Carbonatite melts in geologic environments: formation, composition and evolution

Tibor Guzmics

Summary of Ph.D. thesis

Lithosphere Fluid Research Laboratory

Ph.D. program for Geology and Geophysics at the Ph.D. school of Earth Sciences

Department of Petrology and Geochemistry

Eötvös Loránd University (ELTE), Budapest

Chair of the Ph.D. school: Prof. Miklós Monostori
(Department of Paleontology, ELTE Budapest)

Advisor: Csaba Szabó, Ph.D. associate professor
(Department of Petrology and Geochemistry, ELTE Budapest)

Tutor: Prof. Roger H. Mitchell
(Department of Geology, Lakehead University, Ontario, Canada)

2009 ELTE Budapest

Keywords: carbonatite melt – silicate melt – melt inclusion – fluid inclusion – silicate-carbonatite immiscibility – open system metasomatism – high pressure and temperature experiment – natrocarbonatite – peralkaline melt – Kerimasi, Tanzania – Oldoinyo Lengai – Alcsútdoboz-2, Hungary – lamprophyre

The paper list is updated in 05, May 2010

Table of contents

Introduction

Understanding the nature and origin of carbonatite melts has long focused on petrologic studies with a number of workers concentrating on stability of these melts at high pressure and temperature (e.g., Wyllie and Huang, 1976; Wallace and Green, 1988; Green and Wallace, 1988; Baker and Wyllie, 1990; Dalton and Wood, 1993; Sweeney, 1994; Lee and Wyllie, 1998a, b; Dalton and Presnall, 1998; Lee et al. 2000; Yaxley and Brey, 2004). Some of these studies demonstrate that carbonatite melts can also be formed by partial melting of eclogites and metasedimentary rocks (e.g., Hammouda, 2003; Thomsen and Schmidt, 2008). However, it is difficult to find primary carbonatite melts in the nature because of their reaction with peridotitic releasing CO_2, called decarbonation (Wyllie and Huang, 1976; Green and Wallace, 1988), at relatively low pressure (2.2 GPa). May be due to this phenomenon primary carbonatite melt inclusions have not been reported yet from the mantle. Formation of primary carbonatite melts can be imagined by extremely low degree partial melting (1%>>, e.g., Wallace and Green, 1988; Green and Wallace, 1988; Baker and Wyllie, 1992). This result in their extreme enrichment in incompatible elements such as light rare earths, S, P, Ba, Sr, Na, K, U and Th relative to primitive mantle (e.g., Guzmics et al., 2008a, b; Mitchell, 2009). Their low viscosity, relatively to that of silicate melts (e.g., Hunter and McKenzie, 1989), allows migration along the grain boundaries and reaction with mantle intensively (e.g., Green and Wallace, 1988; Watson et al., 1990; Yaxley et al., 1991; Hauri et al., 1993; Rudnick et al., 1993; Yaxley et al., 1998; Guzmics et al., 2008a, b). It is also a point in their behavior that they can fall through liquid immiscibility, depending of pressure, temperature and bulk melt composition, to form an immiscible carbonatite melt and a silicate melt (Lee and Wyllie, 1998a, b and references therein). Partitioning of major and trace elements and dependence of solubility of minerals between the immiscible melts can be significant (Baker and Wyllie, 1992; Lee and Wyllie, 1997). This is why studying of immiscibility is important in understanding the connection between carbonatite complexes and mineral resources in time and space.

