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Behavior of the Mo, Tl, and U isotope systems during differentiation in the Kilauea Iki lava lake

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ABSTRACT

Stable molybdenum (Mo), thallium (Tl), and uranium (U) isotope ratios were determined in a suite of samples from the 1959 Kilauea eruption and from Kilauea Iki lava lake with the aim of understanding the effects of igneous differentiation on these isotope systems. The samples range from olivine cumulate with MgO up to 27% to internal differentiates with MgO less than 3%, representing a tholeiitic differentiation series. Molybdenum, Tl, and U behave incompatibly during differentiation, and Mo and U isotope ratios do not systematically vary amongst the different samples. δ^{98}Mo values range from −0.17 to −0.31‰ and δ^{238}U values range from −0.20 to −0.38‰. Most individual analyses for both isotope systems overlap within measurement uncertainty (± ~0.7 and ~ 0.6, respectively). Mean δ^{98}Mo and δ^{238}U values are −0.22 ± 0.08‰ (2σ) and − 0.29 ± 0.09‰ (2σ), respectively, which overlap with Pacific mid ocean ridge basalt (MORB). In contrast, Tl isotopes show small but resolvable variations, with ε^{205}Tl ranging from +1.20 to −1.38. The most negative ε^{205}Tl values are confined to some of the lowest [Tl] samples, but the ε^{205}Tl values do not otherwise vary smoothly with MgO or [Tl]. Possible mechanisms for thallium isotope fractionation are considered (e.g., degassing, water leaching, sulfide fractionation) but none are found to be satisfactory. Overall, the lack of resolvable variation in the Mo and U isotope systems and the small magnitude of heterogeneity in the Tl isotope system indicate that differentiation in tholeiitic systems is unlikely to be a major contributor to global variation in these isotope systems.

1. Introduction

The field of non-traditional stable isotopes has greatly expanded in the past decade and a half. One common attribute of nearly all of these emergent tracers is the occurrence of large measurable isotope fractionation at low temperatures, often in oceanographic settings (see Teng et al., 2017 and references therein), and one of the major applications for these systems has been in paleoceanography, particularly research pertaining to the rise of oxygen (e.g., Arnold et al., 2004; Nielsen et al., 2005; Anbar and Rouxel, 2007; Wille et al., 2007; Czaja et al., 2012; Planavsky et al., 2014; Andersen et al., 2016; Wang et al., 2016; Ostrander et al., 2017, 2019; Them et al., 2018). It is inevitable that fractionated isotope signatures diagnostic of Earth-surface conditions will be transferred to solid Earth reservoirs via subduction, and variations in non-traditional isotope ratios in igneous rocks and their minerals perhaps tied to such processes are increasingly being reported (e.g., Nielsen et al., 2006; Wille et al., 2007; Czaja et al., 2012; Andersen et al., 2015; Freymuth et al., 2015; Nielsen et al., 2017a; Rader et al., 2018).

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The Mo, Tl, and U isotope systems are of particular interest as numerous studies in recent years have documented major isotopic variations in igneous systems, especially in arc volcanic rocks (e.g., Willbold and Elliott, 2017; Nielsen et al., 2017a; Andersen et al., 2015; Freymuth et al., 2019). In order to determine if measured isotopic variations can be traced to subduction of isotopically fractionated material, we must first establish if these isotope systems can experience fractionation by igneous processes, such as fractional crystallization.

This contribution explores the behavior of the Mo, Tl, and U isotope systems during the crystallization of Kilauea Iki lava lake, a tholeiitic picrite body. The lava lake has been an ideal locality for testing whether closed-system igneous differentiation leads to isotope fractionation and has been targeted in studies of several other stable isotope systems that include Li, Mg, Ca, Ti, V, Cr, Fe, Cu, Zn, Ga, and Sn (Tomascak et al., 1999; Teng et al., 2007, 2008; Chen et al., 2013; Savage et al., 2015; Badullovich et al., 2017; Kato et al., 2017; Zhang et al., 2018; Johnson et al., 2019; Ding et al., 2020; Shen et al., 2020; Zhao et al., 2020). We show here that negligible isotope fractionation occurs for the Mo and U systems during crystallization. We also report minor heterogeneity in Tl isotope composition that does not correlate straightforwardly with degree of differentiation and discuss potential explanations for this heterogeneity.

2. Background

2.1. The Mo, Tl, and U isotope tracers and their behavior in igneous systems

Early Mo isotope studies identified large fractionations between seawater and certain types of sediments in oceanographic settings (e.g., Barling et al., 2001; Barling and Anbar, 2004), and more recent studies have reported on Mo isotope variations in igneous rocks. A significant range of δ^{98}Mo values (defined as per mil deviation of ^{98}Mo/^{95}Mo in a sample relative to a standard) have been reported from volcanics (Voegelin et al., 2014; Freymuth et al., 2015; Greber et al., 2015; Freymuth et al., 2016; König et al., 2016; Bezard et al., 2016; Liang et al., 2017; Gaschnig et al., 2017; Willbold and Elliott, 2017; Wille et al., 2018; Casalini et al., 2019; McCoy-West et al., 2019; Yan et al., 2019) and granites (Yang et al., 2017), and the possibility that igneous differentiation could be a driver of isotopic diversity has been addressed in several studies. Voegelin et al. (2014) reported Mo isotope compositions in hornblende and biotite separates that were anomalously light relative to whole-rock values from Kos in the Aegean Arc and concluded that crystallization of these minerals can drive the remaining liquid towards heavier isotope compositions. While this study focused on a more water-rich calk-alkaline magmatic system, Yang et al. (2015) analyzed a suite of samples from Hekla in Iceland representing a dry tholeiitic differentiation trend. These authors found a uniformity of isotope composition and concluded that Mo isotopes do not fractionate in such environments. On the other hand, recent studies have suggested that partial melting of the mantle may isotopically fractionate Mo (Liang et al., 2017; McCoy-West et al., 2019).

Thallium can experience fractionation between its two isotopes (Rehkämper and Halliday, 1999), with isotope variations defined as ε^{205}Tl or parts per ten thousand deviation of the ^{205}Tl/^{203}Tl in a sample from the standard. As with Mo, isotope fractionation occurs between seawater and certain sediment types and also oceanic crust (Rehkämper and Halliday, 1999; Rehkämper et al., 2002; Rehkämper et al., 2004).

Significant variation of the Tl isotope composition of arc and ocean island basalts (e.g., Nielsen et al., 2006a; Prytulak et al., 2013; Nielsen et al., 2016, 2017a; Shu et al., 2017; Blusztajn et al., 2018) has led to the consideration of whether these variations could be affected by igneous differentiation rather than reflecting magma sources. Prytulak et al. (2017) studied samples from the dry Hekla differentiation series and also a more water-rich arc differentiation series and found no evidence that igneous differentiation affects Tl isotope composition.

