Miner Petrol (2010) 98:77–89
DOI 10.1007/s00710-009-0059-0

ORIGINAL PAPER

Source of parental melts to carbonatites–critical isotopic constraints

Keith Bell · Antonio Simonetti

Received: 26 December 2008 / Accepted: 4 May 2009 / Published online: 9 June 2009

Abstract The restriction of most carbonatites to continental areas raises questions as to whether the parental liquids to carbonatites are generated within the continental lithosphere, or whether they are derived from deeper parts of the mantle with the lithosphere playing a subsidiary, but important, role in trapping volatile-rich melts/fluids. The constraints imposed by both radiogenic and stable isotopic data from carbonatites world-wide are consistent with a *sub-lithospheric* source for the parental melts, associated with either asthenospheric ‘upwellings’ or more deep-seated, plume-related activity. Crucial evidences that support the generation of carbonated melts from *sub-lithospheric* mantle are: the petrogenetic and temporal association of carbonatites with large igneous provinces (LIPs; e.g., Deccan, Parana), carbonatites with primitive noble gas isotopic signatures, radiogenic isotope ratios similar to OIBs (i.e. involving HIMU, EM1 and FOZO mantle components), and the uniform, time-integrated Rb/Sr and Sm/Nd development lines for Sr and Nd isotopic data for carbonatites from the Superior Province, Canada, and the Kola Peninsula, Russia. Such findings are difficult to reconcile with a lithospheric origin. Even if a metasomatized lithospheric mantle is considered to be the *sole* source of carbonated melts, an unknown mantle process is required, large enough to generate widespread, synchronous metasomatism spanning regions in excess of $1\times10^6\text{km}^2$.

Editorial handling: L. Gwalani

K. Bell
Department of Earth Sciences, Carleton University,
Ottawa, ON K1S 5B6, Canada

A. Simonetti (✉)
Department of Civil Engineering & Geological Sciences,
University of Notre Dame,
Notre Dame, IN 46556, USA
e-mail: simonetti.3@nd.edu

Introduction

Carbonatites, found on all continents, are the products of low-degree partial melting of a carbonate-bearing mantle, and are unique in terms of their geochemistry due to their unusually high concentrations (i.e. 100’s to 1000’s of ppm) of Sr, Nd, and REEs. Carbonatitic melts are now known to play a significant role in mantle metasomatism and as a result are intimately associated with the secular evolution of the sub-continental mantle. Their origin is also closely linked to the source of mantle carbon (C) in which the residence time has been considered to exceed the age of the Earth (Zhang and Zindler 1993; Sleep and Zahnle 2001).

Carbon within the mantle may originate from recycling of continental crust by subduction (e.g. carbonated eclogites), or it may be primitive and juvenile, perhaps stored within the less accessible parts of the mantle. The transfer of C from these sources to melts that can generate carbonatites is no doubt complicated, and probably involves transportation in a variety of phases that migrate along different pathways before the C ultimately resides in a carbonatitic melt. Questions arise about the existence of carbonatitic melts within the mantle, their role in metasomatism as well as depletion of both volatiles and trace elements, and the stability of carbonate phases at various mantle depths.

Recent electrical conductivity experiments (Gaillard et al. 2008) using P-T-oxygen fugacity conditions consistent with those of the upper mantle, indicate that the CO_2 of the mantle (abundance of 10s to 100s ppm) is most likely present in the form of molten carbonate. There are other indications that carbonatites may be generated at *sub-lithospheric* levels. Partition coefficients for 23 trace elements between deep mantle minerals, i.e. majoritic garnet and perovskite and carbonatite liquids at 20 and 25 GPa and 1600ºC were determined by Dalou et al. (2009). When these are used in conjunction with the trace element composition of majoritic garnets found as inclusions in diamonds, these partition coefficients produce trace element abundances similar to those found in natural carbonatites. Thus, this result suggests that carbonatite melts can originate from mantle levels as least as deep as the transition zone (Dalou et al. 2009). It has also been proposed that carbonatitic melts may form via an oxidation melting reaction taking place between elemental carbon (e.g., diamond) within the upper mantle and convective upwellings of deeper, transition zone-type mantle (Luth 2004).

Carbonate phases are known to be stable throughout most of the mantle (i.e. dolomite is present between 1.9 and 4.8 GPa; Falloon and Green 1989; Dalton and Presnall 1998). Others argue that it is limited to <4.8 GPa in natural systems (Dasgupta and Hirschmann 2006). Under lower mantle conditions, magnesite remains stable to depths of at least 100 GPa (Isshiki et al. 2004) depending on whether the redox state of the mantle is suitable and if coexisting phases are present to reduce the carbonate. At pressures >1.9 GPa and appropriate oxygen fugacities, the presence of carbonate depresses the mantle solidus temperature by at least 300°C, and any initial melt generated will be carbonatitic in nature (e.g., Wyllie and Huang 1975). As carbonatitic liquids in equilibrium with lherzolites are stable only at pressures >1.9 GPa, they must have originated in the garnet stability field and thus consistent with their light REE enrichment. The latter is also attributable, in part, to metasomatic activity that may have occurred prior to or contemporaneously with carbonatite melt generation.

Much debate remains, however, as to whether carbonatitic melts are formed exclusively within the lithosphere, asthenosphere, or at much deeper levels within the mantle. Over the past decades, several models have been proposed on the basis of radiogenic isotope data to suggest that carbonatite melt generation is restricted to the lithosphere (e.g., Bell et al. 1982), the sub-lithosphere mantle (e.g., Nelson et al. 1988; Bell and Tilton 2002) and mixing between lithospheric and sub-lithospheric sources (e.g., Gerlach et al. 1988; Simonetti et al. 1998).

Mantle source–isotope perspective

The extensive radiogenic and stable isotope data available to-date from studies of carbonatites world-wide indicate that most young carbonatites (<200 Ma) have Nd, Sr, and Pb isotopic compositions similar to HIMU, EM1 and FOZO mantle components (or mixture thereof) defined on the basis of isotopic data from oceanic island basalts (OIBs; Zindler and Hart 1986; Hart 1988; Hart et al. 1992). We refer the reader to Hofmann (1997 and references therein) for a more detailed overview of the radiogenic isotope characteristics of the various mantle components and models proposed to explain their origins.

The most important findings to emerge from the isotopic studies of carbonatites are:

1. The isotopic similarities between the subcontinental mantle (SCM) and the sub-oceanic mantle.
2. The relatively undisturbed nature of some parts of the SCM over billions of years; e.g. Superior Province Canada, Kola Peninsula (Russia), and Greenland (e.g., Bell et al. 1982; Bizzarro et al. 2002; Bell and Rukhlov 2004) at least in terms of the time-integrated daughter-parent ratios (i.e. Rb/Sr, Sm/Nd).
3. The involvement of HIMU, EM1, and FOZO mantle components in the generation of most young (<200 Ma) carbonatites (e.g., Tilton and Bell 1994; Bell and Tilton 2002; Bell and Simonetti 1996; Simonetti et al. 1995, 1998). All three of these components have been considered to be located within the sub-lithospheric mantle. HIMU and EM1 are prevalent mantle components that underlie most of East Africa.
4. Derivation of some carbonatites from an enriched, ancient deep mantle reservoir marked by an unradiogenic Hf isotope composition (Bizzarro et al. 2002).
5. C and O isotope ratios in carbonatites that are similar to ‘primary’ mantle values based on data from oceanic basalts (e.g., Deines 1989; Keller and Hoefs 1995).
6. Noble gas (Xe, Kr, Ar) and N isotopic data recorded from carbonatites from Brazil, Canada, and Russia indicate derivation from primitive mantle (Sasada et al. 1997; Marty et al. 1998; Dauphas and Marty 1999; Tolstikhin et al. 2002). Sasada et al. (1997) noted that carbonatites of different age characterized by both depleted and enriched Sr and Nd isotopic compositions have similar ^{129}Xe/^{130}Xe and ^{40}Ar/^{36}Ar values suggesting a common source for the volatiles. Several carbonatites from India have experienced a more complex history involving inputs of He and Ne from both MORB and lithospheric mantles (Basu and Murty 2006).

Lithospheric origin?

The generation of carbonated melts within the lithosphere raises many questions. Included among these are: What is the age of the SCL (sub-continental lithosphere)? How is it metasomatized? Are cratonic and off-cratonic lithosphere the same? What are the criteria used to recognize SCL? Throughout our discussion we make the assumption that the lithosphere, either oceanic or continental, has been subjected to metasomatism throughout its history, and that this is still ongoing.

