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KINETIC DISEQUILIBRIUM PROCESSES, (RADIOACTIVE) TRACE
ELEMENTS FRACTIONATION, AND PHASE EQUILIBRIA AS A TOOL TO
CONSTRAIN PRE- AND SYN-ERUPTIVE CONDITIONS

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INTRODUCTION

This habilitation thesis in (experimental) magmatic petrology is a compilation of the major papers of my research, from the period of my doctorate to today, that focuses on a) kinetic disequilibrium processes, b) (radioactive) trace elements fractionation, and c) phase equilibria.

The first focus: I started to be interested in kinetic disequilibrium processes when I was a postdoctoral scholar at Caltech under the guidance of my advisor E.M. Stolper, then some aspect of this topic have been experimentally investigated in co-operation with my colleague F. Arzilli of Manchester University. In parallel, during the last ten years many researchers have started to study this subject showing that the products, i.e. presence of element zoning in minerals, of kinetic disequilibrium processes are common in many natural rock types, including mantle-derived xenoliths (Mallmann et al., 2009; Baziotis et al., 2017, 2019), komatiites, terrestrial basalts, andesites, syenites, dacites, gabbros (Milman-Barris et al., 2008; Tschegg et al., 2010; Sakyi et al., 2012; Shea et al., 2015; Welsch et al., 2013, 2014, 2016; Bouvet de Maisonneuve et al., 2016), various meteorite classes and lunar basalts (Milman-Barris et al., 2008; Boesenberg et al., 2012; Shearer et al., 2013; Elardo and Shearer, 2014; Ennis and McSween, 2014; First and Hammer, 2016; McCanta et al., 2016) as well as in experimentally crystallized mineral phases (Milman-Barris et al., 2008; Bosenberg and Hewins, 2010; Welsch et al., 2014; Shea et al., 2019). In addition, chemical zonation were reported in picritic melt inclusions from Mt Shasta (Anderson 1974), in high-Ca boninitic inclusions from the Tonga arc (Danyushevsky et al., 2002), in inclusions from the Sommata cinder cone on Vulcano Island in the Aeolian arc (Mercier 2009), and in inclusions of Mid-Atlantic ridge pillow basalt (Colin et al., 2012). The reasons for this interest are obvious: minerals and melt inclusions contain hidden information that not only reveal the complexity of magmatic processes in response to cooling but they represent also an open window on an inaccessible area of the Earth's interior given for volcanic systems most of these processes happen in pre- and syn-eruptive contexts. These trapped information, evidenced as chemical zoning in some particular element, are related to the magmatic history experienced by their hosts such as changing temperature, events of magma mixing, episodes of rapid growth. Their preservation is a direct function of the diffusivity of elements in minerals and melt as well as of their exposure at magmatic temperatures for a specific time that will tend to re-homogenize the minerals and melt compositions. In other words, these preserved or relict chemical features in minerals and melt inclusions are the direct expression of a balance between the kinetic disequilibrium process that originated them and the subsequent equilibrium process tending to re-homogenize them. As a consequence our ability in reading and interpreting these features offer to us a powerful tool for a better understanding of otherwise inaccessible magmatic processes and in some case for using them as real geo-chronometer to give a temporal constrain to processes happening in proximity of an eruptive event. The widespread evidence of disequilibrium processes both in natural rocks and in experimental charges question also against the concept of equilibrium conditions that is normally assumed by petrologists.

The focus on (radioactive) trace elements fractionation was developed when I was a postdoctoral researcher at ETH under the guidance of my advisor M.W. Schmidt. The input for this line of research came from the needed to improve the U-series

disequilibria method used to date volcanic rocks younger than 8000 years (Volpe and Hammond, 1991; Reagan et al., 1992; Volpe, 1992; Schaefer et al., 1993; Cooper et al., 2001; Cooper and Reid, 2003; Turner et al., 2003a,b; Rogers et al., 2004; Tepley et al., 2006; Zellmer et al., 2008). In the timescale 0-8000 years ago, the $^{226}\text{Ra}/^{230}\text{Th}$ disequilibrium (^{230}Th decays to form ^{226}Ra with a half-life of 1599 years) can be used to constrain the time scales of magmatic processes given the fractionation of these isotopes produces disequilibrium that will be resorbed after five half-lives of the daughter isotope (i.e. ^{226}Ra). The complication in the $^{226}\text{Ra}/^{230}\text{Th}$ system arose from the fact that no long-lived or stable Ra isotope than ^{226}Ra was available for normalization procedure. Thus, Ba was used as an analog to Ra because of its similar chemical behavior, only a small difference of about 5% in ionic radius between Ra and Ba (Shannon, 1976), assuming that the Ra and Ba crystal/melt partition coefficients were equal. However, modeling trace element partitioning (Blundy and Wood, 1994, 2003) predicted that the 5% difference in ionic radius between Ra and Ba would have resulted in significantly different partition coefficients for the two elements in silicate minerals (Cooper et al., 2001), thus potentially affecting the results of dating by the method ^{226}Ra -Ba- ^{230}Th . This experimental study solved this issue determining the Ra distribution coefficient mineral/melt for leucite, plagioclase, alkali-feldspar, and phlogopite coexisting with silicate liquids. The purpose of this research was, then, to quantify the fractionation of Ra from Ba in these magmatic minerals that may incorporate Ra and thus, to correctly calculate mineral model ages from ^{226}Ra -Ba- ^{230}Th measurements.