Uranium consists of two long-lived radioactive isotopes, ^{238}U and ^{235}U, that can experience isotope fractionation in oceanographic settings (Stirling et al., 2007; Weyer et al., 2008; Tissot and Dauphas, 2015), Reports of isotopic variability (defined by δ^{238}U or per mil deviation of the ^{238}U/^{235}U in a sample relative to the standard) in granites (Telus et al., 2012) and in basalts from different tectonic settings (Andersen et al., 2015) opened the possibility of the use of the U isotope system to understand igneous processes and additional studies have focused specifically on U isotopes in arc rocks (Avanzinelli et al., 2018; Freymuth et al., 2019). As with the Mo and Tl system, interpretation of U isotope ratios as signatures from the magma source requires determining whether igneous differentiation alone can produce significant isotopic fractionation. Thus far, no systematic investigation of this possibility has been conducted.

2.2. Kilauea Iki

Kilauea Iki lava lake formed on the island of Hawaii in 1959 when lava erupted into an existing pit crater (Richter and Moore, 1966; Richter et al., 1970). The lake crystallized inward over several decades, during which it underwent extensive internal differentiation; over this period, it was drilled repeatedly by the USGS and extensive core was recovered (Helz, 1987a). The lava was a tholeiitic picrite with an average melt MgO content of approximately 15.4%. Internal differentiation and crystallization produced a range of compositions from olivine cumulates with MgO of 27% to ferrodiabasic segregation veins with MgO <6%. Rarer, more differentiated compositions occur as small veins or as oozes in boreholes (Helz, 1987a). Samples from the lava lake contain olivine and chromian spinel with plagioclase, augite, and Fe—Ti oxides while the more felsic segregations contain augite, plagioclase, Fe—Ti oxide, and minor apatite. Many samples contain interstitial glass (with SiO_2 up to 74%) and some contain trace amounts of sulfide. By contrast, scoria samples from the 1959 eruption contain mostly glass, with some olivine and chromian spinel, plus rare traces of sulfide.

Kilauea Iki lava lake thus represents a superb natural laboratory for studying the effects of closed-system crystallization and differentiation in a (dry) tholeiitic system. The Kilauea Iki sample suite has a clear advantage over the Hekla sample suite that has been used in other studies of stable isotope behavior during differentiation, where the samples represent multiple eruptions over a millennium. At Hekla, consanguinity of magmas can only be inferred indirectly, and some workers have argued for the role of magma mixing and remelting of the lower crust in the generation of the erupted products (Schuessler et al., 2009; Savage et al., 2011, 2015; Chen et al., 2013; Yang et al., 2015; Prytulak et al., 2017).

Multiple stable isotope systems have been examined in the Kilauea Iki sample suite. The Li, Mg, Ca, Cu, and Ga isotope systems do not show variation in the sample suite (Tomascak et al., 1999; Teng et al., 2007; Savage et al., 2015; Kato et al., 2017; Zhang et al., 2018). In contrast, Teng et al. (2008) reported that Fe exhibits a clear and continuous trend towards heavier isotope compositions with decreasing MgO, Chen et al. (2013) reported that Zn exhibits a small but resolvable shift towards lighter isotope compositions with decreasing MgO, and Badullovich et al. (2017) found a shift in Sn isotopes towards lighter isotope compositions with decreasing MgO. Johnson et al. (2019) and Zhao et al. (2020) observed a step-change to distinctly heavier Ti isotope composition in the most felsic samples due to the crystallization of Fe—Ti oxides, which preferentially removed light Ti isotopes. The same shift towards heavier isotope compositions, driven by Fe—Ti oxide crystallization, was also observed V by Ding et al. (2020). Shen et al. (2020) observed a shift in Cr isotope composition towards lighter isotope composition in the more evolved samples, which they attributed to preferential accumulation of isotopically heavy Cr in spinel.

Previous workers have found that Mo, Tl, and U show similar trends during crystallization, indicating incompatible behavior (Greaney et al., 2017; Helz, 2012). All three elements show slight increases in concentration between ~28% and ~ 7% MgO, followed by a more rapid increase through the remainder of the MgO range. The 7% MgO inflection point corresponds to the point at which clinopyroxene and plagioclase begin to crystallize from the melt. In situ analyses by Greaney et al. (2017) revealed that the major reservoirs of Mo are glass and Fe—Ti oxides whereas Tl is concentrated in glass but also occurs in sulfides. A mineralogical inventory of U has not yet been conducted but based on the similar trend to the other two elements, it is likely concentrated in glass.

3. Methods

3.1. Samples

The Kilauea Iki samples studied here consist of 15 drill core samples collected in the 1967, 1975, 1979, and 1981 drilling campaigns along with eight samples of scoria from the initial 1959 eruption. Major element data are reported in Helz et al. (1994) and Murata and Richter (1966), and trace element data are reported in Helz (2012) and Greaney et al. (2017). Platinum group element data for some of these samples have been reported by Pitcher et al. (2009), and many of these samples were used in the previous stable isotope studies mentioned above.

3.2. Digestion

Initial samples were digested at the Georgia Institute of Technology on a hot plate in screw-top beakers in 4 mL of concentrated HF plus 0.5 mL of concentrated HNO_3 at 140 °C and then uncapped and evaporated. Salts were dissolved in 4 mL of concentrated HNO_3 and evaporated and then repeatedly dissolved in HCl and evaporated until an HCl solution free of precipitates was obtained.

Additional samples of erupted scoria targeted specifically for thallium isotopes alone were digested in the Metal Isotopes Laboratory at Indiana University on a hot plate in screw-top beakers in 3 mL of concentrated HF plus 1 mL of concentrated HNO_3 at 140 °C for three days and then uncapped and evaporated. Salts were dissolved in 4 mL of concentrated aqua regia and evaporated and then repeatedly dissolved in 6 N HCl and evaporated until an HCl solution free of precipitates was obtained.

3.3. Mo separation and isotope analysis

Molybdenum column chromatography was conducted at the Georgia Institute of Technology. Aliquots of dissolved samples were taken and combined with a ^{97}Mo—^{100}Mo double spike in proportions designed to double the Mo concentration of the resulting mixture and then dried down. The single stage Mo column chromatography procedure of Willbold et al. (2016) was used to separate Mo from the sample matrix. This procedure was designed specifically for Mo isotope analysis of igneous samples and entails loading the sample in a mixture of HCl and ascorbic acid, the latter of which is added to reduce all iron to Fe^{2+}, onto columns with AG1-X8 anion exchange resin. Full details of the procedure are provided in Willbold et al. (2016).

Molybdenum isotope analyses were conducted at the Yale Metal Geochemistry Center on a Thermo Neptune Plus MC-ICP-MS. Solutions were introduced with an Apex IR desolvating nebulizer and analyzed in static mode. ^{91}Zr and ^{99}Ru were monitored in addition to the isotopes of Mo in order to correct for isobaric interferences. Groups of three samples were bracketed by analyses of the NIST 3134 Mo standard and also by periodic analyses of the RochMo2 Mo standard. A modified approach of Siebert et al. (2001) was used to process the data. δ^{98}Mo values are reported in per mil relative to the NIST 3134 standard (Goldberg et al., 2013). External reproducibility of the Mo isotope standard was ±0.04‰ (2σ). Gaschnig et al. (2017) reported results for USGS reference materials BHVO-2 (δ^{98}Mo = −0.08 ± 0.03‰, $n = 4$, 2σ) and W-2 (δ^{98}Mo = −0.04 ± 0.08‰, $n = 1$, 2σ). These analyses were conducted during the same analytical sessions as the Kilauea Iki samples and so demonstrate accuracy and reproducibility, with BHVO-2 overlapping with the range of −0.04 to −0.08‰ reported in the literature (Hin et al., 2013; Burkhardt et al., 2014; Li et al., 2014; Bezard et al., 2016; König et al., 2016; Freymuth et al., 2016; Zhao et al., 2016; Liang et al., 2017) and W-2 overlapping with the range of −0.04 to −0.10‰ reported in the literature (Burkhardt et al., 2014; Bezard et al., 2016; Zhao et al., 2016).

