

## Carbonate Melts and Carbonatites

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### INTRODUCTION

Carbonatites are familiar to students of petrology as rare igneous rocks formed predominantly of carbonate, whose only modern expression is a single active volcano that erupts strongly alkaline carbonate lavas with no direct match in Earth's geological record (see Lengai movie in the electronic version of this chapter or on the MSA RiMG website). Based on their Sr-Nd-Pb isotopic data, stable isotopic compositions, noble gases, and experimental phase equilibria, they are derived from the mantle, showing almost no sign of contamination by the crust.

As liquids, carbonate melts have remarkable physical properties, which set them apart from the alkaline silicate melts with which they are often temporally associated. They show very high solubilities of many elements considered rare in silicate magmas, and they have the highest known melt capacities for dissolving water and other volatile species like halogens at crustal pressures. They are highly efficient transport agents of carbon from the mantle to the crust, remaining mobile over extraordinary ranges of temperature, and their very low viscosity should enhance connectivity along grain boundaries in the mantle where they are implicated in geochemical enrichment processes related to metasomatism.

Most carbonatites have unambiguous origins in the mantle and the limit to their depth is not known, but the likelihood that they may exist in the lower mantle (Kaminsky et al. 2009, 2012; Stoppa et al. 2009) needs to be appraised since they may exert a fundamental control on the mobility and long-term storage of deep carbon in Earth. Ultimately the stability of carbonate melt is an extension of the stability of carbonate minerals (Hazen et al. 2013a,b) subject critically to the mantle oxidation state (Luth 1993; Frost and McCammon 2008); carbonate-melts have also been predicted in the oceanic low-velocity zone and deep mantle (Hauri et al. 1993; Presnall and Gudfinnsson 2005) by laboratory petrology experiments (Wyllie 1995). Much remains to be discovered about carbonate melts at very high-pressures.



**VIDEO:** Erupting Lengai volcano. For readers of the electronic version of this chapter, the video can be activated by either clicking on the play button or the image above. The video shows black natrocarbonatite lava spewing from one of several white “hornito” structures at the summit of Oldoinyo Lengai volcano in the East African Rift, Tanzania. This carbonatite lava is the lowest temperature (< 600 °C) and lowest viscosity lava known, and is seen dissolving a channel for itself before it rapidly overflows the rim of the crater. The last part of the movie shows a standing wave caused by a small obstruction near the crater rim. Besides the scientists’ voices, the soundtrack records the strange clinking and water-like murmurs of the lava itself. The movie was filmed by Tobias Fischer, University of New Mexico during a 2005 Oldoinyo Lengai expedition led by Pete Burnard and Bernard Marty, CNRS, France. The volcano has a recent history typified by passive eruption of natrocarbonatite as shown in the movie, interspersed with larger dangerous explosive eruptions every few decades. The last major eruption in 2007-8 destroyed all of the crater hornitos in the movie and excavated a deep new summit crater; it was preceded by tremors measuring up to 6 on the Richter scale.

Beyond the current solid media experiments with piston cylinder, multi-anvil press, and diamond-anvil cell (e.g., calcite-dolomite-aragonite; Kraft et al. 1991), we may look to carbonate inclusions in diamonds (Kaminsky et al. 2001, 2009; Brenker et al. 2007; Kaminsky 2012) and high-pressure shock wave environments for clues, including shocked carbonate from impact craters, which can show isotopic shifts ( $\delta^{13}\text{C}$  vary 5 per mil; Martinez et al. 1994, 1995; Jones et al. 2000a). Another unique property of carbonate melts is their high electrical conductivity—up to three orders of magnitude greater than silicate melts and five orders of magnitude higher than hydrated mantle material (see section “*Occurrence of carbonatites*”). Consequently, carbonate melts have been invoked to explain deep regions of the mantle asthenosphere characterized by anomalous conductivity. The presence of low volume (0.1%) carbonate melts are contenders to explain electrically conductive mantle regions, previously thought to be caused by silicate melts or water-bearing olivine (Gaillard et al. 2008).

Several books and reviews have been written about the systematic geochemistry and mineralogy and origin of carbonatites (Tuttle and Gittins 1966; Bell 1989; Bell et al. 1998; Jones 2000; Mitchell 2005; Woolley and Church 2005; Woolley and Kjarsgaard 2008a; Downes et al. 2012). Fundamental understanding of carbonatites was largely achieved in the last century when engineering developments in technology enabled experimental petrology to unlock the secrets of how carbonatites actually form, including their important connections with water, enabling early formative predictions about the stability of carbonate minerals in the upper mantle; the significance of free  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the mantle transition zone; the derivation of kimberlitic and carbonatitic melts; and mantle metasomatism (Wyllie and Tuttle 1960, 1962; Wyllie and Huang 1976). The purpose of this review is to provide a framework for understanding carbonate melts, to highlight their potential role in providing vertical connectivity and pathways for deep carbon

to be transferred from the mantle to Earth’s surface, and to illustrate how further technological advances are still required to answer even the most basic questions about the abundance and mobility of carbon in Earth’s deep interior.

## CARBONATE MELTS

### Physical properties

Very low magmatic temperatures and very low viscosity are striking features of alkali-carbonatite lavas at low pressure, for example at the sole active volcano Oldoinyo Lengai in Tanzania (Treiman and Schedl 1983; Krafft and Keller 1989; Dawson et al. 1990; Oppenheimer 1998). The low carbonate melt viscosity was first measured accurately in experiments using in-situ synchrotron radiation to track rapidly falling spheres (Dobson et al. 1996) and is compared with other data (Wolff 1994; Jones et al. 1995a) in Table 1. We note that only natural high  $PT$  iron-rich melts in Earth’s core may approach such extremely low viscosities (Dobson et al. 2000).

Calculated physical properties by Genge et al. (1995b) predict that  $\text{CaCO}_3$  melt densities increase from  $2000 \text{ kg m}^{-3}$  at  $P = 0.1 \text{ GPa}$  to  $2900 \text{ kg m}^{-3}$  at  $P = 10.0 \text{ GPa}$ , suggesting carbonate melts are significantly more compressible than silicate melts. Estimates of the constant pressure heat capacity of  $1.65\text{-}1.90 \text{ J g}^{-1} \text{ K}^{-1}$ , isothermal compressibilities of  $0.012\text{-}0.01 \times 10^{-10} \text{ Pa}^{-1}$  and thermal expansivities of  $1.886\text{-}0.589 \times 10^{-4} \text{ K}^{-1}$  were also calculated (Genge et al. 1995b). Self-diffusion coefficients qualitatively suggest that  $\text{CaCO}_3$  melts have very low viscosities at high-pressures to 11 GPa.

Although no other atomic simulations of carbonate melts have been performed, quantum mechanical *ab initio* evolutionary models, which allow the most energetically stable atomic

**Table 1.** Carbonate melt physical data measured *in situ* using synchrotron X-ray falling sphere method and calculations for pressures up to 5.5 GPa. Source references [1] Dobson et al. (1996), [2] Genge et al. (1995b) [3] Wolff (1994).

Composition	Pressure (GPa)	$T$ (°C)	Density ( $\text{g/cm}^3$ )	Comment	Viscosity (PaS)	Reference
$\text{K}_2\text{Mg}(\text{CO}_3)_2$	atm	500	2.262			[1]
$\text{K}_2\text{Ca}(\text{CO}_3)_2$	atm	859	2.058			
$\text{MgCO}_3 = \text{Mc}$	atm		2.30			[2]
$\text{K}_2\text{Mg}(\text{CO}_3)_2$	3.00	800			0.036	[1]
	3.00	900			0.022	[1]
	5.50	1200			0.006	[1]
$\text{K}_2\text{Ca}(\text{CO}_3)_2 = \text{Kc}$	2.50	950	2.75		0.032	[1]
	2.50	1150	2.58		0.018	[1]
	4.00	1050	2.80		0.023	[1]
$\text{Mc}_{.25}\text{Kc}_{.75}$	2.00	1250			0.065	[1]
$\text{K}_2\text{CO}_3$	4.00	1500	3.10		0.023	[1]
RE-Carbonatite	3.00	530	4.10		0.155	[1]
$\text{CaCO}_3$				Thermal expansivity		[2]
Ca-carbonatite	atm	800		calculated	0.08	[3]
Natrocarbonatite	atm	800		calculated	0.008	[3]

structures to be predicted, suggest that radical transformation of carbonate mineral structures occur at lower mantle pressures (Oganov et al. 2008, 2013). Simulations predict that the stable  $\text{MgCO}_3$  and  $\text{CaCO}_3$  phases at pressures  $>82$  GPa and  $>19$  GPa respectively are dominated by corner-sharing  $\text{CO}_4$  tetrahedra networks, with those of  $\text{CaCO}_3$  adopting a  $\beta$ -cristobalite structure, and  $\text{MgCO}_3$  adopting a pyroxene-like structure at pressures  $>110$  GPa. Such predictions are supported experimentally by recovered Mg-Fe carbonates with polymerized structures (Boulard et al. 2011). The formation of  $\text{CO}_4^{4-}$  at high-pressure was predicted (Genge 1994) because it is compatible with the similar electronic configurations of C and Si, which satisfy the requirements of both  $sp^2$  (trigonal) and  $sp^3$  (tetrahedral) hybridization. Transformation from carbonate structures to tetrahedral  $\text{CO}_4$  groups, however, requires the breaking of  $pp$  bonds and the formation of antibonding orbitals and is likely to be associated with significant activation energy. Metastable carbonate phases, therefore, are likely to be present across the transition region of the mantle at which such transformations occur. Indeed *ab initio* models predict that numerous energetically similar metastable phases exist for  $\text{MgCO}_3$  (Oganov et al. 2013).

### Atomic structure of carbonate melts

The atomic structures of carbonate melts have been little studied in comparison to the structure of silicate melts, but are fundamental in controlling their physical and chemical behavior in natural systems. Carbonate melts are ionic liquids consisting of carbonate  $\text{CO}_3^{2-}$  molecular anions and metal cations that interact principally due to coulombic interactions and are thus very different from silicate melts, which have network structures characterized by polymerization (Mysen 1983). Ionic carbonate melts have been considered to be structureless with no definite association between metal cations and carbonate molecules (Treiman and Schedl 1983). However the combined evidence from phase relations of carbonates, the solubility of metals in carbonate liquids, and the spectroscopy of carbonate glasses and atomic simulations, suggests that carbonate liquids have structure at scales larger than their component molecular groups.

