. 5).

Detailed geochronological studies indicate that polyphase alkaline-silicate magmatic systems are emplaced over geologically short timescales (<3 m.y., sometimes within the uncertainty of modern U-Pb techniques; Ilímaussaq Complex and Nechalacho Layered Suite; Krumrei et al., 2006; Möller and Williams-Jones, 2016b; Borst et al., 2019). By contrast, some mineralized silica-saturated systems appear to be monogenetic or dominantly emplaced in a single pulse (e.g., Ivigtût, Baerzhe, Strange Lake; Goodenough et al., 2000; Yang et al., 2014; Siegel et al., 2018). Short, inferred timescales represent minima, as they may result from overprinting of earlier magmatism or from only shallow levels of exposure where the complexity of the precursor feeder system is not represented at surface and is hence unrecognized.

To allow for the extensive fractionation required to form agpaite compositions, the ascent rate of alkaline-silicate magmas must be sufficiently slow (and probably persistent). The rapid melt ascent associated with the formation of monogenetic diatreme breccia pipes, a common feature of alkaline magmatic provinces, appears to be incompatible with REE-HFSE mineralization (2.5–60 m/s; Spera, 1984). These pipes, however, can pre- and postdate mineralization (e.g., Genge et al., 1995; Woolley, 2003; Humphreys et al., 2010), their permeability representing a potential trap for later hydrothermal mineralization (e.g., Dalucao, China; Liu and Hou, 2017). The processes that result in some alkaline-silicate systems being apparently short-lived while others remain intermittently active for millions of years are not yet well understood.

The presence of highly evolved peralkaline magmas and the complexity of growth zoning patterns in their autocryst and antecryst cargo indicate the crucial role for mafic staging chambers in the crust (Larsen, 1976; Bédard et al., 1988). Such magmatic bodies (dark green in 3-D geomodel and Fig. 6) have been inferred at a depth of >14 km below the modern East African rift via magnetotelluric techniques (Samrock et al., 2018) and are consistent with a positive Bouguer gravity anomaly in the Gardar province, Greenland (Blundell, 1978).

In postcollisional systems, common rock types include sheeted syenitic, phonolitic, and trachytic intrusions and carbonatite dikes, with REE, F, and Ba mineralization hosted in stockworks, breccia pipes, carbonatite dikes, and carbohydrothermal veins (e.g., Hou et al., 2009; Guo and Liu, 2019; Goodenough et al., 2021). Carbonatite is commonly more abundant than in continental rift systems, but alkaline-silicate rocks are usually still volumetrically dominant. A comprehensive description of the types of mineralization is not within the scope of this review.

Volcanic connections and the depth of emplacement

Linking alkaline-silicate volcanism to mineralization in the underlying plutonic systems has proved challenging, as exposure of mineralization tends to occur where volcanic sequences have been largely eroded. Extensive volcanism is thought to be incompatible with mineralization, as the associated volatile release may dissipate the commodity into the environment (cf. Sillitoe, 2010). However, minor, late eruptions—for example, of lamprophyre or carbonatite diatremes—have the potential to carry mineralized rocks to surface and offer a window into

the magmatic system at depth (e.g., Monte Vulture, Italy, Becaluva et al., 2002; Teide, Tenerife, Wiesmaier et al., 2012).

The East African rift has been considered as a potential active analogue for the Mesoproterozoic Gardar province, Greenland (Macdonald and Upton, 1993; Macdonald et al., 2014). Cenozoic volcanoes of the East African rift are characterized by major pyroclastic eruptions ($>10 \text{ km}^3$) of evolved peralkaline rhyolite, smaller effusive eruptions ($<10 \text{ km}^3$), and the development of caldera structures (Macdonald et al., 2014; Hutchison et al., 2016b; Rooney 2020a; see 3-D geomodel). Calderas are typically associated with the development of ring faults and associated intrusions (Cole et al., 2005; Coumans and Stix, 2016), which in turn can be recognized in many alkaline igneous complexes, including those from the Gardar province (Macdonald et al., 2014). Furthermore, caldera structures may represent foci for permeability and mineralization.

The Ambohimirahavy Complex in Madagascar (Fig. 5) represents an emplacement depth of $<2 \text{ km}$ and comprises a syenitic ring intrusion surrounding a central mass of volcanoclastic rocks, indicating the presence of a now partially eroded caldera (Estrade et al., 2014a). At the margins of the ring intrusion, REE- and HFSE-rich peralkaline granitic dikes are exposed, demonstrating that mineralization had developed in the underlying magma chamber (Estrade et al., 2014b). However, the volcanoclastic rocks preserved in the complex show no hint of mineralization. The Poços de Caldas Alkaline Complex in Brazil (Schorscher and Shea, 1992) and Pilanesberg Complex in South Africa (Cawthorn, 2015; Andersen et al., 2017; Elburg and Cawthorn, 2017) also represent eroded caldera systems, with late agpaitic nepheline syenites intruding the volcanic succession (Fig. 5). Pyroclastic ejecta from alkaline-silicate and carbonatite volcanoes may also contain REE minerals, but to attain economic grades and tonnages these minerals must be concentrated by sedimentary processes to form placer deposits, as reported at Aksu Dıamas in Turkey (Deady et al., 2019).

In the 3-D geomodel (App. 1), the surface-level lithologies are based on the Ambohimirahavy Complex, Madagascar (Estrade et al., 2019). The caldera fault system is based on analogue sandbox experiments (Coumans and Stix, 2016).

In the absence of volcanic rocks, depth of emplacement is difficult to constrain for alkaline-silicate systems, because of a dearth of calibrated mineral equilibrium barometers (Putirka, 2008; Masotta et al., 2013). Depth of emplacement may, however, influence mineralization potential because higher-pressure systems may more effectively retain dissolved volatiles. This is because pressure influences (1) the mineralogy of the crystallizing assemblage (Pilet et al., 2010; Iacovino et al., 2016; Romano et al., 2018) and, thus, the effectiveness of residual enrichment of REEs and HFSEs (Beard et al., 2019), (2) melt structure and phase equilibria associated with immiscibility of melts and fluid phases (Veksler, 2004; Massuyeau et al., 2015), and (3) the tendency for brittle fractures to form in country rocks (Brantut et al., 2013), which in turn influences the effectiveness of wall-rock assimilation and metasomatism, as well as the potential for volcanism or the venting of volatiles.

On passive or rifted continental margins, overburden at the time of emplacement has been used to estimate emplacement

depth, especially in ultrabasic and carbonatitic systems (Frolov, 1971; Epshteyn and Kaban'kov, 1984). Map compilations from these studies suggest that intrusion geometry may represent a qualitative indicator of pressure because of the greater plasticity of crust at depth and, thus, a greater tendency for emplacement structures to be circular in plan view (Frolov, 1971). Additionally, paleodepth constraints have been made using the intersections of fluid inclusion isochores (Konnerup-Madsen and Rose-Hansen, 1984; Krumrei et al., 2007; Vasyukova et al., 2016; Walter et al., 2021), phase equilibria (Möller and Williams-Jones, 2016a), and mineral geobarometers from adjacent and contemporaneous intrusive units (Mumford, 2013). Typical inferred emplacement depths for mineralized alkaline-silicate systems are 3–5 km, as shown in the interactive 3-D geologic model (Fig. 6; App. 1).

