The Behavior of Re & the Platinum Group Elements during Fractional Crystallization of the Kilauea Iki Lava Lake, Hawaii

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Abstract

Through the use of the isotope dilution method, concentrations of Rhenium and the Platinum Group Elements in picritic basalts from the Kilauea Iki lava lake were measured in order to improve our understanding of the behavior of these elements during volcanic events. The lava lake was formed as a result of the 1959 eruption of the Kilauea volcano. Olivine was the dominant phase during eruption and fractional crystallization of the lake. The lake has a high average MgO content of approximately 15.5%. In the basalts studied MgO varies from 26.8 to 2.3 wt%. Osmium and Ruthenium behave as compatible trace elements with a positive correlation with MgO. Iridium did not correlate with MgO as well as osmium and ruthenium but also appears to be incompatible. Rhenium, Palladium, and Platinum do not well correlate with MgO, although both Re and Pd tend to decrease with increasing MgO, consistent with incompatible trace element behavior. The poor correlation for these elements may be an indication that their abundances are controlled by a phase other than olivine. The low abundances and variability of Re may also be the result of degassing during the eruption Kilauea volcano.

Kilauea Iki Lava Lake

- Formed during the 1959 eruption of the Kilauea volcano (Figure 1).
  - (Nov. 14 – Dec. 20, 1959)
- Prior to the eruption, Kilauea Iki was a empty collapsed crater.
  - 1610 meters long
  - 804 meters wide
  - 213 meters deep
- Picritic tholeiite lava filled the crater.
  - High MgO Content (15.4%)
- Crystallized as a closed system.
  - 39 million cubic meters of picritic tholeiite basalt.
    - Average 15.5 wt.% MgO
  - 102 meters thick.
- Inward crystallization
  - Figure 2.
- Ideal for studying fractional crystallization in basaltic systems.

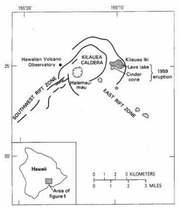


Figure 1. Index map of the summit area of Kilauea Volcano, showing the location of Kilauea Iki lava lake and the 1959 cider cone relative to the main caldera. From: Helz et al., 1983

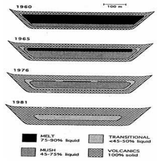


Figure 2. Inward crystallization of the Kilauea Iki Lava Lake. From: Helz et al., 1984

Hypothesis

- Ir, Ru, and Os are compatible in basaltic systems.
- Pd, Pt, Re are incompatible in basaltic systems.

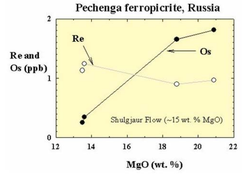
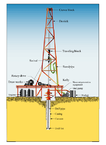


Figure 3. Plot of Re and Os versus MgO, illustrating Re as an incompatible element and Os as a compatible element. From : Walker et al., 1999



Samples

The cores used for this project (Table1) are recoveries from the 1967, 1975, 1979, and 1981 drillings (Figure 4). The Kilauea Iki rocks range from olivine rich cumulates, olivine tholeiites to ferrodiabase, and silicic veins, all of which were produced by internal differentiation in the lava lake.

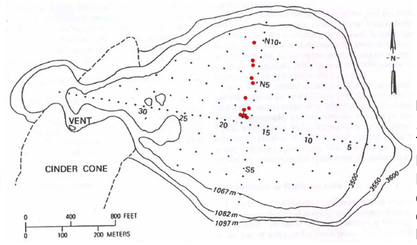
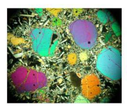


Figure 4. Plan view of the post 1959 surface of Kilauea Iki. The small black dots show the locations of the network of leveling stations. Larger red dots are locations of holes drilled between 1967 and 1988. From: Helz et al., 1983

Table 1. Samples examined for this study, in decreasing MgO content, their identification numbers, and measured Re and PGE concentrations in nanograms per gram (ng/g). MgO from Helz (1983)

