Final research report
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During the project, fluid inclusions enclosed in spinel lherzolite xenoliths from Jeju-island (South-Korea), Mt. Quincan (northeastern-Australia), Rio Grande Rift (New Mexico, USA) and Barombi, Cameroon Volcanic Line (Cameroon) were studied. All xenoliths represent subcontinental upper mantle fragments at either continental rift or backarc environment. As a consequence, main results of this research project allowed us to better understand the main charcteristics of the free fluid phase that might have interacted to the surrounding peridotitic rocks at extensional setting.

Besides, I took part, as consultant, in fluid inclusion studies in mantle xenoliths from Styrian basin and Perşani Mountains with the cooperation of László Aradi and Ábel Szabó, respectively (PhD students at Eötvös Loránd University). Both locations likely represent an above position of a suspected subducted slab (mantle wegde).

Research started with preparation of double-polished thin section (~100 micrometer) and careful petrography. For further analyses we selected parts of the xenoliths out of any visible petrographic sign of the host basalt infiltration, which is regularly restricted to the outermost few mm of the xenolith. Interestingly, spinel lherzolites that enclose negative crystal shaped fluid inclusions (as precursors of fluids trapped at mantle depth, Roedder, 1984; Berkesi et al, 2012) show very similar petrographic features despite the significant geographic distances. Samples are characterized as Group-I spinel lherzolites having porhyroclastic texture with mainly orthoproxenes and subordinately olivines as porphyroclasts. As a general rule, fluid inclusions are enclosed in orthopyroxene porphyroclasts, subordinately in clinopyroxenes. Appearance of fluid inclusions suggests one fluid invasion event recorded in the studied rocks (except for Rio Grande Rift samples, see details below). Moreover, as they are always present along the same orientation as the lamellae in the orthopyroxene porphyroclast never reaching the edge of the host crystal, they can be regarded as an indication for early trapping (e.g., Frezzotti et al., 2010).

Fluid inclusions are mostly filled by one (liquid) or, less commonly, two visible phases (liquid and solid) at room temperature. The smaller inclusions (2–8 µm) show 'undisturbed' features (no visible sign of stretching and/decrepitation or any kind of partial fluid loss after entrapment). As a consideration, the smaller fluid inclusions are rather representative for mantle fluids than the disturbed ones. Microthermometry (in other words, heating-freezing experiments) was thus carried out solely on the undisturbed fluid inclusions. Melting temperatures always indicated CO_2-rich fluid phase within the inclusion cavity (melting temperature of pure CO_2 is at -56,6, Span and Wagner, 1996) ranging between 56.8-59.7 °C (e.g., Berkesi et al., 2017a; Berkesi et al in prep.). In general, fluid inclusions show high (between 0.8 and 1 g/cm^3) or even extremely high density (≥ 1 g/cm^3) as indicators of entrapment at mantle depth. In case of fluid inclusions from **Jeju-Island, Rio Grande Rift and Mt. Quincan**, the melting point depression can be explained by the presence of small amount (between 0.2 and 3.1 mol%) of N_2 besides the CO_2. The results suggest that microthermometric measurements and/or Raman spectrometry with an inferior spectral resolution may leave N_2 undetected in CO_2-rich upper-mantle FIs (Fig 1). One of the most significant finding in this project is that nitrogen, may be a minor but very common component in subcontinental lithospheric upper-mantle fluids. This assumption may give better insight into the global cycle of nitrogen on the Earth that involves the deep lithosphere. Results and their impliciations of microthemometry and Raman spectroscopy on fluid inclusions from these three locations has been published at *European Journal of Mineralogy* (Berkesi et al., 2017a).

