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Evaluation of the Habilitation Thesis submitted by Dr. Aleesanfro Farbbrizio

Dear Habilitation Committee

It is a great pleasure to provide an evaluation of the Habilitation thesis submitted by Dr. Alessandro Fabbrizio to the Faculty of Science of the Charles University of Praha. I know Alessandro from his postdoctoral stay at our institute 10 years ago working with my colleague Max Schmidt and followed his academic career since then.

The submitted thesis is a comprehensive document composed of an introductory summary of the most pertinent publications outlining rational of the studies and their mutual interrelations followed by nine publications divided into 3 major topics: (1) kinetic disequilibrium processes, (2) solid-liquid trace element partitioning and (3) phase equilibria studies of evolved alkaline systems.

In the following, I shortly comment on the nine publications before providing a general summary of the thesis:

(1) The first publication (Fabbrizio, 2019) concerns the zoning of major and trace elements of olivines from the Kilauea Iki lava lake (Hawaii) to unravel the solidification processes and potential disequilibrium formed during rapid cooling of basaltic magmas. This work that was evidently much earlier initiated, bases on a large number of elemental profiles through olivines from various depths within the lava lake demonstrating that cooling rates influence the type and extent of zoning which in turn can be utilized to constrain the cooling history. Phosphorous zoning is of particular interest as it clearly retains zoning features associated with rapid, kinetically driven crystallization. Overall, this is solid work based very careful analyses of natural rock samples and fundamental understanding of growth and diffusion related processes operating during solidification of magmas in shallow level reservoirs.

(2) The paper by Arzilli et al (2018) addresses a pertinent issue regarding application of trace element partitioning in magmatic systems. The work bases on experimental phase equilibria of a trachytic system (from the Campi Flegrei igneous system) combined with trace element partitioning of major and trace elements between trachytic melt and alkali-feldspar. The authors performed time series experiments at conditions of crustal magma reservoirs to evaluate and quantify the potential influence of rapid, kinetically driven disequilibrium versus equilibrium growth on trace element partitioning and found a clear dependence with generally increasing partition coefficients for compatible trace elements such as Ba and Sr with increasing growth rate (or extent of undercooling). To my knowledge, this is the first time this has been experimentally confirmed under controlled conditions in evolved alkaline magmas and has profound impact in the way we apply trace element partitioning to volcanic systems. They finally provide easy applicable equations to estimate crystallization time scales of alkali-feldspars from apparent (measured) trace element partitioning for Sr and Ba and could constrain that for the Campi Flegrei system investigated, residence time of magmas showing disequilibrium Ba and Sr partitioning were in the order of a few days before eruption. This is a very nice study, with the only caveat that the application might be restricted to highly polymerized evolved alkaline rocks, as diffusional re-equilibration might be much faster in hotter, less polymerized basaltic systems.

(3) Newcombe et al. (2014) is a publication devoted to the chemical zonation in olivine-hosted melt inclusions (MI) from a variety of (tholeiitic) basalts from oceanic fracture zones and the Galapagos Island. This is seminal contribution, excellently written tackling a fundamental issue regarding the use of melt inclusions to constrain the liquid line of descent of magmas. Careful profiles through melt inclusions reveal strong and systematic zonation of the MI for major elements. Analysis of the zoning profiles clearly reveals that crystallization of olivine along the wall of the inclusion in combination with diffusion in the boundary layer adjacent to the growing crystal is responsible for the observed zoning patterns. The authors modelled the zoning pattern using a 1-dimensional code combining crystal growth and diffusion of MgO in the adjacent melt successfully reproducing the observed zoning patterns as a function of cooling rates in the magma. This paper represents an exclamation mark for the community using (reconstructed) melt inclusions neglecting boundary layer diffusion to constrain liquid lines of descent. The paper further shows that the zoning patterns can, however, be utilized to constrain the cooling history of basaltic magma.

(4) Papers 4-6 contain the results of experimental studies to determine the partition coefficients of Radium for a variety of crucial mineral species in alkaline magmatic systems. These papers are directly relevant for the geochemical community dealing with U-Th-Ra disequilibrium dating to delimit the residence time of magmas in crustal magma reservoirs prior to eruption. The first paper of this series (Fabbrizio et al., 2008) contains the results of an experimental study on the Ra partitioning between leucite ($KAlSi_2O_6$) and a phonolitic melt typical for the Vesuvius volcanic system at ambient pressure. The results indicate that Ra is much more compatible in leucite than Ba that was previously used as a proxy for Ra. This has significant impact on the calculated ages using U-Th-Ra disequilibrium, basically resulting unconstrained (i.e. negative) ages for most of the cases studied to date. This and the following two studies are unique as the determination of Ra partitioning coefficients was not possible before due to the fact that Ra is highly radioactive and can thus only be studied under specific security measures and requires unprecedented

analytical precision in terms of detection limits. This was achieved conducting experiments optimizing the size of leucite crystals together with large melt pools and laser-ablation ICP method that were absolute state-of-the-art at the time (2007-2009).