### Carbonate melts as ionic liquids

The ionic nature of carbonate melts and their inability to polymerize to form network structures is their most fundamental property and is a consequence of the electronic structure and intra-molecular bonding of the carbonate ion. Consideration of the electronic structure of  $\text{Si}^{4+}$  and  $\text{C}^{4+}$  demonstrates that the outer shells of both atoms have identical electron occupation, that is,  $\text{Si}^{4+}$  ( $3s^23p^2$ ) and  $\text{C}^{4+}$  ( $2s^22p^2$ ), and hence similar bonding characteristics might be expected. However, the differing electronegativities of Si and C, 1.9 and 2.6 respectively (Pauling 1960), result in Si-O bonds that are less polarized than C-O bonds, with a 50% ionic character and localized charge distribution on oxygen atoms. The small ionic radius  $\text{Si}^{4+}$  of 0.34 dictates tetrahedral coordination with oxygen,  $\text{Si}^{4+}$  readily adopts  $sp^3$  hybrid covalent bonds, whereas  $\text{C}^{4+}$  is less restricted by the requirements of close packing and adopts an  $sp^2$  hybridization in order to reduce coulombic interaction of the oxygen atoms. In both  $\text{C}^{4+}$  and  $\text{Si}^{4+}$  the adoption of hybrid bonding orbitals is facilitated by excitation of an electron from an  $s$  orbital to occupy an empty  $p$  orbital. A consequence of the  $sp^2$  hybridization of the carbonate ion is the formation of  $sp^2s$  bonds between C and O and the formation of two  $pp$  bonds (Fig. 1) above and below the plane of the molecule by interaction of C and O  $p$ -orbitals. Not only does the presence of a  $pp$  bond result in a double bond, shared over the three C-O bonds, but it also leaves only lone pair  $p$  orbital per oxygen orientated in the plane of the molecule. Hence, unlike  $\text{SiO}_4^{4-}$  tetrahedra, the  $\text{CO}_3^{2-}$  trigonal group has no unpaired orbitals available for covalent bonding, and is hence, unable to polymerize.

### Cation electronegativity ( $\chi$ )

The dissociation temperatures of crystalline unary carbonates indicate that metal cations exert an important control on carbonate melt structure since they control the stability of the carbonate ion. Carbonate dissociation temperatures decrease with increasing electronegativity

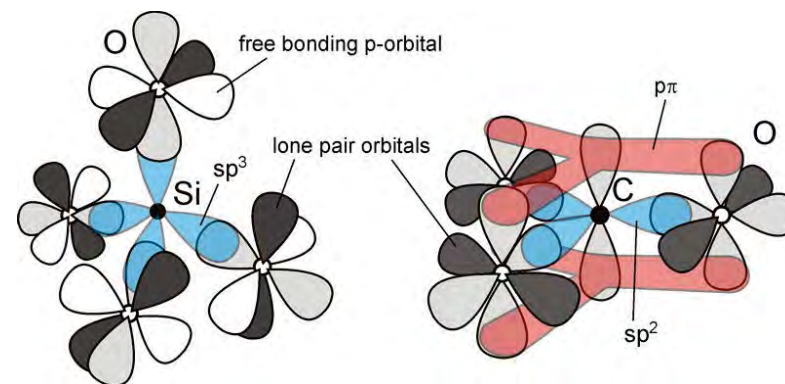


Figure 1. Showing the electronic configurations and molecular bonding of  $\text{SiO}_4$  and  $\text{CO}_3$ .

( $\chi$ ) of the metal cation for any particular polytype (Fig. 2; West 1972). Since  $\chi$  relates to the ability of an atom to attract electrons, the variation in dissociation temperatures of crystalline carbonates with  $\chi$  suggests that intra-molecular bond strengths are moderated by charge delocalization on  $\text{CO}_3^{2-}$  molecules due to the influence of nearby metal cations. Similar control by metal composition on  $\text{CO}_3^{2-}$  intra-molecular bond strengths within carbonate melts will be an important control on dissociation reactions that determine the abundance of carbonate ions available for complexation with metal cations (Genge 1994).

Different dissociation temperature- $\chi$  trends are observed for carbonates with different structures. Aragonite structure carbonates with 8-fold coordinated metal cations have higher dissociation temperatures than 6-fold coordinated calcite structure carbonates. The dependence of C-O bond strength on metal cation site coordination suggests that carbonate melt structure is likely to be as important in the dissociation of carbonate ions as composition. Transition metal carbonates have higher dissociation temperatures than predicted by  $\chi$  of their metal cations, indicating that delocalization of intra-molecular bonding electrons is not the only control on carbonate dissociation (Fig. 2). Transition metals, however, are capable of coordinate bonding with carbonate ions, utilizing the lone pair orbitals of the carbonate ion to donate electrons to empty metal ligands. Coordinate bonding results in charge redistribution that will reduce delocalization of electrons from carbonate ion molecular orbitals, resulting in increased bond

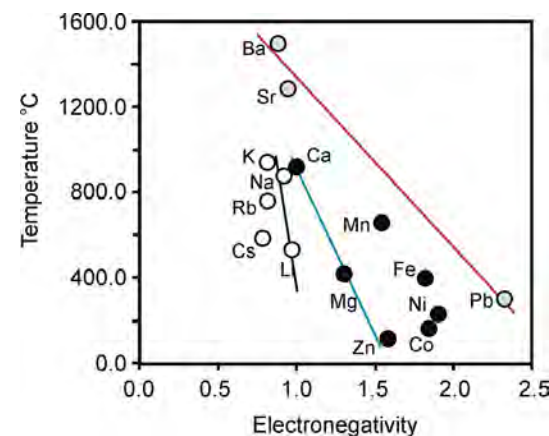
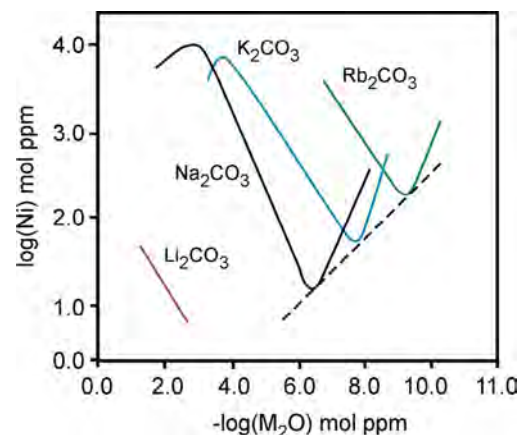


Figure 2. Showing the dissociation temperatures of crystalline carbonates at 1 atm compared with the electronegativity of metal cations.



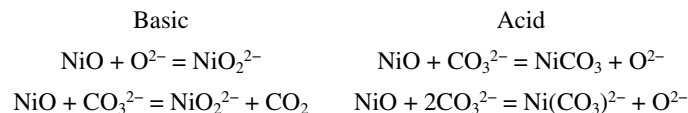
**Figure 3.** The solubility of NiO in unary alkali carbonate melts. After Orfield and Shores (1989).

strengths and greater carbonate stability. Carbonate ion dissociation is thus very important in the nature of speciation of components within carbonate melts.

### Speciation

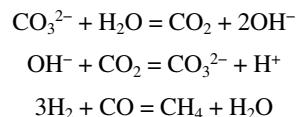
The solubility of metal oxides in carbonate melts can provide constraints on carbonate melt structure, and several studies have been performed on alkali carbonates at atmospheric pressure for use in molten carbonate fuel cells (MCFCs) focused on transition elements/oxides like NiO (Orfield and Shores 1988, 1989) and alkaline earth metal ceramics (Lessing et al. 1988). Solubility experiments for transition and alkaline earths in alkaline carbonate melts

show solution as basic oxides or acid carbonate complexes (Fig. 3). Basic dissolution occurs at low abundances of the added metal oxide while carbonate dissolution is dominant at higher abundances. Illustrative reaction mechanisms for dissolution of NiO are shown below:



Further details of speciation related to dissolution mechanisms in alkaline carbonate melts like  $\text{Na}_2\text{CO}_3$  are provided by Orfield and Shores (1988), while Doyon et al. (1987) show that dependence on carbonate activity within the melt, oxygen fugacity, and partial pressure of  $\text{CO}_2$  will also be important factors in controlling the speciation of metals. Orfield and Shore (1989) report experimentally derived NiO solubility in binary  $\text{Na}_2\text{CO}_3$ - $\text{K}_2\text{CO}_3$  melts, which exhibits significant divergences from ideal mixing behavior, and they provide additional data for  $\text{Rb}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  melts (Fig. 3).

Studies of MCFCs show that water can influence carbonate melt structure through coupled reactions with carbonate ions (Lu and Selman 1989) with a wide range of possible reactions prevalent under different oxygen fugacity and partial pressure of  $\text{CO}_2$ :

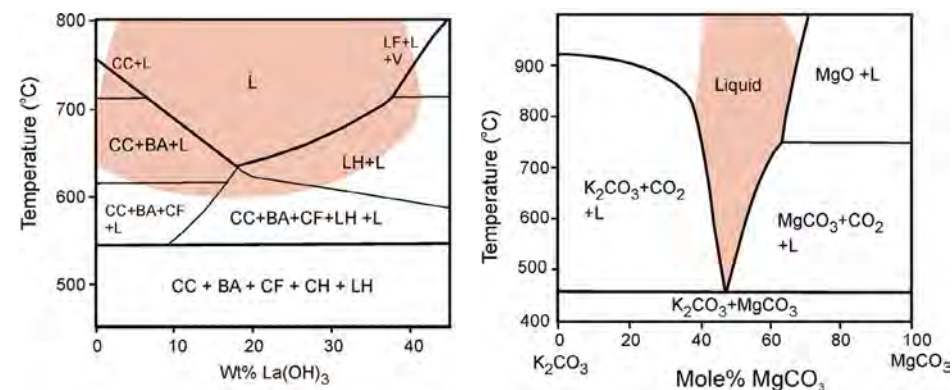


The solubility of species in competition with  $\text{CO}_3^{2-}$  for metal cations, for example P, which in silicate melts is stabilized by divalent cations (Mysen et al. 1981) or  $\text{OH}^-$  are likely to decrease with increasing metal-carbonate complexation. Experimental studies on P solubility in  $\text{CaCO}_3$  melts (Baker and Wyllie 1992) demonstrate that solubility is reduced with increasing partial pressure of  $\text{CO}_2$  and decreasing temperature, consistent with increased formation of metal-carbonate associations in the melt (Genge et al. 1995b). The solubility of cations and molecular species within carbonate melts imply that these are present either as complexes with carbonate ions or as oxide and hydrate complexes, but the solubility data do not provide constraints on the sites or degree of order of these structural components.