3.4. Tl separation and isotope analysis

Initial thallium column chromatography and isotope analysis was conducted in the National High Magnetic Field Laboratory at Florida State University. Purification of Tl was achieved using a two-column procedure described in detail by Rehkämper and Halliday (1999), Nielsen et al. (2004), and Baker et al. (2009). Purified Tl was doped with the NIST 981 Pb standard in order to monitor for instrumental mass bias and for external normalization (Rehkämper and Halliday, 1999; Nielsen et al., 2004; Baker et al., 2009). Isotope analyses were conducted on a Neptune MC-ICP-MS with an Aridus II desolvating nebulizer at the National High Magnetic Field Laboratory of Florida State University. Sample analyses were bracketed by analyses of NIST 997 thallium standard. Results are reported in ε^{205}Tl, referenced to NIST 997. Analyses of USGS reference materials BCR-2 and BHVO-2 yielded mean ε^{205}Tl values of −2.24 ± 0.04 and − 1.78 ± 0.61 (2σ), respectively, which are consistent with literature values (−2.5 ± 0.5 for BCR-2 and -1.5 ± 0.4 for BHVO-2; Prytulak et al., 2013). The error bars are the two standard deviations of replicate analysis unless only one analysis was available, which is then given as an error of the individual analysis.

Thallium column chromatography and isotope analysis for a subset of erupted scoria samples were conducted in the Metal Isotopes Laboratory at Indiana University. Purification of Tl was achieved using the same protocol as mentioned above. Purified Tl was doped with NIST 981 Pb standard to monitor for instrumental mass bias and for external normalization (Rehkämper and Halliday, 1999; Nielsen et al., 2004; Baker et al., 2009). Isotope analyses were conducted on a Nu Plasma II MC-ICP-MS with an Aridus II desolvating nebulizer. Sample analyses were bracketed by analyses of NIST 997 thallium standard. Multiple analyses of USGS reference material BCR-2 yielded mean ε^{205}Tl = −2.5 ± 0.4 (2σ), consistent with literature values (Baker et al., 2009; Prytulak et al., 2013). Error bars represent two standard deviations of replicate analyses.

3.5. U separation and isotope analysis

Uranium column chromatography was conducted at the Georgia Institute of Technology. Aliquots of dissolved samples were taken and combined with a ^{233}U—^{236}U double spike in amounts appropriate to yield a ^{238}U/^{236}U of ~30. Uranium was purified on columns with UTEVA resin, using the methods of Wang et al. (2016) (modified from Weyer et al., 2008). Uranium isotope analyses were conducted at the Yale Metal Geochemistry Center on a Thermo Neptune Plus MC-ICP-MS, with samples normalized to bracketing analyses of spiked CRM 112a standard solution. Additional details are provided in Wang et al. (2018). δ^{238}U results are reported per mil relative to the CRM 112a standard. The long-term reproducibility of this standard is 0.07‰ (2σ). Four analyses of USGS reference material BHVO-2 yielded a mean δ^{238}U of −0.34 ± 0.05‰ (2σ), which overlaps with published values (Andersen et al., 2015; Tissot and Dauphas, 2015).

4. Results

Results are presented in Table 1 and Figs. 1 through 4 and compared to the range of isotopic variation seen in various common rock types in Fig. 5. For Mo isotope results, the data might suggest an increase in δ^{98}Mo with decreasing MgO starting at ~7% MgO, but this largely hinges on a single outlier sample (which has the lowest δ^{98}Mo observed

Table 1
Mo, Tl, and U isotope results

Sample	Aprox latitude (degrees)[a]	Aprox longitude (degrees)[a]	1959E (%)[b]	MgO[c]	SiO_2[c]	δ^{98}Mo	2SE[d]	[Mo][e]	δ^{238}U	2SE[d]	(^{234}U/^{238}U)	[U][e]	ε^{205}Tl	2σ[d]	n	[Tl][e]
67-2-85.7	19.416	−155.247		2.6	56.2	−0.17	0.05	3.55	−0.31	0.05	3.7	1.73	−0.28	0.05	2	0.100
67–3-27.5	19.414	−155.247		12.0	48.6	−0.26	0.07	0.73	−0.34	0.05	6.2	0.24	−0.49	0.35	2	0.030
67–3-6.8	19.414	−155.247		25.8	44.6	−0.20	0.04	0.50	−0.20	0.06	2.6	0.32	−0.48	0.06	2	0.012
75–1-38.9	19.414	−155.247		10.7	50.0	−0.25	0.07	0.78	−0.27	0.05	2.6	0.37	−1.38	0.31	2	0.015
75–1-121.5	19.414	−155.247		7.8	48.9	−0.23	0.07	1.13	−0.28	0.05	2.7	0.49	−0.80	0.18	2	0.031
75–1-75.2	19.414	−155.247		5.8	50.1	−0.22	0.06	1.45	−0.35	0.06	3.8	0.61	−0.26	0.19	2	0.036
79-1R1–170.9	19.414	−155.247		3.5	54.6	−0.20	0.05	2.94	−0.25	0.04	−2.0	1.28	−0.27	0.37	3	0.08
79–3-150.4	19.414	−155.247		13.5	48.4	−0.19	0.06	0.73	−0.33	0.06	3.0	0.32	−0.06	0.49	2	0.019
79-3R2–168	19.414	−155.247		5.1	50.9	−0.28	0.08	1.94	−0.29	0.07	4.6	0.80	−0.96	0.23	2	*0.0001*
81–1-117.8	19.414	−155.247		4.9	50.2				−0.32	0.04	1.5	0.73	−0.94	0.22	1	*0.014*
81–1-119.2	19.414	−155.247		6.7	50.6	−0.31	0.05	1.08	−0.32	0.05	1.7	0.48				
81–1-169.9	19.414	−155.247		26.9	43.7	−0.19	0.09	0.56	−0.31	0.05	3.0	0.24	−0.47	0.00	2	0.020
81–1-190.1	19.414	−155.247		21.9	45.7	−0.21	0.08	0.46	−0.38	0.07	9.8	0.20	−1.27	0.24	2	*0.016*
81–1-230.6	19.414	−155.247		26.6	44.9	−0.21	0.08	0.33	−0.28	0.06	16.4	0.13				
81–2-88.6	19.414	−155.247		2.4	57.1	−0.21	0.06	3.67	−0.30	0.07	−39.2	1.61	−0.47	0.44	2	0.080
Iki 22	19.41	−155.25	27	19.5	46.7	−0.17	0.09	0.66	−0.29	0.07	3.5	0.27	−1.02	0.43	3	0.021
Iki 3	19.41	−155.25		17.2	47.2				−0.21	0.05	2.2	0.30				
Iki 58	19.41	−115.25	100	8.1	49.9	−0.22	0.07	0.87	−0.24	0.05	7.0	0.41	−0.87	0.02	1	0.027
Iki 5	19.41	−115.25	12	10.5	49.1								−1.10	0.7	4	0.012
Iki 9	19.41	−115.25	0	8.2	49.6								−1.00	0.5	4	0.015
Iki 10	19.41	−115.25	0	8.9	49.4								−0.9	0.9	3	0.016
Iki 26	19.41	−115.25	21	19.3	46.7								1.2	0.4	4	0.016
Iki 33	19.41	−115.25	19	18.3	47.0								−0.4	0.9	3	0.013
BCR-2													−2.2	0.4	6	
Mean						−0.22			−0.29				−0.61			
2stdev						0.08			0.09				1.13			
BHVO-2[f]						−0.08	0.03		−0.34	0.05			−1.78	0.61	2	
BCR-2													−2.24	0.0425	3	
W-2[f]						−0.04	0.08									