Wall-rock influences and fenite alteration halos

Mineralized alkaline-silicate rocks are hosted by a variety of igneous, metamorphic, and sedimentary lithologies, giving the initial impression that country-rock type does not play an influential role in mineralization. In some classes of alkaline-silicate-associated deposits, this is probably true, whereas for others, host lithology may play an important role in mineralization—for example, in roof zone deposits (see “Silicate roof zone deposits” section below).

The retention of magmatic volatiles is important for maintaining a depolymerized melt structure and thus delaying the crystallization of common HFSE phases, such as zircon (e.g., Boehnke et al., 2013) that can terminate residual enrichment of the REEs and HFSEs. Consequently, fine-grained host rocks that are impermeable and lack structures to facilitate fluid escape (Walter et al., 2018) or that react readily with magmatic fluids to seal off permeability may increase the potential for focused mineralization (e.g., Fe-rich country rocks; Elliott et al., 2018).

Country-rock assimilation can trigger saturation of crystal phases in the melt that either harbour or reject the REEs or HFSEs, affecting both the relative and absolute abundance of metals in the residual melt (e.g., Giebel et al., 2019). Via this mechanism, reactions with country rock represent a metal-trapping mechanism as they can abruptly decrease the metal carrying capacity of melt and fluid phases by triggering saturation of REE-HFSE minerals (“Silicate roof zone deposits” section below; Motzfeldt SØ, Finch et al., 2019). Indeed, assimilation of silica-rich lithologies may be the origin of oversaturated alkaline rocks in general (e.g., Eby, 1984; Stevenson et al., 1997; Harris et al., 1999; Marks and Markl, 2001). Interaction between alkaline-silicate melt and country rocks can alternatively trap rare metal mineralization in a reaction zone, as seen in skarn-hosted deposits at the Ambohimirahavy Complex, Madagascar (Estrade et al., 2015). Where fluid or melt phases escape the main intrusion, the REE tenor can be dispersed into the country rock, as seen at the Illerfissalik Complex, Gardar province (Sokół et al., 2022). This contrasts with world-class agpaitic layered syenite REE-HFSE mineralization at the neighboring Ilımaussaq intrusion (Borst et al., 2016).

In the 3-D interactive geomodel (App. 1), the blue alkaline intrusive phase highlights the interaction between alkaline magmatic systems and their country rocks. It is based

dominantly on features observed in the Motzfeldt Complex, Gardar province, Greenland (e.g., Finch et al., 2019) where the upper intrusive margin is a laterally continuous and structurally complex roof zone, generated via the reaction between alkaline-silicate melt and the country rocks that overlie the intrusion. Xenoliths of silica-rich Eriksfjord formation sandstones (yellow) have rounded shapes and appear to have reacted readily with the alkaline-silicate magmas. By contrast, basalt xenoliths (black) preserve angular forms and appear to have been relatively unreactive with the magma. Xenoliths up to kilometer scale are found throughout the main intrusive body of several systems in the Gardar province (Upton et al., 2003; Upton, 2013; Finch et al., 2019).

Alteration halos in wall rocks have been used during exploration for some classes of mineralization associated with magmatic systems, such as porphyry Cu deposits (Sillitoe, 2010). These aureoles can have a large footprint relative to the mineralization itself, and systematic variations in alteration mineralogy and composition can aid in the targeting of deposits. The alkali metasomatic aureoles that surround alkaline-silicate and carbonatite intrusions are termed “fenite.” Because fenite composition is controlled by protolith mineralogy, fluid composition, pressure, and temperature, it has potential for use as a vectoring tool during exploration (Elliott et al., 2018; Broom-Fendley et al., 2021). The extent of fenite is additionally controlled by country-rock permeability. Fenitization is typically less pronounced around alkaline-silicate systems than around carbonatite bodies (usually <100 m vs. 1–2 km; Ferguson, 1964; Al Ani and Sarapää, 2009; Arzamastsev et al., 2011). Fenites that formed at depth are typically sodium dominated, containing conspicuous green veins of sodic clinopyroxene and amphibole that cross-cut rocks dominated by alkali feldspar (Elliott et al., 2018). Fenites formed in shallower settings or more proximal to intrusive bodies tend to be potassium dominated and brecciated, containing abundant K-feldspar (~90%), with albite and minor assemblages of apatite, clinopyroxene, and rutile (Elliott et al., 2018). The potassium enrichment in fenite can be mapped by radiometric surveys and used as a vector toward mineralization (Simandl, 2015; Simandl and Paradis, 2018). Because fenite aureoles are formed via fluid expulsion from a parental intrusion, their extent, mineralogy, and geochemistry record information about the metal tenor of the parent intrusion (Downman et al., 2017; Broom-Fendley et al., 2021). This effect is not yet characterized to a sufficient level for widespread use in exploration.

As country-rock lithology and structure influence the type of deposits that may have formed and the extent of reaction halos, the exploration approach at the district scale will need to be adjusted depending on the geology into which the alkaline-silicate system was emplaced.

Prospect and Deposit-Scale Characteristics

The critical raw material deposits associated with alkaline-silicate systems occur either within igneous layered cumulates (orthomagmatic type) or within the upper margins of intrusive bodies where the magmatic system has interacted with country rocks (silicate roof zone type, peralkaline granite type). Alkaline-silicate intrusions containing mineralization are typically circular to oval in plan view (4–650 km²; Fig. 5).

The largest intrusions may be composites of several smaller bodies. Glacial erosion, exploration drilling, and geophysical surveys have revealed the 3-D structure of several REE-HFSE-mineralized alkaline-silicate systems, indicating the thickness, horizontal extent, and structural controls on mineralization (Upton, 2013; Kalashnikov et al., 2016a). These have been used to build the 3-D geomodel presented here (Fig. 6; App. 1).

At the prospect (~5 km) scale, ground geophysical methods offer insight into the 3-D structure of the subsurface in order to target with drilling campaigns promising geologic features at the deposit scale. These surveys include magnetic, gravity, seismic, resistivity, induced polarization, and audio magnetotelluric (AMT) techniques. None of these image REE mineralization directly, because associated unmineralized igneous rocks usually have similar petrophysical properties. However, these techniques can constrain the thickness of volcanic units and the morphology of intrusive bodies, especially where their properties contrast strongly with their host rocks (e.g., Brauch et al., 2018). Recent developments in joint 3-D inversion of gravity and magnetic data were used to map a nepheline monzogabbro pipe in the Kaiserstuhl alkaline silicate and carbonatite complex in Germany (www.terratec-geoservices.com; dos Santos et al., 2019).