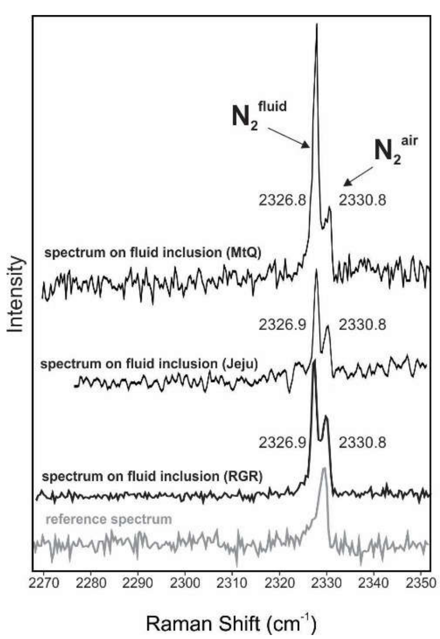

Fig. 1 Representative Raman spectra of fluid inclusions at the spectral region around 2300 cm^{-1} from each location studied. N_2 as the only nitrogen-bearing species was identified at ~2327 cm^{-1}, as the "spectrum on fluid inclusion" indicates. Spectra are shown after the subtraction of a reference (host) spectrum, recorded close to the inclusion of interest using the same parameters as those used for the fluid inclusion. All spectra were taken at 32 °C. Abbreviations: N_2^{air} – nitrogen band in air, N_2^{fluid} –nitrogen band in the fluid inclusion, RGR – Rio Grande Rift, MtQ – Mt. Quincan. Figure taken from Berkesi et al., 2017a

In case of spinel lherzolite xenoliths from **Rio Grande Rift (New-Mexico, USA)** two generations of fluid-inclusion assemblages, both hosted in orthopyroxenes, namely Type-1 (earlier) and Type-2 (later) were observed. Both types of fluid inclusions were characterized combining microthermometry, high-resolution Raman micro-spectroscopy, and focused ion beam–scanning electron microscopy (FIB-SEM). The results indicated that the timing and depth of entrapment, as well as the composition of trapped fluid were different between Type-1 and Type-2 FIs. The earlier fluid infiltration (C–O–N–S) happened at higher depth before or during formation of exsolution lamellae and was trapped as Type-1 FI in the cores of orthopyroxenes. Likely related to the latest metasomatic event recorded in the xenoliths, late fluid infiltration (C–O–H–S) was trapped at shallower depth as Type-2 FI after the formation of the orthopyroxene porphyroclasts with exsolution lamellae. Detailed study on fluid inclusions from Rio Grande Rift has been published in *European Journal of Mineralogy* (Park et al., 2017) in the framework of a cooperation with the Seoul National University. Overall, the paper gives a better insight to understand the relationship between multiple fluid metasomatic event beneath the region.

Fluid inclusions, enclosed in deformed spinel lherzolites from **Mt. Quincan, northeastern Queensland, Australia** of asthenopheric origin were also the subject of this research project. Previous major and trace element geochemical data, together with combined Sr, Nd and Os isotopic composition of whole rocks, from spinel lherzolite suite of Mt Quincan suggest variable degrees of melt extraction at around 275 Ma from a Depleted MORB Mantle (DMM) – like source (Handler et al., 2005). In addition, helium, argon and xenon compositions found in the xenoliths from Mt Quincan indicate the preservation of a MORB-like character in relatively recent fluid entrapment, which might be related to the rifting of Eastern Australia after the Paleozoic subduction events (Czuppon et al., 2009). Major and trace element composition of the consituent minerals (olivine, orthopyroxene, clinopyroxene and spinel) by EPMA, microthermometry compiled with Raman spectroscopy together with FT-IR hyperspectral imaging and in situ FIB-SEM or LA-ICPMS on the fluid inclusions were used as analytical tool for the understanding fluid-peridotite interaction beneath the region. As it was originally planned, LA-ICPMS analyses were obtained at GeoRessources laboratory, Université de Lorraine, Nancy, France, based on the longterm and fruitful scientific cooperation between M. Berkesi and the laboratory. Besides, EPMA analyses could have been performed due to the recent cooperation with Universität Potsdam, Germany; precisely with Silvio Ferrero. FT-IR imaging was carried out in a cooperation with Andrea Perucchi in Elettra Trieste (Italy), at which the infrared beam was induced by a synchrothron beam.

Fluid inclusion, entrapping along lamellae in pyroxene porphyroclasts are having compositional range of CO_2: 75-89 mol%, H_2O: 9-18 mol%, N_2: 0.1-1.7 mol% and H_2S: $\leq$ 0.5 mol% with dissolved trace elements. CO_2-rich fluid phase can be the representative of a residual fluid left behind after metasomatic enrichment of lherzolite at spinel stability beneath the area. Metasomatism resulted in the enrichment of LREE, Nb, Sr and Ti in clinopyroxene and the formation of pargasite of small modal proportion (less than 1 %). Our findings suggest that that the metasomatic agent could have been a fluid-rich silicate melt, which might have been deliberated by asthenophere upwelling at higher depth than pargasite stability. Further cooling of the fluid and their environment, possibly due to the thermal relaxation of the isotherms and by the upward migration of the fluid resulted in reaching the pargasite stability zone and thus froming pargasite (Fig. 2a). We conclude that pargasite, at continental rift-backarc setting could be a common phase at spinel lherzolite sability in the lithospheric upper mantle. Further cooling of the inclusions resulted in the interaction of the CO_2-rich fluid with their host enstatite, as a result, magnesite and quartz (Fig. 2b) formed during or after the entrainment of the xenoliths by the alkali basaltic volcanism to the surface. The manuscript about the fluid inclusion study from Mt. Quincan is now at the final stage of preparation and will be submitted to the Special Issue of the ECROFI conference (acronym of European Current Research on Fluid inclusion) to the journal of *Chemical Geology* as soon as the submission opens in November.

