The Behavior of Rhenium and the Platinum Group Elements during Fractional Crystallization of the Kilauea Iki Lava Lake in Hawaii

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Abstract

Through the use of the isotope dilution method, concentrations of Rhenium and the Platinum Group Elements in 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 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 may be an indication that the 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.

Introduction

The behavior of Rhenium (Re) and the Platinum Group Elements (PGE) are studied in a picritic system, the Kilauea Iki Lava Lake (KILL), Hawaii. The investigation documents the compatibility or incompatibility of these elements by determining their concentrations in KILL samples as a function of known crystal-liquid fractionation sequence (e.g. MgO content in each rock). Concentration variations are used to estimate bulk-distribution coefficients (D-values). I have successfully measured the concentrations of these elements in sixteen of the basalts.
Background

Problem

The behavior of Re and PGE in mafic systems is not well understood due to their low abundances; for this reason studying these elements in samples from the well-characterized KILL will help improve our understanding of how these elements behave during injection and crystallization of a magmatic system.

Kilauea Iki Lava Lake

The Kilauea Iki Lava Lake (Figure 1) was produced by the 1959 eruption of Hawaii’s youngest volcano, Kilauea. Prior to the eruption, Kilauea Iki was an empty collapsed crater approximately 1610 meters long, 804 meters wide, 213 meters deep, and lay to the east of the main Kilauea volcano caldera. The eruption lasted 36 days (November 14 – December 20, 1959) and consisted of 17 separate eruptive phases, which lasted in duration from 1 week to 1 hour (Richter et al., 1970). At the beginning of the eruption, multiple fissures formed a discontinuous line along the crater’s walls in both directions and grew to heights ~15 meters (Richter et al., 1970). By November 15\textsuperscript{th} only one fissure remained active growing from 45 to 304 meters high and throughout the remainder 17 eruptive spurs this single active vent poured 39 million meters cube of picritic tholeiitic lava, containing on average 15.5 wt% MgO (Wright 1973), into the crater, forming a lava lake 102 meters deep (Richter et al., 1970).

Figure 1. Index map of the summit area of Kilauea Volcano, showing the location of Kilauea Iki lava lake and the 1959 cinder cone relative to the main caldera. From: Helz et al., 1983
Weeks after the eruption, the surface cooled forming a solid layer, but with liquid remaining inside for more than 30 years. Over the course of 30+ years, the lake cooled and crystallized inward as a self-roofed magma chamber (Helz et al., 1989); essentially as a closed system where there was no additional volcanic activity and minimal chemical weathering, and the chemistry of the lake was not affected by the composition of the surrounding walls of the crater. While the lava lake was solidifying, 23 successive series of deep boreholes were drilled into the lake (1960, 1961, 1962, 1967, 1975, 1976, 1979, and 1981) recovering roughly 1,200 m of drill core (Helz 1987), and giving an in-depth look at the differentiation of the lava lake (Figure 2). Samples from these cores are the focus of this study.

The KILL is an ideal setting to investigate Re and PGE behavior in a closed system due to the fact that the lava lake is:

1. A natural system that provided an opportunity to observe the behavior of these elements in an environment where they occur in natural abundances.
2. A closed system; the lava lake has not been affected by additional volcanic activity (Helz et al., 1989), chemical weathering (e.g. rain), etc.
3. With constant drilling, the natural course of crystallization, differentiation processes, and composition of KILL can be monitored in detail (Helz et al., 1989).

Figure 2. -- 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., 1994
4. The PGE and Re in KILL basalts have not previously been studied.

As a side benefit, the data generated from this study can contribute towards broadening geological knowledge about the Earth’s deep mantle processes. Mantle melting is not completely understood, so analyzing the end products of mantle melting is crucial to our understanding of the mantle. With updated knowledge about the Earth’s mantle, educated guesses can be made about element partitioning and mantle processes on other planetary bodies; particularly within the moon’s mantle where the composition may be similar to Earth’s. Moreover, insight about hot spots can be enhanced; questions about why hot spots appear in the mantle and why they arise at a particular spot can be potentially answered.