At the deposit scale, exploration campaigns typically use a variety of core logging techniques and handheld devices. The data acquired by industry-standard downhole logging probes allow for automated discrimination of lithology and potentially of mineralized zones. These probes typically measure (1) spectral gamma as an indicator for uranium, thorium, and potassium concentrations (2) magnetic susceptibility to indicate the presence of ferromagnetic minerals, and (3) resistivity and chargeability as indicators for the presence of clay minerals, which are key to understanding the geometry of REE-HFSE deposits in weathered alkaline-silicate rocks. Since it is not possible to measure REE concentration directly with standard geophysical probes, it is necessary to correlate borehole logging results with handheld X-ray fluorescence measurements carried out on the core. Some recent borehole logging instruments allow for direct measurements of the REE content (e.g., oreLOG by UIT Dresden, Germany; Märten et al., 2015). However, these probes are not yet standard equipment in the exploration industry. Petrographic investigations are recommended because modal mineralogy and species mineralogy are crucial for understanding the deposit metallurgy and therefore economic potential (see “Metallurgical Challenges and the Importance of REE Profiles” section). The association of Th radiometric anomalies with REE mineralization as observed in numerous exploration projects worldwide plays a key role in this case (e.g., Tukiainen et al., 1984).

Orthomagmatic deposits in layered agpaitic syenite suites

Agpaitic syenite systems that host orthomagmatic mineralization represent the most evolved and alkali-rich melt compositions known on this planet (Marks and Markl, 2017) and contain some of the largest known REE deposits (Fig. 7; Goodenough et al., 2016; Smith et al., 2016). Several intrusions dominated by silica-undersaturated agpaitic rocks and exceeding 10 km in diameter are known: Ilímaussaq, Greenland (8 × 18 km; Marks and Markl, 2015; Borst et al., 2018),

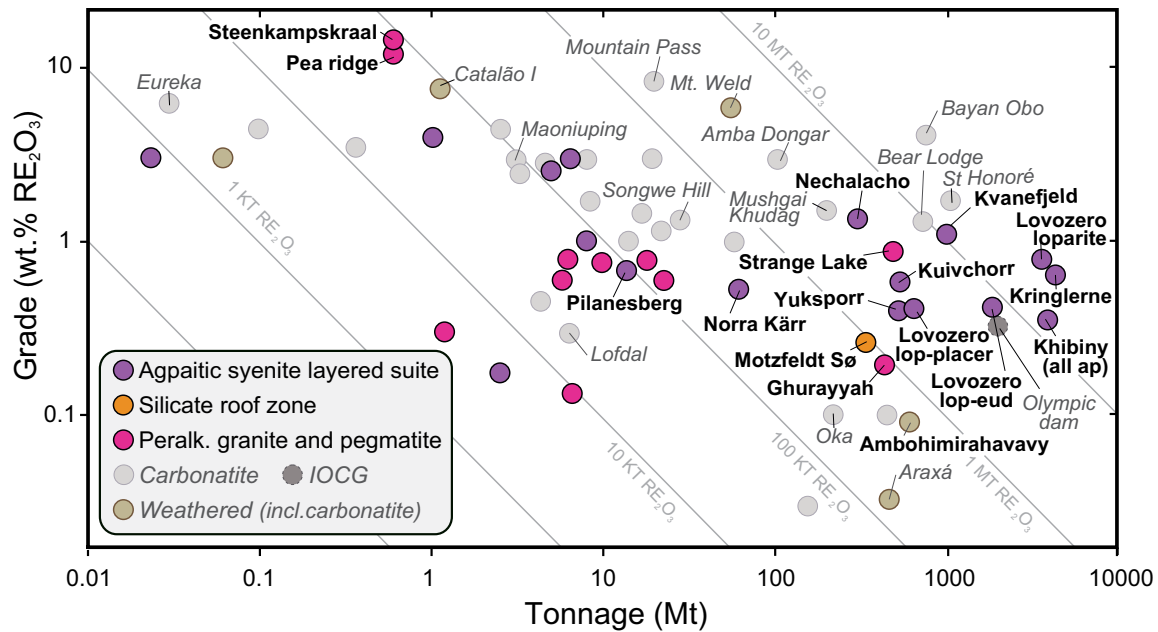


Fig. 7. Total RE_2O_3 grade (total rare earth oxide; TREO) versus tonnage diagram showing a global set of deposits. Diagonal gray lines indicate rare earth element (REE) tenor. Alkaline-silicate-associated REE deposits occupy a similar range of grade-tonnage space to carbonatite-associated REE deposits. Deposits in agpaitic syenite layered suites extend to greater REE tenor than most granite, pegmatite, or silicate roof zone deposits. Data from Woolley and Kjarsgaard (2008), Smith et al. (2016), and various company reports. The classification of deposits is based on the text in the “Prospect and Deposit-Scale Characteristics” section. A compilation of Joint Ore Reserves Committee (JORC) and NI 43-101 code-compliant resource estimates is in Appendix 3. Abbreviations: ap = apatite, eud = eudialyte, IOCG = iron oxide copper-gold, lop = loparite.

Khibiny and Lovozero, Russia (both ~40 km; Kalashnikov et al., 2016a), and Pilanesberg, South Africa (25 km; Cawthorn, 2015). These are layered intrusions consisting mainly of feldspathoid syenites and include early sodalite-rich roof rocks that are interpreted as flotation cumulates (Krumrei et al., 2007; Fig. 8; 3-D geomodel). Their stratified floor sequences are rich in sodic clinopyroxene, sodic amphibole, and ferrous fluorine-rich biotite. Late carbonatite is known from only a few examples (e.g., Gardiner, Khibiny) but is volumetrically minor compared with the silicate rocks (Kalashnikov et al., 2016a; Marks and Markl, 2017). Polyphase intrusive complexes that contain minor agpaitic units about 2 km in outcrop diameter are much more abundant (Mt. St. Hilaire, Poços de Caldas, Nechalacho, Motzfeldt, Norra Kärr; Fig. 5); therefore, these are what the 3-D interactive model is based on (Fig. 8; App. 1). Note that the subsurface extent of agpaitic units can be larger (e.g., Nechalacho; Möller and Williams-Jones, 2016a) but has only been drill defined in a few systems. The agpaitic portions of these polyphase systems may include igneous stratification similar to that described above (Möller and Williams-Jones, 2016a), and several contain Joint Ore Reserves Committee (JORC) or NI 43-101 code-compliant REE-HFSE resources (Fig. 7; App. 3). The majority of agpaitic rock occurrences are as minor late dikes and pegmatites within composite magmatic systems or as discontinuous blebs in otherwise miaskitic intrusions (Marks and Markl, 2017). Few, if any, of these constitute deposits of economic significance.

