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**Isotopic evidence for a lithospheric origin of alkaline rocks
and carbonatites: an example from southern Africa**

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1 Isotopic evidence for a lithospheric origin of alkaline rocks
2 and carbonatites: an example from southern Africa

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55 **Abstract:** Alkaline rocks and carbonatites, including nepheline syenites, are well
56 established as mantle-derived magmatic products, but the nature and location of their
57 mantle sources is debated. Some workers have used isotopic compositions to infer mixed
58 mantle plume type sources such as EM1, HIMU and FOZO, implying derivation from the
59 subcontinental asthenosphere. Other models favour an entirely lithospheric source,
60 whereby the magmas, originally formed during intracontinental rifting, became deformed
61 and subducted into the mantle lithosphere during later continental collisions, and
62 constituted part of a source component for later rift-related alkaline and carbonatite
63 magmatism. We tested this model using Sr, Nd and Hf isotopic compositions of
64 deformed and undeformed nepheline syenites and carbonatites from 3 occurrences in
65 southern Africa, representing emplacement over a ~1 Ga time span. These include: Bull's
66 Run, South Africa (1134 Ma), Tambani, Malawi (726 Ma) and the Chilwa Alkaline
67 Province, Malawi (130 Ma). Mixing modelling indicates that the isotopic compositions of
68 the early Cretaceous Chilwa samples can be accounted for if their source consisted of a
69 blend of ~99% depleted subcontinental mantle lithosphere (DM) and ~0.5-1% of a
70 subducted component similar to the Neoproterozoic Bull's Run nepheline syenites. We
71 do not consider the Bull's Run material specifically as the component involved in the
72 Chilwa source, but our model illustrates an example of how recycled, older, alkaline
73 magmatic rocks can contribute to the mantle sources of younger alkaline rock and
74 carbonatite magmatism. This model accounts for the observation of recurrent alkaline
75 rock and carbonatite magmatism over hundreds of m.y. in spatially restricted areas like

southern Africa. Carbonatite and related alkaline magmatic rocks, therefore, need not owe their origin to deep, sublithospheric melting processes.

Keywords:
Carbonatite
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Lithosphere
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Draft

Introduction

Isotope geochemistry shows that young (<200 Ma) alkaline rocks and carbonatites (acronym: ARCs), including nepheline syenites, syenites and nephelinites, are mantle-derived. Evidence includes the variable, but generally low initial Sr ratios (0.703-0.705), positive initial ϵ_{Nd} values (to +7), $\delta^{18}\text{O}$ values mainly between 6 and 9 ‰, and Pb isotopic compositions consistent with known or inferred mantle sources (e.g. Bell and Blenkinsop 1989; Nelson et al. 1988; Kwon et al. 1989; Deines 1989; Sasada et al. 1997). Because of their very high concentrations of Sr, Nd (and to a lesser extent, Pb), carbonatites and related rocks can be used as mantle probes throughout geologic time, unhindered by the effects of crustal contamination and in-situ decay of parent isotopes (Bell et al. 1982; Bell and Blenkinsop 1987a, 1989).

Early isotopic work on Precambrian ARCs from Canada, based on Sr and Nd systematics (Bell et al. 1982; Bell and Blenkinsop 1987a), implied derivation from a long-lived, depleted source with $\text{Rb/Sr} = 0.017 \pm 0.002$ and $\text{Sm/Nd} = 0.358 \pm 0.008$ that was interpreted to represent sub-continental lithospheric mantle. Later work, mainly on young ARCs from East Africa, revealed that their initial Sr and Nd isotopic compositions are negatively correlated and fall on a so-called East African Carbonatite Line (EACL), implying the involvement of two mantle sources, one depleted, and one enriched relative to bulk Earth and CHUR (Bell and Blenkinsop 1987b; Bell and Tilton, 2001). This initiated debate as to whether the ARC sources were situated in the lithospheric or asthenospheric mantle, or both (e.g., Bell and Blenkinsop 1989), and through the addition

of Pb and Hf isotopic measurements (e.g. Kwon et al. 1989; Bizzarro et al. 2002), the number of mantle sources under consideration increased to include DMM, EM1, HIMU and FOZO (Bell and Tilton 2002). Some now argue for the dominance of just two asthenospheric sources (EM1 and HIMU) (Bizimis et al. 2003; Bell and Simonetti 2010).

The association of ARCs with intracontinental rift zones is well established (e.g. Bailey 1974, 1977, 1992), and a prominent example is the East African Rift, where a large fraction of the world's carbonatite and associated alkaline plutonic and volcanic rock occurs (Woolley 2001). Bailey (1974, 1977, 1992) also drew attention to the repeated emplacement over 100s of millions of years of ARC materials within spatially restricted regions, an observation that we address in this paper. In addition, ARCs have been credibly connected to deep mantle plumes (e.g. Bell 2001), a suggestion that is borne out by rare examples of carbonatites in ocean islands such as Cape Verde, the Canary Islands, and Hawaii (Gerlach 1988; Hoernle et al. 2002; Dixon et al. 2008).

Burke et al. (2003) proposed a Wilson cycle model in which ARCs intruded during intracontinental rifting become deformed (acronym: DARCs) during later continental (or oceanic arc - continent) collisions. They suggested that DARC material subducted prior to and during collision to depths of 100-150 km, became part of the mantle lithosphere, and could thereby represent a source component for later rift-related ARC magmatism. This model would account for Bailey's observation of recurrent ARC magmatism over hundreds of m.y. in reactivated rifts and rifts developed over suture

zones, such as has characterized southern Malawi (Fig. 1). It also implies an entirely lithospheric source for ARC magmatism.

In this paper we test the hypothesis of Burke et al. (2003) using Sr, Nd and Hf isotopic data for three occurrences of ARCs and DARCs emplaced in southern Africa over a time span of 1 b.y., from the Neoproterozoic to the Late Cretaceous. Our results suggest that a combination of lithospheric mantle sources is a viable possibility for the origin of at least some ARCs.

Geology and Sampling

The locations of deformed and undeformed alkaline rocks and carbonatites in Africa, based on the compilation of Woolley (2001), are shown in Fig. 1. Age information is not available for many of these occurrences, although many of the undeformed examples are Mesozoic or younger, and are associated with Jurassic to Cretaceous (~184 – 132 Ma) and Cenozoic (~34 - 0 Ma) magmatic activity of the East African rift system (Burke et al. 2003). Undeformed occurrences as old as ~2 Ga include the Phalaborwa and Schiel carbonatites of South Africa (Eriksson 1989; Walraven et al. 1992) and the Hassi-El-Fogra nepheline syenite of Mauritania (Lameyre and Lasserre 1967). Deformed occurrences are mainly Pan-African in age (500-750 Ma), although the nepheline syenite gneisses at Nhonglong, Cameroon may be as old as 2890 Ma (Lasserre

and Soba 1976); the deformed carbonatites of In'ouzzal, Algeria are ~2 Ga (Bernard-Griffiths et al. 1988).

In this paper, we report new Sr, Nd and Hf isotopic data for three occurrences in southern Africa (Fig. 1), ranging in age from Neoproterozoic (Bull's Run DARC, South Africa) to Pan-African (Tambani DARC, Malawi) to Late Cretaceous (Chilwa Alkaline Province ARCs, Malawi). Brief descriptions of the geological settings of these occurrences are given below.

Bull's Run, South Africa. In the Natal part of the 1000-1100 Ma Namaqua-Natal Metamorphic Belt (NNMB), a variety of alkalic gneisses referred to as the Bull's Run Complex occurs in an elongate sliver ~15 km long and up to 2 km wide (Charlesworth 1981; Scogings and Forster 1989). The Complex forms part of a set of thrust-bounded slices in the Tugela terrane (Johnston et al. 2003), just south of the south-dipping Natal Thrust Front, which juxtaposes rocks of the NNMB against the Archaean Kaapvaal Craton (Fig. 2). Metamorphic grade is upper amphibolite. The Complex consists of an inner zone of nepheline-bearing biotite syenite gneisses of variable grain size, some of which contain abundant scapolite. These rocks are enveloped by nepheline-free biotite-muscovite syenitic gneisses. Three small bodies (largest = 100 x 20 m) of deformed carbonatite occur at the eastern margin of the Complex, within the biotite-muscovite syenite gneiss. The carbonatites are dominated by calcite, with lesser microcline, albite, apatite and biotite, and accessory ilmenite, pyrite and pyrochlore. Some of the syenitic gneisses contain mm- to cm-sized zircon crystals, one of which yielded U-Th-Pb ages of

1140 $\pm$ 35 Ma and 1100 $\pm$ 40 Ma; these are some of the first U-Pb zircon ages measured in southern Africa (Nicolaysen and Burger 1965). These authors also determined an imprecise Rb-Sr age of 900 Ma from biotite taken from a syenitic gneiss.