*Platinum Group Elements (PGE)*

Platinum (Pt), Palladium(Pd), Iridium (Ir), Ruthenium (Ru), Rhodium (Rh), and Osmium (Os) together form a group of elements known either as the Platinum Group Elements (PGE), the Platinum Group Metals (PGM), or the Precious Metals (PM). These elements are highly chalcophile (sulfur loving), and are called PM because they’re the rarest elements commonly found together in Earth’s crust and are mined dominantly in Russia and South Africa. They have similar physical properties, e.g. high density and melting points, and are non reactive with other elements and ions. Platinum and Pd are found in nature as pure forms while the other PGE occur in nature as natural alloys with platinum and gold. Platinum has multiple uses, for example it acts as a catalyst for the control of automobile and industrial plant emissions, and for the production of acids, organic chemicals, and pharmaceuticals. The PGE are used to make reinforced plastic, electrical contacts, conductive and resistive films in electronic circuits, and in jewelry (Mineral Info. Institute).

For this thesis project Rh was not measured because it has only one stable isotope; elements with at least two stable isotopes are required in order to conduct isotope dilution. Standard information about the PGE is given in appendix A.

*Rhenium (Re)*

Rhenium is a silvery white metal with a metallic luster. It is a chalcophile element and is found in nature as a minor component in the mineral gadolinite. It has an atomic mass of 186.207,
atomic number of 75, and has two naturally occurring isotopes \(^{185}\text{Re}, ^{187}\text{Re}\). Rhenium is used for mechanical and chemical purposes (e.g. wires in photography flash lamps).

**Fractional Crystallization**

Fractional Crystallization (FC) is an igneous process during which the crystallizing mineral is physically separated from the parental magma so that the two phases can no longer maintain chemical equilibrium (the newly formed crystals do not further interact/equilibrate with the melt). FC is important in geochemistry because it can lead to the major changes in melt compositions. Figure 3 is a Fenner diagram from Winter (2001) showing the effects of olivine crystallization on a variety of major elements for the 1959 eruption of the Kilauea volcano.

![Fractional Crystallization Diagram](image)

Figure 3. Variation diagram using MgO as the abscissa (sometimes called a “Fenner” diagram) for lavas associated with the 1959 Kilauea eruption in Hawaii. The parent melt (asterisks) was estimated from the most primitive glass found. Subsequent studies have suggested that the parent melt had MgO of about 15.5 wt.%. All the variation can be accounted for by the extraction and accumulation of olivine phenocrysts (after Murata and Richter, 1966, as modified by Best, 1982). From: Winter 2001.

**The Partition Coefficient**

The partition coefficient \((K_d)\) is important in crystal-liquid fractionation because it is a measure of the incompatibility or compatibility of a trace element in a mineral. Trace elements rarely
form their own phases; therefore they must reside in major or minor mineral phases. To be compatible or incompatible refers to a trace element’s preference to replace a major element in available sites in the crystal structure of a mineral; an incompatible element favors the melt; a compatible element favors the solid. A \( K_d \) value is the concentration of an element in a crystallizing mineral divided by the concentration of the element in the melt from which the mineral is crystallizing.

**The Bulk Distribution Coefficient**

The bulk distribution coefficient (D-values) differs from the partition coefficient in that D-values are used to deal with multiple mineral systems; but like the partition coefficient, D-values reflect the compatibility or incompatibility of a trace element. The equation to calculate the D-Value is given below, where \( D > 1 \) is a compatible element and \( D < 1 \) is an incompatible element.

\[
D = \left( \begin{array}{c}
\text{fraction of mineral A} \\
K_d \text{ of mineral A}
\end{array} \right) + \left( \begin{array}{c}
\text{fraction of mineral B} \\
K_d \text{ of mineral B}
\end{array} \right) + \cdots
\]

**Hypothesis**

I hypothesize that Ir, Ru, and Os are compatible in the KILL system and that Pd, Pt, and Re are incompatible. My hypothesis was generated by examining previous studies of Re and PGE partitioning in igneous systems. For example Walker et. al. (1997), a study of Proterozoic picritic rocks, reported Os was compatible during crystallization of a single flow (Figure 4). As the melt crystallized the concentration of the element decreased. Figure 2 also shows Re displaying a negative slope when plotted vs. MgO, consistent with it being an incompatible element in this system.