(5) Fabbrizio et al. (2009) is a similar experimental study conducted at ambient pressure on the partitioning of Ra and other trace elements between feldspars (plagioclase and alkali-feldspar) and trondhjemitic (plagioclase) and rhyolitic (alkali-feldspar) liquids respectively. Whereas Ra behaves incompatibly in plagioclase with a rather strong dependence on anorthite (Ca) content, it behaves compatibly in alkali-feldspar. Similar to leucite, there is significant difference in the partitioning of Ra and Ba (used as proxy before), in this case Ba being more compatible then Ra due to its larger ionic radius fitting less well into the 6-9 coordinated A- site of feldspar. The paper extensively discusses the consequences of the newly obtained partition coefficients on the results of Ra-Th model ages that generally become younger than previously inferred.

(6) The final paper of this series – Fabbrizio et al. (2010) likewise reports the results of an experimental study devoted to the partitioning of Ra between phlogopite mica and a lamproitic melt at 1GPa pressure in a piston cylinder apparatus. Identical analytical methods were employed to determine the trace element partitioning. Results show that Ra is the most compatible element (even exceeding K), basically positioned at the top of the Onuma parabola describing the partitioning of trace elements between solid and liquid as a function of ionic radius of the elements. In this paper, the authors provide a comprehensive summary of Ra partition and Ra/Ba distribution coefficients as a function of temperature, mineral composition and/or Ba-partitioning (that is commonly determined instead of Ra) for all important minerals crystallizing in igneous systems over a wide range of pressure and temperature conditions. They use this as bases to discuss the impact of partitioning of Ra among the liquid and the different minerals during crystallization of magmas on the U-series disequilibrium dating. They conclude that due to the different Ra and Ba partitioning between melt and the most important (Ra hosting) minerals, Ra/Ba-Th isochrones do not work, but alternatively two mineral isochrones based on true partition coefficients might indeed provide a more successful approach to constrain pre-eruptive storage timescales in magmatic systems.

Despite the importance of this research for the isotope geochemical community, these papers have not (yet) received the attention they deserve. This does neither disqualify the work nor the author(s) but rather the community that did not realize the impact of this work on their time-scale determinations!

(7) The final three papers contain the results of the research conducted during the PhD thesis of Alessandro dealing with phase equilibria of magmas from the Phlegraean Fields. Fabbrizio & Carroll (2008) reports the results of a classical phase equilibria study on trachytes (pumice and obsidian) conducted under water-saturated conditions and pressures ranging from 50-200 MPa and temperatures of 700 (subsolidus) to 880 (near liquidus). The study was designed to constrain the pre-eruptive conditions of the specific eruption (20 ky Breccia Museo Eruption) that was delimited to 780°C and 140-200 MPa. These values are, however, only strictly valid of the fluid was pure H_2O, which is unlikely, at least CO_2, but possibly also sulfur species (e.g. melt inclusion record from the Phlegraean Fields, composition of fumaroles) are present that would decrease

H_2O-activity and shift temperatures to higher values. This is mentioned in the manuscript, but should have been evaluated also experimentally as phase equilibria most likely change in addition (influence on biotite stability, potentially shifting the pre-eruptive conditions to even greater depths (>135 MPa)?

(8) Fabbrizio et al. (2006) – The last two papers provide experimental data to constrain the geohygrometer biotite + magnetite + sanidine to estimate water fugacities of fluid-saturated, hydrous evolved magmas. The hygrometer has been proposed earlier but the paper provides novel experimental data conducted under controlled oxygen- and H_2O-fugacity conditions. In detail, the work evaluates the various proposed activity models for biotite solid-solutions and demonstrates that the partly ionic model of Czamanske and Wones (1973) best reproduces the experimental data. They finally applied the newly calibrated model to various examples ranging from calc-alkaline to alkaline differentiated magmas and concluded that the model generally provides “reasonable” values (whatever that means?).

(9) Fabbrizio et al. (2008) is basically an extension of the previous paper providing additional experimental data on the Phlegraean Fields trachytes; in particular data on experiments containing CO_2 (i.e. at H_2O-activities less than unity) and under strictly buffered fO_2 conditions (critical as magnetite is an essential component of the hygrometer and the equation contains free oxygen). They employed internally-heated pressure vessels in addition to cold-seal pressure vessels used in the previous phase equilibria studies. The paper contains a comprehensive discussion of the impact of various activity models on the hygrometer concluding again that the partly ionic model performs best and finally extract the H_2O-fugacity of Phlegraean Field trachytes in the magma reservoir.