Generating carbonatitic melts from lithosphere must involve metasomatism of some sort and if this is so, then the role of lithosphere can take various forms. Either the lithosphere can be metasomatized *in situ* and then tapped intermittently throughout geologic time, or the metasomatized lithosphere can be subducted and later melted to form carbonatitic melts. Another variant is subduction of lithosphere which then becomes metasomatized but at sub-lithospheric levels.

A variety of metasomatic agents have been invoked for the lithosphere including hydrous or carbonic fluids (e.g, Lloyd and Bailey 1975; Erlank et al. 1987), lamproitic or kimberlitic melts (e.g. Menzies et al. 1987; Bonadiman et al. 2005), carbonatitic melts (e.g., Rudnick et al. 1993; Kogarko et al. 2001; van Achterbergh et al. 2002; Moine et al. 2004), and volatile-rich, alkaline silicate melts (e.g., Meen 1987; van Achterbergh et al. 2001), to name but a few. Less specific agents include “reduced metasomatic agent” (e.g., Thomassot et al. 2007), and “asthenospheric melt” (e.g., Choukroun et al. 2005). The interaction of the metasomatic agents with the mantle ledge at depths of ~75 km (~2.5 GPa) is a consequence of the phase relationships in the system peridotite-H_2O-CO_2 (Olafsson and Eggler 1983; Meen et al. 1989; Wyllie 1989, and references therein).

In many cases, multiple metasomatic events have to be invoked in order to explain the complex mineralogy in samples of upper mantle, and these can sometimes be reflected even within a single mantle xenolith. The idea of a ‘closed loop’ involving only lithosphere and asthenosphere seems to form a pervasive ideology in many current models, in part driven by data derived from xenoliths enclosed in kimberlites. The important features to emerge from the many detailed studies of such xenoliths are that the lithospheric mantle has been subjected to metasomatism over billons of years in which metasomatic agents vary from one locality to another, and that multiple metasomatic events can take place even within the same mantle volume. There remains little doubt that lithospheric mantle is targeted by incursions of chemically different melts/fluids throughout its history.

Both HIMU and EM1, recognized in many carbonatites, are two mantle components once considered to be metasomatized lithosphere. The presence of HIMU and EM1 signatures in both oceanic island basalts (OIBs), and in many carbonatites would argue for the involvement of subducted rather than *in situ* lithosphere. Nevertheless, there are problems with this model. Although it is easy to attribute mantle heterogeneities to contamination by slab subduction and metasomatism, the extensive spatial distribution of basalts with similar isotopic ratios implies that the isotopic heterogeneities have remained chemically closed for billions of years. And, equally as important, is the implicit assumption that the isotopic systematics of the slab material had to have been very similar, if not identical, over large geographic areas. It seems unlikely to us that metasomatic processes could generate end-members with similar isotopic signatures, unless the metasomatism was carried out on a global scale and that it was coeval over extensive areas.

Of particular relevance to this discussion is the isotopic data from young carbonatites. We use the data from East African carbonatites to bring out some of these features (see Fig. 1). Isotopic data from the East African Rift carbonatites describe a pattern that define a mixture with varying proportions between just two end members HIMU and EM1 (Bell and Dawson 1995; Bell and Tilton 2001; Bell and Tilton 2002), a process noted even at single volcanic centres within the rift (e.g., Napak – Simonetti and Bell 1993, 1994). It appears that both HIMU and EMI components underlie a large portion of East Africa that includes Kenya, Tanzania and Uganda. In addition to the linear array shown in Fig. 1, another important feature to note is that the isotopic data from Oldoinyo Lengai, the only active carbonatite volcano erupting natrocarbonatites (sodium-rich carbonatites), lie along the same mixing trend. If both of these components, i.e. HIMU and EM1, are sequestered within the continental lithosphere and they reflect metasomatic events characterized by high U/Pb (HIMU) and Rb/Sr (EM1) time-integrated values, then the problem emerges as to why two quite distinct metasomatic events affecting the whole of East Africa have somehow retained their isotopic identities (Fig. 1). In other words, the lithosphere seems to have retained the distinct isotopic signatures of two, quite separate metasomatic events.

The basis of the main argument for *in situ* lithospheric involvement is the repeated incursions of carbonatitic material at the same spot on the Earth’s surface over periods of billions of years (e.g., Greenland; Larsen and Rex 1992). The argument is made that the source of the carbonatitic melts has been retained within the migrating lithosphere, only to be periodically tapped during times of melt generation initiated by plate tectonism. Bailey (1993a, b) cites magmatic activity in East Africa as one example and has argued for localization of carbonatitic activity by old lesions in the lithosphere, and the repetition of post-Jurassic magmatism during distinct magmatic episodes. Bailey (1993a) prefers “an origin linked to permissive release of energy and materials flux from the deep mantle into the lithosphere”.

A lithospheric source for carbonated melt generation, from our perspective, presents problems. We agree that the lithosphere does indeed play a key role in both focussing and concentrating volatiles (see Bailey 1993a), but we

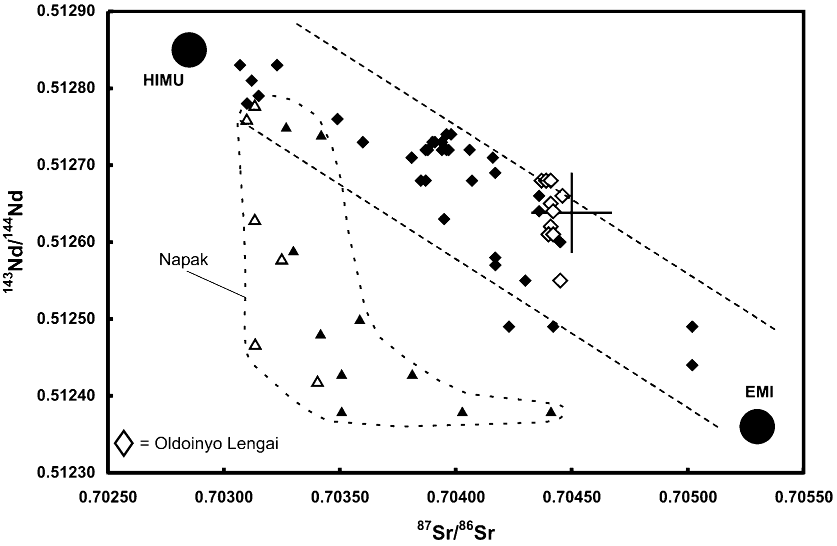

Fig. 1 Nd and Sr isotopic data from young East African carbonatite centres. Note the near-linear array that suggests mixing between two distinct mantle sources, similar to those found in oceanic island basalts (HIMU and EMI). The data from Oldoinyo Lengai cluster close to the cross that marks the composition for the undifferentiated silicate part of the Earth. Although the natrocarbonatites from Oldoinyo Lengai are quite unique in chemical composition relative to other carbonatites, their Sr and Nd isotopic nature conform to those from neighbouring alkaline/carbonatitic centres. Also shown are data for whole rock nephelinites (triangles) and clinopyroxene phenocrysts (open triangles) from Napak, a single nephelinite-carbonatite volcanic centre (Simonetti and Bell 1993, 1994)

remain unconvinced that the source of carbonatites is strictly within the lithosphere itself. Both Bailey (1993a) and Bailey and Woolley (2005) seem unclear about the nature of the triggering mechanisms for carbonatitic magmatism and especially the causes of metasomatism. The latter is related to undefined processes tied in with deep mantle 'upwellings' and initiated by plate collisions and changes in plate directions. The same criticisms can be applied to other models where undefined convective mantle 'upwellings' are invoked (e.g., Tappe et al. 2007).

Many of the arguments Bailey (1993a) uses against plume-related carbonatite magmatism are, in fact, consistent with plume activity. His proposed migration of volatiles and other materials from mantle disturbances seem somewhat similar to plume-related mechanisms. Bailey and Woolley (2005) also claim that the change in lithospheric distribution and the core dynamo reflect thermal and stress regimes within the mantle. However, any model that involves deep mantle processes, variation in thermal distributions, utilization of zones of weakness within the lithosphere, extensive synchronous magmatism, and restriction to continental areas are, more than ever, consistent with plume-related magmatism or at the very least 'upwellings' from deeper, convecting (asthenospheric) mantle below the continental lithosphere.

More recently, Burke and Khan (2006) have emphasised lithospheric involvement based on the widespread acceptance that many carbonatites are associated with rifting. They argue that carbonatites are produced by partial melting of deformed (existing) alkaline rocks and carbonatites along with depleted lithospheric mantle components subsequent to oceanic basin closure (formation of suture zones). Unfortunately, Burke and Khan (2006) do not discuss the ultimate source of carbonatites, and they have ignored the extensive isotopic radiogenic data base from carbonatites that presently exists that can be used to place constraints on mantle sources. Many of their supposed sutures are also questionable.