Figure 4: Plot of Re and Os versus MgO from Walker et. al. (1997), illustrating Re as an incompatible element and Os as compatible.
Brenan et. al. (2005) reported the olivine-melt partition coefficients ($K_d$) of some PGE for an experimental system. Figure 5 shows how the olivine-melt partition coefficients ($K_d$) of the PGE and Re vary with decreasing Oxygen Fugacity ($fO_2$). It illustrates Ir and Ru as compatible and Pd, Ru, Pt, and Re as incompatible. Note how the $K_d$ values of Ir and Ru increase with decreasing log $fO_2$ ($K_d > 1$). Observe also that Ru, Pd, Pt, and Re $K_d$ values decrease with decreasing log $fO_2$ ($K_d < 1$), but Re is more incompatible than the other elements.

![Figure 5: Graph from Brenan et. al. (2005) illustrating how the olivine-melt partitioning coefficients ($K_d$) of the PGE and Re vary with decreasing log $fO_2$.](image)

**Sample Descriptions**

Tables 1-3 and Figure 6 describe and classify the rocks and thin-sections and their compositions. All the cores and thin-sections used were obtained by Dr. Rosalind Helz from the United States Geological Survey (USGS). The samples are recoveries from the 1967, 1975, 1979, and 1981 drillings (Helz et al., 1989) as shown in Figure 6. 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 (Tomascak et al., 1999).
Figure 6. Cross-section of Kilauea Iki lava lake, taken along the N-S line of closely-spaced levelling stations shown in Figure 2. The present surface of the lava lake and two pre-eruption profiles are shown. The two pre-eruption profiles are taken from two different topographic maps: one (at 1:2000) is based on air photos taken in 1948; the other (at 1:5000) is based on air photos taken in 1955. Both maps were prepared by R. Jordan, U.S.G.S., Flagstaff. The present position of the lake bottom (dashed line) has been intersected only at the location of drill hole KI79-5. The vertical exaggeration is 4:1.

The drill holes, which mostly lie along a line 100 feet to the west of this section, are shown as vertical lines projected onto this cross section. Several of the drill hole locations have been reoccupied more than once, in order to sample the same section of the crust in several stages of development. Spacing between these closely-spaced holes is not to scale in this figure.

From: Helz et al., 1989
Table 1. *Sample Chart*. Samples examined for this study, in decreasing MgO content, and their identification numbers. The check marks (✓) indicates which rock I have a thin-section of, and the X indicates which cores I do not have a thin-section of. From: (Helz1989