More than 520 occurrences of carbonatite rocks are known in the world (e.g., Wooley and Kjarsgaard, 2008) in both the continents and the oceanic islands such as for example Canary Islands, Cape-Verdes and Kerguelen. Bulk rock compostions of carbonatites worldwide (e.g., Le Bas, 1977; Wooley and Kempe, 1989; Kogarko et al., 1991; Hoernle et al., 2002; Ionov and Harmer, 2002; Wooley and Church, 2005; Hou et al., 2006) however contains much lesser amount of alkalis and silica than it is expected, based on high T experiments and relevant phase diagrams (Huang and Wyllie, 1974; Wyllie and Huang, 1976; Eggler, 1978; Huang and Wyllie, 1980; Wallace and Green, 1988; Baker and Wyllie, 1992; Sweeney, 1994; Kjarsgaard et al., 1995; Dalton and Presnall, 1998; Lee and Wyllie, 1997, 1998a, b; Lee et al., 2000; Hammouda, 2003; Yaxley and Brey, 2004; Thomsen and Schmidt, 2008). Similarly, huge alkaline and silica deficit can be observed in composition of mantle xenolith-hosted carbonate globules and ocellis (Kogarko et al., 1995; Ionov et al., 1996; Lee et al., 2000; Bali et al., 2002; Van Achterberg et al., 2002; Demény et al., 2004; van Achterberg et al., 2004) in a comparison to that of experimental melts. While the experimentally determined carbonatite melts in carbonate-silicate systems always contain several wt.% of silica, the globules and ocellis are „pure" carbonates. These carbonate compositions, called „forbidden melts" by Wyllie and co-workers; indicate that these compositions cannot represent melts in carbonate-silicate systems.

Thus, it seems that the role of alkalis is huge in carbonatite melts systems at crustal environment (Lee and Wyllie, 1998a, b; Kjarsgaard et al., 1995; 2000; Lee et al., 2000) whereas silica plays role in composition of carbonatite melt systems in mantle conditions. The role of volatiles (H-O-C-Cl-F-S) is also great in characterization of physical and chemical properties of carbonatite systems however, in exception of CO_2, we have pure information about the volatiles coexisted with natural carbonatite melts.

Aim of this Ph.D. thesis

The aim of this Ph.D. thesis is to find a solution for problems mentioned above. I show carbonatite melt inclusions from different geological environments (hosted in phases of mantle xenoliths and crustal carbonatite rocks). In this thesis I discuss the physical and chemical properties of the studied melts. The results based on natural melt inclusions are compared to that of high pressure (2.2 GPa) and temperature (1200 °C) experiments carried out in a similar chemical system to that represented by CAKP mantle xenoliths-hosted melt inclusions. This Ph.D. thesis goes in three divisions. In the first I show major and trace element composition of unique metasomatic mantle xenoliths, consisting of clinopyroxene, apatite, K feldspar and phlogopite (CAKP), and their carbonatite melt inclusions, collected in lamprophyres from Alcsútdoboz-2 boreholes, Hungary. I shed light traces of an open system carbonatite metasomatism in clinopyroxene. I discuss major and trace elements behavior during this process. In the second division I introduce carbonatite melt inclusions hosted by coexisting magnetite, apatite and monticellite in Kerimasi calciocarbonatite, Tanzania. I show the carbonatite melt evolution at Kerimasi volcano. I discuss compositions of possible melt that can crystallize a typical calciocarbonatite rock and I have answers for problem of alkaline deficit in carbonatites worldwide. In the third part I demonstrate results of our piston cylinder experiments. I focus on immiscibility between the experimentally produced melts and, stability of crystals coexisted with these melts.

In summary, I study the possible causes of immiscibility and, compositional changes of immiscible melts from high pressure (mantle) to lower pressure (crust). The main aim of this research is give a picture of formation, evolution and composition of carbonatite melts formed in different geological environment in petrogenetic and geochemical aspect.

Fulfilled work

1/ Petrographic, detailed EMPA and LA-ICP-MS measurements (including quantification) on phases of nine CAKP xenoliths, 60 apatite-hosted and 20 K-feldspar-hosted melt inclusions. 2/ Petrographic measurements of Kerimasi calciocarbonatites as well as on melt and fluid inclusions hosted by magnetites, apatites, monticellites and calcites. 3/ Homogenization experiments of 60 apatite-hosted carbonatite melt inclusions and Raman microanalyses of apatite-hosted melt and fluid inclusions. 4/ Heating and quenching experiments of several hundred grains of apatite and magnetite including their melt inclusions enclosed. 5/ EMPA analyses of the quenched magnetite-hosted-(n=103) and apatite-hosted (n=30) carbonatite melt inclusions, as well as that of magnetite-hosted silicate melt inclusions (n=6). 6/ EMPA analyses of rock forming minerals of Kerimasi calciocarbonatite. 7/ Five piston cylinder experiments at 2.2 GPa and 1000-1300 °C in systems of K-feldspar–apatite–calcite–magnesite–Na-carbonate and plagioclase–apatite–calcite–magnesite–Na-carbonate. 8/ Petrographic measurements, EMPA and RAMAN analyses on piston cylinder run products.