We wish to comment on a more recent model that may have implications for lithospheric sources. On the basis of He, N, Ar isotopes and $CO_2/^3He$ ratios of gases emitted from Oldoinyo Lengai, Fischer et al. (2009) proposed a homogeneous (global) reservoir in the upper mantle that supplies volatiles to both mid-ocean ridges and continental rifts. $^3He/^4He$ ratios for Oldoinyo Lengai do show considerable overlap with those for samples of MORB and lithospheric mantle but this feature generates an important *paradox* between the isotopic composition of the volatiles and the radiogenic isotopes measured from the mineral phases in the lava flows, an important *paradox* that eluded Fischer et al. (2009). As stated earlier in our paper, almost all of the East African carbonatites, including Oldoinyo Lengai, and many young carbonatites (<200 Ma) world-wide have radiogenic isotope compositions that reflect mixing between HIMU and EM1 mantle components. Of equal importance is that few (if any) have Sr, Nd, and Pb isotopic compositions that overlap with those from MORBs (e.g. Bell and Tilton 2002). The Sr and Nd isotopic data from Oldoinyo Lengai, in fact, cluster close to the CHUR- bulk earth intersection (see Fig. 1).

This apparent 'decoupling' between the isotopic compositions of volatiles and the radiogenic isotopic data was also noted by Sasada et al. (1997). Carbonatites from both Brazil and Canada are characterized by both depleted and enriched Sr and Nd isotopic compositions, but yet have similar (primitive) $^{129}Xe/^{130}Xe$ and $^{40}Ar/^{36}Ar$ values suggesting a common source for the volatiles. Thus, the findings from Oldoinyo Lengai are quite different to the noble gas (Xe, Kr, Ar) and N isotopic data for carbonatites reported by Marty et al. (1998), Dauphas and Marty (1999), and Tolstikhin et al. (2002).

On the basis of these studies, it is clear that the volatile components in carbonatites can be derived from different mantle sources, whereas the major elements (Ca, Mg as proxied by Sr, Nd, and Pb) tap distinct mantle components/sources (e.g. EM1 and HIMU). Thus, it is extremely important to emphasize that the findings from Fischer et al. (2009) cannot be used to infer the origin of volatiles in other carbonatites, especially in lieu of the uniquely Na- and K-enriched nature of the erupted lavas at Oldoinyo Lengai.

Crustal recycling?

An alternative model for in situ lithospheric control of carbonatite melt generation involves the role of subducted lithosphere into the mantle. Recycling C into the mantle during subduction produces not only chemical inhomogeneity, but variation in redox conditions. On the basis of phase equilibrium studies, it has been argued that the deep carbon cycle would seem to be restricted to depths of <300 km (see Hammouda 2003; and references therein), although others, such as Yaxley and Brey (2004) and Dasgupta et al. (2004, 2005), argue for much greater depths. Falloon and Green (1989) emphasise the role of dolomitic carbonatite in metasomatism of the mantle wedge and if the Falloon-Green model is correct, then carbonatitic melts with quite distinctive compositions can be generated at convergent margins. Sweeney et al. (1992) have also shown a connection between carbonatitic melts and subduction-related settings, and argue for the metasomatism of a harzburgitic source at >2.5 GPa. However, it should be remembered that carbonatites are virtually absent in present-day, subduction-related settings.

Barker's (1996) arguments for the importance of crustal recycling in carbonatite melt generation are: 1. calcite and dolomite can survive in subducted oceanic crust as refractory phases, and 2. estimates of exhaled CO_2 from most volcanoes can be accounted for by crustal recycling. Barker (1996) also states that both the $^{87}Sr/^{86}Sr$ and C isotope ratios of carbonatites are consistent with limestone input into the mantle. Unfortunately, this model is at variance with the relatively systematic, secular variations of Sr and Nd isotope ratios over an extensive period of time shown by most carbonatites from the Superior Province, Canada, and the Kola Peninsula, Russia (e.g., Bell et al. 1982; Bell and Blenkinsop 1987; Kramm 1993; Bell and Rukhlov 2004). In addition, abundant evidence from diamonds shows that subducted C is scarce and that large variations observed in the isotopic composition of both C and O can be produced by redox/Rayleigh fractionation methods rather than by contamination with crustal material (e.g., Thomassot et al. 2007).

Constraints imposed by Sr and Nd isotopic compositions further negate the role of subduction in providing a source suitable for generating carbonatites. The most recent compilation of data for carbonatites from Canada, Fennoscandia and Greenland is shown in Fig. 2 (after Bell and Rukhlov 2004). What emerges from the data is that the most depleted isotopic signatures fall along a single development line that corresponds to a Rb/Sr ratio of 0.02 that is quite different from those of the carbonatites (Rb/Sr≈0). Overall, the isotopic data shown in Fig. 2 suggest the involvement of at least two mantle sources with intermittent mixing between the two. The distribution of Nd and Sr isotopic data from the 370 Ma Kola carbonatites indicates the involvement of at least three end-members (Kramm 1993; Bell and Rukhlov 2004) with a convergence of the data towards a common end-member considered to be a depleted reservoir of Archean age (Bell and Rukhlov 2004). These findings imply that the carbonatitic melts involved a mantle source whose Rb/Sr, Sm/Nd and perhaps U/Pb ratios were retained over long periods of time (in some cases at least 3 Ga). This is especially brought out by the data shown in Fig. 2a. The data are systematic and not random. Moreover few, if any, of the $^{87}Sr/^{86}Sr$ ratios from carbonatites approach crustal values, ruling out crustal recycling, especially sedimentary limestones whose Sr isotope values are significantly higher. Most values from limestones are greater than 0.707 (e.g. Veizer 1989).

The nature of the depleted mantle source for the Canadian and Fennoscandian carbonatites in Fig. 2 needs further discussion. It appears that the Precambrian source has remained relatively unaffected by mantle convection, and as a result must be situated either in the lithosphere or at deeper levels in the mantle. It might be argued that the development line marks the evolution of lithosphere depleted in the Archean but if this is the case then the lithosphere must have been subjected to a major metasomatic event involving an unknown mantle process large enough to generate widespread, synchronous metasomatism spanning regions in excess of $1\times10^6 km^2$. These arguments, as well as many others, could also be applied to "crustal carbonatites"; i.e. formation of "carbonatites" by pneumotolytic skarn processes (Lentz 1999).