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>MgO (wt%)</th>
<th>Thin-Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI-81-1-169.9</td>
<td>26.87**</td>
<td>✓ VORB (Vertical Olivine Rich Bodies) contains glass</td>
</tr>
<tr>
<td>KI-81-1-239.9</td>
<td>26.55</td>
<td>✓ Contains glass</td>
</tr>
<tr>
<td>KI-67-3-6.8</td>
<td>25.83</td>
<td>X Phase 4 &amp; 5 of eruption</td>
</tr>
<tr>
<td>KI-81-1-210.0</td>
<td>24.5</td>
<td>X Contains glass</td>
</tr>
<tr>
<td>Iki-22</td>
<td>19.52</td>
<td>✓</td>
</tr>
<tr>
<td>KI-79-3-150.4</td>
<td>13.5</td>
<td>X</td>
</tr>
<tr>
<td>KI-67-3-27.5</td>
<td>12</td>
<td>✓</td>
</tr>
<tr>
<td>KI-75-1-139.3</td>
<td>11.7</td>
<td>X Contains glass</td>
</tr>
<tr>
<td>KI-67-3-39.0</td>
<td>10.73</td>
<td>✓</td>
</tr>
<tr>
<td>Iki-58</td>
<td>8.08</td>
<td>✓</td>
</tr>
<tr>
<td>KI-67-3-81</td>
<td>7.73</td>
<td>✓ Contains glass</td>
</tr>
<tr>
<td>KI-75-1-121.5</td>
<td>7.5</td>
<td>✓</td>
</tr>
<tr>
<td>KI-75-1-75.2</td>
<td>5.77</td>
<td>✓ Segregation vein</td>
</tr>
<tr>
<td>KI-67-2-85.7</td>
<td>2.60*</td>
<td>X</td>
</tr>
<tr>
<td>KI-81-2-88.6</td>
<td>2.37*</td>
<td>X Vein – in - vein</td>
</tr>
</tbody>
</table>

*(Sample with the lowest amount of MgO).
***(Sample with the highest amount of MgO)
Table 2: *Hand Sample Classification.* Descriptions of hand samples available, as listed in table 1, for classification. Note that the hand samples and thin-sections were not available for all samples analyzed.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Textures</th>
<th>Minerals Present and their % Abundance</th>
<th>Color Index (CI)</th>
<th>Rock Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI-67-3-6.8</td>
<td>Vesicular Aphanitic porphyritic</td>
<td>Olivine (green mineral) 85%</td>
<td>Mafic 70-85%</td>
<td>Vesicular Porphyritic Aphanitic Basalt</td>
</tr>
<tr>
<td>KI-75-1-75.2</td>
<td>Vesicular Aphanitic</td>
<td>Plagioclase (white elongated minerals) 70% Olivine (green minerals) 10%</td>
<td>Mafic 45-85%</td>
<td>Vesicular Aphanitic Basalt</td>
</tr>
<tr>
<td>KI-75-1-121.5</td>
<td>Aphanitic</td>
<td>Plagioclase (white minerals) 90% Olivine (green minerals) 5% Pyroxene (dark minerals) 5%</td>
<td>Mafic 50-85%</td>
<td>Basalt</td>
</tr>
<tr>
<td>KI-75-1-139.3</td>
<td>Aphanitic porphyritic</td>
<td>Olivine (green minerals) 75%</td>
<td>Mafic 45-85%</td>
<td>Porphyritic Basalt</td>
</tr>
<tr>
<td>KI-81-1-169.9</td>
<td>Aphanitic porphyritic</td>
<td>Olivine (green minerals) 90%</td>
<td>Mafic 45-85%</td>
<td>Porphyritic Basalt</td>
</tr>
<tr>
<td>KI-81-1-210.0</td>
<td>Aphanitic porphyritic</td>
<td>Olivine (green minerals) 85%</td>
<td>Mafic 45-85%</td>
<td>Porphyritic Basalt</td>
</tr>
<tr>
<td>KI-81-1-239.9</td>
<td>Aphanitic porphyritic</td>
<td>Olivine (green minerals) 90%</td>
<td>Mafic 45-85%</td>
<td>Porphyritic Basalt</td>
</tr>
</tbody>
</table>
Table 3: Chemical compositions of each rock studied. From: Helz et al., 1989.