Tambani, Malawi. In the Tambani-Salambidwe region of southwestern Malawi there is an elongate mass of nepheline syenite gneiss $\sim 75 \text{ km}^2$ in areal extent referred to as the Tambani body (Fig. 3, Cooper and Bloomfield 1961; Ashwal et al. 2007). The nepheline-bearing gneisses were described as typically “migmatitic”, composed of alternating bands of varying colour index on a cm-scale. Coarser bands of pegmatitic material contain nepheline crystals up to 7 cm across. Contacts of the Tambani body are conformable with the country rocks, which include dominantly biotite- and/or hornblende-bearing paragneisses and quartz-muscovite schists. To the north of the Tambani body the country rocks are dominated by hornblende-clinopyroxene-plagioclase gneisses, which may represent metavolcanics or metabasic intrusives (Cooper and Bloomfield 1961). Metamorphic grade in the Tambani body and the immediately surrounding country rocks appears to have reached amphibolite facies. Mineralogically, the Tambani rocks consist of varying proportions of microcline microperthite, plagioclase, nepheline, biotite, muscovite, and zircon, with or without corundum, apatite and magnetite

Some of the Tambani nepheline syenite gneisses contain euhedral zircon crystals up to 5 cm across (Ashwal et al. 2007). Near our sampling locality (Fig. 3) an entrepreneurial venture has been set up whereby the villagers are actively collecting and

stockpiling zircon crystals that have weathered out into the local fields; some 60 tons of zircon have been amassed. Some of these zircons are amongst those used for age determinations by Pb- α methods (Cooper and Bloomfield 1961), which yielded a range of results between 515 and 659 Ma. More recent results using TIMS and SHRIMP methods give an age of 726 ± 6 Ma, interpreted as representing the time of magmatic crystallization of the nepheline syenites (Ashwal et al. 2007). The age of amphibolite facies metamorphism was constrained at 522 ± 17 Ma by TIMS analysis of monazite (Ashwal et al. 2007).

The Tambani nepheline syenite gneisses represent a good example of repeated alkaline and carbonatitic magmatism occurring over long periods of geological time in a spatially restricted area. Just over 15 km SW of the Tambani body lies the Salambidwe intrusion, a circular ring complex of phonolitic trachytes, agglomerates, pulaskites and assorted alkaline syenites (Fig. 3, Garson 1965). The Salambidwe intrusion crosscuts and domes Karoo sediments (Permian to Jurassic in age). A dense, radial swarm of sölvbergite (aegirine syenite) dykes emanates from the complex, crosscutting normal faults that separate the Karoo sedimentary sequence from Precambrian basement to the NE (Fig. 3). These dykes establish the proximity of the post-Triassic Salambidwe intrusion to the latest Neoproterozoic Tambani body.

Chilwa Alkaline Province, Malawi In southern Malawi and adjacent Mozambique there is a series of Late Cretaceous alkaline and carbonatitic intrusive and extrusive rocks exposed over about 64,000 km² that is referred to as the Chilwa Alkaline

Province (Garson 1966; Woolley 1991). This Province lies at the southern end of the East African Rift system, and includes the first carbonatites to be recognized in Africa (Woolley 2001). The most extensive occurrences of syenite and nepheline syenite occur to the west of Lake Chilwa as a series of coalescent annular plutons oriented E-W over about 40 km (Fig. 4). These bodies were emplaced into Precambrian gneisses, which have been variably fenitized near their intrusive margins. The principal intrusions include the nepheline syenite – syenite plutons at Chinduzi, Mongolowe, Chaone and Chikala, and the granite – syenite plutons at Zomba-Malosa (Fig. 4). The dominant rock types include pulaskite (5-10% nepheline + 1-50% mafic minerals), foyaite (5-15% nepheline $\pm$ sodalite) and perthosite (mainly microperthite $\pm$ quartz, with mafic minerals). The mafic minerals include alkalic amphiboles, aegirine and/or biotite. About 20 km southeast of the Chikala pluton, there is a ~4 km diameter body of carbonatitic rocks on Chilwa Island, in the southwestern part of Lake Chilwa (Garson and Smith 1958) (Fig. 4). The main rock types in that body include sövite (calcite-dominant carbonatite), ankeritic sövite and sideritic carbonatite; the surrounding Precambrian basement rocks have been extensively fenitized (Woolley 1969). Based on a variety of K-Ar, U-Pb and fission track ages (summarized in Woolley 2001) the nepheline syenites and carbonatites were emplaced at about 130 Ma; the granite-syenite plutons at Zomba-Malosa appear to be somewhat younger, at ~115 Ma. Our sample suite consists of pulaskites and foyaite from the Mongolowe pluton and a variety of carbonatitic rocks from Chilwa Island.

Analytical Methods

245

246 Whole-rock samples were crushed using a steel jaw crusher and ring mill, and
247 were pulverized with an agate mortar and pestle at the Hugh Allsopp Lab (HAL),
248 University of the Witwatersrand. Major and selected trace element concentrations were
249 determined by XRF at the School of Geosciences, University of the Witwatersrand, using
250 standard techniques (Norrish and Hutton 1969; Feather and Willis 1976). Rb-Sr, Sm-Nd
251 and Lu-Hf isotopic and concentration measurements were carried about at the Carnegie
252 Institution of Washington, Department of Terrestrial Magnetism.

253

254 For Rb-Sr isotopic analyses, 100 mg of powders were dissolved with 5 ml 29M
255 HF + 15M HNO₃ (3:2) in Parr pressure vessels at 200°C for 72 hours, dried and re-
256 dissolved in 5 ml 6M HCl at 120°C for 48 hours. A 10% aliquot of the solution was
257 spiked with ⁸⁷Rb and ⁸⁴Sr tracers, fluxed overnight, dried and re-dissolved in 5 ml 1M
258 HCl + 0.1M HF at 120°C overnight. Rb and Sr were separated by standard cation
259 exchange chemistry (elution in 2.5M on 6ml (wet) AG-50W-X8 resin). The Rb fraction
260 was treated with 29M HF to precipitate residual alkaline earths, the supernatant diluted
261 with 1M HNO₃ and the ⁸⁷Rb/⁸⁵Rb measured on the P54 MC-ICPMS. The ⁸⁷Sr isobar was
262 corrected with the ⁸⁸Sr/⁸⁵Rb ratio, and the instrumental mass bias correction was
263 estimated by natural Rb standard bracketing between samples. Sr was loaded on a bed of
264 Ta₂O₅ with 4M HNO₃ on single degassed Re filaments, and isotope ratios analysed in
265 dynamic mode on the 354 TIMS. The Sr isotopic composition was fractionation-
266 corrected with an exponential law relative to ⁸⁶Sr/⁸⁸Sr = 0.1194, and is reported as spike-
267 stripped and bias-corrected relative to the accepted value of the NBS-987 standard

(0.71025). The quoted uncertainty for each analysis is the internal standard error; the external reproducibility of the NBS-987 standard over the course of this study was 0.71026 ± 3 (2σ); uncertainty in Rb and Sr concentrations and $^{87}\text{Rb}/^{86}\text{Sr}$ are estimated at $\leq 0.2\%$ (2σ).