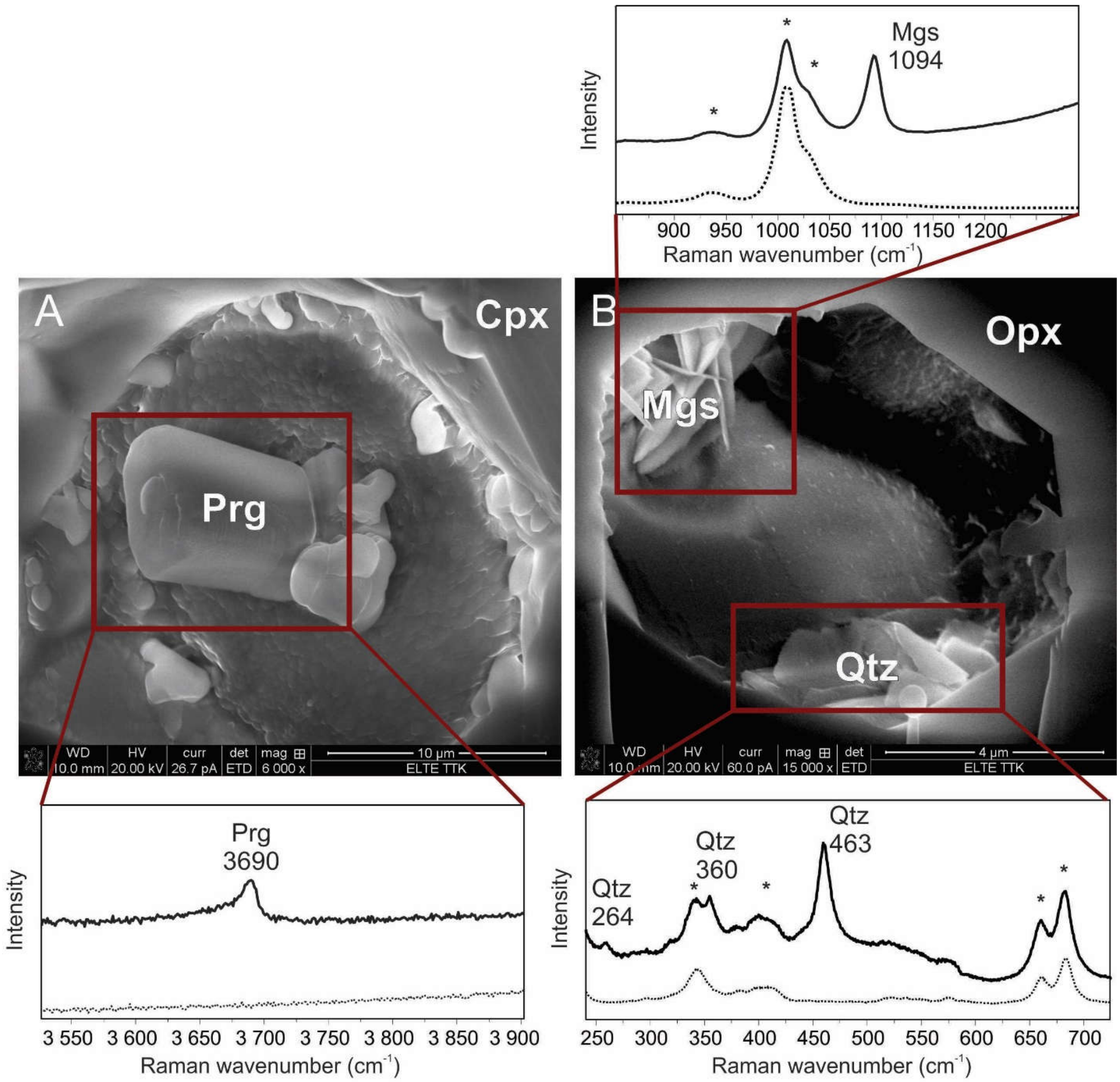

Fig 2. Secondary electron images on exposed inclusions from Mt. Quincan xenoliths by focused ion beam (FIB) technique in A) clinopyroxene- and B) orthopyroxene-hosted fluid inclusion. Solid phases within the cavity of inclusions were previously determined as pargasite (Prg), magnesite (Mgs) and quartz (Qtz) by point measurement of Raman spectroscopy. Dashed lines on the Raman spectra indicate host mineral spectrum of the same focal depth and acquisition parametes that was used on the solid phase beforehand. Asterisks denote the Raman bands of the host minerals. Figure taken from Berkesi et al., in prep.

Xenoliths from **Barombi, Cameroon Volcanic Line** has been the subject of the study by Pintér et al., (2015) giving a strong petrological and geochemical background to understand the evolution of the lithospheric rocks mantle beneath the region. Thus, Barombi xenolith have been concluded to represent a juvenile lithospheric segment, which had been originally part of the asthenosphere. Striking similarities have been observed with the results of Mt. Quincan samples when studying fluid inclusions from Barombi xenoliths (Berkesi et al., 2017b). Occurrence of the fluid inclusion is similar to the Australian samples, namely they are present parallel to the exsolution lamellae of orthopyroxene porphyroclasts. Fluids in the inclusions are high density CO_2-H_2O-H_2S based on microthermometry and Raman spectrsocopy, it is to note that no nitrogen was observed. FT-IR spectroscopy revealed pargasite and phlogopite associated with the cavity of fluid inclusions. Their formation is likely linked to the interaction of a fluid-rich melt of asthenospheric origin with the lherzolite. In situ LA-ICPMS, however, did not show any trace element undoubtedly linked to the inclusions and the FIB-SEM slicing revealed pargasite and phlogopite only at nanometer scale. To sum up the main results from Barombi xenoliths, the technique used in this project shed light on a seemingly complex evolution of fluid infiltration at mantle depth, however, further investigation will be needed to clarify the origin of such fluids (e.g., determination of noble gas composition and their isotopic ratios as it had been done for Mt. Quincan xenoliths in Czuppon et al., 2009).