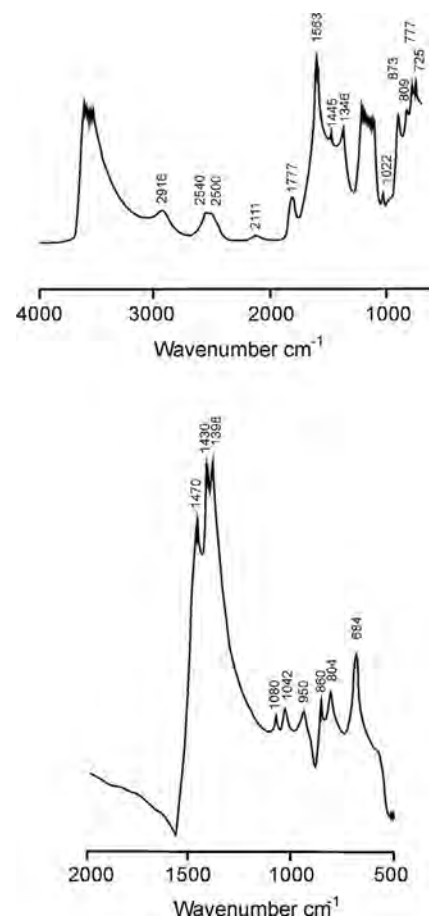
### Carbonate glasses

Two carbonate melt systems are known to quench to glasses at 0.1 GPa under laboratory conditions: (1)  $\text{MgCO}_3$ - $\text{K}_2\text{CO}_3$  (Faile et al. 1963; Ragone et al. 1966) and (2)  $\text{La}(\text{OH})_3$ - $\text{Ca}(\text{OH})_2$ - $\text{CaCO}_3$ - $\text{CaF}_2$ - $\text{BaSO}_4$  (Jones and Wyllie 1983) and provide a means of investigating melt structure directly by spectroscopy. The phase relations of both systems are shown in (Fig. 4). Glass is a supercooled liquid and forms by cooling through the glass transition, a second order phase transition during which the translational and vibrational motions of molecular groups become restricted. Crucial in the formation of glasses is their failure to crystallize during cooling below the liquidus/solidus; thus high viscosity melts and those with low melting temperatures are most likely to form glasses due to the dependence of both crystallization and nucleation on diffusion (Turnbull 1956). The majority of glasses, therefore, form from melts with network structures, such as silicate melts, in which covalently bonded polymers resist rearrangement. Although both carbonate systems that form glass have low eutectic temperatures, they are likely to have low melt viscosities (Dobson et al. 1996). Glass formation in these systems is also not restricted only to low temperature melts. The formation of these carbonate glasses from ionic liquids is, therefore, anomalous and implies that an extended structural association occurs between molecular component groups. Infrared and Raman spectra of carbonate glasses (Genge et al. 1995a) indicate at least two structural populations of  $\text{CO}_3^{2-}$  (Fig. 5, Table 2); one vibrational frequency like common 6-fold coordinated carbonate, and a highly asymmetric site with large vibrational splitting of its  $\nu_3$  mode. The existence of two general structural populations of carbonate ion in the glasses may correspond to a flexible pseudo-network structure where alkaline earth elements (Ca and Mg) act as bridging cations linking carbonate groups by ionic bonds and having similar coordination to equivalent crystalline carbonates, while other components, such as K, act as network modifiers that support ring-structures within the flexible network (Genge et al. 1995b). The structure of carbonate melts is, therefore, envisaged as a network of metal-carbonate complexes held open by modifying species. In this context asymmetric carbonate sites were suggested to represent carbonate ions with non-bridging oxygen atoms without first neighbor bridging cations.

The spectral activity of the O-H stretching region within hydrous La-bearing glasses furthermore suggests that water exists both as molecular  $\text{H}_2\text{O}$  and OH, interacting variably with carbonate ions and as metal complexes occupying relatively high symmetry sites in these glasses. The presence of bicarbonate groups, however, is prohibited by the absence of their character-



**Figure 4.** Phase relations in  $\text{La}(\text{OH})_3$ - $\text{Ca}(\text{OH})_2$ - $\text{CaCO}_3$ - $\text{CaF}_2$ - $\text{BaSO}_4$  and  $\text{MgCO}_3$ - $\text{K}_2\text{CO}_3$  glass forming systems showing regions of melt which quench to glass (shaded areas). Abbreviations: CC-calcite, BA-barites, CF-fluorite, LH - lanthanum hydroxide, L - liquid. After Jones and Wyllie (1986) and Dobson (1995).



**Figure 5.** Background subtracted infrared reflectance spectra of La-bearing (upper) and Mg-K carbonate glass (lower); (Genge et al. 1995a).

istic O-H stretching frequencies. The absence of a molecular  $\text{CO}_2$   $\nu_3$  stretching mode from the infrared spectra of both carbonate glasses suggests, by comparison with IR spectra for silicate melts (Fine and Stolper 1986) very low concentrations of  $\text{CO}_2$  in carbonate melts. In summary, IR and Raman spectroscopy of carbonate glasses, implies that for these restricted compositions, the carbonate melt structure comprises metal-carbonate complexes where a transient pseudo-network of ring structures with interstitial spaces occupied by modifying species and molecular groups (Genge et al. 1995b).

#### Atomic simulation of carbonates

Molecular dynamics simulations (MDS) of  $\text{CaCO}_3$  from atmospheric pressure to 11.5 GPa (Genge et al. 1995b) suggest that  $\text{CaCO}_3$  melts have the closest similarity to calcite structures, rather than aragonite, with similar bond lengths (Table 3) and broadly 6-fold Ca coordination (Table 4). The presence of second-nearest neighbor peaks, however, in particular for Ca-O and C-C suggest a degree of medium-range order consistent with associative metal-carbonate complexes (Fig. 6). Snapshots of melt structure (Fig. 7) indicate the occurrence of local density fluctuations, relating to spatial associations of carbonate groups and metal cations. The results of atomic simulations of  $\text{CaCO}_3$  liquids are, therefore, broadly compatible with the implications of infra-red studies of carbonate glasses since they exhibit carbonate ions linked into a flexible network by ionic bonding to metal cations.

### CARBONATITES

Understanding the geological context of carbonatites observed as volcanic products and magmatic rocks now at Earth's surface should not only consider their connections with other families of carbon-bearing igneous rocks like nephelinites, melilitites, and kimberlites, but also the direct evidence provided by experiments on their synthetic counterparts as carbonate melts. This section summarizes the current status of carbonatites.

Carbonatites are commonly defined as magmatic rocks with high modal abundance of carbonate minerals (>50 wt%) and geochemistry typified by high abundances of Sr, Ba, P and the light rare-earth elements (LREE) (Nelson et al. 1988). They have been subdivided (Fig. 8) on the basis of their dominant modal carbonate mineral, such as calcite-, or dolomite-carbonatites and on their corresponding major element geochemistry with Mg-, Ca, Fe- and REE-carbonatites (Woolley 1982; Le Bas 1987; Woolley and Kempe 1989). In parallel, a process-related classification would divide them into two groups: *primary carbonatites* and

**Table 2.** Infra-red absorption, reflectance and Raman frequencies with band assignments from carbonate glasses in  $\text{cm}^{-1}$  (Sharma and Simons 1980; Genge et al. 1995a). Symbols relate to the form of the band s-shoulder, b-broad, i-intense, w-weak.

La(OH) <sub>3</sub> -Ca(OH) <sub>2</sub> -CaCO <sub>3</sub> -CaF <sub>2</sub> -BaSO <sub>4</sub> Glass			
Raman	Reflectance	Absorption	Assignment
623(w)			CO <sub>3</sub> u <sub>4</sub> out of plane bend
690 (w)			
722 (w)	725 (w)		
	777 (w)		
	809 (w)		
870 (w)	873 (i)		CO <sub>3</sub> u <sub>2</sub> in plane bend
999 (i)	1022 (w)	999 (i)	CO <sub>3</sub> u <sub>3</sub> stretch
1123 (w)			SO <sub>4</sub> stretch
1300 (w)	1346 (i)		CO <sub>3</sub> u <sub>3</sub> stretch
1437 (i)			
1452 (s)			
1508 (w)			
1570 (b)	1563 (i)		
	1777 (i)	1770 (i)	2u <sub>2</sub> or u <sub>1</sub> +u <sub>4</sub>
1945 (i)			
2211 (i)	2111 (w)	2130 (w)	u <sub>1</sub> +u <sub>2</sub>
2521 (i)	2500 (w)	2504 (i)	u <sub>1</sub> +u <sub>3</sub>
	2540 (w)	2549 (i)	
2929 (i)	2916 (w)	2920 (i)	2u <sub>3</sub>
3100 (b)			O-H stretch
	3550 (b)	3550 (b)	
MgCO <sub>3</sub> -K <sub>2</sub> CO <sub>3</sub> Glass			
Raman	Reflectance	Absorption	Assignment
690 (w)	684 (i)	621 (w)	CO <sub>3</sub> u <sub>4</sub> out of plane bend
720 (w)	804 (w)	690 (w)	
		724 (w)	
		804 (i)	
	860 (w)	872 (w)	CO <sub>3</sub> u <sub>2</sub> in plane bend
	950 (w)		
1053 (i)	1042 (i)	1060 (i)	CO <sub>3</sub> u <sub>1</sub> stretch
1072 (i)	1080 (s)	1075 (s)	
1387 (w)	1398 (s)		CO <sub>3</sub> u <sub>3</sub> stretch
1447 (i)	1430 (i)		
	1470 (s)		
1525 (w)		1745 (s)	2u <sub>2</sub> or u <sub>1</sub> +u <sub>4</sub>
		2455 (w)	u <sub>1</sub> +u <sub>3</sub>
		2560 (w)	
		3100 (b)	O-H stretch

*carbothermal residua* (Mitchell 2005). In this scheme, primary carbonatites can be further divided into groups of magmatic carbonatites associated with nephelinite, melilitite, kimberlite, and specific mantle-derived silicate magmas, formed by partial melting, whereas carbothermal residua carbonatites form as low-temperature fluids rich in  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and fluorine.

**Table 3.** Atomic separations (in nm) for simulated CaCO<sub>3</sub> melt at 1600 K and 0.06 GPa, and simulated crystalline polymorphs.

i-j	CaCO <sub>3</sub> melt	Calcite	Aragonite
O-O	0.2434	0.2251	0.2102
O-O(1)	0.3200	0.3210	0.3320
O-C	0.1364	0.1310	0.1276
O-Ca	0.2327	0.2320	0.2401
C-Ca	0.3424	0.3202	0.2953
C-C	0.2541	0.4002	0.2844
Ca-Ca	0.4173	0.4043	0.3902