Applied techniques and instruments

NIKON E600 polarization microscope (ELTE Department of Petrology and Geochemistry, Lithosphere Fluid Research Laboratory, Budapest)
NIKON E4500 digital camera (ELTE Department of Petrology and Geochemistry, Lithosphere Fluid Research Laboratory, Budapest)
CARL ZEISS Jena electric furnace (ELTE Department of Petrology and Geochemistry, Lithosphere Fluid Research Laboratory, Budapest)
Linkam TS 1500 heating stage mounted on NIKON E600 polarization microscope (ELTE Department of Petrology and Geochemistry, Lithosphere Fluid Research Laboratory, Budapest)
AMRAY-1860 IT-6 scanning electron microscope (ELTE Department of Petrology and Geochemistry, Budapest)
CAMECA SX-100 electron microprobe (University of Vienna, Austria)
JEOL JXA-8200 electron microprobe (ETH Zürich, Switzerland)
LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry), using a 193 nm ArF laser with energy homogenized beam profile, coupled with an ELAN 6100 ICP quadropole mass spectrometer (ETH Zürich, Switzerland)
JEOL JXA-8200 electron microprobe (University of Bayreuth, Bayerisches Geoinstitut, Germany)
VOGGENREITER high pressure piston cylinder apparatus (University of Bayreuth, Bayerisches Geoinstitut, Germany)
JEOL JXA-8200 electron microprobe (Free University, Berlin, Germany)

JEOL-JSM5900 scanning electron microscope equipped with LINK ISIS 300 Energy Dispersive Spectrometer incorporating with a Super ATW light element detector (Lakehead University, Thunder Bay, Canada)

Summary

1/ The studied CAKP (*C*linopyroxene-*A*patite-*K* feldspar-*P*hlogopite) xenoliths were formed by an open system carbonatite melt metasomatism in an ultramafic environment. The degree of modal metasomatism correlates with the composition of the altered mantle clinopyroxene, resulting in marked depletion of Cr and enrichment of Zr and Hf. Trace and major element content of the apatite- and K feldspar-hosted carbonatite melt inclusions indicates that there was liquid-liquid separation between a P-bearing carbonatite and a carbonate-bearing alkali aluminosiliceous melts, initiated by compositional changes due to reaction with the ultramafic wall-rock.

2/ Clinopyroxene/carbonatite melt partition coefficients, especially for REE and alkalis, depend on the P and Si content of the carbonate-bearing melts.

3/ Our suggested model together with trace element signature of the CAKP carbonatite melt inclusions indicate that their initial melt was produced by extremely low degree partial melting of a carbonated and mafic silicate rock.

4/ Piston Cylinder experiments, carried out in system K-feldspar–apatite–calcite–magnesite–Na-carbonate, supported that at 2.2 GPa and 1200 °C phase assemblage of apatite–diopside–K-feldspar can be coexisted with two fluid-saturated immiscible melts where the one melt is a phosphorous carbonatite and the other melt is an alkaline aluminosiliceous one. Additionally, our experiments shed light that this supercritical fluid is mainly consisting of C-O-H-S components.