Fluid inclusions from **Jeju-island**, South Korea did not show any evidence for fluid metasomatism. Beside CO_2, only N_2 could have been detected (see above). Raman spectroscopy and FT-IR spectrsocopy proved that the inclusions are water-free, moreover, FIB-SEM exposure of the inclusions did not show the presence of any solid phases that might indicate lack of fluid metasomatism. In situ LA-ICPMS, in agreement with the previous observations did not show any trace element related to the inclusions. As a consideration, despite the effort made on the research on Jeju-island xenoliths result of this part of the project did not give more scientific novelty deserving further publication.

The Styrian Basin Volcanic Field (SBVF, Eastern Austria and Northern Slovenia) situates at the transition zone between the Eastern Alps and the Pannonian Basin, above the suspected already detached Penninic-slab (Aradi et al., 2017 and their references therein), whereas at the **Perşani Mountains** locates at Eastern Transylvania where the subduction of the European platform is suspected underneath (Szabó et al., 2017 and their references therein).

From both locations, amphibole-rich peridotites and/or lherzolite xenoliths with amphibole-rich veins enclose abundant fluid inclusions, both hosted by orthopyroxene and amphibole. In addition to the presence of amphibole, modal metasomatism is evidenced by the presence of phlogopite and apatite, as well. In both locations various examples of subduction-related volcanism and upper mantle metasomatism suggest that the lithospheric mantle of the region may have been in a mantle-wedge position, where fluids may have been released from the subducted slab. The entrapped fluid in incluions, therefore, might represent subduction related mantle fluids. We discovered that within the inclusions, besides CO_2, significant amount of Na, H_2O, N and S (+ K, P, Cl) is present, based on microthermometry, Raman imaging and FIB-SEM exposure (Aradi et al., 2017). A manuscript including the fluid inclusion data together with major and trace element composition of the xenoliths is now in preparation.

During this project, in the framework of international scientific cooperations on fluid and melt inclusions from La Galite Archipelago we gained to better understand the fluid-present anatexis in the region (Ferrero et al., 2014 *Journal of Metamorphic Geology*). Besides, a manuscript has been submitted to the journal of *Contribution of Mineralogy and Petrology* (and is still under revision) due to the cooperation with Júlia Dégi about multi-stage fluid-assisted alteration of symplectites on a composite mafic granulite xenolith from the Bakony-Balaton Highland Volcanic Field. The manuscript is under revision. Although these studies were carried out on crustal fluid inclusions, it is noteworthy that without the experiences on the previously described mantle fluid inclusion these studies could not have been carried out.