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>MnO</th>
<th>CO₂</th>
<th>Cr₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI-67-3-6.8</td>
<td>44.63</td>
<td>7.58</td>
<td>2.10</td>
<td>10.13</td>
<td>25.83</td>
<td>6.25</td>
<td>1.22</td>
<td>0.30</td>
<td>1.32</td>
<td>0.12</td>
<td>0.18</td>
<td>0.01</td>
<td>0.24</td>
</tr>
<tr>
<td>KI-67-3-27.5</td>
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<td>11.74</td>
<td>3.30</td>
<td>8.19</td>
<td>12.01</td>
<td>10.59</td>
<td>1.95</td>
<td>0.49</td>
<td>2.31</td>
<td>0.24</td>
<td>0.17</td>
<td>0.02</td>
<td>0.09</td>
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<td>KI-67-3-39.0</td>
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<td>4.14</td>
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<td>10.73</td>
<td>10.71</td>
<td>2.05</td>
<td>0.54</td>
<td>2.48</td>
<td>0.24</td>
<td>0.17</td>
<td>0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>KI-67-3-81</td>
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<td>5.77</td>
<td>10.01</td>
<td>2.73</td>
<td>0.79</td>
<td>4.12</td>
<td>0.38</td>
<td>0.18</td>
<td>0.02</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>KI-75-1-121.5</td>
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<td>13.46</td>
<td>1.64</td>
<td>9.07</td>
<td>7.77</td>
<td>11.00</td>
<td>2.49</td>
<td>0.64</td>
<td>3.06</td>
<td>0.37</td>
<td>0.16</td>
<td>0.03</td>
<td>0.06</td>
</tr>
<tr>
<td>KI-75-1-139.3</td>
<td>48.77</td>
<td>12.37</td>
<td>1.54</td>
<td>9.34</td>
<td>11.64</td>
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<td>2.06</td>
<td>0.52</td>
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</tr>
<tr>
<td>KI-81-1-210.0</td>
<td>44.87</td>
<td>7.64</td>
<td>1.10</td>
<td>11.24</td>
<td>24.53</td>
<td>7.66</td>
<td>0.98</td>
<td>0.21</td>
<td>1.09</td>
<td>0.10</td>
<td>0.18</td>
<td>0.01</td>
<td>0.20</td>
</tr>
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<td>KI-81-1-239.9</td>
<td>44.21</td>
<td>6.92</td>
<td>0.98</td>
<td>11.93</td>
<td>26.55</td>
<td>6.73</td>
<td>0.95</td>
<td>0.20</td>
<td>1.00</td>
<td>0.11</td>
<td>0.18</td>
<td>0.01</td>
<td>0.25</td>
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<tr>
<td>KI-81-2-88.6</td>
<td>57.07</td>
<td>12.86</td>
<td>2.44</td>
<td>9.41</td>
<td>2.37</td>
<td>6.08</td>
<td>3.55</td>
<td>1.90</td>
<td>2.59</td>
<td>0.96</td>
<td>0.18</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>IKI-22</td>
<td>49.18</td>
<td>12.1</td>
<td>nd</td>
<td>11.33</td>
<td>nd</td>
<td>11.17</td>
<td>2.33</td>
<td>0.52</td>
<td>2.49</td>
<td>0.22</td>
<td>0.13</td>
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<tr>
<td>IKI-58</td>
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<td>nd</td>
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<td>nd</td>
<td>11.5</td>
<td>2.62</td>
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<td>2.91</td>
<td>0.26</td>
<td>0.14</td>
<td>nd</td>
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</tr>
</tbody>
</table>
Petrology of Thin-Sections

Olivine (Figure 7a), pyroxene (Figure 7b), and plagioclase (Figure 7c) are the minerals dominantly found in the thin-sections.

A notable feature in the large olivine phenocrysts are opaque inclusions observed in samples KI-67-3-39.0 and KI-81-1-169.7 (Figure 8a-b). According to Helz (1983) the inclusions occur mainly in olivine phenocrysts. The inclusions are sulfides and it is theorized that the sulfides formed at unique temperatures, silicate melt compositions, and at locally high sulfur fugacities (Helz 1983).

Figure 7: Thin sections from KILL core samples in crossed polarized light with a 3mm field of view; (a) Olivine phenocrysts surrounded by glass from the eruption sample Iki-22; (b) pyroxenes from KI-67-3-39.0 core; (c) subhedral plagioclase phenocrysts in a matrix made entirely of smaller sized plagioclase.