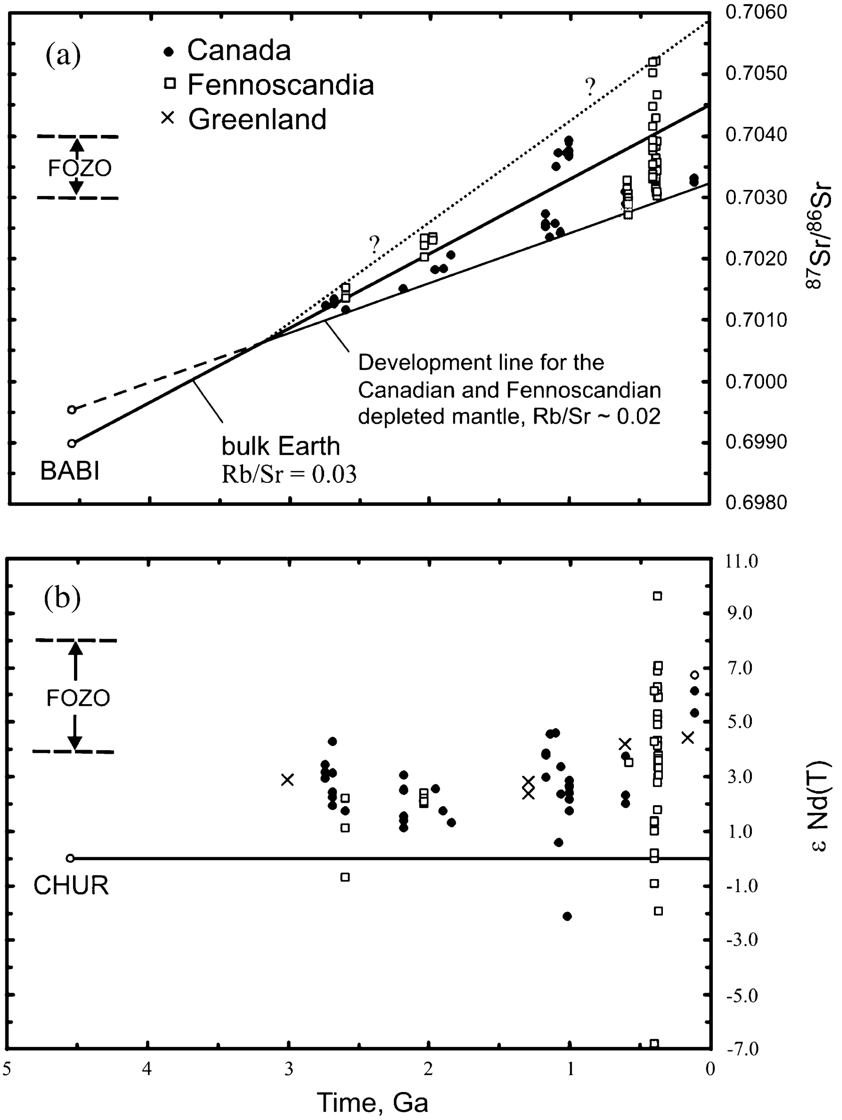

Fig. 2 (**a**) Development lines for Sr and Nd. $^{87}Sr/^{86}Sr$ ratio versus time are shown for Canadian and Fennoscandian carbonatites (after Bell and Rukhlov, 2004). The development line indicates the presence of an ancient mantle reservoir at least 3.0 Ga old. The Earth is considered to have started with a $^{87}Sr/^{86}Sr$ ratio similar to that found in basaltic achondritic meteorites. The initial value is shown by the point marked BABI. (**b**) εNd(T) versus time where $\varepsilon Nd(T) = \left[\left(\frac{^{143}Nd/^{144}Nd_{sample}}{^{143}Nd/^{144}Nd_{CHUR}}\right) - 1\right] \times 10^4$ where $^{143}Nd/^{144}Nd_{sample}$ is the initial ratio in the sample and $^{143}Nd/^{144}Nd_{CHUR}$ is the initial ratio of CHUR at the same point in time (after Bell and Rukhlov 2004) The data points above the horizontal line reflects an ancient reservoir that has undergone depletion relative to achondritic meteorites. Note that the depletion event must have occurred before 3.0 Ga

Two (Cape Verde and the Canary islands) of only three, "oceanic" carbonatite occurrences, have been interpreted as recycled, subducted marine limestones based on their distinct, enriched isotopic signatures (Hoernle et al. 2002). Continental carbonatites were also considered to be the result of melting of metasomatized, sub-continental lithosphere by CO_2-rich fluids/melts generated by partial melting and decarbonation of subducting crust, although some limestone, oceanic crust, and perhaps detached sub-continental lithosphere might sink into the mantle only to be returned by deep-mantle plumes (Hoernle et al. 2002). Although these models help explain the differences in isotopic composition between oceanic and continental carbonatites they are still subject to many of the problems outlined earlier; i.e. the marked absence of carbonatitic activity in present-day subduction zones, a feature that is commonly overlooked in most of the models that invoke crustal recycling.

One of the main arguments that has been used for invoking the recycling of carbon by subduction is the similarity between the C and O isotopic compositions of some carbonatites and continental crust, but this reasoning is hardly unequivocal. There are many other ways to generate variations in the stable isotopic composition of carbonatitic melts without recycling carbonate of crustal origin. Among these are included replacement by secondary carbonates, low-temperature magmatic and hydrothermal processes, crustal contamination, deuteric processes, and reactions with the atmosphere (e.g., Deines 1989; Simonetti et al. 1995; Comin-Chiaramonti et al. 2005).

Further assessment of the stable isotopic data brings out more interesting features. The summary of C and O isotopic data shown in Fig. 3 includes carbonatites from different parts of the Earth, as well as two fields that encompass the isotopic data from Precambrian and Phanerozoic lime-

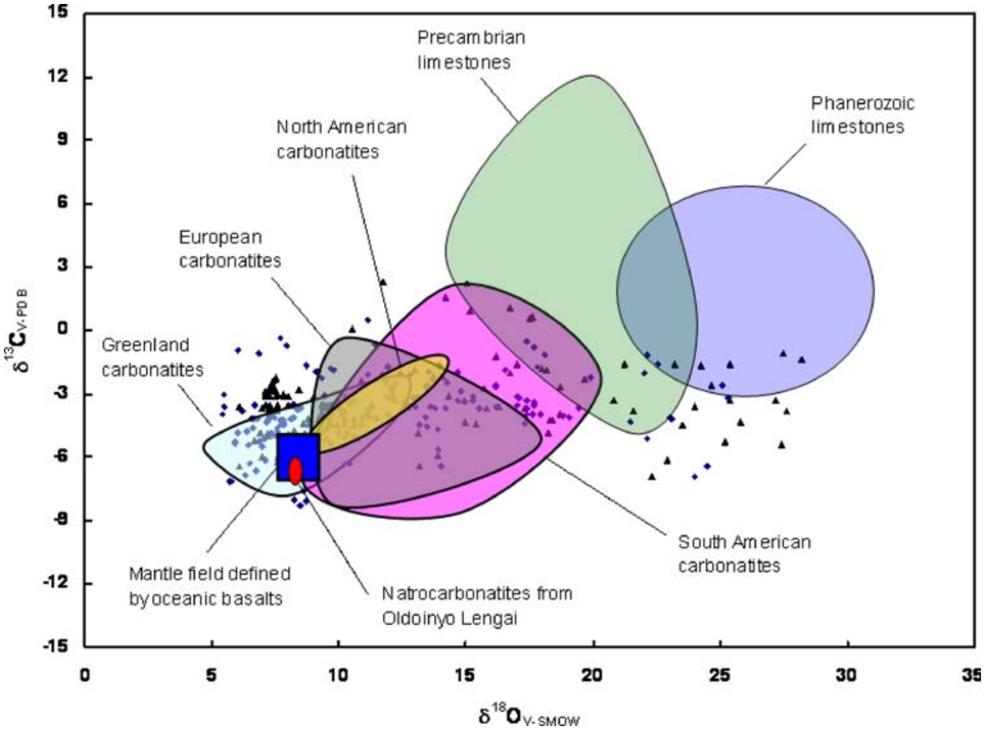

Fig. 3 Comparison of the stable isotope signatures between limestone and carbonatite (after Bell 2005). Note that the isotopic data from carbonatites converge towards the mantle box based on oceanic basalts. Each of the fields enclose >90% of the data points for each particular group. The data from African carbonatites are marked by diamonds, those from India by triangles. Note the extensive range of δ ^{18}O values compared to the δ^{13}C values

stones. The carbonatite fields enclose data from carbonatites of different ages. Particular reference is made to: i. the generally higher delta^{18}O and ^{13}C values for the limestones than the carbonatites, ii. the convergence of the carbonatite data to mantle values defined by data from oceanic basalts, and iii. the wide range of delta^{18}O values shown by carbonatites from India and Africa. If there is any tendency, it is for the carbonatite data to converge towards the mantle field defined by data from oceanic basalts. From the distribution of the data shown in Fig. 3, it therefore seems improbable that limestones have played any role in the generation of the carbonatitic melts, unless both the radiogenic and stable isotopic compositions of the limestones were dramatically changed during subduction.

Additional causes of concern are the criteria used to assess whether carbonates in mantle xenoliths really fall under the definition of carbonatites. We cite one example. Carbonate-silicate globules from lherzolitic clinopyroxene macrocrysts from 200 km below the Slave Province are assumed by van Achterbergh et al. (2002) to be natural samples of mantle carbonatite yet they state that “the carbonatite globules are geochemically distinct from other carbonatites worldwide”! Of importance, these carbonatite gobules are characterized by significantly higher SiO_2 contents (16-20 wt%.) and LREEs abundances roughly one order of magnitude lower compared to the average composition of carbonatites world-wide (e.g., Woolley and Kempe 1989). The subduction-related/crustal signature is based on an ^{87}Sr^{86}Sr ratio of 0.70666+/-0.00003 and a 10 per mil difference in delta ^{18}O between the host clinopyroxene and the inclusions. We would argue that these carbonate globules are certainly not mantle carbonatites for the following reasons: i. the unusually high ^{87}Sr^{86}Sr ratio, and ii. the unusual chemical composition of these carbonate globules.

Mantle “upwellings”/plumes and lithosphere interaction?