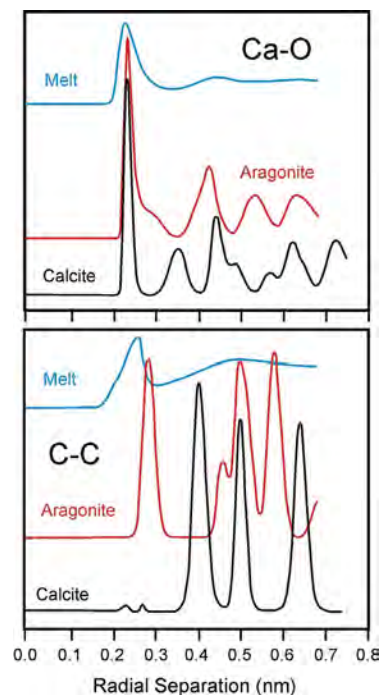
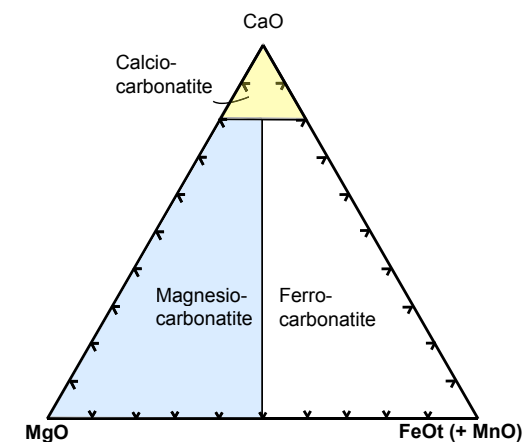
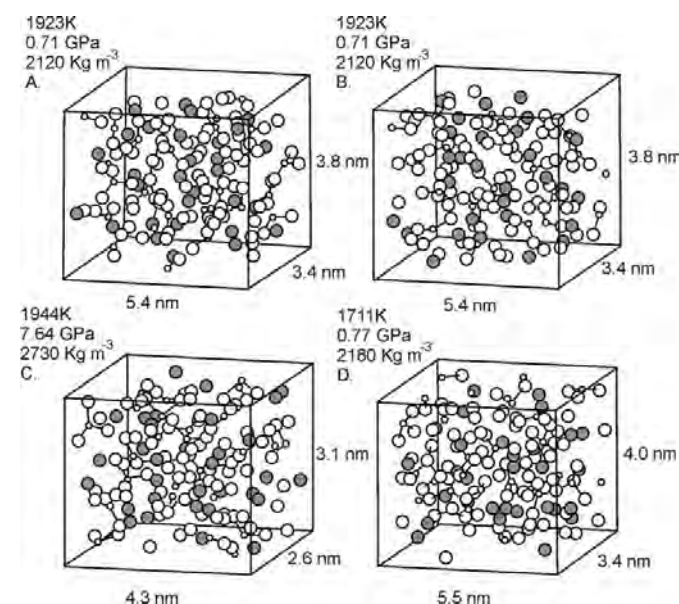
**Table 4.** First-neighbor coordination numbers for CaCO<sub>3</sub> melts simulated at 1700 K at different simulated pressures.

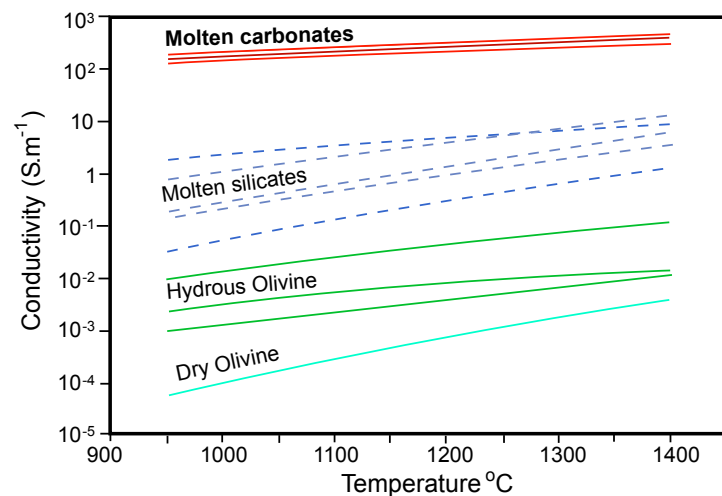
Pressure (GPa)	0.067	3.27	11.56
Density (Kg m <sup>-3</sup> )	2090	2500	3000
O-O	2.912	3.157	4.848
O-C	2.826	2.853	2.544
O-Ca	5.128	5.316	6.320
C-Ca	1.433	1.410	1.911
C-C	5.434	5.420	5.006
Ca-Ca	6.310	6.210	6.102

### Occurrence of carbonatites

**Tectonic setting of carbonatites.** Primarily, carbonatites are located within stable, intra-plate settings, over half of which are in Africa, often occurring in peripheral regions to orogenic belts showing an apparent link to orogenic events or plate separation (Garson et al. 1984; Le Bas 1987; Bell 1989; Veizer et al. 1992). Carbonatite concentrations are also associated with topographic swells up to 1000 km across (Le Bas 1971; Srivastava et al. 1995). The occurrence of carbonatites in continental crust has perpetuated interpretation of their geochemistry in terms of a genetic connection (Bell and Blenkinsop 1987) and they have also been variously related to mantle plumes and large igneous provinces (LIPs); for thematic reviews see Gwalani et al (2010). A recent survey of the most complete world database shows striking lithological control with repeated activation of old carbonatites in Archaean-aged crust. This distribution precludes a direct link with mantle plumes and favors a fundamental link to the same underlying mantle source of carbon, which manifests in kimberlites (Woolley and Bailey 2012). The surface manifestation of carbonatites may belie their distribution in the underlying mantle, where some of their extreme physical properties, such as very high conductivity (Fig. 9) make them sensitive to remote geophysical testing (Gaillard et al. 2008). Understanding their deep origins must explain the growing number of carbonatites reported from unconventional tectonic associations, i.e., not continental rifts, but including oceanic islands, ophiolites, shear zones, deep subduction zones (Woolley 1991; Coltorti et al. 1999; Moine et al. 2004a; Rajesh and Arai 2006; Walter et al. 2008; Nasir 2011) and even connections to ultra-high pressure (UHP) metamorphic terranes (Attoh and Nade 2008).

Carbonatites overlying oceanic lithosphere are rare (Silva et al. 1981; Kogarko 1993; Hoernle et al. 2002; Jørgensen and Holm 2002), but discovery of carbonatite melt as interstitial

**Figure 6.** Showing radial distributions for CaCO<sub>3</sub> melt, calcite and aragonite from MDS simulations (Genge et al. 1995b).**Figure 8.** Carbonatite classification diagram; redrawn after (Woolley and Kempe 1989). Note: ferrocarbonatite can also be rich in REE.**Figure 7.** Showing snapshots of simulated carbonate melt structure (Genge et al. 1995b).

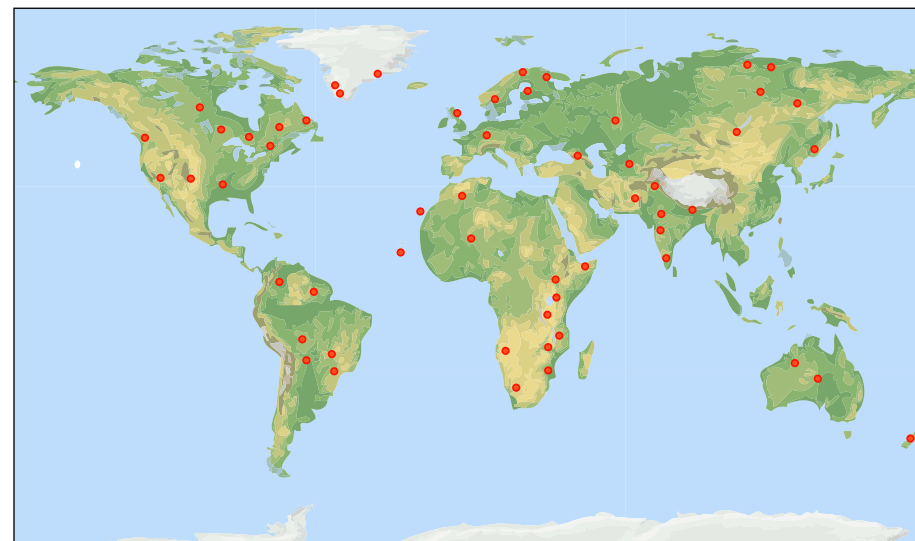


**Figure 9.** Electrical conductivity versus temperature shows very high values for molten carbonates compared with molten silicates, hydrous olivine and dry olivine mineral phases stable in the mantle as a function of temperature. Drawn after Gaillard et al. (2008). See also Sifre and Gaillard (2012).

pockets within dunite xenoliths from the Kerguelen Archipelago (Moine et al. 2004b) indicates that oceanic carbonatites may be more widespread. Geographical areas of carbonatitic activity are often very long-lived and, where unrelated to the migration of mantle plumes, a direct relationship with underlying lithosphere is likely (Genge 1994; Woolley and Bailey 2012), yet others are thought to be related to deep mantle plumes, for example Kola Peninsula (Marty et al. 1998), Canary Islands (Widom et al. 1999), Cape Verde Islands (Holm et al. 2006), Brazil (Toyoda et al. 1994), Deccan Traps (Simonetti et al. 1998), and Greenland (Larsen and Rex 1992). New regions with carbonatites are still being discovered, for example in the Middle East including Saudi Arabia, United Arab Emirates, and ophiolite-related carbonatite in Oman (Woolley 1991). A remarkable series of books dedicated to reviewing the systematic geographical distribution with individual maps of all carbonatites sourced from thousands of references, is provided by Woolley and has been used to publish a comprehensive global map and database of all known carbonatites (Woolley and Kjarsgaard 2008a).

**Temporal distribution of carbonatites.** Globally from just 56 known in 1987 (Fig. 10), there are now ~527 carbonatite occurrences, of which 49 are extrusive, ranging in age from Archaean to present (Woolley and Church 2005; Woolley and Kjarsgaard 2008a). The most commonly reported oldest dated carbonatite and associated silicate rocks are from Phalaborwa carbonatite in South Africa at 2063 to 2013 Ma (Masaki et al. 2005) and Siilinjärvi, Finland circa 2047 million years old (Puustinen 1972; Woolley and Kempe 1989). The Siilinjärvi age is typical, and based upon K-Ar dates of  $1790 \pm 30$  to  $2030 \pm 30$  Ma on phlogopite,  $2530 \pm 45$  Ma on richterite, and  $2260 \pm 42$  Ma on actinolite (Puustinen 1972), as well as  $1850 \pm 40$  Ma and  $2280 \pm 40$  Ma on phlogopite and richterite respectively from the main carbonatite. However, older ages are also discussed for Siilinjärvi, with reports of U-Pb dating of zircon from sövite indicating an age of  $2580 \pm 200$  Ma (Patchett et al. 1982) along with unpublished Sm-Nd data supporting an age of 2600 Ma (Basu et al. 1984).

Of the known extrusive carbonatites, 41 are calcio-carbonatites, 7 are dolomitic carbonatites, and only one extrusive carbonatite is alkaline natrocarbonatite (Woolley and Church 2005). Carbonatites tend not to occur as single rock units but rather as a suite in association with



**Figure 10.** Global distribution of carbonatites from Le Bas (1987); this early compilation shows 56 carbonatites distributed across all continents, but mostly associated with continental modern and ancient rifting. In just over 25 years the number has transformed to over 500 today, culminating in a new metabase called “Carbonatite occurrences of the world: map and database” compiled by Woolley and Kjarsgaard (2008a), which is held at the Site of the Natural Resources in Canada, and is free to access at <http://geoscan.ess.nrcan.gc.ca/starweb/geoscan/servlet.starweb>.

alkaline silicate rocks, including a wide variety of ultramafic to felsic silicate igneous rocks from dunites to syenites, as in the Siberian Massif (Egorov 1970; Kogarko and Zartman 2007; Vladykin 2009), with only ~20% of carbonatites occurring without associated silicate rocks (Woolley and Kjarsgaard 2008a).

