THE ROLE OF FLUIDS IN THE LITHOSPHERIC MANTLE (CENTRAL PANNONIAN BASIN, WESTERN HUNGARY): DETAILED FLUID INCLUSION STUDY IN MANTLE XENOLITHS

Márta Berkesi

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: Dr. Gyula Gábris, D.Sc.
(Department of Physical Geography, ELTE Budapest, Hungary)

Chair of the Ph.D. Program: Dr. Andrea Mindszenty, D.Sc.
(Department of Physical and Applied Geology, ELTE Budapest, Hungary)

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

Consultent: Jean Dubessy, D.Sc.
(Faculté des Sciences, Nancy Université, Vandoeuvre-lés-Nancy, France)

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Introduction

Transport of melts and/or fluids through the convecting mantle are the least understood and, therefore, state-of-the-art problems among a series of processes of formation and evolution of the deep lithosphere. Although percolation of metasomatic agents through the continental lithospheric mantle and their interaction with the peridotic wall rock is petrographically and/or geochemically documented, the compositions of the metasomatic melts/fluids recorded in mantle materials differ widely. For these origins many previous and recent explanations are available and are a matter of debates including silicate melts (Schiano and Clochciatti, 1994; Bali et al., 2007; 2008a, b; Dantas et al., 2009; Scambelluri et al., 2009; Hidas et al., 2010), hydrous melts/fluids (Hartmann and Wedepohl, 1993; Zanetti et al., 1999) and carbonatite melts (Green and Wallace, 1988; Guzmics et al., 2008a, b) that interacted with the mantle. The nature and composition of the metasomatic agents are inferred from the modal and chemical variations induced into the mantle by reactive carbonatite (Rudnick et al., 1993; Watson et al., 1990; Yaxley et al., 1991; Yaxley et al., 1998) or silicate (Szabó et al., 1996; Wulf-Pedersen et al., 1996; Scambelluri et al., 2009) melt percolation. One example is for the latter one the orthopyroxene-enrichment in mantle xenoliths. Orthopyroxene-rich lithologies untraveled in peridotites worldwide may also be explained by several processes. The early models suggest the role of partial melting that shifts modal composition of thherzolite towards harzburgite and dunite (e.g., Arai, 1980). Recently, the significance of modal metasomatism and melt/wall rock reactions has come to the foreground (Kelemen et al., 1992; 1998) by (a) the circulation of SiO$_2$-rich slab-derived melts or fluids formed during the dehydration or the partial melting process of the subducting oceanic crust (Arai et al., 2006; Dantas et al., 2009; Melnès et al., 2001) and (b) the circulation of Si-oversaturated alkaline melts or sub-alkaline melts (Wulf-Pedersen et al., 1996; Arai et al., 2006).

Besides the obvious metasomatic effect of the percolating melt in the lithospheric upper mantle, the role of fluids as metasomatic agents has also become significant in the last decades. The composition and behavior at upper mantle depths of the supercritical aqueous fluids have been intensively studied (Keplinger, 1996; Newton and Manning, 2000; Scambelluri and Philpot, 2001; Kessel et al., 2005; Hermann et al., 2006; Spandler et al., 2007), although the majority of the fluids that present in the lithospheric mantle is CO$_2$-dominated (Roedder, 1984; Szabó and Bodnar, 1996; Andersen and Neumann, 2001; Frezzotti et al., 2002; Frezzotti and Pecceirillo, 2007; Berkesi et al., 2009), less information is available on CO$_2$-rich supercritical mantle fluids and their interactions with peridotitic mantle wall rocks. These interactions can cause cryptic metasomatism in the mantle (Rosenbaum et al., 1996; Scambelluri et al., 2004; Malaspina et al., 2006; Hidas et al., 2010). These facts shed light on the importance of the intensive study of fluid inclusions hosted in peridotite xenoliths. As study on fluid inclusion is the most suitable method to obtain information and evidences on upper mantle fluid systems (Roedder, 1984; Szabó and Bodnar, 1996; Andersen and Neumann, 2001), I aimed to carry out a complex study of a representative series of such fluid inclusions in this thesis.