For the purposes of this paper we adopt the more permissive definition of a mantle plume cited by Lustrino and Wilson (2007) that includes “passive, diapiric upwellings of the upper mantle” such as the hot fingers proposed by Wilson and Patterson (2001). Phase assemblages and magma generation in relation to what might be called the more conventional, larger mantle plumes have been investigated (e.g., Wyllie 1988) and these provide a basis for evaluating carbonatitic melts in the context of mantle upwellings. Wyllie (1989) has modelled the thermal and chemical variation within a plume and notes that within the centre of a plume, temperatures probably exceed 1500° C with a systematic change towards the cooler, outer parts. The volatile components transported by the plume from depths greater than 300 km are subsequently dissolved within interstitial melts as the plume crosses the peridotite-C-O-H solidus. From the outer parts of the plume, any volatile-rich melt enters the lithosphere and aborts at the solidus ledge (depth of ~75 km) producing metasomatism, perhaps accompanied by explosive activity and/or the escape of low volume, low viscosity melts. Plume dynamics and the relative movement of vapours, liquids and host rocks are difficult to evaluate; however, the work by Wyllie and Ryabchikov (2000) indicate that a mantle plume can rise with traces of interstitial vapour perhaps from great depths, or vapours released by dehydration/decarbonation reactions at a depth of about 300 km. More recent studies also indicate that water can be trapped in small amounts in supposedly anhydrous mineral assemblages, such as pyroxene and olivine (e.g., Ingrin and Skogby 2000; Kevin et al. 2007). Dissolution of the vapour within a trace of interstitial volatile-rich liquid is controlled by the thermal structure of the plume and the oxygen fugacity. Such volatile-rich magmas and the vapour phase are enriched in incompatible elements (e.g., Mysen 1978) and the trace element patterns vary radially from the plume centre depending on depth. At the outer, cooler, volatile-rich margins of the plume trace melts can be generated, some of which may be carbonatitic in composition. The behaviour of these liquids and their passage to the lithosphere then depends on the fluid dynamics associated with the migrating liquid, the rheology and fracturing of the lithosphere, and re-equilibration with the host rock during migration. However, the overall effect of upward migration is the redistribution of mobile elements in the mantle, and "preparing sources capable of providing the geochemical signatures from kimberlites, lamproites and other types of alkaline primary magmas during subsequent melting events" (Wyllie and Ryabchikov 2000).

Gerlach et al. (1988) were among the first to relate carbonatitic melts to plume activity; they suggested that carbonatitic magmatism in the Cape Verde islands was spatially controlled by plume geometry and that the melts were generated by low degrees of partial melting at the outer, cooler margins of an isotopically heterogeneous plume. Plume-related magmatism can take several forms. One might imagine: 1. direct melting of the plume itself at low temperatures; 2. metasomatism of the surrounding asthenosphere and/or lithosphere along with subsequent melting; and 3. attachment of a plume head to the lithosphere followed by episodic melting. Cited evidences in favour of plume-related activity are: i. similarity between the Pb-Sr-Nd isotopic signatures of OIBs and carbonatites; ii. spatial association of plumes and carbonatites with continental flood basaltic provinces; iii. primitive noble gas signatures found in some carbonatites, iv. presence of carbonatites in plume-related tracks, e.g. the Monteregian province (Canada). Carbonatites and kimberlites were also linked by Haggerty (1994) to plume activity, who suggested that they form continental recorders of superplumes that date back to at least 2.8 Ga. Plume-lithosphere interaction has also been invoked, since the isotope systematics of some carbonatites record mixing between two distinct mantle end-member compositions (e.g., Gerlach et al. 1988; Simonetti et al. 1995). As an alternative, Bell and Tilton (2002) proposed a model that involved direct melting of an isotopically heterogeneous plume independent of any lithospheric involvement.

In spite of the present controversy about plumes, [compare discussions of Sleep (1990, 2006) and those in Ernst and Buchan (2001) versus the papers in Foulger et al. (2005)], they nevertheless provide a useful working model that embraces many aspects of Earth history, including the origin of continental flood basalts, oceanic island magmatism and continental break up. It is inappropriate here for us to review all of the arguments for or against plumes, and until the model has been more rigorously tested and shown to be without merit, we accept the plume model as a useful, comprehensive, working model for magmatic activity. The plume model has the advantage of explaining metasomatic activity, explosive volcanism at relatively low temperatures, and the generation of small volume, low degree partial melts rich in volatiles. For example, phase equilibrium studies of the solidus of carbonated peridotite shows that melting can occur beneath ocean ridges at about 300 km, with the production of 0.03 to 0.3 vol % carbonatitic liquid (Dasgupta and Hirschmann 2006). If such liquids have cation ratios similar to the silicates there is little change in the peridotite solidus, but excess CO_2 can increase the solidus if the carbonatitic liquid has a cation ratio different from the bulk, or if the excess melt dilutes concentrations of components such as Na_2O or K_2O that lower the solidus. Extraction of incipient carbonatite melts drom deep mantle generates an abundant source of metasomatic fluids that can scavenge highly incompatible elements such as K, U, Th as as well as C, He and Ar. Small-degree carbonatite melts will be strongly enriched in, and residual peridotite markedly depleted of, highly incompatible elements, including those that produce heat (U, Th, K), rare gases and alkali-earths (Cs, Rb, Ba). Consequently, key radiogenic parent-daughter pairs (for example, U-Th-Pb-He and K-Ar, Rb-Sr) may be strongly fractionated in the depleted residual peridotite. On the other hand, such melting could leave most of the H_2O in the residual peridotite.

Preferred model

A considerable number of papers have lent support to models of plume involvement in the origin of carbonatitic melts. Included among these are those of Gerlach et al. (1988), Hoernle and Tilton (1991), Haggerty (1994), Simonetti et al. (1995, 1998), Bell and Simonetti (1996), Sasada et al. (1997), Marty et al. (1998), Dauphas and Marty (1999), Dunworth and Bell (2001), Bell (2001), Bell and Tilton (2001, 2002), Tolstikhin et al. (2002), Bizzarro et al. (2002), Hoernle et al. (2002), Bell and Rukhlov (2004), Kogarko (2006) and Stoppa (2007). In addition to these many papers, we also draw the reader's attention to a series of proceedings edited by Vladykin that include several papers that relate alkaline magmatism as well as carbonatites to plume activity (Vladykin 2007).

In order to generate a mantle source capable of producing carbonatitic (or carbonated) melts, the lithosphere has to undergo major chemical changes but the constraints imposed by the radiogenic isotopic data are severe. Even if the isotopic characteristics are assigned to lithospheric sources, the data suggest that some of the isotopic signatures were established, at least in the cases of the Superior Province and the Fennoscandian Shield, sometime in the Archean and more importantly that the source has remained chemically intact for billions of years. However, the vast amount of information relating to the chemical nature of the sub-continental mantle stemming from kimberlite-/alkaline melt-hosted mantle xenolith studies makes the latter scenario seem highly unlikely. Of the many examples we cite only a few. Cohen et al.'s (1984) isotopic study of separated minerals from a garnet lherzolite xenolith from the recent volcanics of the Lashaine tuff cone, Tanzania, indicated that the lithosphere beneath Tanzania has recorded a complex history including major chemical fractionations *ca*. 2.0 Ga ago. The Lashaine lherzolite xenolith is characterized by extremely unradiogenic Pb isotope values (i.e. ca. $^{206}Pb/^{204}Pb=15.55$) and a $^{87}Sr/^{86}Sr$ value of 0.83604, both geochemical characteristics that cannot be reconciled with the isotope data from East African carbonatites (Fig. 1). As another example, Rudnick et al.'s (1993) investigation of the chemical and isotopic nature of peridotite xenoliths from the Olmani cinder cone in northern Tanzania, led them to attribute the distinctive mineralogical and chemical nature of the Olmani peridotites to the interaction of ultra-refractory residues with carbonatite melts. In addition, they noted that the radiogenic isotope data for the Olmani peridotites are