For Sm-Nd isotopic analyses, 100 mg of powders were spiked with ^{149}Sm - ^{150}Nd and ^{176}Lu - ^{178}Hf tracers, dissolved with 5 ml 29M HF + 15M HNO_3 (3:2) in Parr pressure vessels at 200°C for 72 hours, dried and re-dissolved in 5 ml 6M HCl at 120°C for 48 hours. After Rb-Sr aliquoting, samples were dried and re-dissolved in 5 ml 1M HCl + 0.1 M HF at 120°C overnight. Rare earth elements were separated by standard cation exchange chemistry (following Rb-Sr and Lu separation by elution in 4M HCl on 6 mm i.d. x 20 cm columns of AG-50W-X8 resin, H^+ form, 200-400 mesh); Sm and Nd were separated by cation exchange in 0.2M α -bishydroxybutyric (methylactic) acid on 2 mm i.d. x 10 cm columns of AG-50W-X8 resin (NH_4^+ form, 200-400 mesh). Sm and Nd isotopes were measured on the P54 MC-ICPMS in static and dynamic Faraday modes, respectively. Instrumental mass fractionation of Sm and Nd isotopes was corrected with an exponential law relative to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, and $^{152}\text{Sm}/^{147}\text{Sm} = 1.783$. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are reported as spike-stripped and bias-corrected relative to the accepted value of JNdi-1 standard (0.512102). The quoted uncertainty in $^{143}\text{Nd}/^{144}\text{Nd}$ represents the last significant digits of the internal measurement standard error for each analysis; the external reproducibility of the JNdi-1 standard over the course of this study was 0.512098 ± 9 (2σ); uncertainty in Sm and Nd concentrations, and $^{147}\text{Sm}/^{144}\text{Nd}$ are estimated at $\leq 0.2\%$ (2σ).

291

292 Lu and Hf were separated by standard cation exchange chemistry (initial elution
293 of Hf in 1M HCl + 0.1 M HF; Lu following Rb-Sr separation by elution in 4M HCl on 6
294 mm i.d. x 20 cm columns of AG-50W-X8 resin, H⁺ form, 200-400 mesh, after Patchett
295 and Tatsumoto 1980). Hf was further purified by the method of Munker et al. (2001) on 6
296 mm i.d. x 3.5 cm columns of Eichrom Ln-spec resin (HDEHP-coated resin, 100-200
297 mesh); Lu was separated from the bulk of Yb by elution with 2.5M HCl on 4 mm i.d. x
298 7.2 cm columns of Eichrom Ln-spec resin. Lu and Hf isotopes were measured on the P54
299 MC-ICPMS in static Faraday mode. Instrumental mass fractionation of Hf isotopes was
300 corrected with an exponential law relative to $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$. The $^{176}\text{Lu}/^{177}\text{Hf}$ ratio
301 is reported as spike-stripped and bias-corrected relative to the accepted value of the JMC-
302 475 standard (0.282610, Blichert-Toft et al. 1997). The quoted uncertainty for each
303 analysis is the internal standard error; the external reproducibility of the JMC-475
304 standard over the course of this study was 0.282156 ± 14 (2 σ). Mass fractionation of the
305 $^{176}\text{Lu}/^{175}\text{Lu}$ ratio was corrected using the mass bias in $^{173}\text{Yb}/^{174}\text{Yb}$, renormalized to a
306 value of 0.5075 (McCulloch et al. 1977), and the ^{176}Yb isobaric interference was
307 corrected using a value of $^{173}\text{Yb}/^{176}\text{Yb} = 0.7848$, which optimally recovered the true
308 $^{176}\text{Lu}/^{175}\text{Lu}$ of variably Yb-doped natural and spike Lu standards. Uncertainty in Lu and
309 Hf concentrations and $^{176}\text{Lu}/^{177}\text{Hf}$ are estimated at $\leq 0.3\%$ (2 σ). Insufficient Hf was
310 extracted from the carbonatite samples to allow measurement of $^{176}\text{Hf}/^{177}\text{Hf}$, although Lu
311 and Hf concentrations were able to be determined by isotope dilution. For these samples,
312 Hf may have been scavenged by CaF₂ precipitates during ion exchange chemistry.

313

Rb-Sr, Sm-Nd and Lu-Hf isotopic data, and calculated initial ratios and epsilon values are given in Table 1.

Results

Petrography.

Nepheline syenite gneisses (samples BRM02-1, -02) from Bull's Run consist of granoblastic aggregates of practically unaltered nepheline and perthitic microcline, with lesser green or brown biotite, calcite, titanite and Fe-Ti oxides, and accessory epidote, monazite, apatite and zircon. The gneissic fabric is caused by alignment of dark layers dominated by biotite flakes, abundant euhedral titanite crystals and Fe-Ti oxides. In some samples the abundance of nepheline declines to <5% (BRM02-07), and in these rocks albitic plagioclase becomes prominent, in some cases with zoned riebeckitic amphibole (BRM02-06). Bull's Run carbonatites (BRM02-03) are sövitic, and dominated by calcite, with minor brown biotite, apatite and microcline, and accessory albite, pyrochlore and ilmenite. Further petrographic descriptions and details can be found in Scogings (1989) and Scogings and Forster (1989).

The Tambani DARC's are nepheline monzodiorites dominated by unzoned, fresh albitic plagioclase (70-80%), with lesser, variably altered nepheline (10-20%), dark brown to dark greenish brown biotite (10-15%) and muscovite (2-5%), with accessory apatite, calcite, Fe-Ti oxides (Ashwal et al. 2007). K-feldspar, alkali amphiboles and

pyroxenes and cancrinite are notably absent. The gneissic fabric is formed by aligned plagioclase and micas.

Our samples from the Mongolowe pluton (Chilwa Alkaline Province, Malawi) are all medium grained (1-5 mm), undeformed nepheline syenites, with variable proportions of euhedral to subhedral coarsely exsolved microcline perthite, nepheline, arfvedsonitic amphibole, aegirine and red-brown biotite, with minor sphene, albite, cancrinite and Fe-Ti oxides. Small amounts of sodalite occur in some samples. Plagioclase is absent, except as exsolution products in perthitic feldspars. The major variability in mineralogy relates to the abundance of nepheline (5-15 modal %) and the color index (volume % mafic minerals, 2-25 modal %). Carbonatites are dominated by calcite, with minor Fe-Ti oxides and traces of apatite.

Ages.

No precise ages are extant for the Bull's Run nepheline syenite or carbonatitic gneisses beyond the results of Nicolaysen and Burger (1965), which yielded 1140 ± 35 Ma and 1100 ± 40 Ma from U-Th-Pb isotopic analyses of a single zircon crystal. Regression of Rb-Sr whole-rock data for 11 nepheline syenite gneisses and 5 carbonatites, representing our new results combined with those of Scogings (1989) yields an age of 1134 ± 23 Ma, with $I_{Sr} = 0.70324 \pm 12$ and $MSWD = 21$ (Fig. 5), which is coeval with the zircon ages mentioned above. One sample (nepheline syenite gneiss BRM02-7) has an aberrant isotopic composition and is not included in the regression. This sample has lower Rb concentration compared to similar lithologies, and may have

been affected by secondary leaching effects. A regression excluding the carbonatites yields an age of 1117 ± 31 Ma ($I_{Sr} = 0.70336 \pm 19$, $MSWD = 5.7$), which is within error of the full data regression. There is insufficient spread in Sm/Nd to yield any isochron relationship, and only two samples yielded usable Lu-Hf isotopic data. For this paper we assume an age of magmatic emplacement of 1134 Ma, but we recognize that further geochronology is needed to unravel the complex magmatic and metamorphic events in this complex and understudied terrane (e.g. Johnston et al. 2003).

For the Tambani body, a magmatic crystallization age of 726 ± 6 Ma is well established from U-Pb zircon analyses using TIMS and SHRIMP (Ashwal et al. 2007), but Lu-Hf isotopic data for 3 whole-rock samples (Table 1) yield an array corresponding to an age of 582 ± 18 Ma ($MSWD = 0.34$, $I_{Hf} = 0.28248 \pm 2$, $\epsilon_{Hf} = +2.49$; Ashwal et al., 2007). This result indicates that the Lu-Hf whole-rock isotopic system is resettable at least at amphibolite grade, but given that zircon megacrysts (which essentially preserve magmatic U-Pb ages) are collinear with the 582 Ma Lu-Hf array, Ashwal et al. (2007) interpreted the Lu-Hf “isochron” as a mixing line representing the presence in whole-rocks of variable (but generally small) amounts of magmatic zircon. The age of metamorphism, therefore, must be younger than 582 Ma, and has been constrained by TIMS analysis of monazite to be 522 ± 17 Ma (Ashwal et al. 2007).

