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FELLOWSHIP FINAL REPORT

Timing magma transit in the earth using crystal clocks: re-evaluating element diffusion in minerals

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REPORT INFO

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ABSTRACT

The booming field of diffusion chronometry allows geoscientists to extract the timing and duration of subsurface magmatic processes that occur prior to volcanic eruptions. The technique relies on modeling step-wise, concentric chemical gradients that form within magmatic minerals as they grow or get perturbed by new incoming magma prior to volcanic unrest. These chemical ‘tree rings’ are smeared with time by element diffusion, so that the amount of time between perturbation and eruption can be recovered if the mobility (diffusivity) of elements is calibrated in the lab at magma temperatures. This project aims to resolve recently uncovered discrepancies between widely-used element diffusivities obtained in simplified systems (e.g., mineral-mineral couples) and those obtained in melt bearing systems (mineral-melt couples). The new experiments carried out during a STUDIUM-supported sabbatical in 2024-2025 confirmed that the presence of melt is responsible for important differences in element mobilities for olivine, perhaps via the presence of H_2O. Diffusivities in plagioclase, by contrast, are not influenced by melt or H_2O, implying that current community practices are robust. The underlying mechanisms by which these differences in element behavior appear are still being investigated, and new tools recently tested (hyperspectral cathodoluminescence) may hold important clues as to the presence and distribution of point defects in these minerals.

1- Introduction

The earth counts no less than 47 currently active volcanoes, about half of which erupt yearly. Eruptions vary significantly in frequency, intensity and can cause devastating human and infrastructure losses across the globe. In the last 15 years, eruptions across the world have been responsible for >1300 deaths, the destruction of tens of thousands of homes and critical infrastructure, and enormous economic impact for certain countries [1]. Volcanologists strive to understand the magmatic ‘pulse’ of active volcanoes by combining field work and sampling with geophysical (earthquakes, deformation) monitoring, laboratory experiments, mineralogical and chemical characterizations and modeling studies. Tracking the storage and movement of magma from its genesis in the mantle to the surface is crucial for volcano scientists to better anticipate future behavior. In this regard, obtaining robust constraints on the time it takes for magma to transit and evolve within the earth’s crust is one of the chief objectives of petrologists. In recent years, there has been a revolution in the decoding of zoning in minerals: petrologists are developing techniques to leverage the smearing of growth zones within crystals that occurs with time, as these crystals reside in magma to extract time information ("crystal clocks") [2]. Modeling the diffusive smearing of chemical zoning patterns in minerals is a modern tool to quantify how long magmas stay underground before erupting. Volcanologists correlate time obtained from crystal clocks with other types of datasets (deformation of volcano flanks, seismicity, volcanic gas fluxes) to answer the question of what primes and what triggers volcanic eruptions. Where geophysical monitoring data provides information about the location and evolution of unrest, petrology and crystal clocks pinpoint the cause and nature of unrest and the timing of perturbations in the magmatic system.

Diffusion modeling is a booming subfield of petrology. Robust timescales of magma transit can only be obtained if element diffusivities are well calibrated in the lab for individual minerals. A recent article from our group has highlighted a significant issue with current applications of crystal clocks: it appears that for some minerals at least (olivine, a common mineral in basalt), lab-calibrated diffusion rates applied by our community over the last ~30 years are not valid for magmatic system, where minerals are surrounded by silicate melt and not by other minerals [3]. The existing diffusion coefficients used to extract timescales are nearly all derived from experiments where crystals of olivine, plagioclase or other minerals are placed in contact with solid diffusion sources (e.g., other minerals, powders, solid films). These configurations help avoid reactions between the mineral of interest and the diffusant source at the interface, and have been the method of choice since diffusion studies started. In the 2023 study, we found that diffusion coefficients were about 10 times faster with melt present compared with experiments involving only solids. Therefore, our previous estimates of timescales between magma perturbation and eruption may be too long by a factor of 10. We hypothesized that the presence of H_2O in the melt was possibly responsible for enhancing diffusion in the minerals. The aim of the current project is to replicate similar experiments with basalt melt containing olivine or plagioclase with or without water added to the system to (1) confirm the prior results in different lab setups, and (2) investigate whether the presence of water has an effect on element mobility.