Despite the occurrence of carbonatites throughout the majority of geological periods since the Archaean, their increase in frequency with decreasing age, and episodic clustering of activity, has led to the suggestion that conditions required for carbonatite formation are becoming more widespread (Woolley 1989). Alternatively Veizer et al (1992) argue that the apparent increase is a preservation artifact, with crustal erosion and preferential recycling of orogenic-related carbonatites, with a geodynamic half-life of carbonatite bodies close to ~445 m.y. Carbonatite rocks (orogenic and anorogenic) are relatively easily weathered in comparison to silicate rocks, so bias towards young ages in the geological record might be expected. However the argument for carbonatite age bias due to preservation presented by Veizer et al (1992) has been further debated through the consideration that cratonic material in which carbonatites are concentrated and not readily subducted; therefore, the backward projection through Precambrian time of the modern pace of recycling by subduction is not valid. Instead, Woolley and Bailey (2012) argue that the concentration of carbonatite material in late Archaean cratonic regions is the result of re-opening and use of pre-existing lesions during plate movements. This activity is thought to occur in episodes, with some areas showing up to five events, with gaps of millions of years between episodes.

#### Geochemistry of carbonatites

Carbonatites occur as intrusive, extrusive and hydrothermal or replacement bodies that contain more than 50 vol% primary igneous carbonate minerals derived from carbonate magma (Streckeisen 1980) and with less than 20%  $\text{SiO}_2$  (Le Maitre 2002). A summary classification

is provided in Table 5 (Woolley and Kempe 1989; Le Maitre 2002). The category of REE-carbonatites have no formal definition, and they can be associated with variable Ca:Mg:Fe carbonatites and widely varying grain sizes and textures from fine-grained (Bayan Obo, Inner Mongolia, China), to pegmatitic (Kangankunde, Malawi), and porphyritic (Mountain Pass, California). Their modal REE-minerals may contribute notable colors in hand specimen either yellow, caused by bastnasite, synchisite, and REE-fluocarbonates, or vivid green, caused by monazite and REE phosphates (Wall and Mariano 1996). We suggest a whole-rock value of >1% RE<sub>2</sub>O<sub>3</sub> as a working definition of REE carbonatite. Higher values (>5%) have been used by some mining geologists (Castor 2008); however, these deposits are often also rich in iron and thus have been termed ferrocarnatite. The field relations of REE carbonatites and their association with elevated Th and U suggest primary mechanisms of crystal fractionation of carbonatite magma associated with secondary enrichment by volatile-rich metasomatic fluids (Le Bas et al. 2007; Yang et al. 2011), although relationships with alkaline silicate rocks may need further study as in the case of Mountain Pass (Castor 2008). Their residual magmatic nature is supported by experiments in mixed Ca-Ba-Sr-REE carbonate systems, which show the persistence of melts at low crustal pressures to very low-temperatures (Jones and Wyllie 1983, 1986; Wyllie et al. 1996).

**Major element signatures.** Carbonatites have high abundances of Sr, Ba, P, and light rare earth elements (LREEs), often > 3 orders of magnitude higher than those of chondritic meteorites or bulk Earth, and show a negative Zr and Hf anomaly (Nelson et al. 1988). Their chemical composition makes them powerful chemical probes for understanding the mantle, because the effects of crustal contamination are minimized. The average chemical compositions for carbonatite (Bell 1989) show that concentrations of Si, Ti, Mn, Ba, Fe, and F increase through the series calcicarbonatites – magnesiocarbonatites – ferrocarnatites, but this sequence is unlikely to represent a simple crystal fractionation series (Gaspar and Wyllie 1984; Le Bas 1987). Al, Na, K, Sr, and P are variable throughout the carbonatite divisions (Table 6), with the exception of natrocarbonatite, which is dominated by Na<sub>2</sub>O and K<sub>2</sub>O.

Natrocarbonatite contains up to ~40 wt% (Na<sub>2</sub>O+K<sub>2</sub>O) with very low SiO<sub>2</sub>, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, high amounts of CaO and CO<sub>2</sub>, and considerable BaO, SrO, P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>, Cl, F, and MnO in comparison to silicate igneous rocks (Ridley and Dawson 1975). Natrocarbonatite lavas erupted during the last ~50 years (especially in 1960-1966, 1988-1993, and 2006-2008) have similar compositions and their detailed geology and regional context are comprehensively reviewed in a monograph by Dawson (2008).

**Table 5.** Carbonatite nomenclature extended here from (Woolley and Kempe 1989)\* to include Rare Earth (RE)-carbonatite and natrocarbonatite; FeO<sup>T</sup> is total iron, RE<sub>2</sub>O<sub>3</sub> = total REE oxides.

Class	Sub-division	Chemical Characteristic
Calcicarbonatite*	Sövite (coarse-grained); Alvikite (medium-to fine-grained)	CaO/(CaO+FeO+MgO) > 0.80
Dolomite carbonatite	Beforsite	(Ca,Mg)-rich
Ferrocarnatite*	—	(FeO <sup>T</sup> + MnO) > MgO
Magnesiocarbonatite*	—	MgO > (FeO + MnO)
Rare earth carbonatite	Variable grain sizes modal REE minerals	RE <sub>2</sub> O <sub>3</sub> > 1% wt
Natrocarbonatite	Lava at Oldoinyo Lengai volcano	(Na <sub>2</sub> O + K <sub>2</sub> O) > (CaO+MgO+FeO)

**Table 6.** Major element compositions of carbonatites (wt%).

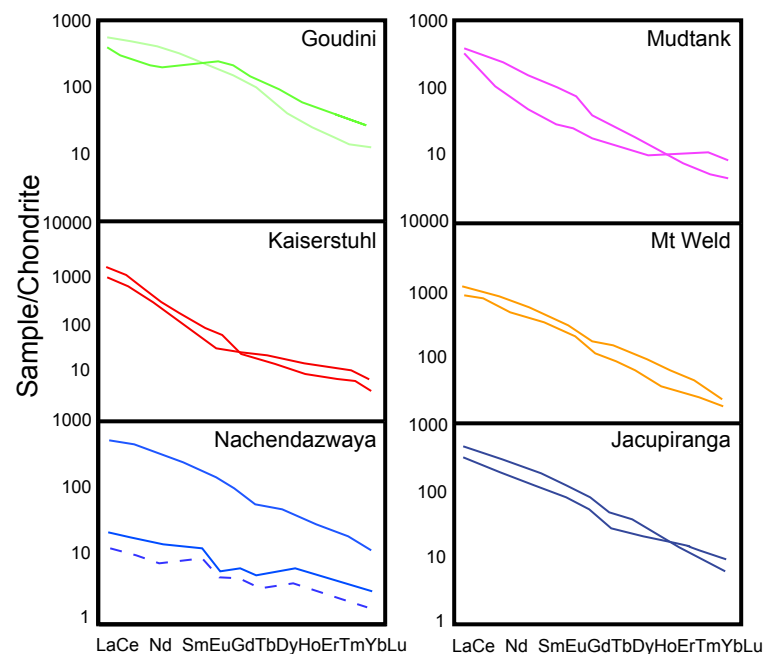
	1	2	3	4	5	6	7
SiO <sub>2</sub>	0.05	0.88	0.16	6.12	3.24	0.83	—
TiO <sub>2</sub>	0.01	0.18	0.07	0.68	0.00	0.07	—
Al <sub>2</sub> O <sub>3</sub>	0.11	0.37	0.17	1.31	0.20	0.65	—
Fe <sub>2</sub> O <sub>3</sub>	0.41	2.62	4.04	7.55	11.50	11.00	—
MnO	0.48	0.39	0.41	0.75	5.18	5.53	1.56
MgO	0.48	0.31	0.67	12.75	10.74	0.36	19.0
CaO	14.43	53.60	51.20	29.03	25.85	43.60	28.8
Na <sub>2</sub> O	33.89	0.09	0.25	0.14	—	0.05	—
K <sub>2</sub> O	8.39	0.03	0.01	0.79	—	0.06	—
P <sub>2</sub> O <sub>5</sub>	0.93	3.18	1.52	2.66	1.27	0.42	—
CO <sub>2</sub>	30.53	38.38	39.50	37.03	32.62	30.42	—
F	2.71	0.06	—	0.09	—	—	—
Cl	3.81	Trace	—	—	—	—	—
SO <sub>3</sub>	2.88	—	—	0.89	0.49	—	—
SrO	1.35	0.23	0.10	0.01	0.73	0.07	1.10
BaO	1.26	0.08	0.17	0.11	2.48	>4.0	—
REE	0.1	0.05	0.3	—	2.82	1.5	—

Notes: Analyses 1-6 from Humphreys et al. (2010) and Le Bas (1987). Analysis 7 from Bailey (1989). 1. Natrocarbonatite from Oldoinyo Lengai; 2. Sövite dyke from Tundulu, Malawi; 3. Alvikite cone sheet, Homa Mountain, Western Kenya; 4. Beforsite (dolomite carbonatite) dyke, Alnö, Sweden; 5. Ferrocarnatite with high Mg, Kangankunde, Malawi; 6. Ferrocarnatite (low Mg), Homa Mountain, Western Kenya; 7. Magnesiocarbonatite, Rufunsa, Zambia.

**Trace elements.** Several “trace” elements achieve major levels in carbonatites. Steep light rare-earth element (LREE)-enriched patterns are typical (Fig. 11) and can occur as modal REE-minerals attractive for economic mining. Through the series of carbonatites from magnesiocarbonatites and calcicarbonatites to ferrocarnatites, trace elements such as Co, Cr, Ni, and V decrease whereas the REE are most abundant in ferrocarnatites and REE-carbonatites, often accompanied by U and Th. Few experiments have determined quantitative element partitioning in carbonate melts, but data exist for Zr, REE, and P (Jones and Wyllie 1983, 1986; Woolley and Kempe 1989; Jones et al. 1995b; Klemme and Meyer 2003; Wall and Zaitsev 2004; Ruberti et al. 2008; Xu et al. 2010). Natrocarbonatite lava contains high concentrations of LREEs with La/Yb and U/Th ratios being amongst the highest of all terrestrial lavas (Dawson 2008, and references therein).

Local chemical variations occur within the natrocarbonatites, with aphyric, phenocryst-poor lavas having a more fractionated pattern with enrichments in Mn, Mg, Fe, V, Ba, Rb, Nb, Y, and several volatile species in comparison to phenocryst-rich lavas and water contents are low (Keller and Krafft 1990). The 1993 natrocarbonatite lavas of Oldoinyo Lengai in Tanzania are particularly enriched in Ba, Cs, K, Mo, U, and LREEs relative to primitive mantle with slight variation between the lava types, i.e., spheroid-free or spheroid-bearing (Simonetti et al. 1997). Natrocarbonatite lava can have Ba/Sr > 0.7, which is the inverse to most primary calcite carbonatites, and Au contents are anomalously higher than continental crust. Natrocarbonatite also occurs as quenched melt in pyroclastic eruptions typified by proximal lapilli beds and tuffs (Church and Jones 1994) and natrocarbonatite tephra may have occurred at other volcanoes in the East African Rift, although there is controversy about whether such ash extends to the area of early hominid footprints at Laetoli (Hay 1983; Barker and Milliken 2008).