Our Rb-Sr isotopic data for rocks from the Chilwa Alkaline Province (including pulaskite, foyaite and carbonatite), when regressed with the previously published results of Simonetti and Bell (1994) (including nepheline syenite, carbonatite, olivine

nephelinites and a variety of other alkaline intrusive and extrusive rocks) yield an age of 131 ± 24 Ma ($I_{Sr} = 0.70349 \pm 8$, MSWD = 226, $n = 21$) (Fig. 6). This is within error of all ages determined previously using K-Ar, U-Pb and fission track methods (summarized in Woolley 2001), which range between 122 ± 11 Ma and 138 ± 14 Ma. We consider 130 Ma as the age of emplacement of our samples from the Chilwa Alkaline Province, and this value is used in all initial ratio calculations discussed below, despite the high MSWD for the isochron shown in Fig. 6.

Isotopic Compositions

Excluding the aberrant sample mentioned above, I_{Sr} values for Bull's Run nepheline syenite and carbonatite gneisses, calculated at their presumed time of crystallization (1134 Ma), range from 0.70284 to 0.70351 (avg. = 0.70320 ± 17 , $n = 16$), using data from our work and from Scogings (1989). Carbonatite gneisses have slightly lower average I_{Sr} (0.70310 ± 20 , $n = 5$) relative to nepheline syenite gneisses (0.70325 ± 15), but the values overlap considerably, and the difference is not significant. Average $\epsilon_{Nd\ 1134}$ and $\epsilon_{Hf\ 1134}$ values are $+3.3 \pm 2$ and -1.1 ± 2 , respectively (Table 1). We failed to recover Hf isotopic data from carbonatite gneiss sample BRM02-3.

For the Tambani body, I_{Sr} values calculated at the crystallization age of 726 Ma range from 0.70285 to 0.70298 (avg. = 0.70292 ± 6 , $n = 3$); ϵ_{Nd} values range from 3.57 to 3.84 (avg. = 3.70 ± 0.14 , $n = 3$) (Table 1). Due to metamorphic resetting and isochron rotation (Ashwal et al. 2007), the initial Hf isotopic composition of two nepheline syenite gneiss samples with high $^{176}\text{Lu}/^{177}\text{Hf}$ (TH-2, TH-5) are unusually low ($\epsilon_{Hf\ 726} = -3.61 -$

3.11). A better estimate of primary initial Hf values is given by samples with low $^{176}\text{Lu}/^{177}\text{Hf}$, such as zircon megacrysts and nepheline syenite sample TH-3, which yield $\epsilon_{\text{Hf}726}$ values of 4.36 to 5.51 (avg. = 4.96 ± 0.50 , $n = 4$).

Samples of carbonatite and nepheline syenite (including ijolites) from the Chilwa Alkaline Province, including our data and those of Simonetti and Bell (1994) and Bizimis et al. (2003), form a cluster of compositions on a plot of I_{Sr} vs. ϵ_{Nd} (Fig. 7), with values of I_{Sr} ranging from 0.70319 to 0.70384 (avg. = 0.70348 ± 18 , $n = 22$), and ϵ_{Nd} values range from 2.52 to 4.56 (avg. = 3.50 ± 0.61 , $n = 21$), excluding one aberrant ijolite sample with $\epsilon_{\text{Nd}} = -0.24$, Simonetti and Bell 1994). Carbonatite samples seem to have a slightly higher average ϵ_{Nd} value (3.79 ± 0.43 , $n = 13$) compared to nepheline syenites ($\epsilon_{\text{Nd}} = 3.04 \pm 0.58$, $n = 8$), although there is some overlap. Initial Hf values for nepheline syenites range from $\epsilon_{\text{Hf}130} = 1.09$ to 2.50 (avg. = 1.60 ± 0.78 , $n = 3$). As with Bull's Run samples, we were not able to acquire Hf isotopic data from Chilwa carbonatites, but Bizimis et al. (2003) reported results for a single carbonatite sample and a replicate that gave $\epsilon_{\text{Hf}130} = 7.37$ to 7.83. Chilwa carbonatites, therefore, appear to have both higher ϵ_{Hf} and ϵ_{Nd} relative to nepheline syenites, but more data are needed to confirm this.

Mixing Calculations

We carried out mixing calculations to evaluate the possibility that the isotopic compositions of sources for alkaline rocks and carbonatites (ARCs) could be accounted

for by blending between known mantle sources and older, deformed ARC (DARC) that were subducted prior to and during continent-continent collisional events, as proposed by Burke et al. (2003). Specifically, our calculations were aimed at testing the possibility that the Sr-Nd-Hf isotopic compositions of the sources to the 130 Ma Chilwa nepheline syenites and carbonatites could be modelled as mixtures of a depleted mantle (DM) component and an older DARC component represented by the 1134 Ma Bull's Run nepheline syenites. We stress that we are not suggesting that Bull's Run type material represents a specific component in the Chilwa source; we are merely exploring the possibility that older DARC material could contribute to such a source. Results are shown in Fig. 7, where the isotopic compositions of all considered samples and possible sources were adjusted to their positions at 130 Ma, the age of the Chilwa alkaline province. For the DM component we used the concentration data for average DM given by Workman and Hart (2005) and the isotopic composition for Sr, Nd and Hf given by Rehkamper and Hofmann (1997), Peucat et al. (1989) and Griffin et al. (2000), respectively. Based on our data and those of Scogings (1989), the Bull's Run nepheline syenites will have variable isotopic compositions at 130 Ma, especially for Sr. Since Scogings reported only Rb-Sr isotopic data we assumed an average $\epsilon_{\text{Nd } 130}$ value of -11.37 based on our own results. For concentrations of Bull's Run nepheline syenites, we used average values of Sr = 470 ppm, Nd = 50 ppm and Hf = 16 ppm based on our own data and those of Scogings (1989) as well as from a larger database of late Precambrian nepheline syenites from the North Nyasa Alkaline Province of Malawi (Eby et al. 1998). A Bull's Run carbonatite component is shown for comparison, but is not modelled because we consider the volume

of carbonatites to be insignificant relative to the nepheline syenite components in most ARC and DARC occurrences.

The results show that the isotopic compositions of Chilwa sources can be successfully modelled as mixtures of DM with ~0.4 - 0.6 % of Bull's Run nepheline syenites, using the mixing equations of DePaolo and Wasserburg (1979). The models also account for the isotopic variability of Chilwa nepheline syenite and carbonatite samples (Fig. 7). The small amount of DARC material required is due to their concentrations of Sr, Nd and Hf, which are ~50-100 times larger than those of the DM component. The most successful models are those in which the DARC components have Sr/Nd ~10 and Nd/Hf ~ 4-5; these ratios are consistent with those of most nepheline syenites, from worldwide compilations. Too few data exist to evaluate the suitability of younger DARC material as a mixing component, such as the 582 Ma Tambani nepheline syenites, but preliminary mixing calculations suggest that such material, blended with DM, would need to be present in amounts of about 1-2%.

Discussion

Our mixing calculations constitute permissive, but not demonstrative evidence for the sources of ARC magmatism as representing mixtures of recognized lithospheric mantle materials such as DM, with subducted, older DARC materials. This model, therefore, serves as a viable alternative to the perhaps more traditional view that involves

an entirely sub-lithospheric source for such magmatism, in which the sources represent mixtures of enriched, asthenospheric mantle components such as HIMU, EM1 and/or FOZO (e.g. Bell and Simonetti 2010). We cannot specify whether the two components we propose (DM and DARC materials) become blended in the upper mantle, or whether they remain physically discrete and produce separate partial melts that mix. However, we envisage a similar process to that which produces ocean-island basalt melts from mantle heterogeneities caused, for example, by subduction of oceanic lithosphere (e.g. Hofmann, 1997). The physical problem of deriving hybrid melts from heterogeneous mantle sources was addressed in studies such as that of Kogiso et al. (2004), who investigated the length-scales of mantle heterogeneities with respect to the relative time-scales between diffusion and melt segregation. More work along these lines is needed.

Arguments against a lithospheric source for ARC magmas, as summarized by Bell and Simonetti (2010), included: (1) their spatial and temporal association with plume-related large igneous provinces (LIPs) such as Deccan and Paraná, (2) “primitive” noble gas signatures in some carbonatites, (3) the similarity of putative mantle sources (HIMU, EM1, FOZO) to those of some ocean island basalts (OIB), and (4) the apparently simple Rb/Sr and Sm/Nd evolution lines of carbonatites in some regions (e.g. eastern Canada, Fennoscandia). We address these points below.