A notable feature in the large olivine phenocrysts are opaque inclusions observed in samples KI-67-3-39.0 and KI-81-1-169.7 (Figure 8a-b). According to Helz (1983) the inclusions occur mainly in olivine phenocrysts. The inclusions are sulfides and it is theorized that the sulfides formed at unique temperatures, silicate melt compositions, and at locally high sulfur fugacities (Helz 1983).

Figure 8 (a-b): olivine phenocrysts with opaque inclusions in thin sections of KILL cores in crossed polarized light. Field of view: 0.25 mm across. (a) KI-67-3-39.0. (b) KI-81-1-169.7

Planar extinction (Figure 9a-b), and reverse zoning where the composition of the mineral changes from exterior to interior of the mineral are additional features in some of the olivine phenocryst.
Another characteristic visible in some olivines are resorption rims (Figure 10). Resorption rims indicate that the olivine phenocrysts were reacting with the remaining liquid at the time of consolidation of the rock (McDonald et al., 1961).

Figure 10: thin-section of KILL eruption pumice sample Iki-22. Field of view: 3mm across. The olivine phenocryst is surrounded by volcanic glass. Resorption rims are located around the edges of the mineral.

Samples KI-67-2-85.5 and KI-79-3-158.0 exhibit a poikilitic texture where the pyroxene, hypersthene occurs as oikocrysts (Helz 1987), the host crystal containing numerous inclusions of plagioclase which they enveloped as the pyroxenes grew (Figure 11).

Figure 11: thin-section of KILL cores. Field of view: 5mm across. (a) KI-79-3-158.0 and (b) KI-67-2-85.5 display poikilitic texture.
All of the samples are generally basaltic with the exception of samples Iki-58 (Figure 12a), Iki-22 (Figure 12b), and KI-67-2-85.5 (Figure 12c). Iki-58 and Iki-22 are eruption pumice rocks from the first phase of the Kilauea eruption. Both rocks have an abundance of vesicular volcanic glass and contain only minor amounts of euhedral olivine minerals ~0.5-2mm long with little to no resorption (Helz 1983). KI-67-2-85.5 is an “ooze”, mostly made of glass. It was formed when the lava lake was drilled to a depth where it intercepted a layer of the lake that was still liquid magma. By capillary rise, the liquid flowed up the borehole and then quickly crystallized. When the same hole was re-drilled, the newly crystallized magma was collected and termed as an “ooze” (Helz et al., 1989). A thoroughly detailed description of the thin-sections can be viewed in appendix D.

Methods of Research
Powders were made from the KILR rocks by crushing them with a jaw crusher and milling to a fine flour-like powder with a disk mill in order to make dissolution of the rocks possible. Once the rocks were dissolved Re and PGE were separated from the solution. The isotopic ratios of the separated elements in each rock were analyzed using a mass spectrometer. The isotope ratios were then used in the isotope dilution equation and the concentrations of the elements were calculated. Once the concentrations were known, some D-values of the elements could be estimated. The step by step chemical separation process can be viewed in the analytical method appendix C.
Re-Os-(PGE) chemical separation techniques

All materials used in the chemical separation needed to be cleaned. Teflon vessels, carius tubes, centrifuge tubes, pipetter tips and transfer pipetters were “acid-washed” in concentrated acids in order to remove any residual contamination (Figure 13a). After cleaning the equipment, appropriate weights of the Os, Re, and other HSE (Highly Siderophile Elements) spikes were calculated on a spread sheet based on the MgO wt% in the rock. In grams, the powders, spikes, and acids were added to the carius tubes (Table 4). Once done each tube was taken to the mineral separation lab, sealed with a torch, placed in a metal jacket, and heated in an oven to 260°C from 12 hours to a week (Figure 13b-c).

![Figure 13](image)

Figure 13. (a) Carius tubes soaking in an “acid bath” of concentrated aqua regia (50% milli-q water, 25% HCl, and 25% HNO₃). (b) Sealing a carius tube containing powders, spikes, and acids with a blow touch. (c) Carius tubes in a metal jacket and placed in an oven for digestion.