Mo, U, and Tl concentrations in ppm. Samples with names in italics were analyzed for Tl isotopes at Indiana University in Bloomington.

[a] Drill hole locations well constrained, but scoria coordinates are inferred from the limited location notes in Murata and Richter (1966).

[b] Percent of more primitive component in erupted scoria samples calculated by Wright (1973).

[c] MgO and SiO2 (wt%) from Helz et al. (1994) and Murata and Richter (1966). Note that original scoria sample names in Murata and Richter were converted to “Iki-” prefixed names used here and elsewhere by Wright (1973).

[d] Uncertainties on Mo and U isotope compositions are standard errors. Uncertainties on Tl isotope compositions are standard deviation of mean of duplicate analyses (n). Samples with only one Tl analysis are listed with internal standard error.

[e] Mo and U concentrations determined by isotope dilution. Listed Tl concentrations are standard addition ICP-MS from Greaney et al. (2017) except for those in italics, which were determined here by comparing the Tl elutions signal intensities to the Tl isotope standard on the MC-ICP-MS.

[f] Mo isotope analysis of BHVO-2 (mean, $n = 4$) and W-2 (mean, $n = 1$) previously reported in Gaschnig et al. (2017). U isotope composition is mean of four analyses of separate digestions.

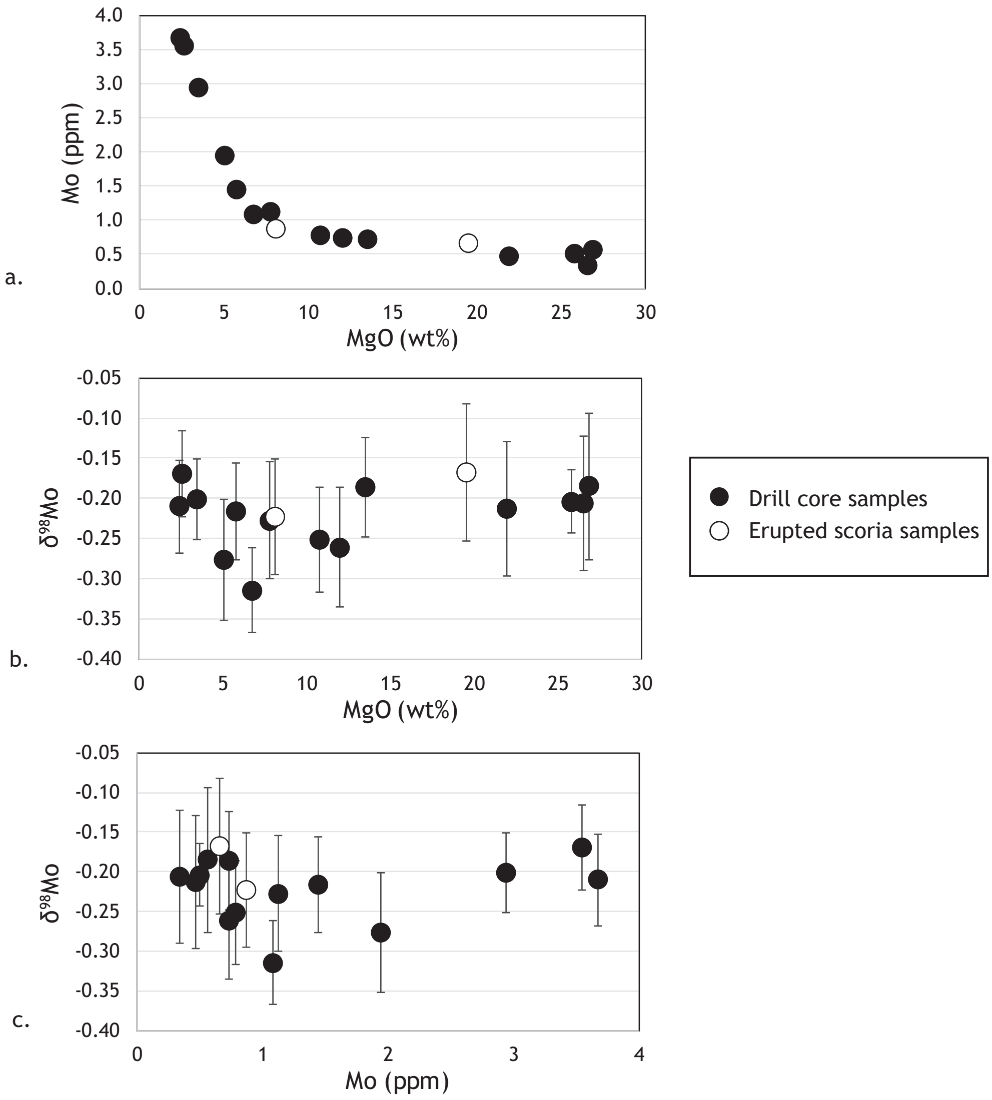

Fig. 1. Stable Mo isotope systematics in Kilauea Iki. Black symbols are drill core samples and white symbols are erupted scoria samples here and in subsequent figures. (a) Mo concentration as a function of MgO (wt%). Samples with MgO greater than ~11% are olivine plus melt cumulates whereas samples with less MgO have experienced fractional crystallization, first of olivine and then of pyroxene, plagioclase, and oxides. Mo behaves incompatibly and is increasingly enriched in the melt during fractional crystallization. (b) δ^{98}Mo (relative to the NIST 3134 standard) as a function of MgO. No systematic change in δ^{98}Mo is observed and nearly all samples are within uncertainty of one another. (c) δ^{98}Mo as a function of Mo concentration. No coherent pattern is seen between isotope composition and concentration.

in this study). The other samples have δ^{98}Mo within analytical uncertainty so there is no real evidence for Mo isotope fractionation at the currently level of precision. The mean δ^{98}Mo is $-0.22 \pm 0.08‰$ (2σ). This composition overlaps with the unweathered Hawaiian basalts reported by King et al. (2016), although it differs from published values for the BHVO-2 reference material (Burkhardt et al., 2014; Hin et al., 2013; Li et al., 2014; König et al., 2016; Bezard et al., 2016; Freymuth et al., 2016; Zhao et al., 2016; Liang et al., 2017; Gaschnig et al., 2017), which is a Kilauea lava collected from a nearby locality. The difference between the Kilauea Iki lavas and BHVO-2 almost certainly stems from the metal contamination to BHVO-2 during preparation that has been extensively documented elsewhere (Weis et al., 2005).