We do not dispute that some ARC magmas were produced as a result of mantle plumes, but these are volumetrically subsidiary, or at least less well characterized than those outcropping in intracontinental rifts (Bailey 1972, 1974, 1992; Burke et al. 2003).

Aside from the rare, obviously plume-related ARC in ocean islands such as Cape Verde, the Canary Islands, and Hawaii (Gerlach 1988; Hoernle et al. 2002; Dixon et al. 2008), well known continental plume-related ARCs include those of the Monteregian Hills, Quebec (e.g. Eby 1994), whose association with a continental hotspot track was outlined by Sleep (1990). However, for continental examples, including those associated with intracontinental LIPs (e.g. Ernst and Bell 2010) we would envisage an entirely lithospheric source for the ARC magmas, with the principal components of DM and subducted, older DARC material. Burke et al. (2008a) explained how the plume-related, Cretaceous Monteregian ARCs could be accounted for using the ARC-DARC model, with the subducted DARC material being represented by Proterozoic nepheline syenites and carbonatites of the Bancroft domain, equivalents of which may have been taken into the mantle lithosphere by Grenvillian collisional events. In our view, mantle plumes may provide the heat, but little to none of the material involved in melting the lithosphere to produce ARCs.

Noble gas isotopic compositions of Precambrian to Cretaceous carbonatites from Brazil, Canada and Russia (e.g. Marty et al. 1998; Sasada et al. 1997; Tolstikhin et al. 2002) have been interpreted to indicate derivation from a deep, sub-lithospheric, primordial mantle source, similar to that advocated for many plume-related products (e.g. Graham 2002) or from the large low shear wave velocity provinces (LLSVPs) situated at the core-mantle boundary (Burke et al. 2008b). For example, Marty et al. (1998) reported $^3\text{He}/^4\text{He}$ of up to $19 R_A$ (where R_A = atmospheric $^3\text{He}/^4\text{He}$) for a component in Devonian carbonatites from the Kola Peninsula (Burke et al. 2007), which would seemingly

represent a strong argument for the involvement of a signature from the deep mantle. We suggest that if ARC magmas contain a plume-related noble gas isotopic signature, the gases may have been added to the mantle lithosphere by diffusion or carried with aqueous and/or carbonic fluids that helped to induce melt production. Indeed, Tolstikhin et al. (2002) have estimated that <2% of the noble gas budget in Kola ARC material could be derived from a deep plume source, with the vast majority (>98%) representing a shallow (i.e. lithospheric) mantle component. They state, therefore, that “a minor contribution from the plume implies that it could only stimulate metasomatism of the subcontinental lithosphere whereas melts from the upper mantle play the major role...” (Tolstikhin et al. 2002, p. 898). We note that all of the ARC occurrences where “primordial” (i.e. with deep) noble gas signatures have been proposed are those associated with well-known mantle plumes, and none are from intracontinental rifts. As shown by isotopic compositions of He, N₂, C, Ar and Ne, the gases presently being emitted from the active natrocarbonatite volcano Oldoinyo Lengai (Tanzania), associated with the East African Rift, resemble those of MORB, and are indistinguishable from the subcontinental lithospheric mantle (Fischer et al. 2009). We conclude that extant noble gas isotopic and concentration measurements in ARC materials do not preclude their origin as partial melts of lithospheric mantle sources.

We do dispute the interpretation of young (or even old) ARC isotopic signatures as representing mixtures between HIMU and EM1 source components, and the inference that these mantle components underlay large areas of the continental lithosphere, such as in East Africa. Rather, the HIMU and EM1 components are rare, and are restricted to a

few places in the oceanic mantle (e.g. Stracke et al. 2005). In our view, arrays formed by different ARC occurrences on diagrams of initial isotopic compositions (e.g. I_{Sr} vs. ϵ_{Nd}) would represent variable amounts of source components DM and older DARC material. Some part of the observed isotopic variability might also be caused by incorporation of DARC material of different ages. The DM component we envisage is usually the dominant one in ARC isotopic signatures (Fig. 7), is compositionally similar to that of the shallow oceanic mantle (e.g. Carlson et al. 2005), and although there is abundant evidence for local metasomatism, depleted mantle typically dominates the sub-continental mantle lithosphere (SCLM) (e.g. Griffin et al. 2003). The simple evolution lines of ARC rocks on age vs. I_{Sr} or ϵ_{Nd} diagrams that imply an ancient (~ 3 Ga) isolated mantle source with low Rb/Sr ~ 0.02 and high Sm/Nd ~ 0.36 precisely track the DM component in the SCLM, as originally suggested by Bell et al. (1982) and Bell and Blenkinsop (1987a). Dispersion of isotopic compositions in such diagrams (e.g. Fig. 2 in Bell and Simonetti, 2010) is likely caused by variable, but small involvement of DARC source components. We would argue, therefore, that the alleged similarity of ARC isotopic signatures to OIB sources is, therefore, more apparent than real, and should not be used to infer the “widespread” presence of oceanic source components in the asthenosphere below continents.

The model we have successfully tested, that ARC magmas could be lithospherically-derived from mixtures of depleted mantle and subducted DARC materials, accounts for the repeated emplacement of ARC and DARC magmas, over long time periods, in the same places. Wilson cycle studies (e.g. Wilson 1966) show that

intracontinental rifts commonly form above previously-formed suture zones, and examples focused on the ARC-DARC hypothesis include Peninsular India (Leelanandam et al. 2006), northwestern Russia and northern Norway (Burke et al. 2007) and east-central Africa (Burke et al. 2003). The triggering mechanism for small-degree, alkaline magmatism is adiabatic decompression melting during uplift and extension of mantle lithosphere (e.g. Bailey 1983; McKenzie and Bickle 1988; Pedersen and Ro 1992; Keen et al. 1994). Heat derived from deep mantle plumes may also be important, as a link between plumes and some intracontinental rifts is well established (Wilson 1973; White and McKenzie 1989; Hill 1991)

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References

- Ashwal, L.D., Armstrong, R.A., Roberts, R.J., Schmitz, M.D., Corfu, F., Hetherington, C.J., Burke, K. and Gerber, M. 2007. Geochronology of large zircons from nepheline-bearing gneisses as constraints on tectonic setting: an example from southern Malawi. *Contributions to Mineralogy and Petrology*, **153**: 389-403.
- Bailey, D.K. 1974. Continental rifting and alkaline magmatism. *In The Alkaline Rocks. Edited by H. Sorenson. Wiley, New York, pp. 148-159.*
- Bailey, D.K. 1977. Lithospheric control of continental rift magmatism. *Geological Society of London Journal*, **133**: 103-108.
- Bailey, D.K. 1983. The chemical and thermal evolution of rifts. *Tectonophysics* **94**: 585-597.
- Bailey, D.K. 1992. Episodic alkaline activity across Africa: Implications for the causes of continental break-up. *In Magmatism and the Causes of Continental Break-up. Edited by B.C. Storey et al. Geological Society of London Special Publication 68, pp. 91-98.*
- Bell, K. 2001. Carbonatites: relationships to mantle-plume activity. *In Mantle Plumes: Their Identification Through Time. Edited by R.E. Ernst and K.L. Buchan. Geological Society of America Special Paper 352, pp. 267-290.*

608

609 Bell, K. and Blenkinsop, J. 1987a. Archean depleted mantle- evidence from Nd and Sr
610 initial isotopic ratios of carbonatites. *Geochimica et Cosmochimica Acta*, **51**: 291-298.

611

612 Bell, K. and Blenkinsop, J. 1987b. Nd and Sr isotopic compositions of East African
613 carbonatites: Implications for mantle heterogeneity. *Geology*, **15**: 99-102.

614

615 Bell, K. and Blenkinsop, J. 1989. Neodymium and strontium isotope geochemistry of
616 carbonatites. *In Carbonatites: Genesis and Evolution. Edited by K. Bell. Unwin Hyman,*
617 *London, pp. 278-300.*

618

619 Bell, K. and Simonetti, A. 2010. Source of parental melts to carbonatites- critical isotopic
620 constraints. *Mineralogy and Petrology*, **98**: 77-89.