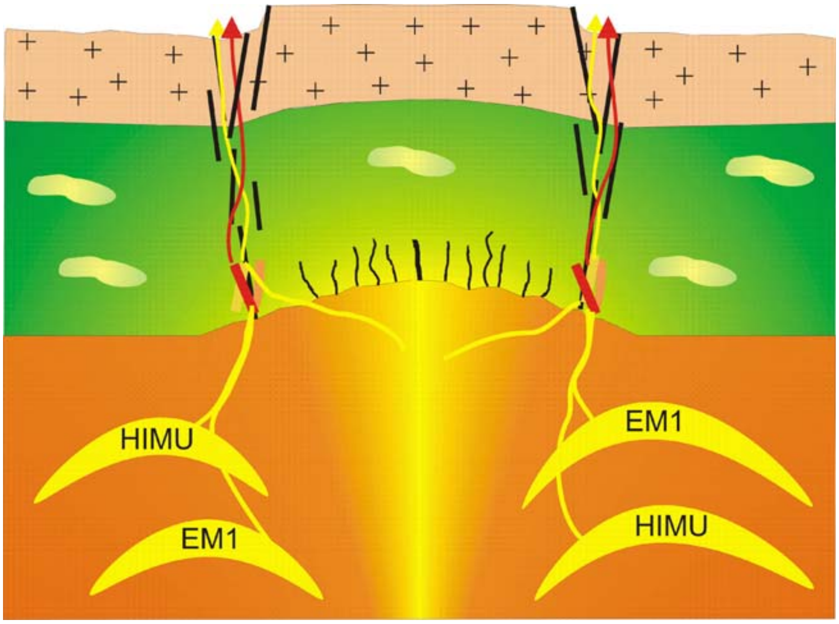

Fig. 4 Cartoon depicting a schematic cross-sectional view of the upper mantle/crust beneath the East African Rift. Green is sub-continental lithosphere (SCL), orange is sub-lithospheric, isotopically-heterogeneous mantle containing pods of HIMU and EM1 material (yellow). A plume/convecting asthenospheric upwelling impinges on the SCL; also shown are associated structural features such as crustal doming and rifting. The convecting asthenosphere/sub-asthenospheric plume is the source of the carbonatite-like/carbonated silicate melts, or metasomatic agents. Any metasomatic activity occurs at depths of about 75 km, the consequence of the phase relationships in the system peridotite-H_2O-CO_2 (Olafsson and Eggler 1983; Wyllie 1989 and references therein). These regions have been the focus of repeated metasomatic events throughout the Earth's history as represented by the different coloured metasomatic veins. As a result, the chemical/isotopic composition of the SCL is extremely heterogeneous and does not track the temporal evolution of any one source since it has undergone a complex chemical history (i.e. partial melting, metasomatism). The sub-lithospheric source for the East African carbonatites is primarily a mixture of HIMU and EM1 mantle components (Bell and Tilton 2001) reflecting either an isotopically heterogeneous, asthenosphere or a sub-asthenospheric plume. Mixing between HIMU and EM1 can occur at various depths. Given the scale of the heterogeneities recorded in one volcanic centre, e.g. Napak (Simonetti and Bell 1934, 1994; see also Fig. 1), mixing probably occurs during source melting

similar to those from the young (<40 Ma) East African carbonatite centres. Thus, Rudnick et al. (1993) concluded that metasomatic activity that affected the peridotites at Olmani occurred recently and that the carbonatites responsible for the metasomatism were ultimately derived from sub-lithospheric sources. On the basis of their chemical and isotopic investigations of nephelinites (and basalts) and peridotite xenoliths from Tanzania, respectively, Paslick et al. (1995) and Aulbach et al. (2008) both argue for the chemical enrichment and modification of the continental lithosphere by OIB/plume components derived from the underlying asthenosphere. In view of these and other reasons, it seems clear that metasomatism involving solely lithosphere-derived components (agents) cannot produce the observed radiogenic isotope evolution of the carbonatite sources, and that the simplest explanation is to generate the carbonated melts in a sub-lithospheric source. Moreover, Harmer et al. (1998) also concluded that the source of the Shawa carbonatites, Zimbabwe (South Africa), lies below the zone of an ancient LREE-enriched lithosphere sampled by nearby silicate magmas, and that the isotopic signatures of the carbonatites more closely approximate an asthenospheric component identified in nearby picrites.

Further supporting evidence for a sub-lithospheric source for carbonatites has emerged from some recent laboratory experiments based on the electrical conductivity of the upper mantle (Gaillard et al., 2008). The latter indicate that the presence of only small amounts of carbonatitic melts (<0.1% by volume) in the asthenosphere is sufficient to match its high conductivity nature; a feature normally attributed to either hydrous silicate melts or water-bearing olivine. It appears that molten carbonates are the most conductive phases of the Earth's mantle and are about 1000 times more conductive than molten silicate at 1000°C. Moreover, Dalou et al. (2009) advocate for the presence of molten carbonate within the mantle's transition zone based on the experimentally determined partition coefficients between carbonatitic melts and deep mantle minerals, such as majoritic garnet and perovskite. Although the results from these recent studies do not provide unequivocal evidence for the sub-lithospheric origin of parental melts to carbonatites, they do add significant and important information that gives credence to their non-lithospheric origin.

Our preferred model for carbonatite melt generation (Fig. 4), therefore, involves partial melts derived from an asthenospheric/plume source, assuming that the redox conditions within the deep mantle promote carbonate stability. The widespread similarity of isotopic signatures between OIBs and carbonatites indicates they are generated from sources that are widespread (Tilton and Bell 1994; Bell and Tilton 2002), i.e. HIMU, EM1 and FOZO mantle components are present within both oceanic mantle and SCL, and hence below the lithospheric mantle. We consider that metasomatism of the lithosphere, although it can occur, has not played a major role in generating the ultimate source of carbonatites. Metasomatism can occur, but if so then it becomes difficult to explain the similarity in isotopic signatures between most young carbonatites (<200 Ma) world-wide and the EM1, HIMU and FOZO components found in oceanic island basalts (Tilton and Bell 1994). The important implication here being that the isotopic signatures were generated from the same mantle sources and acquired by the melts at the time of their formation. The prevalence of carbonatites in continental areas is a consequence of the 'trapping' of low degree partial melts or fluids/volatiles derived from convecting asthenosphere/plume mantle by the overlying lithosphere. The repeated, relatively localized incursions of carbonatite activity over billions of years may be related to mechanically weak regions within the SCM that, once established, remain active as chemical-free pathways for the migration of low viscosity melts generated by plume melting and/or melting initiated by mantle upwellings. The impact of plumes, if they reach lithospheric levels, may indeed impart their distinct isotopic signatures to the lithospheric mantle at depths of about 75 km but the Rb/Sr, Sm/Nd and U/Pb development lines shown by the data from the Superior Province and the Fennoscandian Shield implies that the same closed chemical source was tapped at different intervals during carbonatite formation. In contrast, carbonatite complexes associated with large igneous provinces (LIPS - e.g. Polar Siberia, Brazil, and India) most probably represent products of extreme differentiation of alkaline ultramafic magmas generated by partial melting of plume material whilst maintaining their isotopic signatures inherited from a *sub*-lithospheric source.

Although we realize that there are arguments both for and against a plume origin for carbonatites, any model that involves a solely lithospheric source must explain the similarity of the radiogenic isotopic data from carbonatites to those found in oceanic island basalts. In this paper we have tried to summarize some of the important findings from the isotopic results with the hope that such a foundation will lead to a more objective approach to evaluating the mantle sources of carbonated melts. The constraints imposed by the isotopic data are fairly severe and until HIMU and EMI are found to be ubiquitous components in mantle xenoliths of known lithospheric origin, it seems highly improbable that the source for carbonated melts was the continental lithosphere.

Acknowledgements We sincerely thank Drs. M. Hirschmann, W.L. Griffin, and an anonymous reviewer for providing constructive comments on an earlier version of the manuscript. We are extremely appreciative for all of the stimulating discussions and interactions over the years with former graduate students, postdoctoral fellows and colleagues at Carleton University, as well as those with other carbonatite researchers.

References

Aulbach S, Rudnick RL, McDonough WF (2008) Li-Sr-Nd isotope signatures of the plume and cratonic lithospheric mantle beneath the margin of the rifted Tanzanian craton (Labait). Contr Miner Petrol 155:79–92

Bailey DK (1993a) Carbonate magmas. J Geol Soc London 150:637–651

Bailey DK (1993b) Petrogenetic implications of the timing of alkaline, carbonatite, and kimberlite igneous activity in Africa. South African J Geol 96:67–74

Bailey DK, Woolley AR (2005) Repeated synchronous magmatism within Africa: timing, magnetic reversals, and global tectonics. In: Foulger GR, Natland JH, Presnall DC, Anderson DL (eds) Plates, plumes and paradigms, Geological Society of America Special Paper 388:365-377

Barker DS (1996) Consequences of recycled carbon in carbonatites. Can Mineral 34:373–387

Basu S, Murty SVS (2006) Noble gases in carbonatites of Sung Valley and Ambadongar: implications for trapped components. Chem Geol 234:236–250

Bell K (2001) Carbonatites: relationships to mantle plume activity. In: Ernst R, Buchan KL (eds) Mantle plumes: their identification through time. Geol Soc Am Spec Paper 352, pp.267-290

Bell K (2005) Carbonatites. In: Selley RC, Cocks LRM, Plimer IR (eds) Encyclopedia of Geology. Elsevier, Amsterdam, pp 217–233

Bell K, Blenkinsop J (1987) Archean depleted mantle-evidence from Nd and Sr initial isotope ratios of carbonatites. Geochim Cosmochim Acta 51:291–298

Bell K, Blenkinsop J, Cole TJS, Menagh DP (1982) Evidence from Sr isotopes for long-lived heterogeneities in the upper mantle. Nature 298:251–253