Carbon-dioxide is major component in negative crystal shaped mantle xenolith-enclosed fluid inclusions (e.g., Andersen and Neumann, 2001 and references therein; Berkesi et al., 2007; 2009; Frezzotti et al., 1992; 2002; Frezzotti and Pecceirillo, 2007; Roedder, 1965; 1983; Hidas et al., 2010). This is why up to the recent years, the generally accepted composition for the fluid within the inclusions was a one component (“pure” CO$_2$) system (Roedder, 1984; Andersen and Neumann, 2001). In addition, on the basis of the high temperature and pressure (P~20 kbar, T~1300 ºC) experiments of Eggler (1975), pure CO$_2$ does not play role in dissolving and, therefore, transporting trace elements in the lithospheric mantle. However, there are some trace elements that are undoubtedly linked to mantle fluid inclusions (Rosenbaum et al., 1996; Hidas et al., 2010). This and detection of OH-bearing solids within the mantle fluid inclusions (e.g., Frezzotti et al., 2002; 2010) strongly suggested that the „pure CO$_2$” approach needs to be reconsidered. In this thesis I give direct evidences, besides the CO$_2$, of the presence H$_2$O in the mantle xenolith-hosted fluid inclusions. Additionally, it will be shown that CO$_2$-H$_2$O supercritical fluid contains dissolved silicate melt component at entrapment. The latter one may play great role in trace element transport during fluid metasomatism in the mantle.

Aim of this Ph.D. thesis

In this thesis upper mantle xenoliths, that are commonly contain in fluid inclusions, from the Bakony-Balaton Highland Volcanic Field, Central Pannonian Basin and synthetic capillary inclusions have been studied in detail. The combination of the study of the natural fluid inclusions and the application of the capillary inclusions was to achieve the main aims of this study, such as: 1/ select the fluid inclusion-bearing xenoliths for further study on the basis of detailed petrographic observation of the peridotites, 2/ determine the composition of the phases in the fluid inclusions and look for possibilities to semi-quantify them, 3/ as a result of the abovementioned point, model the bulk composition of the fluid trapped at mantle condition, 4/ moreover, model the bulk density of the trapped fluid to construct the corresponding isochors and to estimate minimum pressure conditions preserved, 5/ reconstruct the post-entrapment processes and, therefore, the fluid/host mineral reactions within the inclusions, and 6/ understand the supercritical fluid/peridotite reaction in geochemical point of view.

In other words, the major goal was the comprehension of the role of fluids that have migrated at lithospheric upper mantle condition beneath the Central Pannonian Basin.

Fulfilled work

1/ Petrographic, detailed EMPA and LA-ICP-MS measurements (including quantification) on constituent minerals of ten xenoliths 2/ Preparation of 24 synthetic silica fused capillary (CO$_2$-H$_2$O) fluid inclusions 3/ Microthermometry of 110 natural fluid and 24 synthetic silica fused capillary fluid inclusions 4/ Raman spectrometry of 60 fluid inclusions and 24 synthetic silica fused capillary fluid inclusions 5/ Focused Ion Beam exposure of 7 natural fluid inclusions 6/ Semi-quantification of the trace
elements in 7 natural fluid inclusions / peak calibration of the Raman peak of dissolved H₂O in CO₂ using the synthetic silica fused capillary fluid inclusions

**Applied techniques and instruments**

NIKON E600 polarization microscope (Lithosphere Fluid Research Laboratory, Department of Petrology and Geochemistry, ELTE, Budapest)

NIKON E4500 digital camera (Lithosphere Fluid Research Laboratory, Department of Petrology and Geochemistry, ELTE, Budapest)

JEOL JXA-8200 electron microprobe (University of Bayreuth, Bayerisches Geoinstitut, Germany)

CAMECA SX-100 electron microprobe (University of Vienna, Austria; Open University, United Kingdom)

USGS-type gas flow heating-freezing stage (Lithosphere Fluid Research Laboratory, Department of Petrology and Geochemistry, ELTE, Budapest)

Linkam TS 1500 heating stage mounted on NIKON E600 polarization microscope (Lithosphere Fluid Research Laboratory, Department of Petrology and Geochemistry, ELTE, Budapest)

Linkam THMS 600 heating-freezing stage mounted on Olympus polarization microscope (Nancy Université, G2R laboratory, France)

HORIBA Jobin Yvon Labram Raman spectrometer (University of Technology and Economics, Budapest; Nancy Université, G2R laboratory, France)

HORIBA Jobin-Yvon LabRam HR spectrometer (Nancy Université, G2R laboratory, France)

Agilent 7500 LA-ICP-MS Laser Ablation Inductively Coupled Plasma Mass Spectrometry (Virginia Tech, USA; Nancy Université, G2R laboratory, France)

Pressure line for the preparation of fused silica capillaries (Nancy Université, G2R laboratory, France)

FEI QUANTA 3D FIB-SEM apparatus (ELTE, TTK, Budapest)

**Summary**

Due to the detailed study of mantle fluid inclusions in peridotite xenoliths from the Central Pannonian Basin (Tihany and Szentbékkálla) with a combination of the application of the fused silica capillary synthetic fluid inclusions, several conclusions can be drawn, as follows:

1. The fluid-inclusion absent (referred to as NOFLUID) Tihany peridotite xenoliths show high modal proportion of orthopyroxene. The petrography and distribution of major and trace elements strongly indicate that the orthopyroxene-enrichment likely formed by a reaction of peridotite and a SiO₂-, and MgO-rich “boninite-like” melt.