621

622 Bell, K. and Tilton, G.R. 2001. Nd, Pb and Sr isotopic compositions of East African
623 carbonatites: Evidence for mantle mixing and plume inhomogeneity. *Journal of*
624 *Petrology*, **42**: 1927-1945.

625

626 Bell, K. and Tilton, G.R. 2002. Probing the mantle: The story from carbonatites. *EOS*,
627 **83**: 273-277.

628

629 Bell, K., Blenkinsop, J., Cole, T.J.S. and Menagh, D.P. 1982. Evidence from Sr isotopes
630 for long-lived heterogeneities in the upper mantle. *Nature*, **298**: 251-253.

631

632 Bernard-Griffiths, J., Peucat, J.-J., Fourcade, S., Kienast, J.-R. and Ouzegane, K. 1988.

633 Origin and evolution of 2 Ga old carbonatite complex (Ihouhaouene, Ahaggar, Algeria):

634 Nd and Sr isotopic evidence. Contributions to Mineralogy and Petrology, **100**: 339-348.

635

636 Bizimis, M., Salters, V.J.M. and Dawson, J.B. 2003. The brevity of carbonatite sources in

637 the mantle: evidence from Hf isotopes. Contributions to Mineralogy and Petrology. **145**:

638 281-300.

639

640 Bizzarro, M., Simonetti, A., Stevenson, R.K. and David, J. 2002. Hf isotope evidence for

641 a hidden mantle reservoir. Geology, **30**: 771-774.

642

643 Blichert-Toft, J., Chauvel, C. and Albarède, F. 1997. Separation of Hf and Lu for high

644 precision isotope analysis of rock samples by magnetic sector-multiple collector ICP-MS.

645 Contributions to Mineralogy and Petrology, **127**: 248-260.

646

647 Burke, K., Ashwal, L.D. and Webb, S.J. 2003. New way to map old sutures using

648 deformed alkaline rocks and carbonatites. Geology, **31**: 391-394.

649

650 Burke, K., Roberts, D. and Ashwal, L.D. 2007. Alkaline rocks and carbonatites of

651 northwestern Russia and northern Norway: Linked Wilson cycle records extending over

652 two billion years. Tectonics **26**: TC4015, doi:10.1029/2006TC002052.

653

- 654 Burke, K., Khan, S.D. and Mart, R.W. 2008a. Grenville Province and Montereian
655 carbonatite and nepheline syenite distribution related to rifting, collision and plume
656 passage. *Geology*, **36**: 983-986.
- 657
- 658 Burke, K., Steinberger, B., Torsvik, T.H. and Smethurst, M.A. 2008b. Plume generation
659 zones at the margins of large low shear velocity provinces on the core-mantle boundary.
660 *Earth and Planetary Science Letters*, **265**: 49-60.
- 661
- 662 Carlson, R.W., Pearson, D.G. and James, D.E. 2005. Physical, chemical and
663 chronological characteristics of continental mantle. *Review of Geophysics*, **43**: RG1001,
664 doi:10.1029/2004RG000156.
- 665
- 666 Charlesworth, E.G. 1981. Tectonics and metamorphism of the northern margin of the
667 Namaqua-Natal mobile Belt near Eshowe, Natal. Ph.D. Thesis, Department of Geology,
668 University of Natal, Durban, 433 pp,
- 669
- 670 Cooper, W.G.G. and Bloomfield, K. 1961. The geology of the Tambani-Salambidwe area
671 (with accompanying geological map, scale 1:100,000). Bulletin 13, Geological Survey of
672 Nyasaland, 63 pp.
- 673
- 674 Deines, P. 1989. Stable isotope variations in carbonatites. *In* Carbonatites: Genesis and
675 Evolution. *Edited by* K. Bell. Unwin Hyman, London, pp. 301-359.
- 676

- 677 DePaolo, D.J. and Wasserburg, G.J. 1979. Petrogenetic mixing models and Nd-Sr
678 isotopic patterns. *Geochimica et Cosmochimica Acta*, **43**: 615-628.
679
- 680 DePaolo, D.J., Linn, A.M. and Schubert, G. 1991. The continental crustal age
681 distribution: methods of determining mantle separation ages from Sm-Nd isotopic data
682 and application to the southwestern United States. *Journal of Geophysical Research*, **96**:
683 2071-2088.
684
- 685 Dixon, J., Clague, D.A., Cousens, B., Monsalve, M.L. and Uhl, J. (2008) Carbonatite
686 and silicate melt metasomatism of the mantle surrounding the Hawaiian plume: Evidence
687 from volatiles, trace elements and radiogenic isotopes in rejuvenated-stage lavas from
688 Nihau, Hawaii. *Geochemistry Geophysics Geosystems*, **9**, doi: 10.1029/2008GC002076.
689
- 690 Eby, G.N. 1994. Montereian Hills 1. Petrography, major and trace element
691 geochemistry, and strontium isotopic chemistry of the western intrusions: Mounts Royal,
692 St. Bruno, and Johnson. *Journal of Petrology*, **25**: 421-452.
693
- 694 Eby, G.N., Woolley, A.R., Din, V. and Platt, G. 1998. Geochemistry and petrogenesis of
695 nepheline syenites: Kasungu, Ilomba, and Ulindi nepheline syenite intrusions, North
696 Nyasa Alkaline Province, Malawi. *Journal of Petrology*, **39**: 1405-1424.
697

- 698 Eriksson, S.C. 1989. Phalaborwa: a saga of magmatism, metasomatism and miscibility.
699 *In Carbonatites: Genesis and Evolution. Edited by K. Bell. Unwin Hyman, London, pp.*
700 *221-254.*
701
- 702 Ernst, R.E. and Bell, K. 2010. Large igneous provinces (LIPs) and carbonatites.
703 *Mineralogy and Petrology, 98: 55-76.*
704
- 705 Feather, C.E. and Willis, J.P. 1976. A simple method for background and matrix
706 correction of spectral peaks in trace element determination by X-ray fluorescence
707 spectrometry. *X-ray Spectrometry, 5: 41-48.*
708
- 709 Fischer, T.P., Burnard, P., Marty, B., Hilton, D.R., Füre, E., Palhol, F., Sharp, Z.D. and
710 Mangasini. F. 2009. Upper-mantle volatile chemistry at Oldoinyo Lengai volcano and the
711 origin of carbonatites. *Nature, 459: 77-80.*
712
- 713 Garson, M.S. 1965, Carbonatites in southern Malawi. Geological Survey of Malawi
714 Bulletin 15, 128 pp.
715
- 716 Garson, M.S. 1966. Carbonatites in Malawi. *In Carbonatites. Edited by O.F, Tuttle and J.*
717 *Gittins. John Wiley, New York, pp. 33-71.*
718
- 719 Garson, M.S. and Smith W.C. 1958. Chilwa Island. Geological Survey of Nyasaland
720 Memoir 1, 127 pp.

- 721
- 722 Gerlach, D.C., Cliff, R.A., Davies, G.R., Norry, M. and Hodgson, N. 1988. Magma
723 sources of the Cape Verdes archipelago: isotopic and trace element constraints.
724 *Geochimica et Cosmochimica Acta*, **52**, 2979-2992.
- 725
- 726 Graham, D.W. 2002. Noble gas isotope geochemistry of mid-ocean ridge and ocean
727 island basalts: Characterization of mantle source reservoirs. *In* Noble Gases in
728 Geochemistry and Cosmochemistry. *Edited by* D. Porcelli, C.J. Ballentine and R. Wieler.
729 *Reviews in Mineralogy and Geochemistry* 47, pp. 247-318.
- 730
- 731 Griffin, W.L., O'Reilly, S.Y., Natapov, L.M. and Ryan, C.G. (2003) The evolution of
732 lithospheric mantle beneath the Kalahari craton and its margins. *Lithos*, **71**: 215-241.
- 733
- 734 Griffin, W.L., Pearson, N.J., Belousova, E., Jackson, S.E., van Achterbergh, E., O'Reilly,
735 S. and Shee, S.R. 2000. The Hf isotope composition of cratonic mantle: LAM-MC-
736 ICPMS analysis of zircon megacrysts in kimberlites. *Geochimica et Cosmochimica Acta*,
737 **64**: 133-147.
- 738
- 739 Hill, R.I. 1991. Starting plumes and continental break-up. *Earth and Planetary Science*
740 *Letters* **104**: 398-416.
- 741
- 742 Hoernle, K., Tilton, G., Le Bas, M.J., Duggen, S. and Garbe-Schönberg, D. 2002.
743 Geochemistry of oceanic carbonatites compared with continental carbonatites: mantle