In orthomagmatic deposits, the ore minerals are located (1) within rhythmic cumulate layering in the floor sequence (Ilímaussaq, Khibiny, Lovozero; Sørensen, 1969; Kalashnikov et al., 2016a; Hunt et al., 2017; Borst et al., 2018; Mikhailova

et al., 2019; Fig. 8) or (2) in late crosscutting dikes or sill-like magmatic bodies (Ilímaussaq, Motzfeldt, Poços de Caldas; Jones, 1984; Ulbrich et al., 2005; Ratschbacher et al., 2015). The former appear to span entire intrusive systems (plan view 4–650 km²) up to a thickness of several hundred meters (Larsen and Sørensen, 1987; Féménias et al., 2005; Upton, 2013; Kalashnikov et al., 2016b). Mineralization occurs as complex Na-HFSE-silicate and Na-HFSE-oxide minerals such as eudialyte, steenstrupine-(Ce), loparite, and pyrochlore and tends to be HREE rich relative to most carbonatite-hosted deposits (e.g., at Ilímaussaq, Khibiny, Lovozero, Nechalacho, Motzfeldt; Sørensen, 1969; Bohse et al., 1971; Tukiainen, 1988; Sørensen, 1992; Möller and Williams-Jones, 2016a; Marks and Markl, 2017). Eight code-compliant resources have an average size of 750 Mt at 1.3 % TREO, the largest being the Kringlerne deposit in the Ilímaussaq Complex, Greenland (Fig. 7; pop-outs in 3-D geomodel).

Cumulate deposits of apatite and titanite are also known from peralkaline syenite intrusive systems and have been mined for phosphate and titanium (e.g., Kovdor, Khibiny; Kalashnikov et al., 2016b; Gerasimova et al., 2018; Kogarko, 2018). Although scandium is *sensu stricto* an REE, scandium deposits known from layered peralkaline systems are spatially separate from other REE deposits. This is because scandium is highly compatible in the M1 site of clinopyroxene (Beard et al., 2019) and is therefore concentrated early on in mafic cumulates (e.g., at Crater Lake, prev. Misery Lake, Canada; Williams-Jones and Vasyukova, 2018). Potentially economic scandium enrichments are also known from weathered carbonatites and granitic pegmatites (Siegfried et al., 2018).

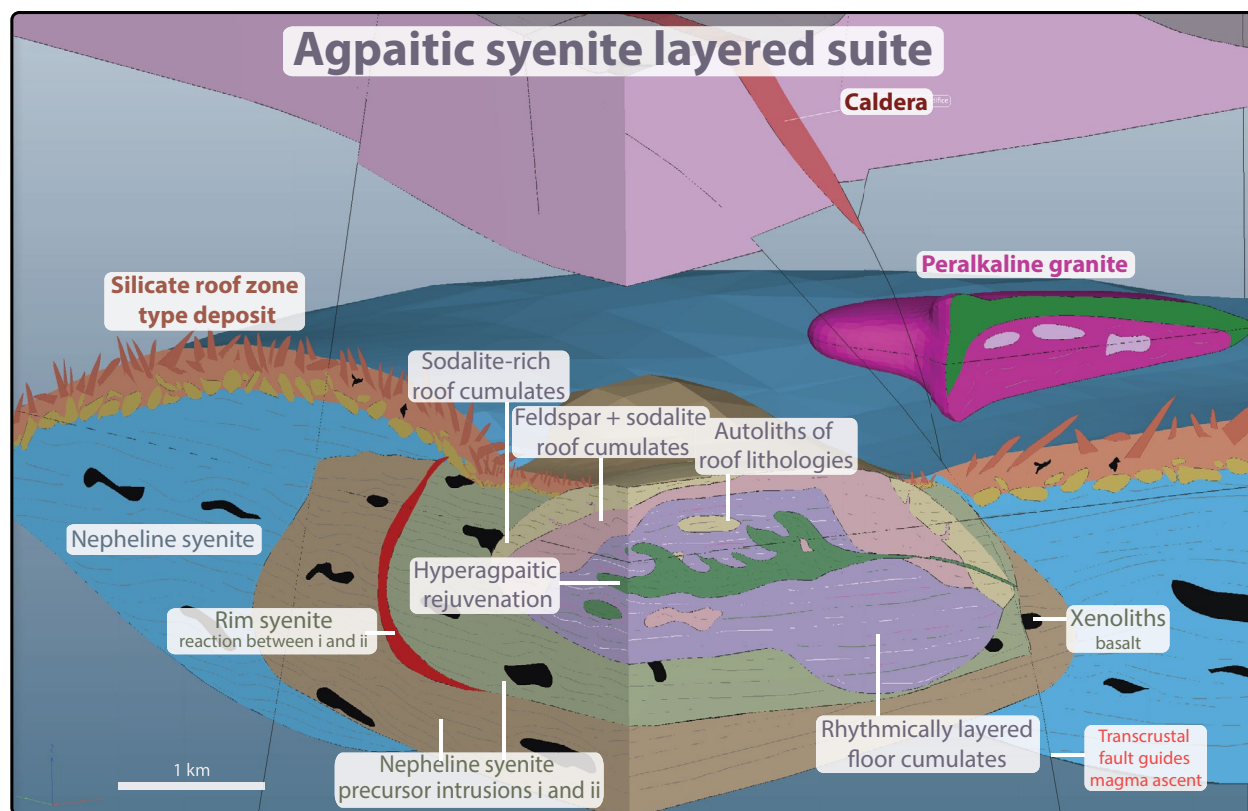


Fig. 8. A detailed view of the 3-D geologic model showing the internal structure of an agpaitic layered suite. Orthomagmatic rare earth element-high field strength element (REE-HFSE) mineralization is in rhythmically layered floor cumulates and in hyperagpaitic rejuvenations. Where present, precursor phases of the intrusion tend to record a general inward decrease in SiO_2 and increase in molar $(\text{Na} + \text{K})/\text{Al}$ (blue, brown, olive). These track decreasing levels of crustal contamination and increasing fractionation. A fine-grained rim syenite may occur on the boundary between intrusive phases (red; cf. Mumford et al., 2014). Detailed views of the silicate roof zone and peralkaline granite are in Figures 9 and 10. The interactive 3-D model is in Appendix 1.

Orthomagmatic deposits of REEs and HFSEs are also known from late hyperagpaitic magmatic bodies that crosscut alkaline-silicate intrusive systems (Fig. 8; 3-D geomodel). At the Ilímaussaq Complex, Greenland, exposure on the walls of fjords reveals that the late-stage lujavrite intrusions may have unzipped floor and roof cumulate layering and splayed both up- and down-section through a preexisting layered suite (combined thickness of 320 m; Ratschbacher et al., 2015). Similar features are reported at the Lovozero Complex, Russia, as the murmanite-lovozerite-bearing porphyritic malignites (Mikhailova et al., 2019). Both deposits are the products of evolved residual melts formed by crystal fractionation that may have pooled under the roof of deeper intrusive bodies or under kilometer-scale xenoliths or may have infiltrated units overlying the main intrusion (Sørensen et al., 2006; Ratschbacher et al., 2015). The largest known example of a cross-cutting hyperalkaline REE-HFSE deposit is at Kvanefjeld in the Ilímaussaq intrusion, Greenland, with 437 Mt at 1.1% TREO (Greenland Minerals Ltd., 2015; Fig. 7). At Kvanefjeld, steenstrupine-(Ce) is the dominant REE-U-Th mineral of economic interest (Khomyakov and Sørensen, 2001; Sørensen and Larsen, 2001; Sørensen et al., 2011; Andersen and Friis, 2014; see pop-up in 3-D geomodel).

