A NEW PETROGENETIC TOOL BASED ON KINETIC ISOTOPE FRACTIONATION ASSOCIATED WITH Mg-Fe INTERDIFFUSION IN OLIVINE. F.-Z. Teng1, N. Dauphas2, R. T. Helz3, S. Gao4 and S. Huang5, 1Isotope Laboratory, Department of Geosciences and Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR 72701 (fteng@uark.edu), 2Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637, 3U.S. Geological Survey, Reston, VA 20192, 4State Key Laboratory of Geological Processes and Mineral Resources, Faculty of Earth Sciences, China University of Geosciences, Wuhan 430074, 5Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138.

Introduction: Understanding the mechanisms of isotope fractionation at high temperature is a prerequisite for using stable isotopes as tracers of geological processes. For example, isotopic fractionation associated with Fe oxidation state has been used to trace the oxygen fugacity of the mantle [1, 2]. Furthermore, recent experimental studies found large Fe isotope fractionation associated with diffusion of Fe along chemical and temperature gradients [3]. Thus, Fe isotopes could potentially be used as geospeedometers or tracers of temperature variations. However, it is difficult to evaluate the extent to which these different processes can affect Fe isotopic variations in natural systems. For example, previous studies on Fe isotopes in Kilauea Iki lava lake revealed large Fe isotope fractionation in bulk rocks and separated olivine grains [4]. These isotopic variations have been interpreted to result either from equilibrium isotope fractionation enhanced by distillation effects or from diffusion-driven kinetic isotope effects.

Mg$^{2+}$ and Fe$^{2+}$ have identical charges and similar ionic radii, so they behave similarly during partial melting and magmatic differentiation. Therefore, coupled studies of Fe and Mg isotopes should help identify the processes that are responsible for Fe isotope fractionation, as change of the oxidation state should not fractionate Mg isotopes whereas chemical and Soret diffusion will fractionate Fe and Mg isotopes in predictable ways [3, 5-8].

Samples: To evaluate the mechanisms governing high-temperature fractionation of non-traditional stable isotopes, we have analyzed Mg isotopes for 28 olivines separated from two drill core samples from Kilauea Iki lava lake that were previously analyzed for Fe isotopes [4]. We also analyzed the Mg and Fe isotopic compositions of six whole-rock basalts as well as 35 olivine grains separated from three basalt samples from Loihi and Koolau volcanoes (Hawaii).

Results: The six whole-rock basalts have homogeneous $\delta^{26}$Mg values (deviation in 0.1 % of the $^{26}$Mg/$^{24}$Mg ratio relative to DSM3 standard) [9] and limited variation in $\delta^{56}$Fe (deviation in 0.1 % of the $^{56}$Fe/$^{54}$Fe ratio relative to IRMM-014) that are within the ranges of typical oceanic basalts [2, 4, 10-13]. By contrast, Mg and Fe isotopes are extensively fractionated in individual olivine grains, with $\delta^{26}$Mg ranging from -0.42 to +0.03 % and with $\delta^{56}$Fe ranging from -1.10 to +0.49 % (Fig. 1). The isotopic compositions of Mg and Fe are linearly, negatively correlated in a $\delta^{26}$Mg vs. $\delta^{56}$Fe diagram, with a slope of -3.3 ± 0.3 (Fig. 1) [14]. Microprobe analysis reveals the presence of strongly zoned olivines in Kilauea Iki lava lake.

Discussion and Conclusions: Three processes could potentially produce large Mg and Fe isotopic variations at high temperature: equilibrium isotope fractionation magnified by distillation effects, isotope fractionation associated with Soret effect [3, 5, 8], and kinetic isotope fractionation during chemical diffusion [3, 5-7].