The last focus on phase equilibria was the subject of my PhD work performed at Camerino University under the guidance of my supervisor M.R. Carroll. Explosive volcanic eruptions represent one of the biggest natural hazard given the profound economic and societal consequences they can produce (Blundy and Cashman, 2008). Although at the current state of knowledge such eruptions are unpredictable a better understanding of the behavior of explosive volcanoes will improve our volcano monitoring and disaster mitigation systems. Because volcanic systems are inaccessible the study of their erupted products provide to us the key for understanding what happens prior to an during an eruption. The determination of pre-eruptive magma storage conditions (T , P , $f\text{O}_2$, $f\text{H}_2\text{O}$, volatile contents) is based on the reproduction of natural phase compositions in experimental charges (Hammer, 2008). A typical approach to constrain the stability fields of the mineral phases in the P - T space is to use a powdered natural rock as starting material and to perform the experimental runs in pressure apparatus for simulating physical conditions relevant to volcanic processes in the Earth's upper crust. Post experiment textural examination and chemical analysis of run products are used to determine the degree of matching with natural samples and thus with natural pre-eruptive conditions. Chemical equilibrium and phase stability are verified by examining crystal texture, by demonstrating the run time-independence of the experimental products, and by approaching the experimental P and T conditions both in forward and reverse way. Pre-eruptive conditions have been determined by phase equilibrium studies both for recent [Santa Maria 1902 (Andrews, 2014); Novarupta 1912 (Coombs and Gardner 2001; Hammer et al., 2002); Mt. Pelée 1929 (Martel et al., 1999; Pichavant et al., 2002); SW Trident 1953-1974 (Coombs et al., 2000); Bezymianny 1956 (Shcherbakov et al., 2013); Arenal 1968-2010 (Parat et al., 2014); St. Helens 1980, (Rutherford et al., 1985; Rutherford and Devine, 1988); Mt. Pinatubo 1991, (Rutherford and Devine, 1996; Scaillet and Evans, 1999; Hammer and Rutherford,

2003); Unzen 1992 (Holtz et al., 2005); Soufriere Hills 1996 (Barclay et al., 1998; Couch et al., 2001); Erebus 1997 (Moussallam et al., 2013); Arenal 2006 (Petermann and Lundstrom, 2006); Tungurahua 2006 (Andújar et al., 2017); Mt. Merapi 2010 (Erdmann et al., 2016); Shinmoe-dake 2011 (Suzuki et al., 2013)]; and historical eruptions [(Chaine des Puys 15000-9200 y.b.p. (Martel et al., 2013); Laacher See 12900 y.b.p. (Harms et al., 2004); Kizimen 12000-8400 y.b.p. (Browne et al., 2010); Black Butte 10000 y.b.p. (McCanta et al., 2007); Santorini 3594 y.b.p. (Cottrell et al., 1999); Aniakchak 3430 y.b.p. (Larsen, 2006); Hekla 2879 y.b.p. (Weber and Castro, 2017); Montana Blanca 2020 y.b.p. (Andújar and Scaillet, 2012); Teide-Pico Viejo 1800 y.b.p. (Andújar et al., 2013); Teide 1150 y.b.p. (Andújar et al., 2010); Mt. Pelée 650 y.b.p. (Martel et al., 1999; Pichavant et al., 2002); Stromboli 800-1600 A.D. (Di Carlo et al., 2006); St. Helens 1480 A.D. (Gardner et al., 1995); Usu 1663 A.D. (Tomiya et al., 2010)] spanning a compositional range from basalt to rhyolite and phonolite, temperature from 725 to 1300 °C, and pressure from 15 to 450 MPa. As expected, the pre-eruptive equilibrium temperatures are negatively correlated with the bulk silica content while the pre-eruption depths of equilibration show no clear correlation with bulk composition or matrix melt composition (Hammer, 2008). The aim of this research was to apply the phase equilibria method for defining the pre-eruptive conditions of an explosive event that occurred 20 ky ago in the Phlegrean Fields Caldera. Then, these experimentally derived pre-eruptive conditions would have been helpful for the Department of the Italian Civil Protection to mitigate the volcanic risk that is considered to be really high given the Phlegrean Fields area is inhabited by about 1.5 million people.

Here is a brief overview of the petrological subject and the paper in which it was described:

	SUBJECT	ARTICLE
1	Zoning in olivines from the Kilauea Iki lava lake	Fabrizio 2019
2	Re-equilibration time and trace element behavior	Arzilli et al. 2018
3	Zoning in olivine-hosted melt inclusions	Newcombe et al. 2014
4	Leucite-phonolite Ra partitioning	Fabrizio et al. 2008
5	Feldspar minerals-silicate melts Ra partitioning	Fabrizio et al. 2009
6	Phlogopite-lamproite Ra partitioning	Fabrizio et al. 2010
7	Pre-eruptive conditions in the Phlegrean Fields	Fabrizio and Carroll 2008
8	Pre-eruptive water fugacity in the Phlegrean Fields	Fabrizio et al. 2009
9	Estimation of magmatic water fugacity	Fabrizio et al. 2006

The following is an extended abstract of the main outcomes for each of these articles, which constitute the main part of this thesis:

Kinetic disequilibrium processes

- 1) Fabrizio, A. (2019) An investigation on the zoning associated with divalent elements, P, Cr, Al and Ti in olivines from the Kilauea Iki lava lake (Hawaii). *Periodico di Mineralogia* 88, 185-201.

In this paper I have studied the preserved chemical zoning in olivine crystals to understand the cooling history of the Kilauea Iki lava lake. The studied samples were recovered by the USGS during the drilling, core KI81-1, of the lake in 1981. Olivine