Tl concentration and isotope results are shown in Table 1 and Figs. 2 and 3. Small but resolvable thallium isotopic heterogeneity is present; the samples here display an overall range of more than 2.6 ε^{205}Tl units. While the Tl isotope composition in the system does not appear to systematically vary with differentiation (Fig. 2), there is a correlation between [Tl] and certain chalcophile elements, such as Cu, As, and Sb (Fig. 3). Uniformly, samples with the greatest [Tl] had heavier Tl isotope compositions whereas lower [Tl] samples had variable ε^{205}Tl. These most enriched samples are the only samples analyzed to have cooled after sulfide saturation at around 5 wt% MgO.

Uranium isotope results are shown in Table 1 and Fig. 4. The majority of δ^{238}U values are identical within analytical uncertainty and no systematic variation between δ^{238}U and MgO or [U] are observed. The mean δ^{238}U is $-0.293 \pm 0.095‰$ (2σ), comparable to BHVO-2.

5. Discussion

5.1. *Lack of fractionation of Mo and U isotopes during differentiation*

The Mo isotope compositions reported here for the Kilauea Iki samples do not vary during crystallization and differentiation in the lava lake. It undoubtedly reflects in part the persistent incompatible behavior of Mo across the crystallization range observed here. The lack of Mo isotope fractionation in this dry tholeiitic system is consistent with the isotopic uniformity that Yang et al. (2015) observed in the similarly tholeiitic sample suite from Hekla in Iceland. This implies that Mo isotopes measured in igneous rocks from such systems should record the composition of the primary melt (assuming that no crustal assimilation has occurred).

As with Mo, U is consistently incompatible across the crystallization range and does not experience systematic isotope fractionation during differentiation. This is the first such study to address directly the question of U isotope fractionation during igneous differentiation in a single system. The question of whether U isotopes are affected by fractional crystallization in a more water-rich and/or granitic system (as has been observed for Mo isotopes) remains an open question.

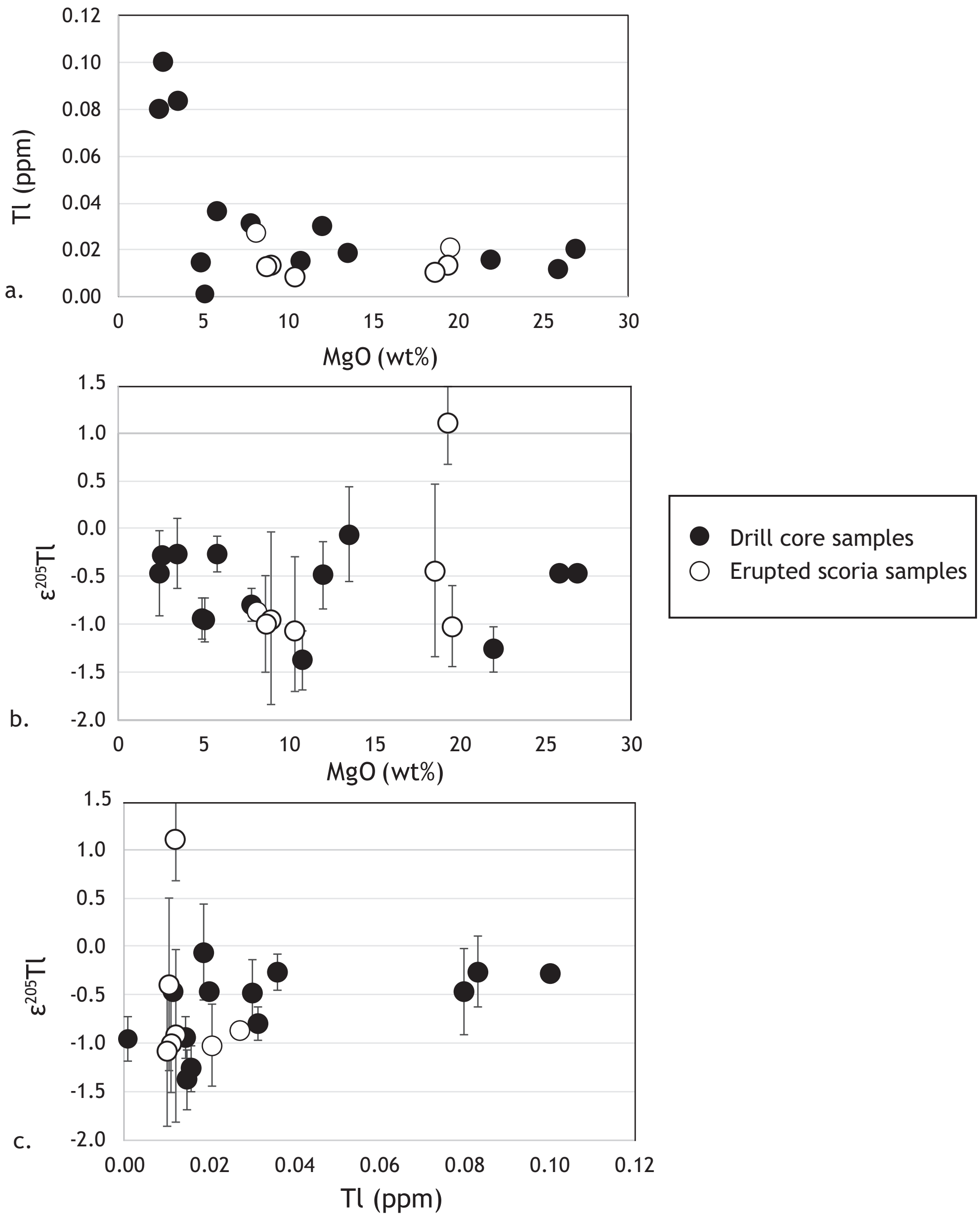

Fig. 2. Stable Tl isotope systematics in Kilauea Iki. (a) Tl concentration as a function of MgO. Tl concentration follows the same trend as Mo, with a rapid increase in concentration after the initiation of fractional crystallization. (b) ε^{205}Tl as a function of MgO. Resolvable variation in the Tl isotope composition is present but it does not correlate with bulk MgO content. (c) ε^{205}Tl as a function of [Tl]. The light Tl isotope compositions are confined to the most Tl poor samples, while heavier isotope compositions are observed in some of the Tl poor samples and all of the more Tl-enriched samples.