**Figure 11.** Typical chondrite-normalized REE concentrations of carbonatites from Goudini, Limpopo; Kaiserstuhl, Germany; Nachendazwaya, Tanzania; Mudtank and Mt Weld, Australia; Jacupiranga, Brazil, drafted after (Nelson et al. 1988) and see also (Lottermoser 1990; Currie et al. 1992; Huang et al. 1995; Verwoerd 2008). Notice the prominent light-REE enriched patterns, and absence of significant anomalies for Europium, consistent with mantle origins.

### Carbonatite mineral deposits

Carbonatites contain minerals enriched in several key elements of immense economic interest, which include the REE (“strategic metals”) niobium, uranium, and tantalum, and to a lesser extent, iron, copper, phosphorus, fluorite, barite, platinum group elements, silver, and gold (Richardson and Birkett 1996; Hornig-Kjarsgaard 1998). Political and economic aspects of their sustainability as producers of REE have recently been re-evaluated (Franks 2011) and currently hinge on large-scale REE carbonatite mineralization of the large Bayan Obo deposit in China (Le Bas et al. 1992, 2007; Smith and Henderson 2000; Yang et al. 2011), with high prices driving resource exploration in some countries such as Malawai (e.g., Kangankunde, AR Woolley, personal communication 2012). Carbonatites have been considered to host the majority of the world’s niobium, with up to 10% of the western world’s niobium once sourced from Niobec mine in the Oka carbonatite, Quebec (Scales 1989), where extreme compositional variation of pyrochlore group minerals may have been caused by magma mixing (Zurevinski and Mitchell 2004).

Table 7 shows data for significant carbonatite mineral deposits showing their potential, including estimated reserves and grades, chemical affinity and mineralogy, for both primary magmatic and secondary metasomatic deposits (Richardson and Birkett 1996). Secondary enrichment is often a result of remobilization of Nb and REEs by hydrothermal or carbothermal fluids enriched in F and CO<sub>2</sub> (Le Bas 1987; Smith and Henderson 2000; Fan et al. 2005). The REE-enriched nature of carbonatites has been linked to the preferential transport of REE by molecular CO<sub>3</sub> complexes in the melt during immiscible separation between coexisting silicate

**Table 7.** Mined carbonatite deposits with reserves (Megatons) and grade of interest for REE, Nb, CaF<sub>2</sub> (fluorite) and P<sub>2</sub>O<sub>5</sub> (as phosphate minerals); for a comprehensive review of ore grades and tonnages for market conditions in the mid 1990’s see Richardson and Birkett (1996).

Deposit	Reserve and Grade	Comments
Oka Carbonatite, Quebec	112.7 Mt at 0.44% Nb <sub>2</sub> O <sub>5</sub> 23.8 Mt at 0.2-0.5% REO	Hydrothermal REE mineralization especially pyrochlore
Phalaborwa, South Africa*	600 Mt at 7% P <sub>2</sub> O <sub>5</sub> 286 at 0.69% Cu 2.16 Mt REO	Banded carbonatite contains Cu sulfides, magnetite and baddeleyite.
Bayan Obo, Inner Mongolia	37 Mt at 6% REO; 1 Mt at 0.1% Nb	Largest mined REE deposit
Amba Dongar, India	11.6 Mt at 30% CaF <sub>2</sub>	Ore associated with fenite units between carbonatite and country rock
Panda Hill, Tanzania	113 Mt at 0.3% Nb <sub>2</sub> O <sub>5</sub>	Disseminated pyrochlore, apatite, magnetite in sövite plug.

\* Alternate spelling for Phalaborwa is Palabora.

and carbonate melts, resulting in an increased La/Lu ratio in the carbonatite relative to silicate melt (Cullers and Medaris 1977).

### Isotopic signatures of carbonatites

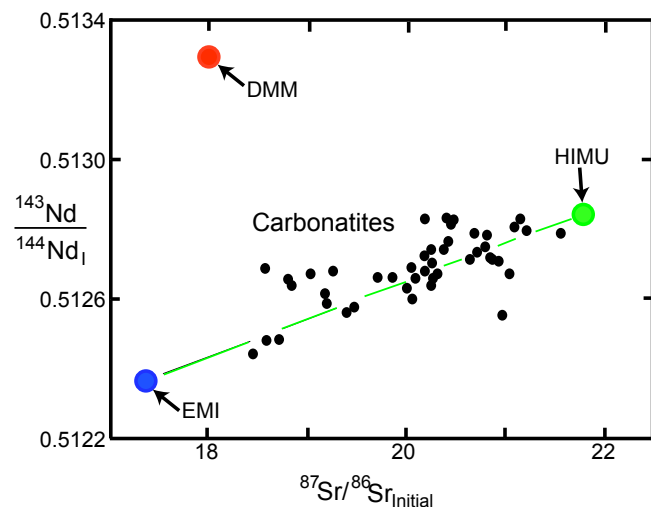
**Radiogenic isotope ratios.** Although carbonatites are volumetrically insignificant compared with silicate igneous rocks, their widespread distribution on most continents coupled with their variation in age provides constraints on the evolution of the sub-continental mantle through time. Young carbonatites share significant isotopic similarities with young oceanic island basalts (OIB; Bell and Tilton 2001). Thus, alkaline silicate magmas and carbonatites in the important East African Rift, including the active carbonatite volcano Oldoinyo Lengai, lie close to the mixing line HIMU-EM1 (Fig. 12) identified in OIB. This mixing may represent either a lithospheric or a deeper mantle sub-lithospheric signature related to a mantle plume (Bell et al. 1998; Bell and Tilton 2001). In general carbonatites contain very low concentrations of Pb, far below crustal levels, offering a clear distinction from crustal carbonates. Their Pb isotopic compositions are not contaminated by crust, and can be used to probe the isotope geochemical signature of unseen deep carbon mantle reservoirs.

A linear array for covariation of Nd-Sr isotope data (Table 8) lies on the East African Carbonatite Line (EACL) and has often been thought to show binary mixing between the mantle reservoirs of HIMU (high <sup>238</sup>U/<sup>204</sup>Pb thought to be the results of recycled ancient, altered oceanic crust) and EM1 (“enriched mantle 1,” caused by the recycling of continental crust or lithosphere; Kalt et al. 1997). However, young carbonatites from the central Italian rift (Stoppa and Principe 1998; Stoppa et al. 2005, 2009) and Mesozoic carbonatites from Shandong China (Fig. 13) have much higher <sup>87</sup>Sr/<sup>86</sup>Sr interpreted to reflect the controlling influence of metasomatized lithospheric mantle (Ying et al. 2004; Woolley and Bailey 2012).

**Stable isotope ratios.** Early studies of carbon and oxygen isotope ratios of carbonatites focused on coarse-grained intrusive carbonatites associated with alkaline silicate rocks in western Germany; Alnö, Sweden; and Colorado, USA, to define *primary igneous carbonatite* (Taylor et al. 1967) reproduced in Figure 14. By observing the origins of divergent trends in oxygen isotopes affected by secondary fluid/hydrothermal alteration, a common origin could be defined. Thus, the co-variation of carbon and oxygen isotopes were used to define the “box” in the range δ<sup>13</sup>C −3.1 to −7.7 and δ<sup>18</sup>O +5.3 to +8.4 for *primary igneous carbonatite*.

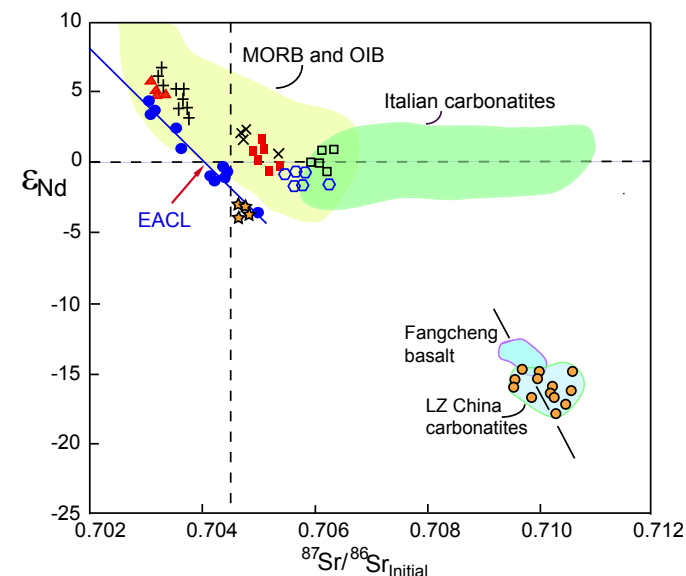
**Table 8.** Range of Sr and Nd isotope ratios for all rock units found at Oldoinyo Lengai natrocarbonatite volcano, and a range of carbonatite complexes with indicative key references.

Complex	$^{87}\text{Sr} / ^{86}\text{Sr}$	$^{143}\text{Nd} / ^{144}\text{Nd}$	Reference
Oldoinyo Lengai, Tanzania	0.70437-0.70445	0.51259-0.51263	(Bell and Dawson 1995)
Homa Bay, Kenya	0.70502	0.51244	(Bell and Blenkinsop 1987)
Panda Hill, Tanzania	0.70423	0.51249	(Bell and Blenkinsop 1987; Bell and Dawson 1995)
Igaliko, Greenland	0.70267-0.70380	0.51191-0.51206	(Pearce and Leng 1996)
Laiwa-Zibo, China	0.7095-0.7106	0.51155-0.51174	(Ying et al. 2004)
Il'mensky-Vishnevogorsky, Russia	0.70356-0.70470	0.51190-0.51231	(Nedosekova et al. 2009)

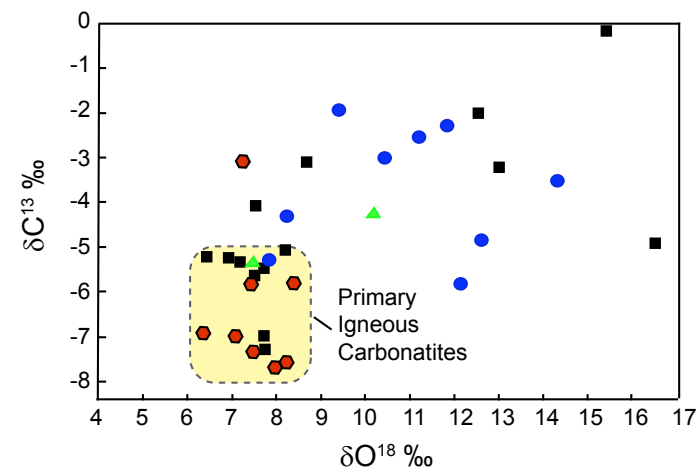


**Figure 12.** Isotopic covariation of Nd and Sr isotopes for geologically young carbonatites, plotted as  $^{143}\text{Nd}/^{144}\text{Nd}$  Initial versus  $^{87}\text{Sr}/^{86}\text{Sr}$  Initial, including positions of end member isotope reservoirs known as HIMU, DMM and EMI. After Bell and Tilton (2001). See also Bell and Blenkinsop (1987).