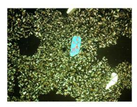
Sample ID	MgO (wt.%)	Os (ng/g)	Ir (ng/g)	Ru (ng/g)	Pt (ng/g)	Pd (ng/g)	Re (ng/g)
KI-81-1-169.9	26.87	0.6333 ± 0.00076	0.3312 ± 0.0018	1.958 ± 0.010	1.401 ± 0.017	1.962 ± 0.051	0.1511 ± 0.0025
KI-81-1-239.9	26.55	0.9669 ±0.01102	0.4801 ± 0.0008	1.613 ± 0.005	10.43 ± 0.019	0.2474 ± 0.058	0.03041± 0.0028
KI-67-3-6.8	25.83	1.065 ± 0.2398	0.3807 ± 0.0025	1.482 ± 0.009	1.151 ± 0.019	1.351 ± 0.056	0.4186 ± 0.0028
KI-81-1-210.0	24.5	0.8207 ± 0.01108	0.7508 ± 0.0011	2.012 ± 0.003	1.921 ± 0.017	0.3490 ± 0.050	0.03901± 0.0024
IKI-22	19.52	0.6044 ± 0.00073	0.3927 ± 0.0021	1.301 ± 0.007	5.564 ± 0.030	1.526 ± 0.050	0.2247 ± 0.0024
KI-79-3-150.4	13.5	0.4343 ± 0.00069	0.5196 ± 0.0007	0.6264 ± 0.003	3.102 ± 0.015	2.463 ± 0.046	0.2269 ± 0.0023
KI-67-3-27.5	12	0.2224 ± 0.00342	0.2668 ± 0.0013	0.5171 ± 0.003	2.394 ± 0.019	2.626 ± 0.057	0.4306 ± 0.0028
KI-75-1-139.3	11.7	0.2403 ± 0.00457	0.7639 ± 0.0008	1.412 ± 31.9	1.636 ± 0.019	0.2868 ± 0.057	0.06889 ± 0.0028
KI-67-3-39.0	10.73	0.1725 ± 0.00624	0.2252 ± 0.0010	0.4530 ± 0.003	3.533 ± 0.016	5.812 ± 0.052	0.2985 ± 0.0024
IKI-58	8.08	0.05603 ± 0.00242	0.1651 ± 0.0003	0.4017 ± 0.004	2.285 ± 0.019	2.083 ± 0.056	0.4141 ± 0.0028
KI-67-3-81	7.73	0.09690 ± 0.00306	0.1227 ± 0.0016	0.1588 ± 0.003	2.360 ± 0.016	3.169 ± 0.050	0.2120 ± 0.0024
KI-75-1-121.5	7.5	0.02664 ± 0.00085	0.2127 ± 0.0004	0.2408 ± 0.003	1.582 ± 0.019	1.239 ± 0.058	0.1873 ± 0.0028
KI-75-1-75.2	5.77	0.01044 ± 0.0006	0.0065 ± 0.0002	0.04781 ± 0.002	2.620 ± 0.014	3.605 ± 0.043	0.9308 ± 0.0021
KI-67-2-85.7	2.6	0.1050 ± 0.00768	0.1170 ± 0.0003	0.1037 ± 0.003	5.180 ± 0.019	3.883 ± 0.058	0.6261 ± 0.0028
KI-81-2-88.6	2.37	0.0006 ± 0.00062	0.0003 ± 0.0002	0.0034 ± 0.002	3.924 ± 0.014	3.125 ± 0.043	2.0293 ± 0.0022

Samples



XPL
Scale of view: 3mm

- KI-81-1-169.9
- 26.87 MgO wt % (Highest)
- Olivine cumulate



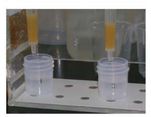
XPL
Scale of view: 5mm

- KI-67-2-82.5
  - Equivalent to KI-67-2-85.7
- 2.60 MgO wt% (lowest)
- Ooze

Methods: Chemical Separation

- Powders were made from rock chips.
- Teflonware and Carius Tubes cleaned in aqua regia.
- Carius Tubes used for sample digestion.
  - Added powders and spikes.
  - Sealed and heated in oven.
    - Ensures that the powder and acid + spike solutions equilibrate.

Methods: Chemical Separation



- Os was extracted into carbon tetrachloride (CCl_4), reduced and stabilized in hydrobromic acid (HBr).
- Re and the remaining PGE were purified using anion exchange columns and concentrated acids.

Methods: Mass Spectrometry

- Osmium was analyzed by Thermal Ionization Mass Spectrometry.

Thermal Ionization Mass Spectrometer

Inductively-Coupled Plasma Mass Spectrometer

- Rhenium, Ru, Ir, Pt, and Pd were analyzed by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS).

Measurement Uncertainties

Factors that may contribute to the uncertainty in concentration are the uncertainty of the sample and spike weights, the isotope ratios, and blank corrections. The largest value is the uncertainty that was applied to final cited concentration. (Note: the uncertainties cited are 2 sigma). Most uncertainties were dominated by blank corrections (Table 2).