5.2. Mo isotope composition of the Hawaiian plume

The Mo isotope system has been applied to igneous systems in many studies in recent years, including studies of arc lavas (Voegelin et al., 2014; Freymuth et al., 2015, 2016; König et al., 2016; Gaschnig et al., 2017; Wille et al., 2018), mid ocean ridge basalts (MORBS) (Bezard et al., 2016; Liang et al., 2017), komatiites (Greber et al., 2015; McCoy-West et al., 2019), and granites (Greber et al., 2014; Yang et al., 2017). However, available data for ocean island basalts, particularly the classic localities for different mantle reservoir end members (e.g., EM1, EM2, HIMU, etc.), are more limited. An abstract by Willbold et al. (2012) reported δ^{98}Mo results for several OIB localities, including a − 0.25 to +0.18‰ range for Hawaiian samples, but these data have not been published in full. Liang et al. (2017) published results for a few OIB samples, including two samples from the Loihi seamount of the Hawaiian chain with an average δ^{98}Mo of −0.05‰. Mo isotopic compositions from the island of Hawaii were also provided by King et al. (2016) in a study of the effects of chemical weathering on Mo and its isotopes, with unweathered volcanic bedrock yielding δ^{98}Mo from −0.11 to −0.26‰.

The Kilauea Iki Mo isotope data presented here may offer new constraints on the Mo isotope composition of the Hawaiian mantle plume, given the lack of isotope fractionation during lava differentiation. While the possibility of isotope fractionation during low degree partial melting of the mantle has been suggested (Liang et al., 2017), the Kilauea Iki magma is not a low degree melt. The average δ^{98}Mo of the sample suite is -0.22 ± 0.08‰ therefore likely reflects the Mo isotope composition of the mantle plume source. This composition falls within range of the East Pacific Rise MORB compositions reported on by Bezard et al. (2016), indicating that the Mo isotope composition of the portion of the Hawaiian plume sampled by the Kea trend (upon which Kilauea lies) is indistinguishable from the ambient Pacific mantle. This is somewhat surprising given the previously reported Tl isotope anomalies that indicate the presence of Fe—Mn sediments in the Hawaiian plume (Nielsen et al., 2006), as such sediments also typically contain isotopically light Mo. This may reflect the lower abundance of Tl in the mantle and the commensurately greater isotopic leverage that can be exerted by sedimentary contamination.

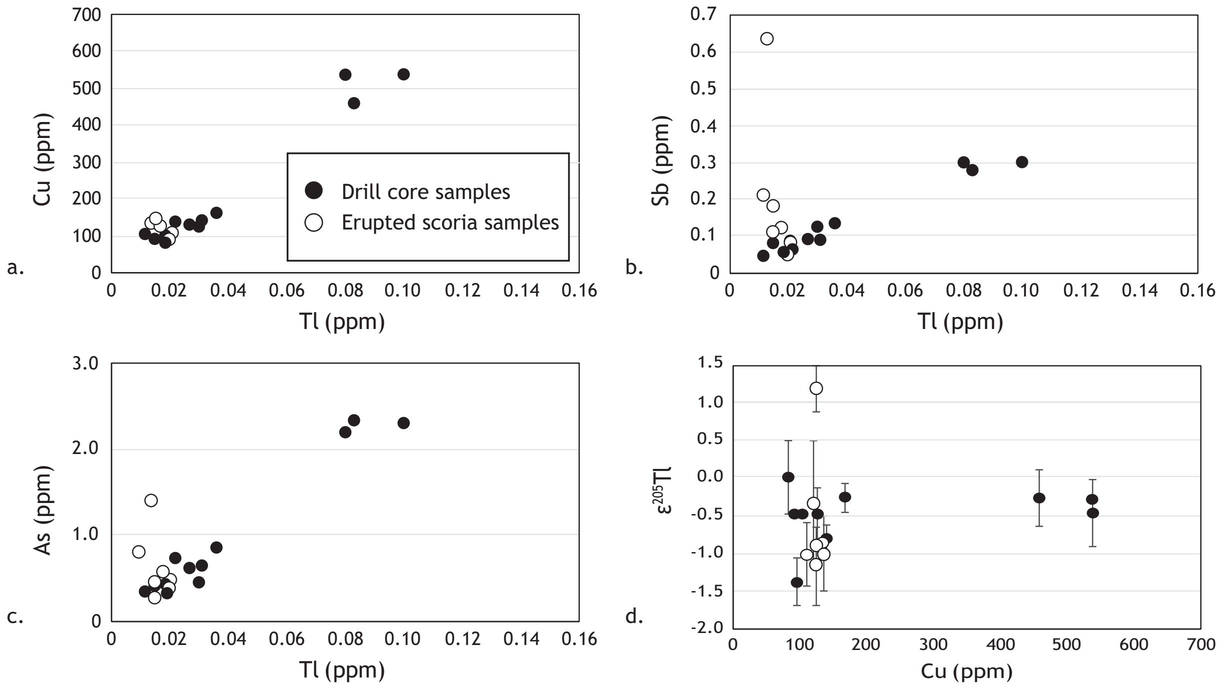

Fig. 3. Thallium concentration and isotope systematics relative to chalcophile elements at Kilauea Iki, with. Tl concentration relative to Cu in (a), As in (b) and Sb in (c). There is some correlation between [Tl] and chalcophile elements, with the three most evolved samples being strongly enriched in Tl. These three are the only samples that represent melts separated after sulfide saturation was reached. (d) ε^{205}Tl as a function of chalcophile concentration (Cu shown here, but similar patterns are observed for the other chalcophile elements).

5.3. Potential causes of Tl isotope heterogeneity Kilauea Iki samples

The Tl isotope system shows discernable but relatively small heterogeneity (Fig. 3) in the Kilauea Iki system, but this does not appear to be directly attributable to fractional crystallization of major phases given the lack of correlation with canonical measures of melt evolution. Here, we explore and discuss potential causes of Tl isotope heterogeneity.

5.3.1. Degassing, water leaching

Thallium is a relatively volatile metal that can be enriched in volcanic gas emissions (e.g., Hinkley et al., 1994). In considering metal output via degassing from several volcanoes, Hinkley et al. (1999) estimated that 9.1 tons per year of Tl were being emitted from Kilauea. If Tl is isotopically fractionated during degassing, this might provide an explanation for the small isotopic heterogeneities seen in Kilauea.

The effect of volcanic degassing on the Tl isotope system was studied in detail by Baker et al. (2009), who analyzed gas condensates and particulates from six volcanoes from around the world. While they reported an average ε^{205}Tl of −1.7 ± 2.0 (comparable to the average composition of the mantle and the continental crust), significant isotopic variation was present amongst individual samples at most of the localities examined. Gas samples from Kilauea were included in this study, and several of these had anomalously negative ε^{205}Tl values. As a result, we would expect degassing from Kilauea Iki lava lake to drive lake samples to higher ε^{205}Tl values as Tl is removed, but we observe the opposite relationship (Fig. 2c). The lava samples with the lowest ε^{205}Tl values have some of the lowest Tl concentrations. Consequently, existing evidence argues against this explanation.

Lastly, it appears that Tl might be vulnerable to leaching by water, either in the geothermal system that circulated in the upper crust of the lava lake, or by the water used during drilling to cool the bit and quench the samples. One sample (KI79-3R2–168), with the extremely low Tl value of ~0.0001 ppm (Table 1), was recovered after having been exposed to three re-entries of the borehole, or roughly three times as much water as any of the other lake samples studied here. However, its ε^{205}Tl value of −0.96, the same as other comparably differentiated samples, confirms that such leaching does not affect the isotopic signature.