The mineralization in layered peralkaline syenite systems may be preserved as fresh, unaltered igneous minerals

but is commonly overprinted or completely obliterated, occurring as complex pseudomorph assemblages of alteration minerals (Feng and Samson, 2015; Borst et al., 2016; Möller and Williams-Jones, 2017; van de Ven et al., 2019). These assemblages might not influence overall ore grades, but finely intergrown secondary phases might be challenging to process and extract with a commercial-scale metallurgical process optimized for eudialyte alone (Zakharov et al., 2011), although work is ongoing to develop beneficiation workflows (Stark et al., 2017; Vaccarezza and Anderson, 2020). This overprinting by autometasomatism occurs due to the flushing of residual Na-rich aqueous fluids, melts, and in some cases magmatic hydrocarbons through the cumulate pile during late stages of crystallization (Markl et al., 2001; Mitchell and Liferovich, 2006; Salvi and Williams-Jones, 2006; Marks and Markl, 2015; Borst et al., 2016). Retrograde solubility of some REE-HFSE phases further promotes breakdown and metal remobilization during cooling (e.g., Aja et al., 1995; Timofeev et al., 2015). Late-stage melts and fluids may therefore (partially) remobilize orthomagmatic mineralization, carrying the metals upward through the crystal pile (van de Ven et al., 2019). If residual melt and fluid phases are retained to low temperatures ($<200^\circ\text{C}$), then the intrusion may also retain its metal budget largely in situ (van de Ven et al., 2019).

Several metamorphosed examples of orthomagmatic peralkaline syenite deposits are known (Norra Kärr, Red Wine, Kipawa, and Sushina Complexes; Chakrabarty et al., 2016, 2018; Atanasova et al., 2017; Sjöqvist et al., 2017). The main REE mineral of interest in all these cases is eudialyte. However, there has been only limited study on the effect of metamorphism on REE minerals and the potential remobilization of REE that such conditions might trigger (Sjöqvist et al., 2020).

Mining of orthomagmatic deposits in agpaitic syenite layered suites has occurred in only a few cases because of metallurgical challenges posed by their complex REE-HFSE mineralogy (pop-up in 3-D geomodel, App. 1). In the Khibiny Complex in Russia, HREE-rich rinkite pegmatites at the Yuksporr Lovshorrite deposit were mined for REEs, Nb and Ti between 1934 and 1939, and apatite mines are currently in production (e.g., Kalashnikov et al., 2016a). The only operating Nb production in an alkali silicate system is the Karnasurt mine in nepheline syenites of the Lovozero Complex, Kola Peninsula, Russia. Here loparite, a perovskite group mineral, is targeted for Ti, Nb, Ta, and REEs (Mitchell, 2015; Kalashnikov et al., 2016a).

Silicate roof zone deposits

Silicate roof zone type deposits occur in the upper portions of layered alkaline-silicate systems and occasionally underneath large xenoliths or autoliths within layered suites (Sørensen, 1992; Sørensen et al., 2011; Fig. 9). In the former case, roof

zones may be continuous across the lateral extent of plutons (up to ~10 km) with a thickness of several hundred meters (Stephenson and Upton, 1982; Upton et al., 2013). The metasomatic reaction of residual melts and fluids with the roof and country rocks forms complex networks of crosscutting lenses and sills as well as late-stage veins and pegmatites (Müller-Lorch et al., 2007). These late-magmatic pegmatites and veins are often enriched in a variety of elements (e.g., Li, Be, U, Th, REEs, Ti, Nb, Ta, Zr, and Zn; Bailey et al., 2001).

Roof zones represent the reaction products of metalliferous residual fluids and melts with roof rocks, which include both igneous roof cumulates and country rocks. They are defined by strong thermal and chemical gradients (Huppert and Sparks, 1988), including redox; thus, ascending melts and fluids that enter the roof undergo abrupt changes in metal carrying capacity, in some cases causing saturation of minerals that can trap a mobile commodity. Deposits in roof zones are less well studied than the orthomagmatic type, and key questions for future work relate to their internal structure, the mechanisms of mineralization, and the physical and chemical relationship between roof zones and their underlying alkaline-silicate plutons. Roof zone mineralization is known from alkaline granitic rocks (Bushveld Complex, Bailie and Robb, 2004; Mutele et al., 2017) and syenite complexes associated with continental rifting (Gardar province, Finch et al., 2019; Ditrău Complex, Romania, Honour et al., 2018; Kola Peninsula, Russia, Kalashnikov et al., 2016a). The Grace Lake granite of the Blatchford Lake Complex, Canada, may represent