crystals were studied for their zoning by electron microprobe to obtain X-ray intensity maps, single spot analyses, and line profiles. Only olivine crystals recovered from the shallower portion of the lava lake (<64 m) display concentric positive (i.e. from high to low concentrations) zoning from core to rim for Fo contents and Ca associated with negative concentric zoning for Mn, crystals from greater depth show no zoning in divalent elements. It is suggested that zoning in divalent elements was driven by the different cooling history of the samples as a function of their position (depth) inside the lava lake and that is better preserved in the crystals that have experienced the lower residence temperature coupled to the highest degree of undercooling (expressed as the difference between the liquidus temperature of olivine and the temperature of the sample at the time of its recovery) and cooling rates (expressed as the degree of cooling per unit of time). High degrees of undercooling associated with high cooling rates promote the formation and development of strong zoning in divalent elements, whereas low residence temperatures permit these zoning to be preserved for longer time respect to higher residence temperatures. Clearly, the shallower samples (< 64 m depth) are those who had experienced the highest degree of undercooling coupled with the highest degree of cooling rate given the surface of the lava lake cooled in air whereas its bottom was in contact with rock and consequently the heat loss was less efficient. Samples from intermediate depths (64-78 m) show no zoning in divalent elements because being trapped between two layers of hot magma they experienced the lower degrees of undercooling and cooling rates but the highest residence temperatures, consequently their zoning in divalent elements was fainter than those observed in shallower crystals and easily rehomogenized with time. Also olivine crystals in samples recovered from the deeper section of the lake (>78 m) have no zoning in divalent elements despite the temperature at the time of drilling for some of these samples is comparable to the sample's temperature of the shallower samples. Given these samples lie between a thick layer of hot magma at their top and a layer of country cold rock at their bottom, it could be supposed they have experienced an undercooling and cooling rate intermediate respect to samples of the upper levels. Despite their temperature at the time of recovery is similar or lower to that of the deepest samples still preserving zoning in divalent elements, it could be supposed that the undercooling itself was powerful enough to generate a strong zoning but it was buffered by the relatively low cooling rates these samples experienced, resulting in a final zoning that was weaker than expected and that was erased by their residence temperature. In addition, the strong linear correlations between Fo contents and concentrations of Ca (positive), Mn (negative), and Ni (positive) can be interpreted as being the result of the cooling and crystallization of the magma body without no recharge event. Also the absence of reversely zoned and/or resorbed olivines is taken as an evidence of the lacking of subsequent events of magma recharge. To summarize, the divalent elements record in the crystallizing olivine crystals only the variations in temperature as the magma body of the lava lake loses its heat and cools down. Other than the zoning in divalent elements an oscillatory and skeletal zoning for P is observed, without any correlation with Fo contents, in all examined crystals independently respect to their recovery depth. The P-zoning is sometime spatially related with zoning in Cr-Al-Ti. The unrelated P-zoning (\pm Cr-Al-Ti) features with the zoning of divalent elements suggest that the P enrichments are provoked by excessive incorporation of P in olivine crystals during rapid events of crystal growth. The entrapment of P in olivine at disequilibrium concentrations well above the equilibrium values coupled with its low diffusivity in olivine permit that the P zoning features are accurately preserved over long exposures at magmatic temperatures. The high-P

features have been used, when possible together with high-Al and -Ti features, to estimate the growth rate of the olivine crystals that entrapped them. The estimated growth rates imply that an olivine 500 μm wide would require only 8 minutes to crystallize and entrap P and other slow diffusing elements to develop the related zoning. These events of rapid olivine growth were followed by period of slow growth during which the P-poor region developed and the crystals acquired their final shape. All the above observations support the idea that the Kilauea Iki lava lake could be viewed as approaching closely an ideal closed system where its continuous and linear cooling provoked both the fast crystallization of olivines, recorded by P zoning and related elements, and their simple and normal zoning recorded by the divalent elements.

- 2) Arzilli, F., Fabbrizio, A., Schmidt, M.W., Petrelli, M., Maimaiti, M., Dingwell, D.B., Paris, E., Burton, M., Carroll, M.R. (2018) The effect of diffusive re-equilibration time on trace element partitioning between alkali feldspar and trachytic melts. *Chemical Geology* 495, 50-66.

High-silica and alkali-rich magmas are often characterized by explosive eruption styles, therefore the determination of kinetic effects on mineral/liquid partition coefficients for highly evolved systems can significantly improve our understanding of magma evolution processes. This should allow the development of new magma chamber and conduit models that take into account disequilibrium crystallization and magma evolution in the conduit and hence constrain timescales of magmatic processes, facilitating the evaluation of volcanic hazards. In this study the influence of kinetic effects involving diffusive re-equilibration, growth rate, and order-disordered crystal growth on trace element partitioning between alkali feldspar and trachytic melt have been investigated at 500 MPa, 870-890 $^{\circ}\text{C}$, and water undersaturation (2 wt% H_2O), through short (18-39 h) and long (192 h) experiments simulating thus, respectively, disequilibrium and near-equilibrium conditions. As expected Ba and Sr behave always compatibly but their partition coefficients are strongly affected by the rapid growth of alkali feldspar crystals that characterize the short-duration experiments. The rapid crystals growth favors a disordered growth (development of anhedral crystals with tabular, prismatic elongated, acicular, skeletal and hopper shapes) and the creation at the interface crystal/liquid of a boundary layer enriched in incompatibles elements and depleted in compatible elements leading to an over-incorporation of Ba and Sr in the crystal lattice that will result in higher values of the partition coefficients than those obtained through long-duration experiments. With increasing the experimental time, the crystals' growth rate decreases and the longer timescale of diffusive re-equilibration, i.e. the chemical composition of the boundary layer tend to re-homogenize with the composition of the far-field liquid depending on the elements diffusivity, facilitates the incorporation of elements within the crystal lattice through ordered growth (development of crystal with tabular and prismatic euhedral shapes) resulting in lower partition coefficient values. These results show that the kinetic of crystals growth and the subsequent process of diffusive re-equilibration have a strong influence on the partitioning behavior of elements between alkali-feldspar and melt, implying that the partition coefficients of some element such as Ba and Sr can be used to establish time-scales of crystallization processes under pre- and syn-eruptive conditions. In natural magmatic systems events such as magma mixing and magma ascent are examples of a rapid change from equilibrium to disequilibrium conditions. The application of our results to alkali feldspar in rocks

from Campi Flegrei (Italy), which is an active volcanic caldera characterized by evolved alkaline rocks (trachytes, trachyphonolites and phonolites) with alkali feldspar as the dominant crystal phase, constrain the magma residence time at subliquidus conditions in a reservoir to a maximum of 6 days under disequilibrium conditions and to a minimum of 9 days upon approaching near-equilibrium conditions. However further studies investigating the influence of other factors such as undercooling, cooling and decompression rate on trace element partitioning behavior are needed to provide definitive constraints of crystallization timescales. These results also highlight the different timescale, several days vs. few hours, needed for the transition from disequilibrium to equilibrium conditions for mineral phases crystallizing in trachytic and basaltic magmatic systems reflecting, probably, the differences in temperature, melt polymerization and diffusivity.