5.3.2. Fractionation by sulfides

Thallium can exhibit chalcophile and lithophile characteristics (Heinrichs et al., 1980; Nielsen et al., 2014), and chalcophile behavior seems to be particularly pronounced in ultramafic and mafic lithologies. Nielsen et al. (2014) found that sulfides dominate the thallium budget in mantle lherzolites. In Kilauea Iki, Fe-Ni-Cu sulfide blebs have been reported in both melt inclusions in olivine crystals and in the interstitial melt in partly molten samples (Stone and Fleet, 1991; Helz, 1987b; Helz and Wright, 1992; Pitcher et al., 2009). Greaney et al. (2017) analyzed several chalcophile elements in the groundmass sulfides and found that thallium concentrations and enrichment relative to adjacent groundmass glass were heterogeneous, suggesting relatively mild chalcophile behavior for thallium. Nonetheless, a few sulfides were significantly enriched in thallium (Greaney et al., 2017) and the thallium contents of olivine-hosted sulfides were not determined.

The possible effect of sulfide crystallization on thallium isotopes in Kilauea Iki is considered here. Rader et al. (2018) found that sulfides often have heavier thallium isotope compositions than coexisting silicate minerals in igneous and metamorphic rocks. In Kilauea Iki, sulfide saturation occurred during differentiation and is thought to be the result of the onset of magnetite crystallization, which takes place when glass MgO content falls between 5 and 3 wt% (Greaney et al., 2017). Sulfide minerals are most abundant in the more evolved bulk compositions and appear to be in equilibrium with their interstitial melt (Greaney et al., 2017), which also has the greatest Tl and chalcophile element concentrations (Fig. 2-3). Prior to sulfide saturation, most primitive samples (bulk MgO > 5 wt%and SiO_2 < 51 wt%) have consistently low Tl and chalcophile element concentrations and variable ε^{205}Tl values, indicating indiscriminate Tl partitioning amongst the major mineral phases. However, once sulfide saturation is attained in the more evolved

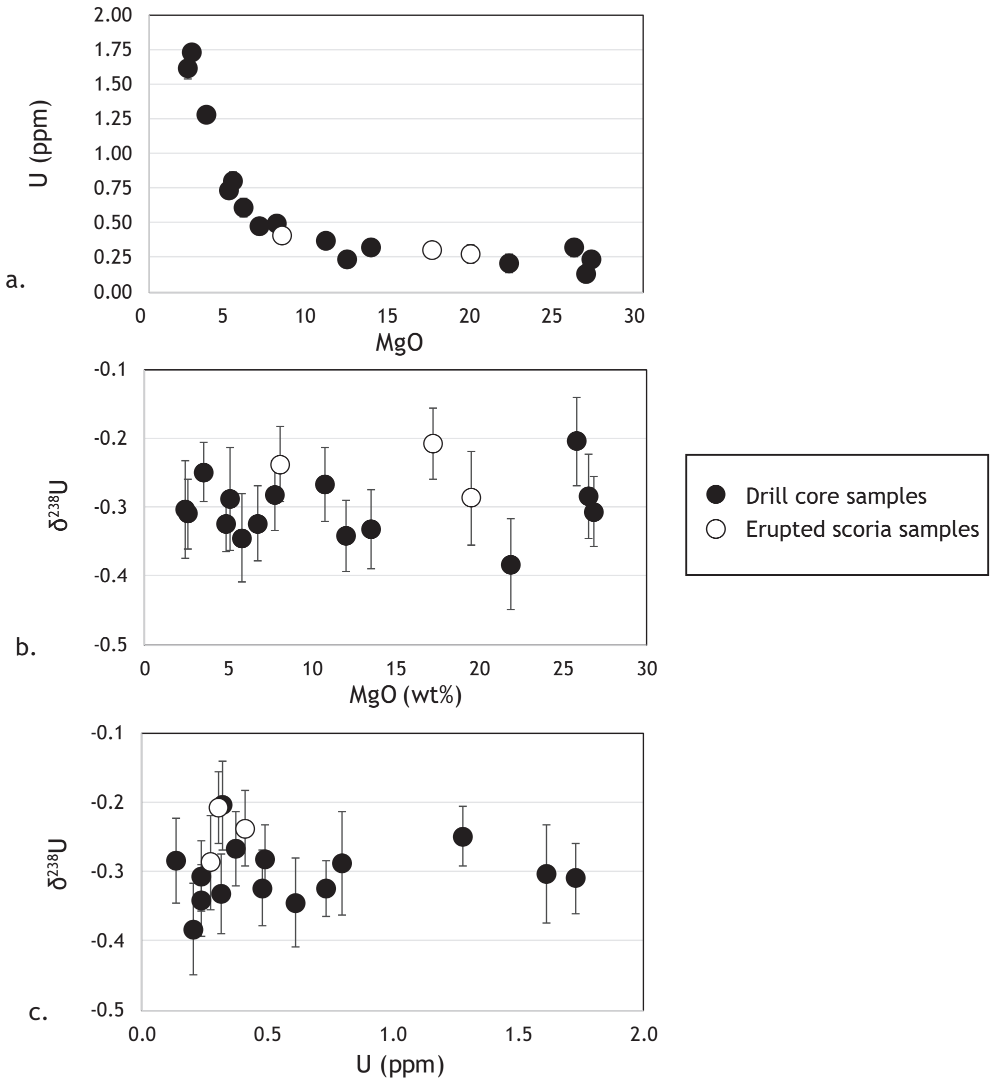

Fig. 4. Stable U isotope systematics in Kilauea Iki. (a) U concentration as a function of MgO. As with Mo and Tl, U content rapidly increases with decreasing below an MgO value of ~10%. (b) δ^{238}U as a function of MgO. The U isotope composition does not vary in any systematic way and most samples overlap within uncertainty. (c) δ^{238}U as a function of U concentration. No coherent variation in isotope composition is observed.

material, Tl may partition into sulfide phases, which have been shown to exert a preference for the heavy isotope of Tl (Rader et al., 2018). This process would induce isotopic fractionation and, overall, push the three evolved samples towards heavier Tl isotope compositions.

This is not observed, however (Figs. 2b and 3d), probably because sulfide is a trace phase in samples from Kilauea Iki lava lake. We can approximate the necessary proportion of sulfide material required to instill the observed fractionation effects. Using the ε^{205}Tl values for sulfide minerals from Rader et al. (2018), which present an overall range from $\varepsilon^{205}\text{Tl} = +1.6$ to $+17.8$ and $\varepsilon^{205}\text{Tl}_{avg} = +5.8$, and solving two-variable simultaneous equations, we note it would require a modal abundance of sulfide blebs between 2 and 17%, with an average of 6%, to shift the ε^{205}Tl values from those of the average primitive samples to those observed for the higher, more evolved samples. The overall abundance of the sulfide blebs observed for the Kilauea Iki samples is insufficient to produce this observed shift, as would be expected from their low bulk sulfur contents (Helz et al., 1994).