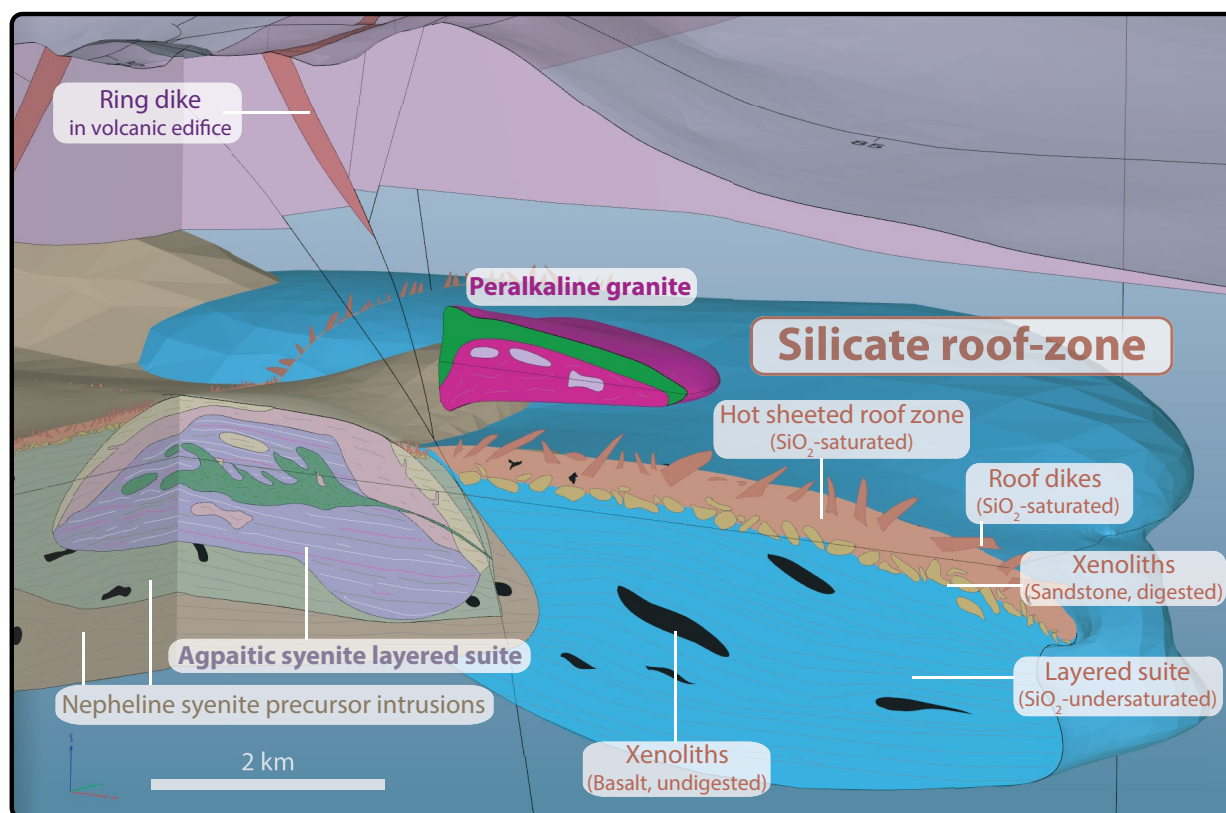


Fig. 9. A detailed view of a roof zone type deposit in the 3-D alkaline-silicate geomodel (overview in Fig. 6). This deposit class represents extensive interaction between alkaline-silicate magmas and their country rocks; this hybridization likely representing the trigger for mineralization. The interactive 3-D model is in Appendix 1.

a similar, but unmineralized, setting (Mumford, 2013; Mumford et al., 2014). In the case of the syenite complexes, the roof zone is characterized primarily by mineralization of Nb-Ta-Zr rather than of the REEs.

The best-studied example of a mineralized roof zone is that at Motzfeldt Sø, Greenland (Finch et al., 2019), where xenolith populations suggest preferential digestion of quartz arenite (yellow, Fig. 9; App. 1) relative to basaltic country rocks (black), resulting in generation of Si-F-rich hybrid melts. The Nb-Ta mineralization at Motzfeldt is hosted high in the roof by a series of discontinuous sheets of pyrochlore micro-syenite, notably without chilled margins (Tukiainen et al., 1984; Tukiainen, 1988; Finch et al., 2019). Their contained pyrochlore preserves oscillatory concentric zonation of Nb and Ta, a record of polyphase crystal growth (McCreath et al., 2013). These pyrochlore grains may have been remobilized upward through the roof zone by several episodes of magma overturning or replenishment (Tukiainen, 1988). Pyrochlore from this type of system typically contains high concentrations of U and Th. However, postmagmatic hydrothermal alteration can increase the U-Th concentration of pyrochlore without

strongly affecting HFSE concentrations (McCreath et al., 2012; Finch et al., 2019). For this reason, airborne gamma radiometric mapping, commonly used in exploration campaigns, may reveal regions rich in U and Th that do not necessarily correlate spatially with the Nb-Ta mineralization most favorable for beneficiation (Tukiainen et al., 1984; Finch et al., 2019). Motzfeldt Sø is the only roof zone type deposit with a code-compliant resource estimate, inferred to be 340 Mt at 120 ppm Ta_2O_5 , 1,850 ppm Nb_2O_5 , 4,600 ppm ZrO_2 , and 2,600 ppm TREO (Ram Resources 2012; Fig. 7; pop-up in 3-D geomodel, App. 1).

Mineralization associated with peralkaline granites and pegmatites

Rare earth element-HFSE mineralization is also associated with peralkaline (A-type) granite magmatism (Fig. 10; 3-D geomodel). This type of deposit has recently been reviewed by Vasyukova and Williams-Jones (2020). The majority of REE-HFSE mineralization described here is in the upper parts of intrusions and associated with hydrothermal alteration and pegmatite formation (Vasyukova and Williams-Jones, 2019a).

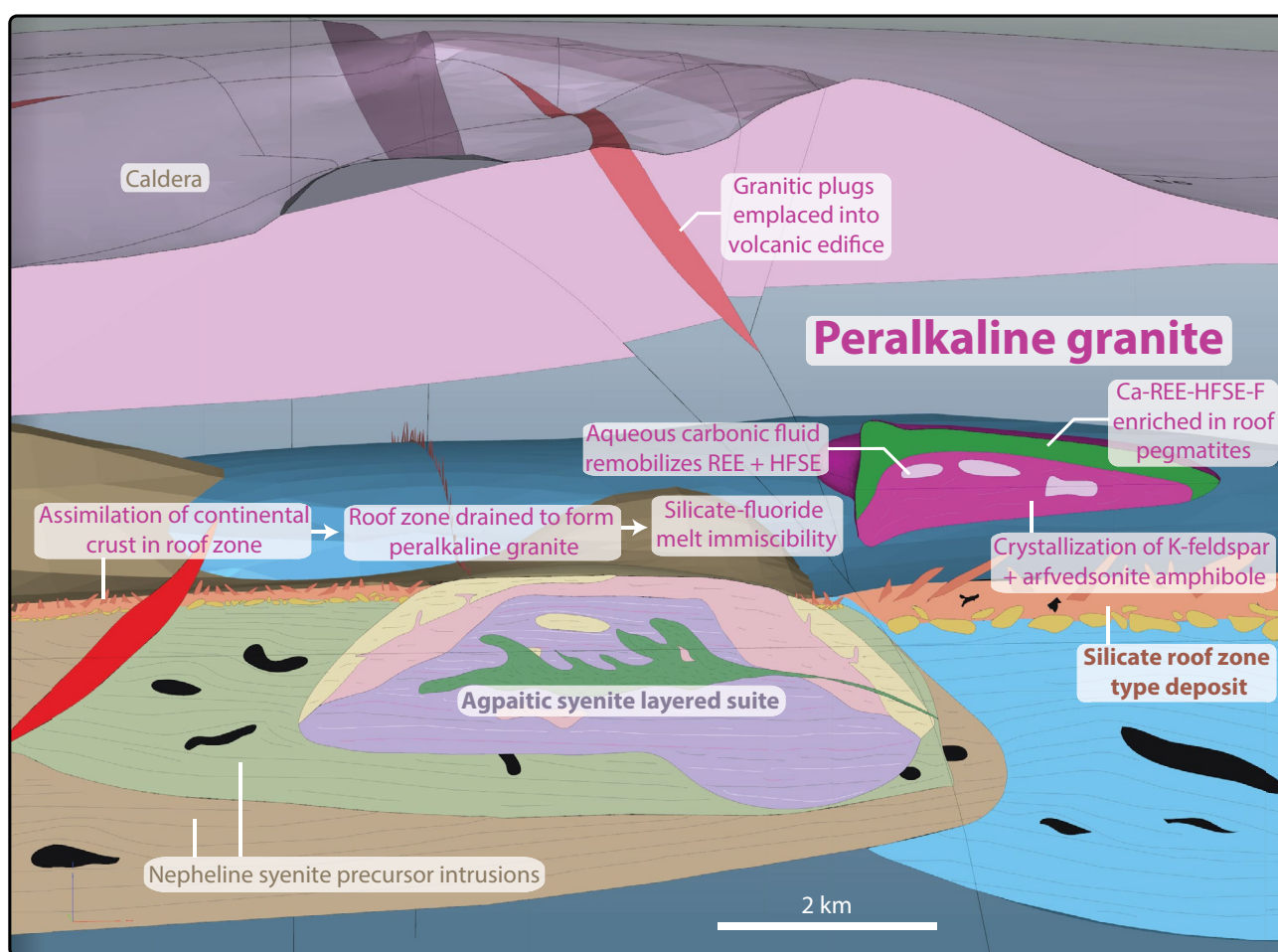


Fig. 10. A detailed view of the internal structure of a mineralized peralkaline granite intrusive body. Mineralization associated with peralkaline granites tends to be spatially associated with the roof where salt (ionic) melts and volatile-rich fluids accumulate. Granitic magmas may also be emplaced as plugs and dikes in the volcanic edifice, peripheral to major silica-undersaturated intrusive bodies (Estrade et al., 2014b). The interactive 3-D model is in Appendix I. REE-HFSE = rare earth element-high field strength element.