Bell K, Dawson JB (1995) Nd and Sr isotope systematics of the active carbonatite volcano, Oldoinyo Lengai. In: Bell K, Keller J (eds) Carbonatite volcanism: IAVCEI Proceedings in Volcanology 4. Springer-Verlag, Berlin, pp 100–112

Bell K, Rukhlov AS (2004) Carbonatites from the Kola Alkaline Province: origin, evolution and source characteristics. In: Zaitsev A, Wall F (eds) Phoscorites and carbonatites from mantle to mine: the key example of the Kola Alkaline Province, Miner Soc Series 10. pp, London, pp 421–455

Bell K, Simonetti A (1996) Carbonatite magmatism and plume activity: implications from the Nd, Pb and Sr isotope systematics of Oldoinyo Lengai. J Petrol 37:1321–1339

Bell K, Tilton GR (2001) Nd, Pb and Sr isotopic compositions of east African carbonatites: evidence for mantle mixing and plume inhomogeneity. J Petrol 42:1927–1945

Bell K, Tilton GR (2002) Probing the mantle: the story from carbonatites. EOS, Amer Geophys Union 83:273 276-277

Bizzarro M, Simonetti A, Stevenson RK, David J (2002) Hf isotope evidence for a hidden mantle reservoir. Geology 30:771–774

Bonadiman C, Beccaluva L, Coltorti M, Siena F (2005) Kimberlite-like metasomatism and 'garnet signature' in spinel-peridotite xenoliths from Sal, Cape Verde Archipelago: relics of a subcontinental mantle domain within the Atlantic oceanic lithosphere. J of Petrol 46:2465–2493

Burke K, Khan S (2006) Geoinformatic approach to global nepheline syenite and carbonatites distribution: testing a Wilson cycle model. Geosphere 2:53–60

Choukroun M, O'Reilly SY, Griffin WL, Pearson NJ, Dawson JB (2005) Hf isotopes of MARID (mica-amphibole-rutile-ilmenite-diopside) rutile trace metasomatic processes in the lithospheric mantle. Geology 33:45–48

Cohen RS, O’Nions RK, Dawson JB (1984) Isotope geochemistry of xenoliths from East Africa: implications for development of mantle reservoirs and their interaction. Earth Planet Sci Lett 68:209–220

Comin-Chiaramonti P, Gomes CB, Cenzi P, Speziale S (2005) Carbonatites from southeastern Brazil: a model for the carbon and oxygen isotope variations. In: Comin-Chiaromonti P, Gomes CB (eds) Mesozoic to Cenozoic alkaline magmatism in the Brazilian platform. Edusp. Fapest, Brazil, pp 629–649

Dalou C, Koga KT, Hammouda T, Poitrasson F (2009) Trace element partitioning between carbonatitic melts and mantle transition zone minerals: Implications for the source of carbonatites. Geochim Cosmochim Acta 73:239–255

Dalton JA, Presnall DC (1998) Carbonatitic melts along the solidus of model lherzolite in the system CaO-MgO-Al_2O_3-SiO_2-CO_2 from 3 to 7 GPa. Contrib Miner Petrol 131:123–135

Dasgupta R, Hirschmann MM (2006) Melting in the Earth's deep upper mantle caused by carbon dioxide. Nature 440:659–662

Dasgupta R, Hirschmann MM, Dellas N (2005) The effect of bulk composition on the solidus of carbonated eclogite from partial melting experiments at 3 GPa. Contrib Miner Petrol 149:288–305

Dasgupta R, Hirschmann MM, Withers AW (2004) Deep global cycling of carbon constrained by the solidus of anhydrous, carbonated eclogite. Earth Planet Sci Lett 227:73–85

Dauphas N, Marty B (1999) Heavy nitrogen in carbonatites of the Kola Peninsula: a possible signature of the deep mantle. Science 286:2488–2490

Deines P (1989) Stable isotope compositions in carbonatites. In: Bell K (ed) Carbonatites: genesis and evolution. Unwin Hyman, London, pp 278–300

Dunworth EA, Bell K (2001) The Turiy Massif, Kola Peninsula, Russia: isotopic and geochemical evidence for multi-source evolution. J Petrol 42:377–405

Erlank AJ, Waters FG, Hawkesworth CJ, Haggerty SE, Allsopp HE, Richard RS, Menzies MA (1987) Evidence for mantle metasomatism in peridotite nodules from the Kimberley pipes, South Africa. In: Menzies MA, Hawkesworth CJ (eds) Mantle Metasomatism. Academic Press, London, pp 221–311

Ernst RE, Buchan KL (2001) Mantle plumes: their identification through time. Geol Soc Am Spec Pap 352:593

Falloon TJ, Green DH (1989) The solidus of carbonated, fertile periodite. Earth Planetary Sci Lett 94:364–370

Fischer TP, Burnard P, Marty B, Hilton DR, Füri E, Palhol F, Sharp ZD, Mangasini F (2009) Upper mantle volatile chemistry at Oldoinyo Lengai volcano and the origin of carbonatites. Nature 459:77–80

Foulger GR, Natland JH, Presnall DC, Anderson DL (2005) Plates, plumes and paradigms. Geol Soc Amer Special Paper 388:1–881

Gaillard F, Malki M, Iacono-Marziano G, Pichavant M, Scaillet B (2008) Carbonatite melts and electrical conductivity in the asthenosphere. Science 322:1363–1365

Gerlach DC, Cliff RA, Davies GR, Norry M, Hodgson N (1988) Magma sources of the Cape Verdes archipelago: isotopic and trace element constraints. Geochim. et Cosmochim Acta 52:2979–2992

Haggerty SE (1994) Superkimberlites: a geodynamic diamond window to the Earth's core. Earth Planet Sci Lett 122:57–69

Hammouda T (2003) High-pressure melting of carbonated eclogite and experimental constraints on carbon recycling and storage in the mantle. Earth Planet Sci Lett 214:357–368

Harmer RE, Lee CA, Eglington BM (1998) A deep mantle source for carbonatite magmatism: evidence from the nephelinites and carbonatites of the Buhera district, SE Zimbabwe. Earth Planet Sci Lett 150:131–142

Hart SR (1988) Heterogeneous mantle domains: signatures, genesis and mixing chronologies. Earth Planet Sci Lett 90:273–296

Hart SR, Hauri EH, Oschmann LA, Whitehead JA (1992) Mantle plumes and entrainment: isotopic evidence. Science 256:517–520

Hoernle KA, Tilton GR (1991) Sr-Nd-Pb isotope data for Fuerteventura (Canary Islands) basal complex and subaerial volcanics: applications to magma genesis and evolution. Schweiz Miner Petrograph Mitteil 71:3–18

Hoernle KA, Tilton GR, Le Bas MJ, Duggen S, Garbe-Schonberg D (2002) Geochemistry of oceanic carbonatites compared with continental carbonatites: mantle recycling of oceanic crustal carbonate. Contrib Miner Petrol 142:520–542

Hofmann AW (1997) Mantle geochemistry: the message from oceanic volcanism. Nature 385:219–229

Ingrin J, Skogby H (2000) Hydrogen in nominally anhydrous upper-mantle minerals: concentration levels and implications. European J Miner 12:543–570

Isshiki M, Irifune T, Hirose K, Ono S, Ohishi Y, Watanuki T, Nishibori E, Takata M, Sakata M (2004) Stability of magnesite and its high-pressure form in the lowermost mantle. Nature 427:60–63

Keller J, Hoefs J (1995) Stable isotope characteristics of recent natrocarbonatites from Oldoinyo Lengai. In: Bell K, Keller J (eds) Carbonatite Volcanism: IAVCEI Proceedings in Volcanology 4. Springer-Verlag, Berlin, pp 113–123

Kevin G, Ingrin J, Lorand JP, Dumas P (2007) Water partitioning between mantle minerals from peridotite xenoliths. Contr Miner Petrol 154:15–34

Kogarko LN (2006) Enriched mantle reservoirs are the source of alkaline magmatism. In: Vladykin NV (ed) Deep-seated magmatism, its sources and plumes. Proceedings of the VI International Workshop, Mirny. Publishing House of the Inst. of Geography SB RAS, pp 46–58

Kogarko LN, Kurat G, Ntaflos T (2001) Carbonate metasomatism of the oceanic mantle beneath Fernando de Noronha Island, Brazil. Contr Miner Petrol 140:577–587

Kramm U (1993) Mantle components of carbonatites from the Kola alkaline province, Russia and Finland–A Nd-Sr study. European J Miner 5:985–989

Larsen LM, Rex DC (1992) A review of the 2500 Ma span of alkaline-ultramafic, potassic and carbonatitic magmatism in West Greenland. Lithos 28:367–402