5.3.3. Variability within the 1959 scoria samples

The 1959 eruption at Kilauea Iki was a mixed-magma eruption, with both a primitive, mantle-derived magma (1959E-rich component) and a more evolved, shallowly stored magma (1959 W-rich component) (Wright, 1973; Helz, 1987b). Initially, only two erupted samples, both rich in the juvenile component (1959E, see Table 1), were analyzed for Tl isotopes in this study and both displayed light ε^{205}Tl values ($\varepsilon^{205}\text{Tl} < -0.85$). This led us to consider the possibility that the two components might have different Tl isotopic signatures. Five additional 1959 eruption samples, which spanned the range of potential mixing ratios (Table 1), were analyzed to evaluate this possibility. These samples display a wider range of ε^{205}Tl values than range of the previously analyzed samples ($\varepsilon^{205}\text{Tl} = -1.1$ to $+1.2$, Fig. 2b), but are not consistently different from the earlier values, and Tl isotope composition does not correlate with the fraction of the evolved component (Fig. 6). This demonstrates that the two source components do not have distinctive signatures. All 1959 eruption samples analyzed here were collected in real time during the eruption and bagged and stored away from any possible subsequent influences so the variation cannot be attributed to any kind of post-eruptive alteration.

To summarize, the cause and significance of the Tl isotope heterogeneity remains uncertain. However, the magnitude of this heterogeneity is small, with values spanning a range of slightly under 3 ε^{205}Tl units. This is broadly an order of magnitude less than the range of Tl isotope variation seen in terrestrial materials; consequently, we see little evidence from the data presented here that tholeiitic differentiation will

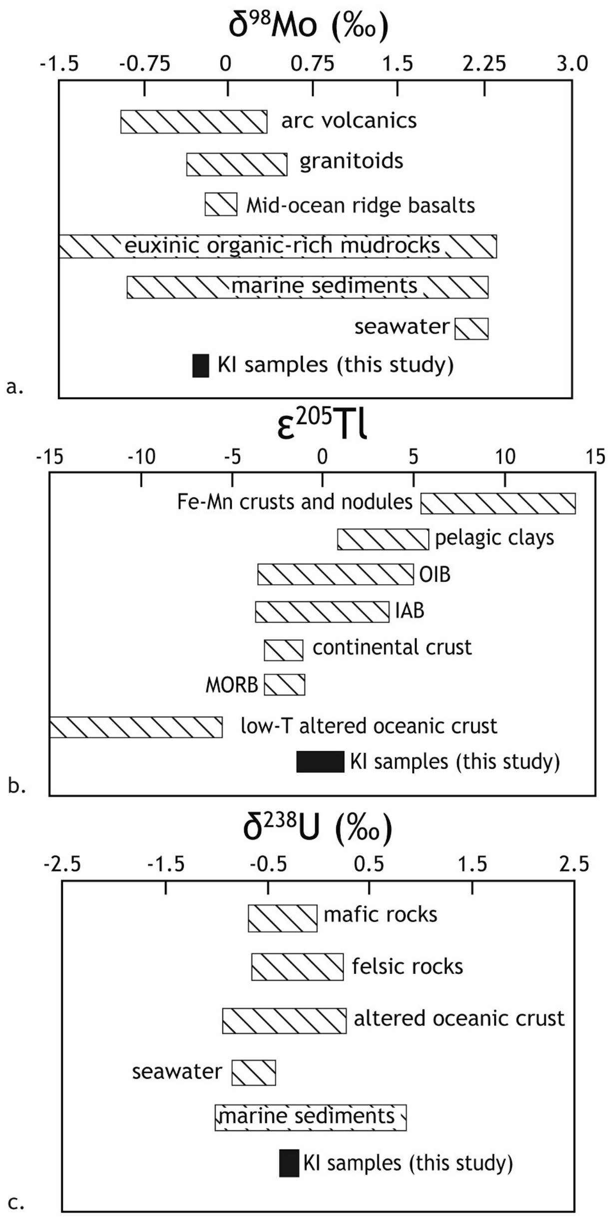

Fig. 5. Kilauea Iki Mo, Tl, and U isotope data compared to range of isotope compositions found in key Earth materials. (a) Mo isotope range modified from Kendall et al. (2017), with additional igneous rock data sources cited in the text of this paper. (b) Tl isotope range modified from Nielsen et al. (2017b). (c) U isotope range modified from Andersen et al. (2017).

contribute significantly to the global variation seen in Tl isotope compositions.

6. Conclusions

Molybdenum, Tl, and U isotope analyses of diverse samples from Kilauea Iki lava lake samples ranging from olivine cumulates to ferrodiabasic segregations and beyond, were obtained, to evaluate whether fractional crystallization in the tholeiitic Kilauea Iki system leads to fractionation in these isotope systems. The Mo and U isotope systems do not systematically vary and mean δ^{98}Mo and δ^{238}U values are -0.22 ± 0.08‰ (2σ) and -0.29 ± 0.09‰ (2σ), respectively. The lack of fractionation in the Mo isotope system is consistent with previous work in another tholeiitic system (Yang et al., 2015), but this is the first systematic study of this question for the U isotope system. The mean Mo isotope composition is comparable to the range seen in Pacific MORB (Bezard et al., 2016) and lacks the clear evidence of recycled sediment influence in the Hawaiian source that is seen in other isotope tracers.

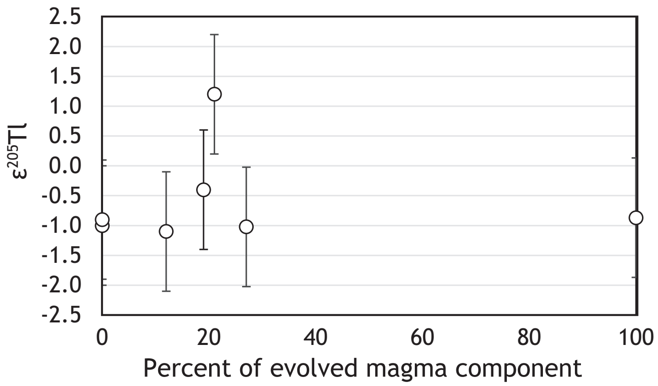

Fig. 6. Tl isotope composition of erupted scoria samples versus the percent of the evolved magma component in the Kilauea Iki system calculated by Wright (1973). Variations in erupted scoria compositions indicate that the eruption tapped two magmas: a primitive one derived directly from the mantle and a more evolved, shallowly stored one (Wright, 1973; Helz, 1987b). Lack of correlation indicates that Tl isotope heterogeneity is not tied to mixing of discrete magmas.

In contrast to the Mo and U systems, Tl isotopes show some heterogeneity, both in Kilauea Iki and in the 1959 eruption samples, with ε^{205}Tl values ranging from $+1.20$ to -1.38. ε^{205}Tl values do not clearly correlate with indicators of differentiation such as MgO or SiO$_2$ or with eruption component proportions. Also there is insufficient sulfide present in samples from Kilauea Iki to impact the ε^{205}Tl compositions. Overall, the magnitude of Tl isotope variation observed here is quite small, both compared to what has been observed across Earth reservoirs and also what has been reported in igneous rocks alone and shows no consistent variation at Kilauea Iki. While there is slightly more heterogeneity in Tl isotope compositions here as compared with U and Mo, there is no systematic behavior during differentiation for Tl.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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