3) Newcombe, M.E., Fabbriozio, A., Zhang, Y.X., Ma, C., Le Voyer, M., Guan, Y., Eiler, J.M., Saal, A.E., Stolper, E.M. (2014) Chemical zonation in olivine-hosted melt inclusions. *Contributions to Mineralogy and Petrology* 168:1030, <https://doi.org/10.1007/s00410-014-1030-6>

A significant chemical zoning in major, minor, trace, and volatile elements has been discovered in naturally glassy olivine-hosted melt inclusions sampled from three different magmatic settings: (a) glassy rims of pillow basalts sampled from the Siqueiros transform fault; (b) a hornito on Santiago Island, (Galapagos); (c) a lava flow on a submarine flank of Fernandina Island (Galapagos). It is proposed that the zoning develops during the last few minutes to hours of a volcanic eruption when the olivine-hosted melt inclusions (MIs) cool and crystallize olivine on their walls, producing olivine-depleted boundary layers in the melt adjacent to their olivine hosts. These boundary layers are depleted in elements that are compatible in olivine and enriched in elements that are incompatible. The preserved concentration profiles in glassy MIs are the result of the competition between diffusive relaxation of these boundary layers into the centers of the MIs and replenishment of the boundary layers by continued olivine crystallization. The extension and preservation of the concentration profile for a given element is a function of several factors such as the diffusivity of the element in the melt, its partition coefficient olivine/melt, the olivine's growth rate, and the thermal history and size of the MI. Consequently, in the same MI the concentration profiles are different from element to element, and the concentration profiles of the same element will differ from inclusion to inclusion. It is observed that compatible elements tend to produce a parabolic shape profile concave downward, symmetrical respect to the center of the MI, whereas for the incompatible elements the parabolic profile is concave upward. Exceptions are represented by the concentration profiles of CaO, H₂O, and F, suggesting that these components are exhibiting multicomponent diffusion effects and/or that volatiles have been lost from the inclusions into the host olivine late in their cooling histories. Evidence of multicomponent diffusion effects are observed also for other components such as FeO showing concentration profiles influenced by uphill diffusion, whereas the resulting concentration profiles of rapidly diffusing components such as Na₂O and K₂O are affected by interaction with slow diffusing components such as SiO₂ and Al₂O₃ given their similar extension. An implication of this chemical zonation is that analyses of zoned MIs, even if made near the centers of the MIs, will be diffusively fractionated from the liquid line of differentiation of their parental melts (i.e., the diffusion of fast-diffusing elements such as Ca can extend to the center of a ~150 μm radius MI). A

model has been developed of the time-dependent evolution of MgO concentration profiles in MIs due to simultaneous depletion of MgO at the inclusion walls due to olivine growth and diffusion of MgO in the MIs in response to this depletion. This model was applied to the observed concentration profiles to constrain their thermal histories. Cooling rates determined by a single-step linear cooling model range from 150 to 13000 °C/h from the liquidus temperatures down to ~1000 °C, consistent with previously determined cooling rates for basaltic glasses. Despite the studied MgO compositional trends are reproduced well by this simple single-step linear cooling, it is observed that MgO concentration profiles in some melt inclusions are better fit by a two-step cooling history, from liquidus temperatures to ~1000 °C, with a slower-cooling first step from 64 to 1100 °C/h followed by a faster-cooling second step from 320 to 22000 °C/h, over a total time period from 40 s to just over 1 h with most MIs having cooling histories ~5 min in length. In general most of the MIs from subaerial samples have MgO profiles that are well described by single-step linear cooling histories, with durations of < 2 mins, consistent with the efficient fragmentation observed during this style of volcanic eruption. Whereas MgO profiles in MIs from submarine samples and some from subaerial samples require a two-step cooling history with the lowest recorded cooling rates of the entire sample set (64 °C/s for ~1 hr, then 320 °C/s for ~20 mins) reflecting, probably, the slow cooling of the MIs as they travel through the magmatic conduit and/or the interior of a lava flow or pillow followed by rapid quenching of the MIs as the host phenocrysts near the melt-water interface in the case of the submarine samples or against air in the case of the subaerial samples. Given all studied MIs from the Siqueiros and Galapagos sample suites exhibit zoning profile and that chemical zonation in MIs from various tectonic setting is widely reported, it is suggested that this feature may be the norm rather than the exception and it may be nearly universal in glassy olivine-hosted melt inclusions. In that case, the zoning profile in MIs have the potential to be used as geochronometer and -speedometer to constrain late-stage syneruptive processes and it could also provide insights as a natural diffusion experiment.

(Radioactive) trace elements fractionation

- 4) Fabbriozio, A., Schmidt, M.W., Günther, D., Eikenberg, J. (2008) Experimental determination of radium partitioning between leucite and phonolite melt and ²²⁶Ra-disequilibrium crystallization ages of leucite. *Chemical Geology* 255, 377-387.