Some of these systems have agpaitic compositions. The host granite intrusions may be monogenetic or polygenetic and are typically hundreds of meters to several kilometers in diameter (Fig. 5). They may also occur as plugs or dikes external to a major silica-undersaturated center (Ambohimirahavavy Complex, Estrade et al., 2014b; T zone, Nechalacho, Möller and Williams-Jones, 2016a). The fluorite-rich breccias that commonly define the margins of these granites suggest fluorine-rich melt compositions (Vasyukova and Williams-Jones, 2014, 2016). Compositional similarities with silicate roof zone deposits (see “Silicate roof zone deposits” section) suggest that A-type granites may be roof zones that were later mobilized through the crust (Fig. 10). REE-Zr-Nb mineralized pegmatites are typically tens of centimeters to tens of meters thick and occur in the upper part (cupola) of these granitic intrusions. Mineralization reflects the combined effects of early immiscible fluoride melts and late hydrothermal fluids (Vasyukova and Williams-Jones, 2019a). The anomalous enrichments of these roof pegmatites in fluorine, calcium, and the REEs are consistent with crystallization of a (REE-) fluoride melt phase (Veksler et al., 2012; Yang and van Hinsberg, 2019), as well as subsequent and extensive late-stage hydrothermal alteration (Salvi and Williams-Jones, 1996; Gysi and Williams-Jones, 2013). The Strange Lake granite, Canada, is presently the best-characterized example of this class of mineralization (Salvi and Williams-Jones, 2006; Siegel et al., 2018; Vasyukova and Williams-Jones, 2019b). REE-HFSE-mineralized pegmatites are additionally known from the Ambohimirahavavy and Manongarivo Complexes, Madagascar (Estrade et al., 2014a, b); the Amis Complex, Namibia (Schmitt et al., 2002; Bernard et al., 2020); Baerzhe, China (Qiu et al., 2019; Wu et al., 2021); Bokan Mountain, Alaska, USA (Dostal et al., 2014); the Evisa Complex, Corsica (Bernard et al., 2020); and Khaldzan Buregtey and Khan Bogd, Mongolia (Kovalenko et al., 1995; Kynicky et al., 2011). An extremely fluorine rich example that lacks REE-HFSE mineralization is the Ivigtût alkaline granite in the Gardar province, Greenland, where the (probably unique) 150-m-wide cryolite deposit within the granite was formed from a fluoride-rich, carbonate-rich fluid or melt (Goodenough et al., 2000; Köhler et al., 2008). Ivigtût has been mined out because cryolite from this deposit was a key ingredient for the smelting of aluminium in the 19th century (Berry, 2012).

Although many peralkaline granitic systems show significant enrichment in the REEs and HFSEs, virtually none have been exploited. This may be due, in part, to their complex mineralogy (Jaroni et al., 2019; Pell et al., 2021; pop-out in 3-D geomodel; “Metallurgical Challenges and the Importance of REE Profiles” section above). The REEs and HFSEs are typically hosted by multiple phases including zircon, elpidite, gittinsite, armstrongite, monazite-Ce, xenotime-Y, allanite-Ce, gadolinite-Y, columbite-tantalite, pyrochlore, bastnäsite-Ce, and REE fluorocarbonate minerals, such as fluocerite-(Ce), gagarinite-(Y), and fluorite-fluocerites (Gysi and Williams-Jones, 2013). Few of these minerals have proven workflows for commercial beneficiation (see “Metallurgical Challenges and the Importance of REE Profiles” section), but various key parameters such as their flotation properties and acid bake chemistry have been determined (Demol et al., 2019; Kursun et al., 2019). Variations in ore

mineralogy and texture within individual deposits represent significant geometallurgical challenges.

The largest REE-HFSE deposits in peralkaline granitic systems have TREO resources about an order of magnitude smaller than their orthomagmatic silica-undersaturated cousins, with similar TREO grades (~1 wt %; Fig. 7). Strange Lake, Canada, has the largest REE resource with 278 Mt at 0.93% total rare earths (TRE; indicated) and 214 Mt at 0.85% TRE (inferred) for a total of 5.1 Mt TREO (Quest Rare Minerals Ltd., 2017).

There are several localities, such as the Erongo Complex in Namibia, Pitinga in Brazil, and the Nigerian younger granites (e.g., Ririwai Complex), where peralkaline granitic complexes may be associated with tin-tungsten mineralization in roof zone pegmatites and marginal facies (Lenharo et al., 2003; Kinnaird et al., 2016). Such mineralization is more characteristic of S-type granites and likely indicates the importance of crustal contamination in these plutons (Costi et al., 2009; Pirajno, 2015; Falster et al., 2018).

The Impact of Weathering

Weathering may extend hundreds of meters from the ground surface and can cause significant changes to both the geochemistry and mineralogy of alkaline-silicate complexes. In rare examples, such as at Tomtor in Russia (Lazareva et al., 2015) and Poços de Caldas in Brazil (Schorscher and Shea, 1992), the REE-HFSE grades have been enhanced by surface weathering as easily weathered components of the igneous rocks have been broken down and removed. At Poços de Caldas, lateritic and allitic weathering of phonolites and nepheline syenites with magmatic hydrothermal U-Th-REE enrichments further elevated metal concentrations and formed the recently mined Osamu Utsumi U-Zr-REE-Th deposit and the Morro do Ferro U-Th deposit (Schorscher and Shea, 1992; Takehara et al., 2016). However, in most cases, weathering breaks down REE minerals, which may then be dispersed into the surface environment, sequestered by secondary REE minerals, some of which are not yet easily processed (e.g., florencite-Ce, Barros De Oliveira and Liguori Imbernon, 1998; Wall and Zaitsev, 2004), or adsorbed in their ionic form onto mineral surfaces, especially clays. The latter process can generate ion adsorption deposits (IADs) from which the REEs are relatively easily recovered.

Global production of HREEs is dominated by IADs from southern China (~80%; Weng et al., 2015; Jowitt et al., 2017). These Chinese deposits formed in the weathering profile of a variety of types of granite (Bao and Zhao, 2008; Sanematsu and Watanabe, 2016), and similar weathering processes control the formation of IADs on syenites and pegmatites elsewhere (Estrade et al., 2019; Borst et al., 2020). IAD ore grades are relatively low (a few 100 to 1,000s of ppm of REE) compared to hard-rock alkaline-silicate and carbonatite deposits, but extraction can be economically viable through in situ or heap leaching of the clay-adsorbed REE fraction (Moldoveanu and Papangelakis, 2016).