5/ During melt evolution of Kerimasi calciocarbonatite, apatite and magnetite enclosed a S- and P-bearing, Ca- and alkali-rich carbonatite melt; whereas magnetite enclosed a Na-metasilicate normative, peralkaline silicate melt, additionally. On the basis of homogenization experiments of apatite-hosted carbonatite melt inclusions and forsterite-monticellite relations, temperatures are estimated to be 900-1000 °C at the early stage of magma evolution. It is postulated that at this time at least three liquid phases coexisted: 1) a Ca-rich, P-, S- and alkali-bearing carbonatite melt; 2) a Mg- and Fe-rich, peralkaline silicate melt; and 3) a C-O-H-S-bearing fluid phase. During development of coexisting melts (carbonatite and silicate), the Si/Al and Mg/Fe ratio of the silicate melt decreased with contemporaneous increase in alkalis due to olivine fractionation, whereas the carbonatite melt increased in alkalis and decreased in CaO as a result of calcite fractionation. Overall, the peralkalinity of bulk melt-system increased resulting in decrease the size of miscibility gap. The carbonatite melt composition leaves the miscibility gap and develops further along the silicate-carbonate liquidus field boundary surface, crystallizing both calcite and monticellite together with apatite and magnetite. This alkali enrichment during melt evolution results ultimately in the crystallization of the Na-Ca carbonates enclosed in calcite. At the final stage of the evolution, the magma composition could be extremely enriched in alkalis, and have a composition similar to that of Oldoinyo Lengai natrocarbonatites.

6/ At mantle pressures and temperatures (e.g., T=1100-1200 °C, P>=2,2 GPa) in the characterization of composition of carbonatite melts Ca, Mg, a Fe, PO_4^{3-} and SiO_4^{4-} have great role, whereas at lower (crustal) pressure and temperatures (T = 500-1000 °C) Ca and alkalis show great significance. The major element distribution between the immiscible melt shows: 1/ Ca, P and F prefer the carbonatite melt while Si and Al partitioned into the silicate melt at both high and low pressure, 2/ in the high pressure systems (CAKP xenoliths, T01 and T04 experiments) the alkalis are compatible in aluminosilicate melt however, the divalent cations prefer the carbonatite liquid, 3/ in contrast, at low pressure (Kerimasi system) the divalent cations (in exception of Ca) partitioned into silicate liquid, whereas the alkalis prefer the carbonatite melt. The sulfate prefers the carbonatite melt instead of silicate melt. The behavior of Cl is similar to that of alkalis.

7/ Liquid-liquid separation caused separation of trace and major elements between the immiscible melts. Uranium, Th, Pb, Nb, Ta, P, Sr, Y and REE partitioned into the P-bearing carbonatite melt, whereas Cs, Rb, Na, Li, K, B, Al, Zr and Hf preferred the carbonate-bearing silicate liquid.

8/ Fluids that boiled in both natural and experimentally produced carbonatite melts can be characterized dominantly by C-O-H-S and alkali components. These carbonatite-coexisted fluids can play great role in crystallizing phases that can be altered easily by weathering, such as e.g., alkaline-hydrocarbonates, alkaline-carbonates and sulfates.

9/ In contrast with the compositions of bulk carbonatite rocks, the melt inclusions show at least 6-10 wt.% Na_2O+K_2O for carbonatite melts that form calciocarbonatites. Pure carbonates (globules and ocellis) and carbonatite rocks do not represent carbonatite liquid. Thus, studying of carbonatite melt inclusions are considered as being more applicable method for estimating of magma composition than study of any bulk rock.

Acknowledgement

I owe thanks to my supervisor, Csaba Szabó, Ph.D. (Eötvös University Budapest, Hungary) and my tutor Prof. Roger Mitchell (Lakehead University, Thunder Bay, Canada) for their great help during my Ph.D work. I am grateful to members of Lithosphere Fluid Research laboratory for the fruitful discussions especially to Márta Berkesi, Enikő Bali, Károly Hidas and János Kodolányi. I am also grateful to my family especially to my Father, Koni, Betti and Ági for their huge patience and support. This work is dedicated to my mother.