Accepted papers during the project (including cooperations):

Márta Berkesi, Réka Káldos, Munjae Park, Csaba Szabó, Tamás Váczi, Kálmán Török, Bianca Németh, György Czuppon (2017a): Detection of small amounts of N_2 in CO_2-rich high density fluid inclusions in mantle xenoliths, *European Journal of Mineralogy*, 3:423-431.

Park Munjae, **Márta Berkesi**, Jung Haemyeong, Kil Youngwoo (2017): Fluid invasions in the lithospheric upper mantle based on fluid inclusion study in spinel peridotites from Adam's Diggings beneath the western margin of Rio Grande Rift, USA, *European Journal of Mineralogy*, DOI: 10.1127/ejm/2017/0029-2658.

S. Ferrero, R. Braga, **M. Berkesi**, B. Cesare, N. Laridhi Ouazaa (2014): Production of metaluminous melt during fluid-present anatexis: an example from the Maghrebian basement, La Galite Archipelago, central Mediterranean, *Journal of Metamorphic Geology*, 32: 209-225.

Book chapter:

Berkesi Márta (2015): Upper mantle xenoliths from the Bakony-Balaton Highland Volcanic Field (In Hungarian with English abstract), In: Kónya Péter (Ed.): A Bakony–Balaton felvidék vulkáni terület ásványai. Miskolc; Budapest (Hungary): Herman Ottó Múzeum; Magyar Földtani és Geofizikai Intézet , 2015. pp. 125-134. (TQS Monopgraphs; 1.)

Manuscript under revision:

Júlia Dégi, Kálmán Török, Bianca Németh, Diether Rhede, Ágnes Takács, **Márta Berkesi**, Gerlinde Habler, Rainer Abart: Complexity of kelyphitic rims after garnet - Part I: Multi-stage fluid-assisted alteration of submicron-sized symplectites, submitted to *Contribution to Mineralogy and Petrology*

Manuscript in preparation:

Márta Berkesi, György Czuppon, Csaba Szabó, István Kovács, Silvio Ferrero, Marie-Christine Boiron and Andrea Perucchi: Pargasite in fluid inclusions of mantle xenoliths from northeast Australia (Mt. Quincan): sign of interaction of asthenospheric fluid. Manuscript will be submitted to *Chemical Geology* in the framework of the Special Issue of XXIII ECROFI conference. Submission opens in November 2017

László E. Aradi, Ábel Szabó, **Márta Berkesi**, Alberto Zanetti and Csaba Szabó: Fluid transfer in the lithospheric mantle beneath the margins of the Pannonian Basin - a xenolith study. Manuscript is planned be submitted to *Lithos.*

Abstracts (with no paper accepted in the same subject):

Márta Berkesi, György Czuppon, Csaba Szabó, István Kovács, Silvio Ferrero, Marie-Christine Boiron and Andrea Perucchi (in preparation): Pargasite in fluid inclusions of mantle xenoliths from northeast Australia (Mt. Quincan): sign of interaction of asthenospheric fluid. ECROFI 2017 conference, Book of Abstracts, p. 114.

Berkesi Márta, Pintér Zsanett, Czuppon György, Kovács István János, Ferrero, Silvio, Boiron, Marie-Christine, Szabó Csaba (2017b): Asztenoszféra-eredetű fluidumok spinell lherzolitokban: esettanulmányok északkelet-Ausztráliából és Kamerunból (in Hungarian). 8. Kőzettani és Geokémiai Vándorgyűlés, abstract book, p 27-29.

Posters (where the mention of the project number was solely allowed on the poster itself):

László E. Aradi, Ábel Szabó, **Márta Berkesi**, Alberto Zanetti and Csaba Szabó (2017): Fluid transfer in the lithospheric mantle beneath the margins of the Pannonian Basin - a xenolith study. Goldschmidt 2017 Paris, Abstracts

Szabó, Á., **Berkesi, M.**, Aradi, L. and Szabó, Cs. (2017): Preliminary results on fluid inclusions in mantle xenoliths from the Perşani Mountains, Eastern Transylvanian Basin, ECROFI 2017 conference, Book of Abstracts, p. 230.

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