The aim of this research was first to experimentally determine at atmospheric pressure the Ra distribution coefficient (D_{Ra}), and for many other trace elements, for the pair leucite-phonolitic melt. Then, the correct D_{Ba}/D_{Ra} ratios were used to recalculate the crystallization ages for leucite in phonothephrite lavas of the 1944 eruption of Vesuvius. Knowing the partitioning behavior of elements for leucite-melt pairs is also of relevance for understanding the nature and the timescales of magmatic processes in young and strongly alkaline volcanoes. To be specific, leucite is reported from lavas of four Holocene volcanoes that have erupted in historical times: the 1944 eruption of Vesuvius, the eruptive periods between AD 1000 and 1250 of Vulcanello Island, Aeolian Island, Italy, the historical eruptions (AD 1719-1721) of the Huoshaoshan and Laoheishan volcanoes in northeastern China, and the eruptions of the Jingpohu volcanoes, northeastern China, that occurred 3490-3430 and 2470 years ago. Because of the flexible and large structure, it is expected that leucite may host significant

amounts of Ra. It is also well known that leucite stability field shrinks with increasing pressure, consequently, leucite crystallization is limited to shallow magma chambers or in the volcanic conduits, possibly only appearing during the final magma ascent. Thus calculated crystallization ages are characteristic for low-pressure (< 2 kbar) magmatic environments. The experimental results showed that Ra is the only compatible divalent cation ($D_{\text{Ra}} = \sim 2$) whereas Ba is moderately incompatible ($D_{\text{Ba}} = 0.5$). Results for monovalent cations showed that their compatibility decreases with decreasing their ionic radius from Cs to K and that Na is moderately incompatible. This experimental study conducted on a synthetic phonolite demonstrated that there is a significant fraction of Ra from Ba between leucite and melt being the ratio $D_{\text{Ba}}/D_{\text{Ra}}$ in the range 0.21-0.27, which in turn has large effect on calculated ages. Accounting for fractionation of Ra from Ba between leucite and melt the ^{226}Ra - ^{230}Th model ages were recalculated for a cumulate, a lava and a tephra, all from the 1944 eruption of Vesuvius. The original Ra-Th ages, that were determined assuming no fractionation of Ra from Ba, were in the range 1763-3270 years before eruption. When the Ra-Th ages were recalculated taking into account the real fractionation of Ra from Ba, undefined ages were obtained. This result evidenced the presence of post-crystallization events that disturbed the equilibrium of the system, i.e., the magmatic system was not a closed system. Considering that natural lava are characterized by insufficient ^{226}Ra concentrations (0.1-1 ppb) for reliable determinations of Ra partition coefficients by current in-situ micro-analytical techniques and because of the difficulties in obtaining trace elements concentrations from a natural groundmass characterized by either abundant microlites or full crystallization an alternative approach was proposed to estimate the D_{Ra} in leucite bearing rocks. The approach consists of four steps: (a) fitting of the Onuma parabola to the four monovalent alkalis Na through Cs, thus calculating their D_0 , E_0 and r_0 parameters; (b) considering that the top of the parabola for the heavy alkaline earths (HAE) is directly below of the apex of the parabola for the monovalent alkalis, it can be assumed that $r_0^{1+} = r_0^{\text{HAE}}$; (c) thus knowing r_0^{HAE} and having determined the partition coefficients of Ba and Sr, D_0^{HAE} and E_0^{HAE} can be calculated to obtain (d) D_{Ra} from the fit parameters of the heavy alkaline earth's parabola. This method was applied to a natural leucite-tephrite lava from Vesuvius obtaining a D_{Ra} value closely in agreement with those measured in the experimental runs.

- 5) Fabbriozio, A., Schmidt, M.W., Günther, D., Eikenberg, J. (2009) Experimental determination of Ra mineral/melt partitioning for feldspars and ^{226}Ra -disequilibrium crystallization ages of plagioclase and alkali-feldspar. *Earth and Planetary Science Letters* 280, 137-148.

In this second paper of the radium series, the mineral-melt partitioning of Ra was investigated for feldspar phases. High-temperature experiments at 1 atm and at 0.8-1 GPa were performed to crystallize anorthitic and albitic plagioclase and alkali-feldspar in equilibrium with silicate melts. The partitioning behavior of Ra was investigated together to those of other trace elements. Results show a strong influence of the plagioclase composition, expressed as the anorthite content in plagioclase (An_{xx}), on the partitioning behavior of trace elements. In anorthitic plagioclase, alkalis and the heavy earth alkalis are incompatibles, in albitic plagioclase Na is compatible, whereas Ca and Sr are always compatible in plagioclase. Radium is always the most incompatible divalent cation but its incompatibility decreases with decreasing the anorthite content in plagioclase. For the only composition crystallizing alkali-feldspar,

Ra was found to be compatible together with K, Rb, Ba, and Sr, whereas Na, Cs, and Ca are incompatible. In total, 5 experiments have led to measured partition coefficients of Ra in plagioclase: the four of this study on An₃₄, An₈₁ and An₉₁, and the one for pure anorthite from Miller et al. (2007). By fitting these 5 results an equation permitting to calculate the D_{Ra} value as a function of the molar fraction on anorthite (X_{An}) in plagioclase and of the crystallization temperature has been proposed. Furthermore, the D_{Ba} values for the same data set were used to derive an equation relating D_{Ba} with X_{An} and temperature. Then, combining these two equations has led to an expression for the D_{Ra}/D_{Ba} ratio that is necessary to calculate ^{226}Ra - ^{230}Th model ages for plagioclase-glass/groundmass pairs. A similar equation to determine D_{Ra}/D_{Ba} ratio as a function of the molar fraction on orthoclase (X_{Or}) and crystallization temperature has been proposed for alkali-feldspar considering the D_{Ra} and D_{Ba} values determined in this study for a single composition and the D_{Ra} values that were calculated from literature data set for experimentally determined partition coefficient of Ba. The purpose of this study was, then to quantify the fractionation of Ra/Ba in the feldspars and thus, to correctly calculate mineral model ages (i.e., crystallization ages) from Ra-Ba-Th measurements for Mount Shasta, Nevado del Ruiz, Mount St. Helens, Kilauea, Sangeang Api Volcano, for volcanoes from the Tonga and lesser Antilles arcs, for Arenal, Torfajökull-Veidivöton area, Mount Erebus, and Longonot volcano. Distribution coefficients of D_{Ra}/D_{Ba} for plagioclase and for alkali-feldspar were calculated employing the above equations at appropriate temperatures and feldspar compositions for each magmatic system. The calculated D_{Ra}/D_{Ba} values were used to recalculate the crystallization ages of feldspars taking into account the fractionation of Ra from Ba. In general, the recalculated Th-Ra-Ba model ages led to generally shorter feldspar residence times that were calculated as difference between the recalculated mineral ages and the eruptive periods. The variations encompass 20 to 90% shorter crystallization ages with respect to the originally calculated ones, in two cases feldspar crystallization ages increase slightly. Some previously undefined model ages become defined and vice versa. The undefined ages might stem from often complex crystallization histories of plagioclase, from the frequent zoning, indicating that for several cases the measured plagioclase and melt have either never been in equilibrium or the Th-Ra-Ba system has been disturbed after crystallization.