Publications connected to this research

Papers:

Guzmics, T., Zajacz, Z., Kodolányi, J., Halter, W. & Szabó, Cs. (2008) LA-ICP-MS study of apatite- and K feldspar-hosted primary carbonatite melt inclusions in clinopyroxenite xenoliths from lamprophyres, Hungary: implications for significance of carbonatite melts in the Earth's mantle. *Geochimica et Cosmochimica Acta,* 72, 1864-1886. [Impact factor (2008): **4,235**; independent citations: 7].

Guzmics, T., Kodolányi, J., Kovács, I., Szabó, Cs., Bali, E., & Ntaflos, T. (2008) Primary carbonatite melt inclusions in apatite and in K-feldspar of clinopyroxene-rich mantle xenoliths hosted in lamprophyre dikes (Hungary). *Mineralogy and Petrology*, 94, 225-242. [Impact factor (2008): **1,511**; independent citations: 2].

Szabó, Cs., Hidas, K., Bali, E., Zajacz, Z., Kovács, I., Yang, K., **Guzmics**, **T**. & Török, K. (2009) Melt-wall rock interaction in mantle as shown by silicate melt inclusions in peridotite xenoliths from the central Pannonian Basin (western Hungary). *The Island Arc*, 18, 375-400. [Impact factor (2007): **0,837**, independent citations: 0].

Berkesi, M., Hidas, K., **Guzmics, T.**, Dubessy, J., Bodnar, R.J., Szabó, Cs., Vajnai, B., & Tsunogaee, T. (2009) Detection of small amounts of H_2O in CO_2-rich fluid inclusions using Raman spectroscopy. *Journal of Raman Spectroscopy*, 40, 1461-1463. [Impact factor (2008): **3,526**; independent citations: 0]

Hidas, K., **Guzmics, T.**, Szabó, Cs., Kovács, I., Bodnar, R.J., Zajacz, Z., Nédli, Zs., Vaccari, L. & Perucchi A. (2010) Coexisting silicate melt inclusions and H_2O-bearing, CO_2-rich fluid inclusions in mantle peridotite xenoliths from the Carpathian-Pannonian region (central Hungary) (2010) *Chemical Geology*, in press, DOI 10.1016/j.chemgeo.2010.03.004. [Impact factor (2008): **3,531**; independent citations: 0]

Guzmics, T., Mitchell, R.H., Szabó, Cs., Berkesi, M., Milke, R. & Abart, R. (2010) Carbonatite melt inclusions in coexisting magnetite, apatite and monticellite in Kerimasi calciocarbonatite, Tanzania: melt evolution and petrogenesis. (2010) *Contributions to Mineralogy and Petrology*, in press, DOI 10.1007/s00410-010-0525-z. [Impact factor (2008): **3,853**; independent citations: 0]

Abstracts and reports

Guzmics, T., Szabó, Cs., Bali, E., Kovács, I. & Ntaflos, T. (2005) S-bearing phosphorous carbonatite melt inclusions in alkali clinopyroxenite xenoliths from lamprophyre dikes (Transdanubian Central Range, Hungary), Abstract book, ECROFI XVIII Conference, Siena, July 6-9, 2005.

Guzmics, T., Szabó, Cs., Bali, E., Kovács, I. & Ntaflos, T. (2005) S-bearing phosphorous carbonatite melt inclusions in ultra high pressure and temperature from pyroxenite xenoliths placed in Ad-2 lamprophyres. Peridotite Workshop 2005, 27-30 September, 2005, Lanzo (Italy), Ofioliti, 30, 175.

Guzmics, **T.,** Kodolányi, J., Kovács, I., Bali, E., Zajacz, Z., Halter, W. & Szabó, Cs. (2007) Primary carbonatite melt inclusions in apatite and in K feldspar from clinopyroxene-rich mantle xenoliths from Hungarian lamprophyres: implications for generation and evolution of carbonatite melts in the Earth's mantle. European Current Research on Fluid Inclusions (ECROFI-XIX) University of Bern, Switzerland, 17–20 July, 2007. Abstract Volume, p. 78.