2. The application of the Raman microspectroscopy at moderately high temperature on the studied fluid inclusions proved the presence of H₂O, beside the main CO₂ component. The results of this work suggest that H₂O in fluid inclusions trapped at subcontinental lithospheric mantle conditions is more common than it was previously thought. Thus, the fluid system can be no longer treated as pure (or nearly pure) CO₂ fluid system. Therefore, the assumption of a pure CO₂ (H₂O-free) fluid in this environment must be reconsidered. Room temperature Raman spectroscopy and microthermometry alone are not suitable for detecting H₂O in such fluid inclusions.

3. The preparation and application of fused silica capillary fluid inclusions played an important role in controlling the analyses when trying to infer the bulk fluid composition by applying the Raman microspectroscopy at moderately high temperature (75-275 °C). Moreover, the study of the synthetic fluid inclusions revealed the CO₂-density dependence on the Raman peak position of the dissolved H₂O in CO₂ liquid. To our best knowledge, this is the first study to calibrate the position of this peak and also observe the dependence of the peak shift. The liquid CO₂ density may be determined at higher accuracy when taking into account the peak of the dissolved H₂O in CO₂, instead of the distance in the Fermi diads of CO₂. Additional feature is the peak broadening of the dissolved H₂O with decreasing CO₂ density, which shed light on the influence of CO₂ molecules on the perturbation of the energy of the symmetric stretching of the H₂O in CO₂.

4. The fluid inclusion exposure, applying the FIB technique, revealed the presence of S-bearing solid phase (Fe-sulfide), and of a glass film covering the wall of the inclusion. These phases, to my best knowledge, have not been previously described in mantle fluid inclusion. The glass has a feature that is typical also for the volcanic glasses, showing numerous spherical-shaped holes (i.e., vesicles) on the surface as a result of the devolatization. The finding proved that the CO₂-rich fluid, existing in the lithospheric mantle, dissolves silicate melt components.
(5) In the studied samples carbonates and quartz were also identified as formed via the reaction of the CO₂-rich fluid and the host pyroxene after entrapment. Water should have been completely dissolved in the CO₂-dominated fluid (i.e., the CO₂-rich and the H₂O-rich phases are single phases) when the reactions took place. On the basis of on the thermodynamic model, the CO₂-rich fluid started to react with the host phases at the temperature of about 400-600 °C. The “quenching” of the glass phase probably excluded the completion of the carbonation reaction, as a result, preserved the residual CO₂ and the daughter phases in the fluid inclusions. As carbonates were previously found in other mantle xenolith-hosted CO₂-rich fluid inclusions, it is suggested that the presence of the glass phase is reasonable in mantle fluid inclusions.

(6) The strong relation between the chemical characteristics and the presence (or absence) of fluid inclusions (e.g., xenolith groups “NOFLUID” or “FLUIDRICH”) indicates metasomatism by a volatile-rich phase on the fluid inclusion-bearing peridotites from Tihany. The metasomatic agent was likely a supercritical CO₂-rich, COH₂S-bearing volatile-rich fluid containing also silicate component.

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Publications connected to this research

Papers:


Field guide:


Selected abstracts:


Berkesi, M., Guzmics, T., Szabó, C. and Dubessy, J. (2011): Advantage of the use of Focused Ion Beam technique to specify mantle fluid inclusions. ECROFI-XXI (European Current Research on Fluid Inclusions), accepted abstract

References


Bali, E., A. Sanetti, C. Szabo, D. W. Peate, and T. E. Waight (2008b), A micro-scale investigation of melt production and extraction in the upper mantle based on silicate melt pockets in ultramafic xenoliths from the Bakony-Balaton Highland Volcanic Field (Western Hungary), Contributions to Mineralogy and Petrology, 155, 165-179.


Egger, D.H. (1975), CO$_2$ as a volatile component of the mantle:the system Mg$_2$SiO$_4$-SiO$_2$-H$_2$O-CO$_2$. Phys. Chem. Earth, 9, 869-881.


Hartmann, G. and K. H. Wedepohl (1993), The composition of peridotites tectonites from the Ivrea Complex, northern Italy: Residues from melt extraction, Geochemica et Cosmochimica Acta, 57, 1761-1782.


Roedder, E. (1965), Liquid CO₂; inclusions in olivine bearing nodules and phenocrysts from basalts, American Mineralogist, 50, 1746-1782.


Spandler, C., J. A. Mavrogenes, and J. Hermann (2007), Experimental constraints on element mobility from subducted sediments using high-P synthetic fluid/melt inclusions, Chemical Geology, 239, 228-249.