- 6) Fabrizio, A., Schmidt, M.W., Günther, D., Eikenberg, J. (2010) Ra-partitioning between phlogopite and silicate melt and $^{226}\text{Ra}/\text{Ba}$ - $^{230}\text{Th}/\text{Ba}$ isochrons. *Lithos* 114, 121-131.

In the last article of the Ra series the phlogopite/lamproitic melt partition coefficients of Ra and other trace elements have been experimentally determined at 1 GPa and 1050-1100 °C. The interest for phlogopite was justified by the fact that phlogopite is an important constituent in mantle xenoliths, alkali basalts, kimberlites, lamproites and in some of the more K-rich suite and that it is an important repository for K, Rb, Ba, and Ra. The use of a laser ablation-ICP-MS with low detection limits (~0.01 fg) permitted the measurement of the very low Ra concentrations feasible in experiments (~1 ppb). Radium is found to be a compatible element in phlogopite given its ionic radius is close to the apex of the lattice strain parabola for earth alkalis in the large XII-coordinated interlayer site of phlogopite. The results confirm that also Ba, K, and Rb are partitioned preferentially into phlogopite, whereas Na, Cs, Sr and Ca are incompatibles. Given the concentrations of Ra in natural phlogopite are below the

detection limit for the current analytical techniques (LA-ICP-MS and ion-probe) a strategy is proposed to obtain reliable Ra partition coefficients through application of the lattice strain model and accurate measurements of Na through Cs and Ca through Ba in phlogopite and groundmass or glass. The proposed approach to estimate D_{Ra} in phlogopite bearing rocks is the following: (a) fitting of the Onuma parabola to the alkalis Na through Cs, thus calculating D_0^{1+} , E_0^{1+} and r_0^{1+} ; (b) the obtained r_0^{1+} is equated to r_0^{2+} , taking advantage of the fact that for many minerals r_0^{1+} of a given site is within error identical with r_0^{2+} , and the E_0^{2+} of the interlayer site is fixed to 68 GPa that represents the best constrained Young modulus for the Ra-doped experiments; (c) thus knowing r_0^{2+} and E_0^{2+} and having determined the partition coefficients of Ca, Sr and Ba, D_0^{2+} can be calculated to obtain (d) D_{Ra} from the fit parameters of the heavy alkaline earth's parabola. From this, $D_{\text{Ra}}^{\text{mineral/melt}}$ can be calculated with sufficient precision for $(^{226}\text{Ra})-(^{230}\text{Th})\text{-Ba}$ model ages. A second aim of this study was to re-evaluate several magmatic minerals for their potentiality to fractionate Ra and Th from Ba in order to understand the (in-)significance of $(^{226}\text{Ra})/\text{Ba}-(^{230}\text{Th})/\text{Ba}$ isochrones. The results show that all mineral phases such as plagioclase, K-feldspar, leucite, phlogopite, clino- and ortho-pyroxene, olivine, amphibole, oxides, zircon, and apatite strongly fractionate Ra and Th from Ba, i.e., $D_{\text{Ra}} \neq D_{\text{Ba}} \neq D_{\text{Th}}$. This evidence implies that the $^{226}\text{Ra}\text{-}^{230}\text{Th}\text{-Ba}$ mineral dating is applicable only to model ages calculated from mineral-glass pairs with known D_{Ra} given the $(^{226}\text{Ra})/\text{Ba}$ ratio in the various minerals is not constant and these minerals do not form a straight line in the $(^{226}\text{Ra})/\text{Ba}-(^{230}\text{Th})/\text{Ba}$ system at the time of crystallization and thus, there is no $(^{226}\text{Ra})/\text{Ba}-(^{230}\text{Th})/\text{Ba}$ isochron at t_0 .

Phase equilibria

- 7) Fabbrizio, A., Carroll, M.R. (2008) Experimental constraints on the differentiation process and pre-eruptive conditions in the magmatic system of Phlegraean Fields (Naples, Italy). *Journal of Volcanology and Geothermal Research* 171, 88-102.