Table 2. The total average blank and blank uncertainties for each element analyzed. n = 3

Os blank (pg)	Ir blank (pg)	Ru blank (pg)	Pt blank (pg)	Pd blank (pg)	Re blank (pg)
8.8 ± 1.5	0.0925 ± 0.06	7.0 ± 6.7	432.7 ± 34	174.3 ± 10	4.2 ± 5.0

Results

Osmium and Ru concentrations range from 0.0006 to 1.06 ppb and 0.0034 to 2.01 ppb, respectively. In plots of MgO (wt. %) versus element concentration (ppb), Os and Ru behave as highly compatible elements with positive correlations. Regressions for both elements have relatively high R^2 values of 0.865 (Ru) and 0.858 (Os), indicating a good linear correlation. Iridium concentrations range from 0.0003 to 0.76 ppb; Ir does not correlate as well as Os and Ru with an low R^2 of 0.41. Rhenium has generally low concentrations (0.030 - 2.0 ppb), a poor correlation with MgO, and a R^2 of 0.32. Palladium concentrations range from 0.24 to 5.81 ppb and Pt concentrations are 1.15 to 10.4 ppb. Both elements have low R^2 values of 0.021 (Pt) and 0.35 (Pd). Figure 5 shows MgO plots for the elements measured

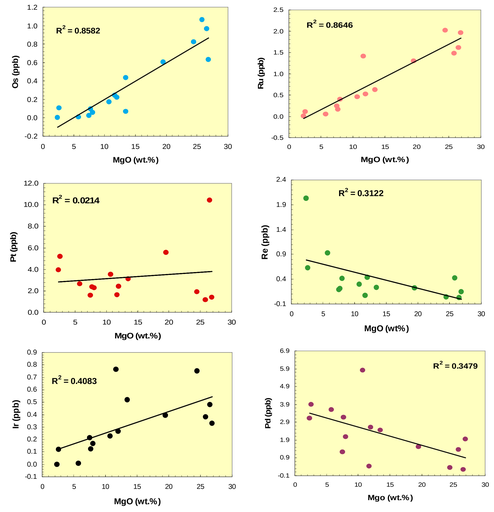


Figure 5. Plots of MgO (wt. %) versus Re, Os, Ir, Pt, and Ru concentrations (in ppb).

Discussion

The positive trends in the MgO plots for Os and Ru illustrate that the elements behave compatibly in this system; as the MgO decreases via olivine fractionation, the concentration of Os and Ru correspondingly decrease. Although Rhenium, Pd, Ir, and Pt do not correlate well with MgO, Ir behaves in a compatible manner; Re and Pd exhibit incompatible behaviors; their concentrations increase as MgO decreases. Therefore Re, Pd, and Ir maybe controlled less by olivine and more by sulfide and chromite precipitation. The low abundances of Re is perhaps also a result of degassing of Re during the eruption of the Kilauea volcano (Norman el at., 2004; Bennett et al., 2000).

Bulk distribution coefficients were estimated for Ru, Re, and Os by calculating model liquid and sold compositions generated by fractional crystallization and empirically changing D-values until a good fit to the actual Iki data was achieved. Calculations were done using the starting concentrations obtained for sample KI-79-3-150.4, a rock with MgO content (13 wt.%) most similar to the estimated parental melt. Figure 6a illustrates Re as an incompatible element with a bulk-D value of 0.45. Os has a bulk-D value of 2.5. Ru has estimated D-value of 3.0 and therefore behaves similar to Os (Figure 6b).

Figure 6. (a) Bulk distribution coefficient model for Os and Re. (b) Bulk distribution coefficient model for Re and Ru.

Conclusions

Concentrations of Re and PGE were measured in borehole samples from the Kilauea Iki lava lake. Osmium (0.0006 to 1.06 ppb) and Ru (0.0034 to 2.01 ppb) displayed a good correlation with MgO content, indicating that olivine controlled these elements during fractional crystallization of the lava lake. Iridium (0.0003 to 0.7 ppb), Pd (0.24 to 5.8 ppb), Pt (1.15 to 10.4 ppb), and Re (0.030 to 2.0 ppb) have limited correlations to changes in MgO, leading to two assumptions; (1) Iridium, Pd, and Pt were influenced less by olivine and more by a co-precipitating phase like chromite, or sulfides found as inclusions in the olivine phenocrysts. (2) Outgassing of Re during the eruption of the Kilauea volcano may have contributed to low Re concentrations. The bulk distribution coefficients for Os, Re, and Ru were estimated (Figure 5).

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Acknowledgments — I wish to thank Dr. Rosalind T. Helz from the USGS. Thanks also go to Dr. Igor S. Puchtel for guidance in the University of Maryland's geochemistry clean laboratories. Thanks to Dr. Roberta L. Rudnick for the use of her digital camera and microscope to photograph thin-sections. Special thanks is due to Dr. Richard J. Walker for taking the role as my thesis advisor, mentor, and teacher.