Overall, this is an impressive collection of predominantly experimental research conducted by Alessandro Fabbrizio over the last 15 years well summarizing the principle research he was conducting over this period and the contributions he made. Alessandro is an excellent experimental petrologist – very carefully and very experienced - tackling some of the most difficult experimental tasks in high-pressure, high-temperature research in igneous systems such as partitioning of radioactive elements and disequilibrium - equilibrium relations that are notoriously difficult because path-dependent by definition. In addition, Alessandro is an experienced igneous petrologist/geochemist and volcanologist with focus on (sub-)volcanic processes constraining them by petrography, petrology, phase equilibria studies and geochemistry (bulk and minerals). More recently he moved towards disequilibrium features including impact of diffusional processes on the evolution of volcanic systems, which, in my opinion, is clearly a very timely topic targeting duration and rates of igneous processes. Alessandro is not the first author on some of the papers contained in this thesis, but in these cases, it is obvious that he provided considerable and essential input both experimentally and analytically, but also intellectually, clearly justifying including them in the thesis. To summarize, this thesis contains three essential parts that I would describe in the following way: (1) phase equilibria on evolved alkaline systems – solid PhD work, not particularly original more classical, but well appreciated by the community, (2) Ra and other trace element partitioning between feldspars, feldspatoids and mica – state-of-the-art experimental petrology, superb experiments and analytics, very significant but did not yet receive the attention it deserves; and

(3) disequilibrium crystal growth and diffusional processes in igneous systems – very original, highly relevant and lots of future potential. From this short summary, it is evident that Alessandro is on the "climbing limb" of his career developing from a well-guided PhD student to an experienced experimental petrologist / volcanologist to a mature scientist.

Basing on the above evaluation, I clearly and with no hesitation recommend acceptance of the Habilitation thesis and promotion of Dr. Alessandro Fabbrizio by the Faculty of Science of the Charles University of Praha.

Sincerely,

Prof. Dr. Peter Ulmer

PS. On the following page I added a few questions that might be asked during the habilitation.

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For the defense of the Habilitation thesis, the following general and more specific questions might be raised (in the order of publications):

1) Fabbrizio (2019, Periodico, olivines Kilauea Iki) – Can you derive minimum residence times of olivines in the Kilauea Iki lava lake from the difference in P, Ti, Al and divalent cation zoning patterns assuming different diffusivities in olivine? Can you separate growth and diffusion related features (how)?
2) Arzilli et al. (2018, Chemical Geology – trace element diffusive re-equilibration) – To what extent boundary layer diffusion affects your partition coefficients derived from the short duration experiment? How can you distinguish between "disordered growth" of the alkali-feldspar crystal and boundary layer effects being responsible for the increased Ba and Sr partitioning coefficients with decreasing run duration?
3) Newcombe et al. (CMP, 2014) – What does the two-stage cooling model physically infer in the course of lava emplacement and solidification? What is the justification for a two-stage model beyond better fitting the profiles?
4) Fabbrizio et al. (2008, Chemical geology, leucite - Ra) – What does the fact that divalent cations smaller than Sr do not fit on Onuma parabola imply? [different lattice sites, interstitial sites, located in the "channel" of leucite].
5) Fabbrizio et al. (2009, EPSL, feldspar – Ra) – You state that Na is compatible in albitic plagioclase – Is this realistic considering well-known anorthite – albite melting relations indicating that plagioclase is always more anorthitic than coexisting melt? [most likely this is an artifact because in such a system one should actually look at the Na/Ca distribution coefficient in order to take additional melt components into consideration as Na is not a trace but a major element of the system; Na/Ca partitioning is still in favor of the melt (Na/Ca plag =1, Na/Ca melt = 1.63)]
6) Fabbrizio et al. (2010, Lithos, phlogopite – Ra):
   Technical question – Why are the iron contents of all runs except the one at 1050 °C basically zero (very low) despite the fact that the starting material contained 5.8 wt.% FeO? [iron-loss? and if so why is this so extensive – very low fO_2?]
   General question – You state that classical Ra/Ba – Th/Ba diagrams do not work to calculate residence times, what do you propose alternatively based on your results?
7) Fabbrizio & Carroll (2008, JVGR, Phase equilibria Phlegraean fields) – The experiments reported are all water saturated, how would the phase equilibria and derived pre-eruptive conditions change when the magmas where either (a) fluid undersaturated or (b) contain other volatiles in particular CO_2 in addition?
8) and 9) Fabbrizio et al. (2006, 2008, bio-mag-san-geohygrometer) – Why is the value you derive (735 bars) for the Phlegraean Field magmas a minimum value when additional CO_2 is present in the fluid? [according to the governing equation the value of fH_2O you get should be independent of fluid composition, but dependent on fO_2 (which is another critical issue), i.e. water contents assuming fluid saturation would actually be maximal and not minimal in case other fluid species are present]