Guzmics, T., Zajacz, Z., Szabó, Cs. & Halter, W. (2007) Apatite- and K feldspar-hosted primary carbonatite melt inclusions from mantle xenoliths, Hungary. Geochim. Cosmochim. Acta 71, Supplement 1, Goldschmidt Conference Abstracts 2007 (A366).

Guzmics, T., Zajacz, Z., Szabó, Cs. & Halter, W. (2007) LA-ICPMS study of clinopyroxene-apatite-K feldspar-phlogopite metasomatic mantle xenoliths from Hungarian lamprophyres and their primary carbonatite melt inclusions: implications for carbonatite melt metasomatism in the Earth's upper mantle. European Mantle Workshop Abstract Volume (unpaged).

Guzmics, T., Gál-Sólymos, K., Németh, B. & Szabó, Cs. (2007) Microthermometric, textural and geochemical study on red calcite veins of Mesozoic carbonates from the Transdanubian Central Range, Hungary HUNTEK Workshop Absract Volume, p. 41.

Guzmics T., Kodolanyi J., Zajacz Z. & Szabo C. (2008) Mantle metasomatism by primary carbonatite melts found in melt inclusions in clinopyroxenite xenoliths from lamprophyre dikes, Hungary European Geosciences Union General Assembly 2008 Vienna, Austria, 13 – 18 April 2008 (A-00319).

Guzmics T., Kodolanyi J., Zajacz Z. & Szabo C. (2008) Liquid immiscibility between a P-bearing and a silicate-bearing carbonatite melts reflected by primary carbonatite melt inclusions in mantle xenoliths, 33rd International Geological Congress Abstract Oslo, Norway, 6 - 14 August 2008 (MPM10304P).

Hidas, K., Szabó, Cs., **Guzmics, T.**, Bali E., Bodnar, R.J., Nédli, Zs., Vaccari, L. (2008) C-O-H-S bearing fluids in upper mantle peridotites from the central Pannonian Basin. Pan-American Current Research On Fluid Inclusions (PACROFI-IX), June 2-5, 2008, Washington (USA), Abstract Book.

Guzmics T., in collaboration with E. Bali, A. Audétat, M. Berkesi and C. Szabó (2008) Liquid immiscibility between a phosphorous carbonatite melt and a carbonate-bearing alkali aluminosiliceous melt, coexisting with apatite, K-feldspar and diopside at 1200 °C and 2.2 GPa: implications for carbonatite metasomatism in the mantle. EU RITA (Research Infrastructure Transnational Access, "The Structure and Properties of Materials at High Pressure") User workshop Abstract, Verbania, Italy, September 28 – October 1, 2008.

Guzmics T., in collaboration with E. Bali, A. Audétat, M. Berkesi and C. Szabó (2008) Liquid-liquid immiscibility between a phosphorous-bearing carbonatite melt and a potassic aluminosiliceous melt coexisting with apatite, K-feldspar and diopside at 2.2 GPa and 1200 °C. Annual Report 2008 Bayerisches Geoinstitut, Germany.

Guzmics, T., Mitchell, R.H., Berkesi M. & Szabó, Cs. (2009) Carbonatite melt inclusions in coexisting magnetite, apatite and monticellite from Kerimasi carbonatite, Tanzania. Geochim. Cosmochim. Acta 73, Supplement 1, Goldschmidt Conference Abstracts 2009 (A483).

References

Baker MB, Wyllie PJ (1992) High pressure apatite solubility in carbonate-rich liquids, Implications for mantle metasomatism. Geochim Cosmochim Acta 56, 3409-3422

Baker MB, Wyllie PJ (1990) Liquid immiscibility in a nephelinite-carbonate system at 25 kbar and implications for carbonatite origin. Nature 346, 168-170

Bali E, Szabó C, Vaselli O, Török K (2002) Significance of silicate melt pockets in upper mantle xenoliths from the Bakony–Balaton Highland Volcanic Field, Western Hungary. Lithos 61, 79-102

Blundy J, Dalton J (2000) Experimental comparison of trace element partitioning between clinopyroxene and melt in carbonate and silicate systems, and implication for mantle metasomatism. Contrib Mineral Petrol 139, 356-371