Lentz DR (1999) Carbonatite genesis: a re-examination of the role of intrusion-related pneumatolytic skarn processes in limestone melting. Geology 27:335–338

Lloyd FE, Bailey DK (1975) Light element metasomatism of the continental mantle: the evidence and the consequences. Phys Chem Earth 9:389–416

Lustrino M, Wilson M (2007) The circum-Mediterranean anorogenic Cenozoic igneous province. Earth Sci Rev 81:1–65

Luth RW (2004) Mantle volatiles–distribution and consequences. In: Carlson RW (ed) The mantle and core volume 2 treatise on geochemistry. Elsevier-Pergamon, Oxford, pp 319–361

Marty B, Tolstikhin I, Kamensky IL, Nivin V, Balaganskaya E, Zimmerman J-L (1998) Plume-derived rare gases in 380 Ma carbonatites from the Kola region (Russia) and the argon isotopic composition in the deep mantle. Earth Planet Sci Lett 164:179–192

Meen JK (1987) Mantle metasomatism and carbonatites: An experimental study of a complex relationship. In Morris EM, Pasteris, JD (eds) Mantle metasomatism and alkaline magmatism. Geol Soc Am Spec Paper 215 pp 91-100

Meen JK, Ayers JC, Fregeau EJ (1989) A model of mantle metasomatism by carbonate alkaline melts: trace-element and isotopic compositons of mantle source regions of carbonatite and other continental igneous rocks. In: Bell K (ed) Carbonatites: genesis and evolution. Unwin Hyman, London, pp 464–499

Menzies MA, Rogers N, Tindle A, Hawkesworth CJ (1987) Metasomatic and enrichment processes in lithospheric peridotites, an effect of asthenosphere-lithosphere interaction. In: Menzies MA, Hawkesworth CJ (eds) Mantle Metasomatism. Academic Press, London, pp 313–361

Moine BN, Grégoire M, O'Reilly SY, Delpech G, Sheppard SMF, Lorand JP, Renac C, Giret A, Cottin JY (2004) Carbonatite melt in ocean upper mantle beneath the Kerguelen Archipelago. Lithos 75:239–252

Mysen BO (1978) Experimental determination of crystal-vapour partition coefficients for rare earth elements at 30 kbar pressure. Carnegie Institute of Washington Yearbook 73:255–258

Nelson DR, Chivas AR, Chappell BW, McCulloch MT (1988) Geochemical and isotopic systematics in carbonatites and implications for the evolution of ocean-island sources. Geochim Cosmochim Acta 52:1–17

Olafsson M, Eggler DH (1983) Phase relations of of amphibole, amphibole-carbonate, and phlogoipite-carbonate peridotite: petrologic constraints on the asthenosphere. Earth Planet Sci Lett 64:305–315

Paslick C, Halliday A, James D, Dawson JB (1995) Enrichment of the continental lithosphere by OIB melts: isotopic evidence from the volcanic province of northern Tanzania. Earth Planet Sci Lett 130:109–126

Rudnick RL, McDonough WF, Chappell BW (1993) Carbonatite metasomatism in the northern Tanzanian mantle: petrographic and geochemical characteristics. Earth Planet Sci Lett 114:463–475

Sasada T, Hiyagon H, Bell K, Ebihara M (1997) Mantle-derived noble gases in carbonatites. Geochim Cosmochim Acta 61:4219–4228

Simonetti A, Bell K (1993) Isotopic disequilibrium in clinopyroxenes from nephelinitic lavas, Napak volcano, eastern Uganda. Geology 21:243–246

Simonetti A, Bell K (1994) Nd, Pb and Sr isotopic data from the Napak nephelinite-carbonatite centre, eastern Uganda: an example of open-system crystal fractionation. Contrib Miner Petrol 115:356–366

Simonetti A, Bell K, Viladkar SG (1995) Isotopic data from the Amba Dongar carbonatite complex, west-central India: evidence for an enriched mantle source. Chem Geol 122:185–198

Simonetti A, Goldstein SL, Schmidberger SS, Viladkar SG (1998) Geochemical and Nd, Pb, and Sr isotope data from Deccan alkaline complexes-inferences for mantle sources and plume-lithosphere interaction. J Petrol 39:1847–1864

Sleep NH (1990) Hotspots and mantle plumes: some phenomenology. J. Geophys Res 95:6715–6736

Sleep NH (2006) Mantle plumes from top to bottom. Earth Sci Rev 77:231–271

Sleep NH, Zahnle K (2001) Carbon dioxide cycling and implications for the climate on ancient Earth. J Geophys Res 106:1373–1399

Stoppa F (2007) CO_2 magmatism in Italy: from deep carbon to carbonatite volcanism. In: Vladykin NV (ed) Alkaline magmatism, its sources and plumes. Proceedings of the VII International Workshop, Naples, Italy. Publishing House of the Inst. of Geography SB RAS, pp 109-126

Sweeney RJ, Green DH, Sie SH (1992) Trace and minor element partitioning between garnet and amphibole and carbonatitic melt. Earth Planet Sci Lett 113:1–14

Tappe S, Foley SF, Stracke A, Romer RL, Kjarsgaard BA, Heaman LM, Joyce N (2007) Craton reactivation on the Labrador Sea margins: $^{40}Ar/^{39}Ar$ age and Sr-Nd-Hf-Pb isotope constraints from alkaline and carbonatite intrusives. Earth Planet Sci Lett 256:433–454

Thomassot E, Cartigny P, Harris JW, Viljoen KS (2007) Methane-related diamond crystallization in the Earth's mantle: stable isotope evidences from a single diamond-bearing xenolith. Earth Planet Sci Lett 257:362–371

Tilton GR, Bell K (1994) Sr-Nd-Pb isotope relationships in late Archean carbonaties and and alkaline complexes-applications to the geochemical evolution of Archean mantle. Geochim Cosmochim Acta 58:3145–3154

Tolstikhin IN, Kamensky IL, Marty B, Nivin VA, Vetrin VR, Balaganskaya EG, Ikorsky SV, Gannibal MA, Weiss D, Verhulst A, Demaiffe D (2002) Rare gas isotopes and parent trace elements in ultrabasic-alkaline-carbonatite complexes, Kola Peninsula: identification of lower mantle plume component. Geochim Cosmochim Acta 66:881–901

van Achterbergh E, Griffin WL, Stiefenhofer J (2001) Metasomatism in mantle xenoliths from the Letlhakane kimberlites: estimation of element fluxes. Contrib Miner Petrol 141:397–414

van Achterbergh E, Griffin WL, Ryan CG, O'Reilly SY, Pearson NJ, Kivi K, Doyle BJ (2002) Subduction signature for quenched carbonatites from the deep lithosphere. Geology 30:743–746

Veizer J (1989) Strontium isotopes in seawater through time. Annual Rev Earth Planet Sci 17:141–167

Vladykin NV (ed) (2007) Alkaline magmatism, its sources and plumes. Proceedings of the VII International Workshop, Naples, Italy. Publishing House of the Inst. of Geography SB RAS, p 192

Wilson M, Patterson R (2001) Intraplate magmatism related to short-wavelength convective instabilities in the upper mantle: evidence from the Tertiary-Quaternary volcanic province of western and central Europe. In: Ernst R, Buchan KL (eds) Mantle plumes: their identification through time. Geol Soc Am Spec Paper 352, pp.37-58

Woolley AR, Kempe DRC (1989) Carbonatites: nomenclature, average chemical compositions, and element distribution. In: Bell K (ed) Carbonatites: genesis and evolution. Unwin Hyman, London, pp 1–14

Wyllie PJ (1988) Solidus curves, mantle plumes, and magma generation beneath Hawaii. J Geophys Res 93:4171–4181

Wyllie PJ (1989) Origin of carbonatites: evidence from phase equilibrium studies. In: Bell K (ed) Carbonatites: genesis and evolution. Unwin Hyman, London, pp 500–545

Wyllie PJ, Huang WL (1975) Peridotite, kimberlite, and carbonatite explained in the system $CaO\text{-}MgO\text{-}SiO_2\text{-}CO_2$. Geology 3:621–624

Wyllie PJ, Ryabchikov ID (2000) Volatile components, magmas, and critical vapours in the upwelling mantle. J Petrol 41:1195–1206

Yaxley GM, Brey GP (2004) Phase relations of carbonate-bearing eclogite assemblages from 2.5 to 5.5 GPa: implications for petrogenesis of carbonatites. Contrib Miner Petrol 146:606–619

Zhang Y, Zindler A (1993) Distribution and evolution of carbon and nitrogen in Earth. Earth Planet Sci Lett 117:331–345

Zindler A, Hart SR (1986) Chemical dynamics. Annual Rev Earth Planet Sci 14:493–571