- 744 recycling of oceanic crustal carbonate. *Contributions to Mineralogy and Petrology*, **142**,
745 250-542.
- 746
- 747 Hofmann, A.W. 1997. Mantle geochemistry: the message from oceanic volcanism.
748 *Nature*, **385**, 219-229.
- 749
- 750
- 751 Johnston, S.T., McCourt, S., Bisnath, A. and Mitchell, A.A. 2003. The Tugela Terrane,
752 Natal Belt: Kibaran magmatism and tectonism along the southeast margin of the
753 Kaapvaal Craton. *South African Journal of Geology*, **106**, 85-97.
- 754
- 755 Keen, C.E., Courtney, R.C., Dehler, S.A. and Williamson, M.-C. 1994. Decompression
756 melting at rifted margins: comparison of model predictions with the distribution of
757 igneous rocks on the eastern Canadian margin. *Earth and Planetary Science Letters* **121**:
758 403-416.
- 759
- 760 Kogiso, T., Hirschmann, M.M. and Reiners, P.W. 2004. Length scales of mantle
761 heterogeneities and their relationship to ocean island basalt geochemistry. *Geochimica et*
762 *Cosmochimica Acta*, **68**, 345-360.
- 763
- 764 Kwon, S.-T., Tilton, G.R. and Grunenfelter, M.H. 1989. Lead isotope relationships in
765 carbonatites and alkalic complexes: an overview. *In Carbonatites: Genesis and Evolution*.
766 *Edited by K. Bell*. Unwin Hyman, London, pp. 360-387.

767

768 Lameyre, J. and Lasserre, M. 1967. Étude géochronologique des syenites alcalines et
769 néphélinitiques du massif annulaire de Hassi-el-Fogra (Mauritanie du Nord). Comptes
770 Rendus des l'Académie des Sciences, Paris, **265D**: 733-736.

771

772 Lasserre, M. and Soba, D. 1976. Age libérien des granodiorites et des gneiss à pyroxène
773 du Cameroun méridional. Bulletin du Bureau de Recherches Géologiques et Minières,
774 Paris, **4**: 17-32.

775

776 Leelanandam, C., Burke, K., Ashwal, L.D. and Webb, S.J. 2006. Proterozoic mountain
777 building in Peninsular India: an analysis based primarily on alkaline rock distribution.
778 Geological Magazine **143**: 195-212.

779

780 Marty, B., Tolstikhin, I., Kamensky, I.L., Nivin, V., Balaganskaya, E. and Zimmermann,
781 J.-L. (1998) Plume-derived rare gases in 380 Ma carbonatites from the Kola region
782 (Russia) and the argon isotopic composition in the deep mantle. Earth and Planetary
783 Science Letters, **164**: 179-192.

784

785 McCulloch, M.T., Rosman, K.J.R. and De Laeter, J.R. 1977. The isotopic and elemental
786 abundance of ytterbium in meteorites and terrestrial samples. Geochimica et
787 Cosmochimica Acta, **41**: 1703-1707.

788

- 789 McKenzie, D. and Bickle, M.J. 1988. The volume and composition of melt generated by
790 extension of the lithosphere. *Journal of Petrology* **29**, 625-679.
791
- 792 Munker, C., Weyer, S., Scherer, E. and Mezger, K. 2001. Separation of high field
793 strength elements (Nb, Ta, Zr, Hf) and Lu from rock samples for MC-ICPMS
794 measurements. *Geochemistry Geophysics Geosystems*, **2**, doi:10.1029/2001GC000183.
795
- 796 Nelson, D.R., Chivas, A.R., Chappell, B.W. and McCulloch, M.T. 1988. Geochemical
797 and isotopic systematics in carbonatites and implications for the evolution of ocean-
798 island sources. *Geochimica et Cosmochimica Acta*, **52**: 1-17.
799
- 800 Nicolaysen, L.O. and Burger, A.J. 1965. Note on an extensive zone of 1000 million-year
801 old metamorphic and igneous rocks in southern Africa. *Sciences de la Terre* **10**, no. 3-4,
802 497-516.
803
- 804 Norrish, K. and Hutton, J.T. 1969. An accurate X-ray spectrographic method for the
805 analysis of a wide range of geological samples. *Geochimica et Cosmochimica Acta*, **33**:
806 431-453.
807
- 808 Patchett, P.J. and Tatsumoto, M. 1980. A routine high-precision method for Lu-Hf
809 isotope geochemistry and chronology. *Contributions to Mineralogy and Petrology*, **75**:
810 263-267.
811

- 812 Pedersen, T. and Ro, H.E. 1992. Finite duration extension and decompression melting.
813 Earth and Planetary Science Letters **113**: 15-22.
814
- 815 Peucat, J.J., Vidal, P., Bernard-Griffiths, J. and Condie, K.C. 1989. Sr, Nd and Pb
816 isotopic systematics in the Archean low- to high-grade transition zone of southern India:
817 syn-accretion vs. post-accretion granulites. Journal of Geology, **97**: 537-549.
818
- 819 Rehkamper, M. and Hofmann, A.W. 1997. Recycled ocean crust and sediment in Indian
820 Ocean MORB. Earth and Planetary Science Letters, **147**: 93-106.
821
- 822 Sasada, T., Hiyagon, H., Bell, K. and Ebihara, M. 1997. Mantle-derived noble gases in
823 carbonatites. Geochimica et Cosmochimica Acta, **61**: 1219-1228.
824
- 825 Scogings, A.J. 1989. Alkaline intrusives from the Tugela Terrane, Natal Metamorphic
826 Province. Ph.D. Thesis, Department of Geology, University of Durban, Westville, 500
827 pp.
828
- 829 Scogings, A.J. and Forster, I.F. 1989. Gneissose carbonatites in the Bull's Run Complex,
830 Natal. South African Journal of Geology, **92**: 1-10.
831
- 832 Simonetti, A. and Bell, K. 1994. Isotopic and geochemical investigation of the Chilwa
833 Island carbonatite complex, Malawi: Evidence for a depleted mantle source region, liquid
834 immiscibility, and open-system behaviour. Journal of Petrology, **35**: 1597-1621.

835

836 Sleep, N.H. 1990. Montereyan hotspot track: A long-lived mantle plume. *Journal of*
837 *Geophysical Research*. **95**: 21983-21990.

838

839 Stracke, A., Hofmann, A.W. and Hart, S.R. 2005. FOZO, HIMU and the rest of the
840 mantle zoo. *Geochemistry, Geophysics and Geosystems*, **6**: 1-20. doi:
841 10.1029/2004GC000824.

842

843 Tolstikhin, I.N., Kamensky, I.L., Marty, B., Nivin, V.A., Vetrin, V.R., Balaganskaya,
844 E.G., Ikorsky, S.V., Gannibal, M.A., Weiss, D., Verhulst, A. and Demaiffe, D. 2002.
845 Rare gas isotopes and parent trace elements in ultrabasic-alkaline-carbonatite complexes,
846 Kola Peninsula: Identification of lower mantle plume component. *Geochimica et*
847 *Cosmochimica Acta*, **66**: 881-901.

848

849 Walraven, F., Frick, C. and Lubala, R.T. 1992. Pb-isotope geochronology of the Schiel
850 complex, northern Transvaal, South Africa. *Journal of African Earth Sciences*, **15**: 103-
851 110.

852

853 White R. and McKenzie, D. 1989. Magmatism at rift zones: The generation of volcanic
854 continental margins and flood basalts. *Journal of Geophysical Research* **94**: 7685-7729.