Experimental studies of phase equilibria have been successful in constraining the likely storage conditions of different magma systems, greatly improving our knowledge about the magma evolution and the state of magma chambers just prior to eruption (e.g., Rutherford et al., 1985). Those results have been confirmed by close agreement between experimentally and geophysically estimated depths of magma chambers (e.g., Cottrell et al., 1999). This study focused on the evolution of the magma storage system for the trachytic magma of the Phlegraean Fields. To better understand the pre-eruptive history of this magma body, phase relations of two samples (i.e., a pumice and an obsidian slightly more evolved than the pumice) of the Breccia Museo Eruption (BME), BME is an explosive event that took place (about 20 ky ago) during the caldera-forming phase of the Ignimbrite Campana eruption, have been determined experimentally as a function of temperature (700 to 885 °C), pressure (50 to 200 MPa) and water content of the melt. The crystallization experiments were carried out at $f\text{O}_2 = \text{NNO}+1$ log unit. Melt water content ranged from 3.4 to 8 wt% (H_2O saturation). Phase equilibrium experiments and analyses of mineral phases and melt compositions provide new experimental and analytical data to explain the observed compositional variations in natural samples. The synthetic products are compared to the natural phases to constrain a range of pre-eruptive conditions (T, P) at which these trachytic magma bodies were stored prior to eruption

in presence of an H₂O-rich fluid. The major phase occurring in the BME have been reproduced. Phase equilibria for the obsidian at 150 MPa reproduce the phase assemblage of the magma only at temperatures below 785 °C. At the same pressure the natural phase assemblage is reproduced for the pumice at temperatures below 810 °C. The stability of biotite is favoured at pressures higher than 135 MPa. The crystallization experiments produced the following textural features: (1) homogeneous distribution of all phases present (glass + crystals + bubbles); (2) homogeneity of crystal sizes and euhedral shapes; (3) bubble sizes that were homogeneous. Crystal sizes ranged from 10 µm (oxide, clinopyroxene, biotite) to 40 µm (alkali-feldspar, plagioclase). Crystalline phases identified in run products were magnetite, clinopyroxene, biotite, apatite, titanite, sanidine and plagioclase. From the viewpoint of phase petrology, crystallization experiments gave results consistent with an overall close approach to bulk equilibrium. The compositions of the synthetic phases are homogeneous in a given charge. Solid solution phases display continuous and smooth compositional changes with variations in temperature. Similarly, the synthetic liquid composition is homogeneous throughout a given experimental charge. Essential features of the phase relations are as follows:

(a) in the experiments performed with the obsidian as starting material, magnetite is the liquidus phase, crystallizing above 870 and 860 °C for pressures of 50 and 200 MPa, respectively. It is followed by clinopyroxene at 870 and 810 °C for pressures of 50 and 200 MPa. Biotite is stable only at pressures above 135 MPa, appearing at temperatures of 820 and 825 °C for corresponding pressures of 150 and 200 MPa, respectively. The first appearance of alkali feldspar is at 840 and 760 °C for pressures of 50 and 200 MPa. Given the scarce occurrence of apatite and titanite, no attempt was made to constrain their stability fields. In all these runs, with the exception of the experiment carried out at 700 °C and 200 MPa, residual liquid was present. The solidus line was identified between 730 °C, 50 MPa and 710 °C, 200 MPa.

(b) In the experiments performed with the pumice as starting material, magnetite, clinopyroxene and biotite are liquidus phases, which were found in the runs at higher temperatures (885 °C, 50 MPa; 880 °C, 200 MPa). The stability field of alkali-feldspar is 50 °C higher than the one in the obsidian, appearing at a pressure of 50 MPa near 900 °C and at a pressure of 200 MPa above 800 °C. The final phase that crystallizes close to the solidus is plagioclase, which is stable below 880 and 770 °C for pressures of 50 and 200 MPa, respectively. The crystallization of plagioclase is probably related to the higher CaO and Al₂O₃ contents in the pumice than in the obsidian. Because of the high crystal content residual liquid was not found in most experimental charges. Consequently, the solidus is placed between 870 °C, 50 MPa and 755 °C, 200 MPa.

The main differences between the obsidian and the pumice are that in the pumice the stability field of all minerals is enhanced by about 50 °C, biotite is stable at lower pressures (below 150 MPa), there is the crystallization of plagioclase, and the quantity of residual liquid is very small. The compositions of the experimental products are compatible with the progressive tapping of a shallow magma chamber that was chemically zoned. The data from phase equilibria suggest that, initially, the less evolved magma was stored at about 200/250 MPa and temperature higher than 800 °C. In order to allow plagioclase crystallization the magma cooled to temperature lower than 800 °C. The differentiation of the less evolved trachyte produced more evolved magma that rose to shallower reservoir in the crust. In these batches of more evolved magma the most abundant phenocryst is sanidine that crystallize at 780 °C and pressures below 170 MPa. The evolved trachyte was stored at a pressure not lower

140-150 MPa just before the eruption, because the experimental results show that biotite is not stable below 135 MPa. This magma could have spent no more than a couple of days at pressures below 135 MPa, or biotite would have broken down in a reaction with the groundmass melt. This suggests that the travel of the magma from the reservoir at 150 MPa to the surface was very fast (from hours to a maximum of 1-2 days). Together, these arguments suggest a final pre-eruption equilibration of the more evolved trachyte at a pressure near 150 MPa at a temperature of 780 °C, assuming H₂O saturation. Assuming that the evolved magma came from the roof of the reservoir, the estimated pressures place the top at a depth of about 5-6 km, which suggests that the entire magma body was stored between 5 and 8 km below the surface. These results suggest that after an early eruptive phase during which the upper, most differentiated level of the magma chamber was tapped, the sudden collapse of the roof of the reservoir triggered drainage of the less evolved remaining magma.

- 8) Fabbrizio, A., Scaillet, B., Carroll, M.R. (2009) Estimation of pre-eruptive magmatic water fugacity in the Phlegrean Fields, Naples, Italy. *European Journal of Mineralogy* 21, 107-116.