Subsequent studies of carbonatites show these features to be global in nature (Pineau et al. 1973; Suwa et al. 1975; Horstmann and Verwoerd 1997) including a more restricted range for fresh natrocarbonatite:  $\delta^{13}\text{C}$   $-6.3$  to  $-7.1$  and  $\delta^{18}\text{O}$   $+5.8$  to  $+6.7$  (Keller and Hoefs 1995; Zaitsev and Keller 2006). Natrocarbonatite undergoes atmospheric alteration towards heavier isotopes (Deines 1989) with  $\delta^{18}\text{O}$  rapidly increasing to  $\sim +24\text{‰}$  and  $\delta^{13}\text{C}$  values changing less to  $-1.5\text{‰}$  (Keller and Zaitsev 2006; Zaitsev and Keller 2006). Scarce representatives of apparent “oceanic” carbonatites from La Palma and Fuerteventura (Canary Islands, Spain), have  $\delta^{18}\text{O}$  of  $+13\text{‰}$  and appear to have been overprinted by fluid alteration (Hoernle et al. 2002; Demény et al. 2008). The role of isotope fractionation has often been neglected, but this can have a major influence on deep-carbon systems in general, including carbonate melts and carbonatites. Isotope fractionation has been considered to be a significant process in (mantle) carbonate systems (Deines 1968, 1970, 2004) and early experiments to 3 GPa showed C isotope fractionation between  $\text{CO}_2$  vapor and carbonate melt (Matthey et al. 1990). Mass-independent fractionation of oxygen isotopes is also known from thermal decomposition of carbonates



**Figure 13.** Covariation of Nd and Sr isotopes for carbonatites: global data set shows 3 primary fields (after Ying et al. 2004): (1) proximity to the EACL = East Africa Carbonatite Line (Bell and Blenkinsop 1987) (2) locus for extension to high Sr for Italian carbonatites (pale green field; Stoppa and Woolley 1997) and (3) steeper trend for Chinese Fangcheng carbonatite (Ying et al. 2004). Individual symbols show carbonatites from Africa (blue circles; Bell and Blenkinsop 1987), Magnet Cove (black crosses; Bell and Blenkinsop 1987), Pakistan (black/orange stars; Tilton et al. 1998), oceanic (triangles; Hoernle et al. 2002), Wallaway Australia (black X's; Nelson et al. 1988), Jacupiranga Brazil (solid red squares; Huang et al. 1995), Amba Dongar India (blue hexagons; Simonetti et al. 1995), Vulture calcio-carbonatites Italy (open squares; Rosatelli et al. 2007), Laiwa-Zibu carbonatites from Fangcheng China (orange circles; Ying et al. 2004). Also shown are global basalt fields for MORB+OIB (pale yellow; Hoffman 1997), and Fangcheng basalts (pale blue; Ying et al. 2004).



**Figure 14.** Stable isotope ( $\delta^{18}\text{O}$  vs.  $\delta^{13}\text{C}$ ) for global carbonatite complexes. Highlighted region of carbonatites thought to be unaffected by deuteric or hydrothermal alteration labeled “primary igneous carbonatite; after (Taylor et al. 1967). Symbols represent carbonatites from Africa (blue circles), Iron Hill (green triangles), Laacher See Germany (red hexagons), and Alnö Sweden (black squares).

(Miller et al. 2002) and there is a measurable effect of thermal decarbonation on stable isotope composition of carbonates (Sharp et al. 2003).

The mantle range for oxygen isotopes, as determined from the study of chondrites, mantle xenoliths and basalts, is relatively restricted to between 5 and 6‰, slightly offset from bulk peridotite silicate minerals such as olivine, orthopyroxene, clinopyroxene, and garnet, which average 7 to 8‰  $\delta^{18}\text{O}$  (Deines 1989). The carbon isotope signature of the mantle is more difficult to determine due to the apparent previous under-estimation of high-temperature isotope fractionation for carbon in the mantle (Mikhail et al. 2011), and also because there is large uncertainty over the average concentration of carbon in the mantle (Marty et al. 2013; Shirey et al. 2013; Wood et al. 2013). A large variability is observed in the isotopic compositions of meteorites, xenoliths, and basalts with respect to carbon, but carbonatites seem to have a relatively restricted range with a mode around -5‰. This value is more positive than average mantle diamond and chondritic meteorite isotope signatures, and may result from an unknown enrichment mechanism during melt formation from an isotopically averaged source region (Deines 2002).

### GENESIS OF CARBONATITE MAGMAS

The three main theories for the origin of carbonatites are essentially:

1. Residual melts of fractionated carbonated nephelinite or melilitite (Gittins 1989; Gittins and Jago 1998).
2. Immiscible melt fractions of  $\text{CO}_2$ -saturated silicate melts (Freestone and Hamilton 1980; Amundsen 1987; Kjarsgaard and Hamilton 1988, 1989; Brooker and Hamilton 1990; Kjarsgaard and Peterson 1991; Church and Jones 1995; Lee and Wyllie 1997; Dawson 1998; Halama et al. 2005; Brooker and Kjarsgaard 2011).
3. Primary mantle melts generated through partial melting of  $\text{CO}_2$ -bearing peridotite (Wallace and Green 1988; Sweeney 1994; Harmer and Gittins 1998; Harmer et al. 1998; Ying et al. 2004).

Combinations of these three theories are also popular; for example carbonatite liquids generated by deep melting of carbonated eclogite in the upper mantle infiltrate overlying peridotite to produce silica under-saturated carbonate-bearing melts, which then penetrate the crust and evolve or un-mix (Yaxley and Brey 2004). Carbonatites have also been considered to be generated in the lithospheric mantle as partial melts rising rapidly above a hot ascending mantle plume. If these mantle carbonate melts stall, for example owing to thermal death, they generate carbonate-melt metasomatism in the mantle (Wyllie 1995). As the much hotter center of the plume approaches, melting is induced in the metasomatic horizon and results in generation of the carbonatite melts that are observed on the surface (Bizimis et al. 2003). Although the plume model is quite attractive, recent recognition of strong and repeated lithospheric controls in the compilation of global carbonatite ages are thought to argue against a direct connection to mantle plumes (Woolley and Bailey 2012).

Alternative models for natrocarbonatite petrogenesis have included anatexis of metasomatized basement (Morogan and Martin 1985), incorporation of trona sediments [ $\text{Na}_3(\text{CO}_3)(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$ ], remobilization of carbonate material already present on the volcano (Church and Jones 1995, and references therein), and condensation from a co-magmatic fluid (Nielsen and Veksler 2001, 2002).

Recently discovered provinces of Neogene- to Quaternary-aged carbonatite-silicate volcanism in Europe (Italy, France, and Spain) are providing important new lines of research for the mantle origins of extrusive carbonatite volcanism (Stoppa and Principe 1998; Stoppa et

al. 2005). These new studies are exciting because, unlike carbonatites in general, the young volcanoes have transported mantle xenoliths, which can help constrain their source regions or wallrocks. Derived geotherms can also constrain transport pathways for deep carbon (Jones et al. 2000b; Downes et al. 2002; Bailey and Kearns 2012). These silico-carbonatite volcanic rocks also preserve high-pressure carbonate minerals like aragonite ( $\text{CaCO}_3$ ; Hazen et al. 2013a) as early high-pressure inclusions in olivine ( $\text{Fo}_{87}$ ) considered to have crystallized in the mantle at depths of >100 km (Humphreys et al. 2010, 2012).

### Carbonate melt metasomatism

The low viscosity and chemical composition of carbonatites and carbonate melts (Table 1) makes them excellent metasomatic agents, and there are both experimental and natural examples. High  $\text{P}_2\text{O}_5/\text{TiO}_2$  or variable solubility in synthetic carbonate melts was used to suggest metasomatized harzburgite by carbonatite melts (Ryabchikov et al. 1989; Baker and Wyllie 1992) and carbonate metasomatism has been inferred to occur in the lower mantle from experiments at 20-24.5 GPa and 1600-2000 °C (Gasparik and Litvin 2002). Thus, while transfer of mobile silicate (basaltic) melts may adequately account for the chemistry of many spinel peridotites and pyroxenites, highly mobile carbonate melts are believed to have played a pivotal role in the formation of apatite pyroxenites/wehrlites (converted peridotites), carbonate-bearing peridotites (reacted wallrock) and metasomatized mantle xenoliths in continental terrains (O'Reilly and Griffin 2000). Carbonate-metasomatism is observed in some eclogitic xenoliths (Pyle and Haggerty 1994, 1997) and massive eclogite terrains, implying an active role for metasomatic carbonate fluids in subduction zones (Selverstone et al. 1992). "Subduction" experiments with carbonated eclogite at 5-10 GPa, corresponding to approximately 150-300 km depth in the mantle show, that the carbonatitic solidus in eclogite is located at 4 GPa higher in pressure than in the peridotitic system; first carbonate partial melts can be calcium-rich [ $\text{Ca}/(\text{Ca}+\text{Fe}+\text{Mg}) \sim 0.80$ ] in contrast to those produced by melting of carbonated peridotite [ $\text{Ca}/(\text{Ca}+\text{Fe}+\text{Mg}) \sim 0.50$ ] (Hammouda 2003) possibly also influenced by the role of garnet in carbonated eclogite (Knoche et al. 1999). The Th/U ratio may be sensitive to mantle metasomatism related to carbonate or silicate melts where clinopyroxene is stable (Foley et al. 2001) and ultrapotassic mantle metasomatism in East Africa can be notably rich in fluorine (Edgar et al. 1994; Rosatelli et al. 2003) and may result during emplacement of immiscible silicate-carbonatite magmas (Rosatelli et al. 2003).

Melt inclusions in deep volcanic minerals and xenoliths from continental rift systems commonly demonstrate the effects of metasomatism caused by carbonate melts (Seifert and Thomas 1995; Jones et al. 2000b; Downes et al. 2002; Woolley and Bailey 2012). Carbonate melt metasomatism in lherzolite has also been related to derivation from kimberlite transport in the mantle (Bodinier et al. 2004). Sometimes direct evidence for high-pressure carbonate-melts occurs trapped as inclusions in minerals, such as in ultramafic xenoliths from Kerguelen related to oceanic upper mantle domains (Schiano et al. 1994), and globally as carbonatitic alkaline hydrous fluid inclusions in diamond (Navon et al. 1988; Guthrie et al. 1991; Schrauder and Navon 1993, 1994; Izraeli et al. 2001; Tomlinson et al. 2005), which in addition to common inorganic carbon-species C-O-H volatiles also may contain hydrocarbons and nitrogen (Tomilenko et al. 1997).