Blundy JD, Wood BJ (1994) Prediction of crystal-melt partition coefficients from elastic moduli. Nature 372, 452-454

Dalton JA, Presnall DC (1998) Carbonatitic melts along the solidus of model lherzolite in the system $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2\text{-}CO_2$ from 3 to 7 GPa. Contrib Mineral Petrol 131, 123-135

Dalton JA, Wood BJ (1993) The composition of primary carbonate melts and their evolution through wall rock reaction in the mantle. Earth Planet Sci Lett 119, 511-525

Demény A, Vennemann TW, Hegner E, Nagy G, Milton JA, Embey-Isztin A, Homonnay Z (2004) Trace element and C–O–Sr–Nd isotope evidence for subduction-related carbonate–silicate melts in mantle xenoliths (Pannonian Basin, Hungary). Lithos 75, 89-113

Eggler DH (1978) The effect of CO_2 upon partial melting of peridotite in the system Na_2O-CaO-Al_2O_3-MgO-SiO_2-CO_2 to 35 kb, with an analysis of melting in a peridotite-H_2O-CO_2 system. Am J Sci 278, 305-343

Green DH, Wallace ME (1988) Mantle metasomatism by ephemeral carbonatite melts. Nature 336, 459-462

Guzmics T, Zajacz Z, Kodolányi J, Werner H, Szabó C (2008a) LA-ICP-MS study of apatite- and K-feldspar-hosted primary carbonatite melt inclusions in clinopyroxenite xenoliths from lamprophyres, Hungary, Implication for significance of carbonatite melts in the Earth's mantle. Geochim Cosmochim Acta 72, 1864-1886

Guzmics T, Kodolányi J, Kovács I, Szabó Cs, Bali E, Ntaflos T (2008b) Primary carbonatite melt inclusions in apatite and in K-feldspar of clinopyroxene-rich mantle xenoliths hosted in lamprophyre dikes (Hungary). Mineral Petrol 94,225-242

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

Hauri EH, Shimizu N, Dieu JJ, Hart SR (1993) Evidence for hotspot-related carbonatite metasomatism in the oceanic upper mantle. Nature 365, 221-227

Hoernle K, Tilton G, Le Bas MJ, Duggen S, Garbe-Schönberg D. (2002) Geochemistry of oceanic carbonatites compared with continental carbonatites, mantle recycling of oceanic crustal carbonate. Contrib Mineral Petrol 142, 520-542

Hou Z, Tian S, Yuan Z, Xie Y, Yin S, Yi L, Fei H, Yang Z The Himalayan collision zone carbonatites in western Sichuan, SW China, Petrogenesis, mantle source and tectonic implication. Earth Planet Sci Lett 244, 234-250

Huang WL, Wyllie PJ (1974) Eutectic between wollastonite II and calcite constrained with thermal barrier in MgO-SiO_2-CO_2 at 30 kbar, with application to kimberlite-carbonatite petrogenesis. Earth Planet Sci Lett 24, 305-310

Huang WL, Wyllie PJ, Nehru CE (1980) Subsolidus and liquidus phase relationships tn the system CaO-SiO_2-CO_2 to 30 kbar with geological applications. Am Mineral 65, 285-301

Hunter RH, McKenzie D (1989) The equilibrium geometry of carbonate melts in rocks of mantle composition. Earth Planet Sci Lett 92, 347-356

Ionov DA, O'Reilly SY, Genshaft YS, Kopylova MG (1996) Carbonate-bearing mantle peridotite xenoliths from Spitsbergen, phase relationships, mineral compositions and trace-element residence. Contrib Mineral Petrol 125, 375-392

Kjarsgaard BA, Hamilton DL, Peterson TD (1995) Peralkaline nephelinite/carbonatite liquid immiscibility, comparison of phase compositions in experiments and natural lavas from Oldoinyo Lengai. In, Bell K, Keller J (eds) Carbonatite volcanism. Springer, Berlin, pp 163–190