855

856 Wilson, J.T. 1966. Did the Atlantic close and then re-open? *Nature* **211**: 676-681.

857

- 858 Wilson, J.T. 1973. Mantle plumes and plate motions. *Tectonophysics* **19**: 149-164.
859
- 860 Woolley, A.R. 1969. Some aspects of fenitization with particular reference to Chilwa
861 Island and Kangankunde, Malawi. *Bulletin of the British Museum (Natural History)*,
862 *Mineralogy* **2**: 189-219.
863
- 864 Woolley, A.R. 1991. The Chilwa Alkaline Province of Malawi: a review. *In* *Magmatism*
865 *in Extensional Structural Settings: the Phanerozoic African Plate. Edited by A.B.*
866 *Kampunzu, A.B. and R.T. Lubala. Springer-Verlag, Berlin, pp. 377-409.*
867
- 868 Woolley, A.R. 2001. Alkaline rocks and carbonatites of the world: Part 3, Africa.
869 Geological Society of London, 372 pp.
870
- 871 Workman, R.K. and Hart, S.R. 2005. Major and trace element composition of the
872 depleted MORB mantle (DMM). *Earth and Planetary Science Letters*, **231**: 53-72.
873
874
875
876
877

Figure Captions

Fig. 1. Locations of deformed and undeformed alkaline rocks and carbonatites of Africa, compiled from the catalogue of Woolley (2001). The three occurrences for which data are reported upon in this study include Bull’s Run, South Africa (Fig. 2), Tambani, Malawi (Fig. 3) and Chilwa, Malawi (Fig. 4).

Fig. 2. Geological map of the Bull’s Run Complex, Natal, South Africa, showing locations of analysed samples. Original mapping is by Charlesworth (1981) and Scogings and Forster (1989).

Fig. 3. Geological map of the Tambani – Salambidwe area of southern Malawi, showing the Tambani sample locality reported upon in this paper. About 15 km southwest of the 726 Ma Tambani body lies the post-Triassic Salambidwe intrusion, representing an example of recurrent alkaline magmatism in a spatially restricted area (Burke et al. 2003). Original mapping is by Cooper and Bloomfield (1961)

Fig. 4. Geological map of the Chilwa Alkaline Province of southern Malawi, showing location of samples from the Mongolowe nepheline syenite body and the Chilwa Island carbonatite.

Fig. 5. Rb-Sr isochron diagram showing regression of isotopic data for Bull's Run (South Africa) nepheline syenite gneisses and carbonatites. Analytical uncertainties (2σ) are smaller than the symbol sizes. Data sources: this study and Scogings (1989).

Fig. 6. Rb-Sr isochron diagram showing regression of isotopic data for nepheline syenites, carbonatites, olivine nephelinites, camptonites, alnöites and ijolites from the Chilwa Alkaline Province, Malawi. Analytical uncertainties (2σ) are smaller than the symbol sizes. Data sources: this study and Simonetti and Bell (1994). The array yields an errorchron with high MSWD, but the resulting age of 131 ± 24 Ma falls within the range of ages for the Chilwa Alkaline Province (122 – 138 Ma) as summarized by Woolley (2001), and is equivalent to the 130 Ma age for rocks of the Province as used by Simonetti and Bell (1994).

Fig. 7. Sr, Nd and Hf isotopic data for southern African alkaline rocks and carbonatites, showing positions of putative mantle source components DM, HIMU, FOZO and EM1. All data are corrected to the emplacement age of 130 Ma for the Chilwa Alkaline Complex. See text for additional details, including data sources. Symbols are as follows: red = Chilwa nepheline syenites, dark blue = Chilwa carbonatites, pink = Tambani nepheline syenites, green = Bull's Run nepheline syenites, light blue = Bull's Run carbonatites.

Table 1. Rb-Sr, Sm-Nd and Lu-Hf isotopic and concentration data for alkaline rocks and carbonatites.

Sample No. Rock Type	Bull's Run, South Africa			Tambani, Malawi						Chilwa Island, Malawi			Mongolowe, Malawi		
	BRM02-1 nepheline	BRM02-7 sy gneiss	BRM02-3 carbonatite	TH-2 nepheline	TH-3 syenite	TH-5 gneiss	78/52 zircon	78/57 megacrysts	78/62 zircon	CI-1 carbonatite	CI-2 carbonatite	CI-3 carbonatite	MM03-30 nepheline	MM03-35 syenite	MM03-45 gneiss
T = Age (Ma)	1134	1134	1134	726	726	726	726	726	726	130	130	130	130	130	130
Rb (ppm)	105	128	69.5	42.2	42.8	36.5				0.313	0.763	3.003	61.1	52.3	71.7
Sr (ppm)	857	532	5759	839	609	847				2917	4445	9020	596	337	210
⁸⁷ Rb/ ⁸⁶ Sr	0.3546	0.6966	0.0349	0.1455	0.2033	0.1246				0.0003	0.0005	0.0010	0.2965	0.4493	0.9891
⁸⁷ Sr/ ⁸⁶ Sr	0.709098	0.709156	0.703406	0.704425	0.704961	0.704276				0.703472	0.703469	0.703481	0.704312	0.704336	0.70509
± (2σ)	17	12	17	15	20	11				13	19	20	16	19	12
I _{Sr} , T	0.703343	0.697854	0.703839	0.702917	0.702854	0.702984				0.703471	0.703468	0.703479	0.703764	0.703507	0.703265
I _{Sr} , 130 Ma	0.708443	0.707870	0.703342	0.704156	0.704585	0.704046				0.703471	0.703468	0.703479	0.703764	0.703507	0.703265
Sm (ppm)	14.04	2.54	24.04	3.29	5.09	2.78				158.8	40.86	115.2	8.85	9.21	4.39
Nd (ppm)	100.5	22.5	152.4	20.2	32.2	17.0				1351	277	971	63.7	70.0	31.8
¹⁴⁷ Sm/ ¹⁴⁴ Nd	0.08445	0.06824	0.09535	0.09846	0.09556	0.09886				0.07106	0.08918	0.07173	0.08399	0.07954	0.08346
¹⁴³ Nd/ ¹⁴⁴ Nd	0.512001	0.511913	0.511961	0.512367	0.512345	0.512355				0.512696	0.512716	0.512693	0.512679	0.512674	0.512671
± (2σ)	4	10	4	4	5	5				5	7	5	4	6	5
I _{Nd} , T	0.511447	0.511465	0.511335	0.511898	0.511890	0.511884				0.512636	0.512640	0.512632	0.512677	0.512606	0.512600
ε _{Nd} (T) ¹	3.89	4.52	1.52	3.84	3.68	3.57				3.22	3.31	3.15	2.67	2.65	2.52
ε _{Nd} (130 Ma) ¹	-10.57	-12.01	-11.53	-3.66	-4.04	-3.90				3.22	3.31	3.15	2.67	2.65	2.52
T _{DM} (Ga) ²	1.290	1.238	1.464	0.962	0.967	0.981				0.416	0.453	0.421	0.479	0.468	0.486
Lu (ppm)	0.326	0.049	1.132	0.070	0.122	0.062				0.880	0.806	0.876	0.386	0.274	0.344
Hf (ppm)	5.621	0.525	0.587	0.100	1.215	0.099				4.624	0.388	0.957	4.656	3.434	7.653
¹⁷⁶ Lu/ ¹⁷⁷ Hf	0.0082	0.0133	0.2726	0.0992	0.0143	0.0884				0.0269	0.2941	0.1294	0.0118	0.0113	0.0064
¹⁷⁶ Hf/ ¹⁷⁷ Hf	0.282175	0.282349		0.282217	0.282443	0.282232	0.282466	0.282475	0.282454				0.282791	0.28275	0.282741
± (2σ)	5	18		32	8	40	57	57	57				9	8	5
ε _{Hf} (T) ¹	-2.24	0.05		-3.61	4.36	-3.11	5.19	5.51	4.77				2.50	1.09	1.21
ε _{Hf} (130 Ma) ¹	-18.97	-13.26		22.54	-3.15	18.79	-7.97	-7.66	-8.40				2.50	1.09	1.21

¹CHUR parameters: ¹⁴⁷Sm/¹⁴⁴Nd = 0.1967, ¹⁴³Nd/¹⁴⁴Nd = 0.512638; ¹⁷⁶Lu/¹⁷⁷Hf = 0.0332, ¹⁷⁶Hf/¹⁷⁷Hf = 0.282772

²Based on depleted mantle model of De Paolo et al. (1991): ε_{Nd,T} = 8.6-1.91T

182x201mm (300 x 300 DPI)

196x110mm (300 x 300 DPI)

157x282mm (300 x 300 DPI)

236x202mm (300 x 300 DPI)

194x276mm (300 x 300 DPI)