It was speculated that Fe isotopes could be fractionated due to equilibrium fractionation between Fe$^{2+}$ and Fe$^{3+}$ and preferential partitioning of isotopi-
cally light Fe into olivine [4]. This model would not predict any Mg isotope fractionation in olivine. Both Mg and Fe isotopes can be extensively fractionated during Soret diffusion, with light Mg and Fe isotopes preferentially concentrated at the hot end relative to the cold end of a thermal gradient [3, 5, 7]. Hence a positive correlation between $\delta^{28}\text{Mg}$ and $\delta^{56}\text{Fe}$ would be expected for this process. The observed negative correlation thus rules out equilibrium redox-control and Soret-diffusion as causes of the large Mg and Fe isotopic variations in the olivines.

By contrast, during inter-diffusion of Mg and Fe in olivines, Mg and Fe form a solid solution, and diffusion of Fe from the melt into the olivine phenocrysts is coupled with diffusion of Mg out of the olivine phenocrysts. Since light isotopes always diffuse faster than heavy ones during chemical diffusion [3, 5–7], a negative correlation between Mg and Fe isotopes is expected before the system reaches equilibrium [15]. The slope of -3.3 in a $\delta^{28}\text{Mg}$ vs. $\delta^{56}\text{Fe}$ diagram is similar to the theoretical ratio of -2.7 for binary diffusion, calculated based on inter-diffusion of Mg-Fe in olivine [15] by assuming $\beta_{\text{Mg}} = \beta_{\text{Fe}} = 0.05$ in the parameterization of diffusion-driven mass fractionation $D_{2}/D_{1} = (m_{1}/m_{2})^{\beta}$ and using an initial olivine composition of Fo$_{85}$. Furthermore, the Fo zoning profile measured in a single olivine phenocryst from a drill core can be reproduced by using a state-of-the-art parameterization of Mg-Fe inter-diffusion coefficient and a total cooling time of ~19 yr, which corresponds approximately to the time span between eruption in 1959 and recovery of the quenched samples in 1981. The predicted isotope fractionations are comparable to those measured in the olivines. Finally, olivines from samples quenched at lower temperature are more Fe-rich and more scattered in chemical composition than those from samples quenched at higher temperature, which directly reflects re-equilibration of the olivines with evolving residual melts [4, 16]. Comparison of compositional zoning in individual olivines shows that highly zoned olivines have larger isotopic variations than intermediately zoned ones.

Compositional zoning in olivines can yield information on the source, magma transport and crystalization history of basaltic magmas. Zoning is mainly controlled by crystal growth and inter-diffusion of Mg and Fe. Studies of Mg and Fe isotopes can unambiguously tease apart the roles of these two processes in olivine zoning. Zoning generated by crystal growth attending magmatic evolution should show little isotope fractionation as equilibrium isotope fractionation at high temperature is small, whereas diffusion-controlled zoning is accompanied with large and negatively correlated Mg and Fe isotope fractionation [15]. Our study indicates that normal zoning in olivine phenocrysts from Kilaeua Iki lava lake is mainly produced by inter-diffusion of Mg and Fe between olivine and evolving melts. The zoning hence can be used to constrain the cooling rate of the lava lake. The cooling history from modeling the diffusion profile of Mg and Fe in olivines from Kilaeua Iki lava lake agrees well with actual observation.

To summarize, studies of Mg and Fe isotope fractionation during chemical diffusion can be used to determine the nature of mineral zoning in igneous rocks and possibly in metamorphic rocks, and constrain the residence times of crystals in magma and the duration of metamorphic events by modeling the diffusion profiles. They can also be used to identify core olivine compositions that have been affected by diffusion and which Fo content cannot be used to estimate the composition of the primary melt as is often done. Our study demonstrates the usefulness of undertaking in situ measurements of Mg and Fe isotopic compositions in olivine phenocrysts using laser-ablation MC-ICPMS or SIMS as this will help interpret chemical profiles that are routinely measured using electron probes.

Acknowledgements: We thank Frank Richter for discussions and Jing-Liang Guo for help with microprobe analyses. This work was supported by NSF (EAR-0838227) and Arkansas Space Grant Consortium (SW19002) to FZT; NSF (EAR-0820807), NASA (NNX09AG59G) and a Packard fellowship to N.D., as well as the NSF of China (40821061) and the Ministry of Education of China (B07039) to SG.