Kogarko LN, Henderson CMB, Pacheco H (1995) Primary Ca-rich carbonatite magma and carbonate-silicate-sulfide liquid immiscibility in the upper mantle. Contrib Mineral Petrol 121, 267-274

Le Bas MJ (1977) Carbonatite-nephelinite volcanism. Wiley-Interscience Publication, Bristol, Great Britain

Lee CT, Rudnick RL, McDonough WF, Horn I (2000a) Petrologic and geochemical investigation of carbonates in peridotite xenoliths from northeastern Tanzania. Contrib Mineral Petrol 139, 470-484

Lee WJ, Wyllie PJ (1997) Liquid immiscibility between nephelinite and carbonatite from 1.0-2.5 GPa compared with mantle compositions. Contrib Mineral Petrol 127, 1-16

Lee WJ, Wyllie PJ (1998a) Petrogenesis of carbonatite magmas from mantle to crust, constrained by the system CaO—(MgO + FeO*)—(Na_2O + K_2O)—(SiO_2 + Al_2O_3 + TiO_2)—CO_2. J Petrol 39, 495-517

Lee WJ, Wyllie PJ (1998b) Processes of Crustal Carbonatite Formation by Liquid Immiscibility and Differentiation, Elucidated by Model Systems. J Petrol 39,2005-2013

Lee WJ, Wyllie PJ (2000) The system CaO-MgO-SiO_2-CO_2 at 1 GPa, metasomatic wehrlites and primary carbonatite magmas. Contrib Mineral Petrol 138, 214-228

Lee WJ, Huang WL, Wyllie PJ (2000) Melts in the mantle modeled in the system CaO-MgO-SiO_2-CO_2 at 2.7 GPa. Contrib Mineral Petrol 138, 199-213

Mitchell RH (2009) Peralkaline nephelinite-natrocarbonatite immiscibility and carbonatite assimilation at Oldoinyo Lengai, Tanzania. Contrib Mineral Petrol, in press, DOI 10.1007/s00410-009-0398-1

Rudnick RL, Barth M, Horn I, McDonough WF (2000) Rutile-bearing refractory eclogites, Missing link between continents and depleted mantle. Science 287, 278-281

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

Sweeney RJ (1994) Carbonatite melt composition in the Earth's mantle. Earth Planet Sci Lett 128, 259-270

Thomsen TB, Schmidt MW (2008) Melting of carbonated pelites at 2.5–5.0 GPa, silicate–carbonatite liquid immiscibility, and potassium–carbon metasomatism of the mantle. Earth Planet Sci Lett 267, 17-31

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

Van Achterbergh E, Griffin WL, Ryan CG, O'Reilly SY, Pearson NJ, Kivi K, Doyle BJ (2004) Melt inclusions from the deep Slave lithosphere, implications for the origin and evolution of mantle-derived carbonatite and kimberlite. Lithos 76, 461-474

Wallace ME, Green DH (1988) An experimental determination of primary carbonatite magma composition. Nature 335, 343-346.

Woolley AR, Church AA (2005) Extrusive carbonatites, A brief review. Lithos 85, 1-14

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

Woolley AR, Kjarsgaard BA (2008) Carbonatite Occurrences of the World, Map and Database; Geological Survey of Canada, Open File 5796, 1 CD-ROM + 1 map

Wyllie PJ, Huang WL (1976) Carbonation and melting reactions in the system CaO-MgO-SiO_2-CO_2 at mantle pressures with geophysical and petrological applications. Contrib Mineral Petrol 54, 79-107.

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 Mineral Petrol 146, 606-619

Yaxley GM, Crawford AJ, Green DH (1991) Evidence for carbonatite metasomatism in spinel peridotite xenoliths from western Victoria, Australia. Earth Planet Sci Lett 107, 305-317

Yaxley GM, Green DH, Kamenetsky V (1998) Carbonatite metasomatism in the southeastern Australian lithosphere. J Petrol 39, 1917-1930