The main factors that determine the mobilization and redistribution of the REEs in IADs are the REE mineralogy of the bedrock and the soil pH (Bao and Zhao, 2008; Li et al., 2020). During weathering, a portion of the REEs is released from minerals in the bedrock and adsorbed to clays and other

secondary phases in the regolith (Yang et al., 2013; Sanematsu and Watanabe, 2016; Estrade et al., 2019; Li et al., 2019; Borst et al., 2020).

Weathering of precursors with high REE grades and easily weathered REE phases produce higher-grade IAD deposits. For example, the Zudong deposit in southern China formed on a granite containing synchysite-Y (Li, et al., 2017, 2019, 2021; Xu et al., 2017), and the Ambohimirahavy Complex in Madagascar formed on peralkaline granite, nepheline syenite, and pegmatite dikes containing eudialyte, apatite, and REE-fluorcarbonates (Estrade et al., 2019; Borst et al., 2020). Lower leachable REE grades have been reported where protoliths contained more resistant REE-bearing phases such as zircon, pyrochlore, monazite, and xenotime (Estrade et al., 2019). At the Bankeng deposit, China, the HREEs that liberated to groundwater by weathering were transported downslope, and where soil pH increases due to water-regolith interaction, they were efficiently fixed by adsorption to clays (Li et al., 2020). LREEs at Bankeng are richest upslope, possibly due to the presence of relatively resistant and LREE-rich monazite-Ce and apatite in the granite bedrock. Other factors that play a role in IAD formation are climate, topography, vegetation, and hydrological factors, such as seasonal variations to the depth of the water table (Yang et al., 2019; Li et al., 2020).

The thickness of the oxidation and weathering zones in IAD-type deposits can be mapped via induced polarization geophysical techniques (Brauch et al., 2018). The formation of clay minerals lowers the resistivity of the rocks relative to their igneous precursors. Their chargeability is also reduced during the oxidation and weathering of sulfide minerals (where present). Various IAD-type deposits are currently under exploration in South America, Africa, and Southeast Asia (Sanematsu and Watanabe, 2016).

Summary and Outlook

Alkaline-silicate-associated REE-HFSE deposits are a relatively understudied ore deposit type that is increasing in importance as global energy and transport infrastructures shift toward renewables. In the last two decades, the magmatic-hydrothermal evolution of these systems and their links to continental-scale geodynamic processes have been clarified. Recent developments in exploration have seen the successful delineation of substantial new REE resources within alkaline silicate rocks. However, mineralogy and mineral processing remain major hurdles to getting alkaline-silicate-associated deposits into production. Numerous pilot studies are underway and aim to develop beneficiation pathways for the diverse family of REE-HFSE ore minerals. As is the case for all mining projects, public trust must be earned early in the exploration process and maintained if commercial extraction is to take place. Special considerations must be made for the risks posed by radionuclides, which are likely to be a social concern even in cases where the actual environmental risk is negligible.

The current state of geologic understanding of alkaline-silicate systems allows for exploration programs to use a combination of geophysical and geochemical tools to progressively reduce the scale of search areas, following a mineral systems approach. Mineralization is known from continental rift,

postcollisional, and intraplate (e.g., plume) tectonic settings. At the continental scale, the key targeting criteria are (1) a trigger for low-degree, ideally persistent, mantle melting, (2) melting at high pressure, for example, under thick continental crust (≥ 40 km) at craton margins, and (3) a mantle source that is enriched in the commodity and a suitable cocktail of alkalis and volatiles to promote extensive fractional crystallization—for example, mantle that was metasomatized by subduction. Also note that (4) All mineralization identified thus far postdates the Archean, as high mantle potential temperatures early in Earth history do not appear to be associated with significant alkaline magmatism. Province-scale exploration should identify and map crustal-scale structures that could have focused magma ascent from the mantle. In continental rifts, the largest intrusive centers straddle long-lived fault systems and are crosscut by them. In postcollisional settings, intrusions are commonly aligned along crustal-scale transcurrent shear zones. At the district scale, exploration should target long-lived or repeatedly reactivated intrusive systems, as these have the greatest potential for the extensive fractional crystallization required for residual enrichments of the REEs and HFSEs. Volcanism does not appear to exclude the possibility of mineralization. However, the retention of magmatic volatiles is important for maintaining a depolymerized melt structure required for extended fractional crystallization. Highly reactive, low-permeability wall rocks are therefore key to the sealing-in of REE-HFSE-rich residual melts and fluid phases, thus preventing dispersal of the commodities into the wider environment. An interactive 3-D model presented at district scale shows the typical relationship between lithologies and places alkaline-associated mineralization within a horizontal and depth reference frame. This includes orthomagmatic mineralization in layered apatitic syenites, silicate roof zone type deposits, and mineralization associated with peralkaline granites and pegmatites.

There is still much to learn. Outstanding questions highlighted by this work include the following:

1. What are the fundamental mantle and crustal factors that determine whether continental rifts or collisional belts are endowed with rich and extensive alkaline-silicate REE-HFSE mineral systems (e.g., Kola and Gardar provinces), smaller and more temporally limited systems (Mianning-Dechang belt), or none at all (mid-continent rift)?
2. Can the systematics of province-scale crustal structures be used as a robust predictor for the main focus of mineralization? What role, if any, does rift asymmetry play?
3. What are the effects of depth (pressure) of crystal fractionation on the residual enrichment of the REEs + HFSEs in transcrustal alkaline-silicate magmatic systems? Is there an important role for country-rock assimilation?
4. What are the processes that result in some alkaline-silicate systems being apparently short-lived, while others remain intermittently active, potentially for millions of years, preserving multiple stages of magma intrusion or volcanism?
5. What is the relationship between depth of emplacement and mineralization in alkaline-silicate intrusions? What influence does depth have on the extent of autometasomatism and on the retention of the metal budget within the intrusion versus that expelled into country rocks?

6. What is the relationship between fenite metasomatic aureoles and their parent intrusive bodies? Can the extent, mineralogy, or geochemistry of fenite alteration be used to indicate metal tenor in the parent intrusion?

Effective study of these and other problems will require integration of diverse approaches. These include the geochemical and mineralogical studies that have thus far been a major focus in alkaline systems, as well as experimental work on the thermodynamics of alkaline magmas, fluids, and metal transport mechanisms, field-based geochemical and geophysical studies, and the assembly and interrogation of global-scale geochemical and geophysical databases. Better and more detailed documentation of geologic relationships is required at all scales, but especially related to structure on the regional to district scale. The acquisition of this spatial data will allow for better targeting of laboratory studies and will hopefully clarify both the evolutionary histories of alkaline-silicate REE-HFSE systems and the fundamental controls on the formation of large and high-grade mineralization.

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