2- Experimental details

A first series of H_2O-free diffusion experiments was performed in 1-atm furnaces was designed according to methods outlined in a pioneering study by Spandler and O'Neill [4], who were among the first to highlight the influence of melt on elemental diffusivities. Instead of placing individual olivine or plagioclase crystals inside basalt melt, as would occur in natural magmas, ~5mm sized An_{59} plagioclase from Chihuahua (Mexico) and Fo_{90} olivine crystals from San Carlos (Arizona, US) were drilled and used as containers for the basalt melt. This configuration solves two problems: (1) other typical containers (platinum, gold palladium, aluminum) can react at the contact with both basalt and plagioclase and induce unwanted reactions (loss of Fe or other elements); (2) the plagioclase-melt interface is well defined (a cylinder), making mathematical modeling and extraction of diffusivities very straightforward. These experiments were run at T=1080-1300°C for durations of 2-8 days.

A second series of higher-pressure, water-bearing experiments was performed in internally heated pressure vessels (IHPV) at ISTO at P=25-100 MPa and T=1025-1200°C. For these experiments, crystals of plagioclase and olivine were cut into ~2mm cubes and placed inside precious metal capsules (Au, AuPd) surrounded by basalt powder and with a small amount of H_2O added to the mix. The capsules were welded shut and experiments run for durations of 1-11 days.

Experimental charges were extracted and embedded in resin as 1-in diameter mounts, before being polished to a mirror and carbon coated for electron microprobe analysis (EPMA). EPMA was used to map the chemical distribution of key elements (Fe, Mg, Ca, Cr, Ni, Al, P, Na) and to collect analytical profiles across zoned crystals. The chemical zoning acquired by diffusion during the experimental durations was then modeled using methods outlined in [2] to extract element diffusivities.

3- Results and discussion

The year at ISTO was fruitful in carrying out a substantial number of experiments (n=30 charges for olivine, n=16 for plagioclase). The olivine experiments performed at 1-atm confirm our prior results [3] and it is now clear that the community will need to revise their interpretation of timescales of runup from unrest to eruption obtained from diffusion chronometry in olivine. Additionally, we find that H_2O may play a major role in switching from slow to fast diffusion because of how its presence influences the defect structure of olivine. Experiments with even small amounts of H_2O yield much faster diffusivities than those that have none at all. Importantly, we discovered a new, promising analytical technique to resolve defects in olivine: hyperspectral cathodoluminescence. This method was previously thought unsuitable for Fe-bearing olivine because of signal quenching, but it turns out that modern instruments at ISTO were well capable of measuring signal. We have therefore started new tests in determining what defects of olivine crystals are being resolved by HS-CL. This could be a real breakthrough for mineralogy and materials science in general because crystal point defects are enigmatic and extremely difficult to image or detect.

By contrast, the main cations used for diffusion chronometry in plagioclase (Mg, Sr) do not seem affected by the experimental configuration. Whether melt or solids are present, whether H_2O is absent, present in low or high abundance, diffusivities obtained for Mg coincide very well with studies done on solid-solid configurations [5, 6]. The results imply that timescales from the literature are based on robust diffusivity data. Additionally, our experiments show that Fe diffuses much faster than other cations in plagioclase and can be developed as a chronometer for days-long timescales, a timeframe currently missing from our chronometer 'palette'. Fe has previously not been calibrated for crystal clock work.

4- Conclusion

We showed that the results of the 2023 paper [3] on olivine are reproducible in another lab and with other experimental setups. The presence of melt influences cation diffusivities. The diffusion rates we obtained in 1-atm and IHPV are consistent with the prior values: there is approximately a 10-fold difference when melt is present or absent. Crucially, it is the presence of even hundreds of ppm of H_2O in the melt that may explain this vast difference.

We verified that current diffusivity data is robust fort plagioclase, and are now developing Fe-in-plagioclase as a new chronometer applicable to most magmatic systems. Importantly, in performing this investigation, we have discovered new promising analytical methods to image the defect structure of minerals.

5- Articles published in the framework of the fellowship

The full results of the experimental work carried out in 2024-2025 are still being treated, analyzed and interpreted. Therefore, no journal article has been published yet. However, we can reasonably expect two, if not three papers could come out of this collaborative work: (1) Diffusion of cations in olivine in the presence of water, (2) Diffusion of Fe and other elements in plagioclase, and (3) Leveraging cathodoluminescence in olivine and plagioclase to detect and image the distribution of point defects. And abstract summarizing the plagioclase work was presented at the EMPG Conference in June of 2025 [7].

6- Acknowledgements

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