The percolation of carbonatitic material through olivine-rock matrix (i.e., mantle peridotite) has been proposed to occur at a rate of several millimeters per hour by a process of dissolution-precipitation (Hammouda and Laporte 2000). These infiltration rates are orders of magnitude higher than those previously found for basalt infiltration in mantle lithologies. However, it could be argued that such quick percolation may result in short residence times, which may inhibit chemical interaction and metasomatism to take place (Dalou et al. 2009). Transient mineral reactions to armor veins may greatly extend metasomatic pathways while

depleting fluids in silicate-compatible and hydrous components (Jones et al. 1983; Menzies et al. 1987; Rudnick et al. 1993; Menzies and Chazot 1995; Dawson 2002). Evidence for carbonatite-related metasomatism has been repeatedly recognized in the East African rift region, as manifest in fenitized rocks and glimmerites with abundant phlogopite, pyroxene, and amphibole (Rhodes and Dawson 1975; Dawson and Smith 1988, 1992; Rudnick et al. 1993; Dawson et al. 1995), as well as across the globe in Italy (Rosatelli et al. 2007; Stoppa et al. 2008, 2009; Stoppa and Woolley, 1997), Australia (Andersen et al. 1984), Canary Islands (Frezzotti et al. 2002), Grande Comore in the Indian Ocean (Coltorti et al. 1999), and Greenland (Ionov et al. 1993).

### Carbonate melt crystallization of diamond

Natural diamondiferous carbonatites are very rare but are known to occur at Chagatai, Uzbekistan, and a few other diamond-bearing carbonatites are likely related to the crystallization of carbonate-kimberlite (Litvin et al. 2001, 2003; Bobrov et al. 2004), where it is thought that the diamond is syngenetic (Palyanov et al. 1994). In principle, carbonate melts, which are over-saturated with respect to dissolved carbon and sometimes visibly bear graphite, are highly efficient diamond-forming systems under the thermodynamic conditions of diamond stability (Borz dov et al. 1999; Bobrov et al. 2004; Kogarko et al. 2010). Several observations of carbonate as inclusions in mantle diamond (Guthrie et al. 1991) lead to models of diamond formation involving carbonated melts in the mantle (Hammouda 2003). Carbonate melt inclusions have also been identified associated with diamond in continental crust from high pressure metamorphic rocks (De Corte et al. 2000; Korsakov et al. 2005), interpreted as very deep subduction (Korsakov and Hermann 2006) with unknown significance of recently recognized lonsdaleite (hexagonal diamond) in crustal rocks (Godard et al. 2011). Diamond is readily synthesized experimentally from simple carbonates (Pal'yanov et al. 1999a, 1999b, 2002a, 2002b), from alkali potassic carbonate (Shatskii et al. 2002), from hydrous-carbonate (Sokol et al. 2000), from carbonate with sulfide (Spivak et al. 2008), from mixed carbonate-alkali-halide systems (Tomlinson et al. 2004), and from mixed carbonate-silicate (kimberlitic) melts (Litvin 2003) to produce artificial diamond rock or "diamondite" with polycrystalline diamond (Litvin and Spivack 2003). Experiments show that "superdeep" diamond can crystallize rapidly from simple Mg-carbonate at pressures up to 20 GPa (Tomlinson et al. 2011). Thus, carbonate melts have been suggested as a medium for the efficient crystallization of diamonds in Earth's mantle, broadly consistent with global distribution of carbonatitic fluids trapped during the growth of natural "coated stone" type mantle diamond (Navon et al. 1988; Tomlinson et al. 2005; Klein-BenDavid et al. 2007) although quantitative details of a genetic connection between carbonate melts and fluids in the mantle are virtually unknown.

### Magmas related to carbonate melts

For at least half a century field observations of alkaline silicate-carbonatite systems have suggested a variety of petrogenetic pathways between carbonatites and alkaline silicate magmas are preserved in surface volcanic products at least from the Proterozoic (Harmer 1999; Andersen 2008) through to Recent volcanism (Le Bas 1987). The associations have been tested with increasing sophistication as experimental technology has advanced. Pioneering phase equilibria studies delineated the important role of water (Wyllie and Tuttle 1962). More recent experiments quantified partial melting of mantle lherzolite using major components CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub> with a CO<sub>2</sub> content of 0.15 wt%, which showed a continuous change in melt composition approximating to carbonatitic through to kimberlitic melts over the minor melting range 0-1%, initially to a few GPa pressure (Dalton and Presnall 1998), to 3-8 GPa (Gudfinsson and Presnall 2005), and to 6-10 GPa pressure (Brey et al. 2008), where additional preconditioning of the mantle by metasomatism is implicated. In general these experimental studies have avoided alkaline-bearing or indeed alkaline-rich and fluid-bearing systems (but see Litvin et al. 1998; Gasparik and Litvin 2002; Safonov et al. 2007; Brooker and Kjarsgaard

2011) and are still lacking in complexity, and for example, understanding of oxygen fugacity compared with natural systems.

Direct experiments with natural carbonatitic rocks and minerals suffer from a host of different problems, but they can provide indicative results (e.g., Bobrov et al. 2004). Carbonatites may share geochemical trace element signatures with kimberlites (Hornig-Kjarsgaard 1998; Le Roex et al. 2003) and associations with other families of ultramafic rocks such as lamprophyres where CO<sub>2</sub>-rich ocelli (Huang et al. 2002) might imply arrested unmixing of immiscible liquids. Round spherical textures, such as ocelli in rocks are sometimes ambiguous (Brooker and Hamilton 1990) and coexisting silicate and carbonatite lapilli have been also used to argue against a genetic association (Andersen 2008). The composition of primary kimberlite from the Slave Craton, based on samples of aphanitic kimberlite from the Jericho kimberlite pipe, Northwest Territories, Canada, have minimum CO<sub>2</sub> contents (10-17 wt%) and geochemistry suggesting carbonatite affinities (Price et al. 2000). Potassic silicate glass occurs with calcite carbonatite in lapilli from extrusive carbonatites at Rangwa Caldera Complex, Kenya (Rosatelli et al. 2003). Group II mantle kimberlites have been shown to be experimentally related to carbonate melts in their mantle source region (Ulmer and Sweeney 2002) and metasomatized mantle xenoliths can show, for example, geochemical signatures transitional between kimberlites and carbonatites (Jones 1989). Detailed potential relationships between distinct families of silicate rocks and carbonatites are given in dedicated books and reviews (Le Bas 1987; Woolley and Kempe 1989; Woolley 2003; Mitchell 2005; Woolley and Kjarsgaard 2008b), and others have blurred the boundaries between carbonatite and kimberlite volcanism (Sparks et al. 2009) as evident in early experiments (Wyllie and Huang 1976).

Other indicative experiments of upper mantle carbonate melts have investigated liquid immiscibility (Brooker and Hamilton 1990; Lee and Wyllie 1996), the transition from carbonate to silicate melts in the simplified CaO-MgO-SiO<sub>2</sub>-CO<sub>2</sub> system (Moore and Wood 1998), mixed carbonate-chloride-silicate systems (Safonov et al. 2007), dissociation of carbonate in low pressure halide melts (Combes et al. 1977; Cherginets and Rebrova 2002, 2003) and the melting behavior of mantle carbonate-phlogopite lherzolite (Thibault et al. 1992).

### FUTURE RESEARCH

Fundamental gaps remain in our knowledge of the petrogenesis of carbonate melts in the deep mantle, which cloud our understanding of the possible origins of carbonatites, including their relationships to mantle silicate rocks and to the deepest known mantle magmas, kimberlites.

### Carbonatites at high-pressure

New geological discoveries that provide insights on carbonatites are still being made, and can be very instructive. For example, carbonatite-silicate volcanism carrying mantle xenoliths, carbonatites in major shear zones, and carbonatites associated with ophiolite belts are providing new tests and ideas for conventional research into mantle-derived carbonatitic melts (Tilton et al. 1998; Nasir et al. 2003; Stoppa et al. 2005; Nasir 2006, 2011; Rajesh and Arai 2006; Attoh and Nudé 2008; Humphreys et al. 2010; Bailey and Kearns 2012). However, we still lack quantitative understanding of high-pressure behavior in several critical areas; for example high-pressure behavior of mixed C-O-H fluids to calculate carrying capacities over the range of compositions transitional between carbonate-silicate mantle systems, and how these operate in fluid-rich pathways escaping from subduction zones (Stalder et al. 1998). What have been the roles of carbonate melts in the distribution of carbon throughout Earth's history, and how do these roles relate to changing mantle dynamics and different plate tectonic settings? Key will be to map out the phase stability of carbonates from the crust into the mantle to connect observations from the deepest natural samples (inclusions in diamond) with predictions from

theory and experiment (Berg 1986; Biellmann et al. 1993a, 1993b; Brenker 2005; Brenker et al. 2006, 2007). Particularly relevant will be to understand the relative stabilities of low-pressure carbonate and newly discovered families of high-pressure tetracarboxates.

### Melt structure of tetracarboxates?

The transformation of carbonate minerals to “tetracarboxates” represents potentially the most significant step-forward in the understanding of the solid reservoirs of carbon at deeper mantle pressures (Oganov et al. 2013), in particular since experimental results suggest the transformation may involve a range of carbon-bearing phases, including nanodiamond (Boulard et al. 2011). The implications for carbonate melt structures, if these are present under lower mantle geotherms, is intriguing to consider. Changes in the density and viscosity in silicate melts occur corresponding to phase changes in the equivalent solid phase due to increases in coordination (Genge 1994; Karki and Stixrude 2010). Thus, jadeite and albite melts display increases in density in both solid and quenched glass phases between 1.0-1.5 GPa and decreases in viscosity relating to the plagioclase to garnet phase transition (Karki and Stixrude 2010). We might therefore expect changes in behavior in carbonate melts corresponding to phase transitions in their crystalline solids with increases in coordination and close packing under compression. Crystalline CaCO<sub>3</sub> transforms from calcite to aragonite structures at ~2 GPa (Suito et al. 2001); however, MDS simulations of CaCO<sub>3</sub> melts suggest no equivalent increase in Ca coordination from 6- to 8-fold (Genge et al. 1995b). The large compressibility of CaCO<sub>3</sub> melts predicted from these simulations, however, would imply that coordination increases are inevitable at higher pressures (>11 GPa). If transformation of CaCO<sub>3</sub> melt structure to a tetrahedral carbonate occurs at lower mantle pressures then a dramatic change in melt properties would be expected owing to the ability of CO<sub>4</sub> to form polymerizable networks. If the theoretical increases in carbonate melt viscosity at high pressures are verified (Jones and Oganov 2010) this behavior would fundamentally inhibit mobility of carbonate melts in the lower mantle and transform previous conceptions (Jones and Oganov 2009; Stoppa et al. 2009). Significant changes in the chemical properties of carbonate melts dramatically change their solubility for metal cations. The site of transformation of tetracarboxate to carbonate magmas in the lower mantle could, therefore, be extremely significant for storage of deep mantle carbon, and we might envisage, for example, precipitation of solid phases from rising carbonate melts.

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