Water is the most abundant volatile component in many magmatic systems, it can influence eruption style, magma physical properties and mineral stabilities. The abundance (or activity) of water can be estimated using a variety of approaches, including melt inclusion studies, phase equilibrium constraints, or devolatilization equilibria involving hydrous phases. The coexistence of sanidine, biotite, and magnetite in erupted magma can be used as a geo-hygrometer to determine the water fugacity ($f_{\text{H}_2\text{O}}$) during crystallization according to the reaction $\text{KAlSi}_3\text{O}_8 + \text{Fe}_3\text{O}_4 + \text{H}_2\text{O} = \text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + 0.5\text{O}_2$ and hence to give a constrain about the depth of crystallization. In this study this geo-hygrometer was used to constrain the $f_{\text{H}_2\text{O}}$ of the Phlegrean Fields magma by performing crystallization experiments on a representative sample of trachytic Breccia Museo Eruption in the temperature and pressure range of 725-870 °C and 50-200 MPa, and redox conditions corresponding to NNO+1 (oxidized) and FMQ (reduced) buffers. Most of the experiments were performed at water saturated conditions ($P_{\text{water}} = P_{\text{total}}$), whereas few runs were made in presence of a mixed H₂O-CO₂ fluid phase to reduce the water activity. All experiments were heated to 925 °C, above the liquidus, for two hours to dissolve any inherited crystal, and then cooled isobarically to run conditions to optimize crystal growth. A total of 23 experiments were successful both for crystallizing the assemblage sanidine-biotite-magnetite and for giving evidence of textural and chemical equilibrium as confirmed by the homogenous distribution of all phases present in the experimental charge, by the homogeneity of crystal sizes, mineral phase compositions and their euhedral shapes. Activity values for sanidine, magnetite and biotite were estimated using appropriate relations based on mineral phase compositions. Among these activity models, those for estimating the activity of biotite influence more the final determination of water fugacity given the complexity of substitution mechanisms that characterize this mineral phase. Water fugacity values were estimated using each of these biotite activity models in combination with those for sanidine and magnetite and the calculated water fugacities were compared with those quantified using a modified Redlich-Kwong equation of state. This comparison permitted to establish which activity model for biotite is the more suitable in this trachytic magmatic system. Estimate of the pre-eruptive $f_{\text{H}_2\text{O}}$, using the appropriate

activity model for biotite, for the trachytic magma of the Phlegrean Fields yields values in the range 309-1646 bars. This range of values may reflect differing magma storage depths or wide variations in the CO₂/H₂O ratio in the coexisting melt (gas phase), or possibly, the fact that the biotite-melt equilibrium may change during magma decompression in which case the spread in water fugacity does not necessarily reflect different depths of magma storage.

- 9) Fabbrizio, A., Rouse, P.J., Carroll, M.R. (2006) New experimental data on biotite plus magnetite plus sanidine saturated phonolitic melts and application to the estimation of magmatic water fugacity. *American Mineralogist* 91, 1863-1870.

In this study new experimental data obtained by crystallization experiments of a peralkaline phonolitic obsidian from the Montaña Blanca pumice deposit, Tenerife, Canary Islands, are used to estimate the water fugacity ($f_{\text{H}_2\text{O}}$) in hydrous phonolitic magmas by using the equilibrium of the mineralogical assemblage biotite-magnetite-sanidine. A total of 19 experimental runs were performed at 720-810 °C, 50-250 MPa, both at oxidized (NNO+1 buffer) and reduced QFM (buffer) conditions. In most of the runs the activity of water was equal to 1 (pure water, $P_{\text{water}} = P_{\text{total}}$), whereas in other runs the presence of a mixed H₂O-CO₂ fluid reduced the activity of water to 0.5. To favor the crystallization of sanidine and to enlarge its stability fields at higher pressures and temperatures with the aim to expand the range of conditions over which the biotite-magnetite-sanidine assemblage could be investigated, 10-20 wt% seeds of natural alkali feldspar were added to the starting material of several experiments. The use of the assemblage biotite-magnetite-sanidine to estimate the pre-eruptive $f_{\text{H}_2\text{O}}$ requires that the activity of each phase be estimated by an appropriate activity model. Sanidine activity were estimated graphically in plot of activity versus orthoclase content in sanidine. Magnetite activity were calculated by the activity-composition relations for magnetite-ülvospinel solid solution taking into account the mole fraction of magnetite in the oxide and its activity coefficient to correct for non ideal behavior in the solid solution. The choice of the appropriate activity model for biotite is more critical because the crystal chemistry of biotite is complex with the possibility for several substitutions in the octahedral sites, because some Fe in biotite can be present as Fe³⁺ and so the Fe²⁺/Fe³⁺ ratio should be accurately determined, and because of the substitution of F for H₂O in the hydroxyl site. In this study, the different activity models for biotite were used to calculate its activity and then, in combination with the calculated activity for sanidine and magnetite, to estimate the subsequent $f_{\text{H}_2\text{O}}$ value for each of the performed experiments. These calculated water fugacity were compared to the ones estimated by using a modified Redlich-Kwong equation of state. This comparison showed that the activity model treating biotite as a pure phlogopite-annite solid solution tend to overestimate the biotite activity and hence the $f_{\text{H}_2\text{O}}$. Whereas the biotite activity model that assume ideal mixing between the components tend to underestimate biotite activity and consequently also the final values of the $f_{\text{H}_2\text{O}}$. Instead, the biotite activity calculated by a model that considers only the molar fraction of Fe²⁺ in the octahedral site and the molar fraction of OH in the hydroxyl site and neglects all the other possible substitutions resulted in final $f_{\text{H}_2\text{O}}$ values that approach better the $f_{\text{H}_2\text{O}}$ values estimated by the modified Redlich-Kwong equation of state. Using this method the pre-eruptive $f_{\text{H}_2\text{O}}$ of the Montaña Blanca magma was estimated to be 676±200 bars, in excellent agreement with an $f_{\text{H}_2\text{O}}$ of about 670 bars estimated from melt inclusions data. Lastly, to demonstrate the wide applicability and usefulness of the geo-hygrometer to any magmatic/metamorphic system in which

biotite-sanidine-magnetite is a stable assemblage the pre-eruptive f_{H_2O} for the Fish Canyon tuff (753-2978 bars), Bishop tuff rhyolite (1065-2440 bars), and for metamorphic rocks from Au Sable Forks (\approx 130 bars) were also calculated.

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