Carbonatite melts in geologic environments: formation, composition and evolution

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Summary of Ph.D. thesis

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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 CO₂, 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, B, 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 carbonate 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 compositions 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 CO₂, we have pure information about the volatiles coexisted with natural carbonate 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 plagiogpote (CAKP), and their carbonatite melt inclusions, collected in lamprophyres from Accoliuboz-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 magnette, 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 calciocarbonate rock and I have answers for problem of alkaline deficit in carbonatitites 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 calcioarbonatites 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 calcioarbonatite. 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 (Clinopyroxene-Apatite-K feldspar-Phlogopite) xenoliths were formed by an open system carbonate 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 carbonate melt inclusions indicates that there was liquid-liquid separation between a P-bearing carbonate and a carbonate-bearing alkali aluminum silicate melts, initiated by compositional changes due to reaction with the ultramafic wall-rock.

2/ Clinopyroxene/carbonate 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 carbonate 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 carbonate and the other melt is an alkaline aluminum silicate 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 calcio-carbonatite, apatite and magnetite enclosed a S- and P-bearing, Ca- and alkali-rich carbonate melt; whereas magnetite enclosed a Na-metasilicate normative, peralkaline silicate melt, additionally. On the basis of homogenization experiments of apatite-hosted carbonate 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 carbonate 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 carbonate 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 carbonate melt composition leaves the miscibility gap and develops further along the silicate-carbonate liquid 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 carbonate melts Ca, Mg, a Fe, PO₄²⁻ and SiO₄⁴⁻ 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 carbonate 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 carbonate 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 carbonate melt. The sulfate prefers the carbonate 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 carbonate 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 carbonate melts can be characterized dominantly by C-O-H-S and alkali components. These carbonate-coexisted fluids can play great role in crystallizing phases that can be altered easily by weathering, such as e.g., alkaline-hydrocarbontes, alkaline-carbonates and sulfates. 

9/ In contrast with the compositions of bulk carbonate rocks, the melt inclusions show at least 6-10 wt.% Na₂O+K₂O for carbonate melts that form calcio-carbonatites. Pure carbonates (globules and ocellis) and carbonate rocks do not represent carbonate liquid. Thus, studying of carbonate melt inclusions are considered as being more applicable method for estimating of magma composition than study of any bulk rock.

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Publications connected to this research

Papers:


Abstracts and reports


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