Table 4. The Kilauea Iki cores used in the studied and the amounts of sample powders and spike weights added to carious tubes. Samples are listed with decreasing MgO content

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MgO Content (wt.%)</th>
<th>Sample wt. (g)</th>
<th>Os spike wt. (g)</th>
<th>Quantity of Os spike added (ng)</th>
<th>Re spike wt. (g)</th>
<th>Quantity of Re spike added (ng)</th>
<th>HSE spike wt. (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI-81-1-169.9</td>
<td>26.87</td>
<td>1.96035</td>
<td>0.03826</td>
<td>0.5156</td>
<td>0.03826</td>
<td>0.1287</td>
<td>0.07313</td>
</tr>
<tr>
<td>KI-81-1-239.9</td>
<td>26.55</td>
<td>1.74627</td>
<td>0.34760</td>
<td>0.6785</td>
<td>0.45487</td>
<td>1.7226</td>
<td>0.40906</td>
</tr>
<tr>
<td>KI-67-3-6.8</td>
<td>25.83</td>
<td>1.78182</td>
<td>0.3110</td>
<td>0.60704</td>
<td>0.45487</td>
<td>1.7226</td>
<td>0.40906</td>
</tr>
<tr>
<td>KI-81-1-210.0</td>
<td>24.5</td>
<td>2.01383</td>
<td>0.33207</td>
<td>0.64817</td>
<td>0.47933</td>
<td>1.8152</td>
<td>0.48680</td>
</tr>
<tr>
<td>IKI-22</td>
<td>19.52</td>
<td>2.01862</td>
<td>0.03458</td>
<td>0.4660</td>
<td>0.03458</td>
<td>0.1163</td>
<td>0.07307</td>
</tr>
<tr>
<td>KI-79-3-130.4</td>
<td>13.5</td>
<td>2.16700</td>
<td>0.10407</td>
<td>0.20313</td>
<td>0.51161</td>
<td>1.9375</td>
<td>0.44369</td>
</tr>
<tr>
<td>KI-67-3-27.5</td>
<td>12</td>
<td>1.79777</td>
<td>0.11456</td>
<td>0.22361</td>
<td>0.50601</td>
<td>1.9163</td>
<td>0.44351</td>
</tr>
<tr>
<td>KI-75-1-139.3</td>
<td>11.7</td>
<td>1.75684</td>
<td>0.11529</td>
<td>0.22503</td>
<td>0.45968</td>
<td>1.7408</td>
<td>0.37934</td>
</tr>
<tr>
<td>KI-67-3-39.0</td>
<td>10.73</td>
<td>2.03020</td>
<td>0.16787</td>
<td>0.32767</td>
<td>0.51423</td>
<td>1.9474</td>
<td>0.44347</td>
</tr>
<tr>
<td>IKI-58</td>
<td>8.08</td>
<td>1.78061</td>
<td>0.55839</td>
<td>0.07537</td>
<td>0.38245</td>
<td>1.4483</td>
<td>0.20968</td>
</tr>
<tr>
<td>KI-67-3-81</td>
<td>7.73</td>
<td>2.04286</td>
<td>0.54567</td>
<td>0.07365</td>
<td>0.52512</td>
<td>1.9886</td>
<td>0.22187</td>
</tr>
<tr>
<td>KI-75-1-121.5</td>
<td>7.5</td>
<td>1.76284</td>
<td>0.18753</td>
<td>0.02531</td>
<td>0.41510</td>
<td>1.5720</td>
<td>0.20850</td>
</tr>
<tr>
<td>KI-75-1-75.2</td>
<td>5.77</td>
<td>2.30437</td>
<td>0.50497</td>
<td>0.06816</td>
<td>0.50935</td>
<td>1.9289</td>
<td>0.22249</td>
</tr>
<tr>
<td>KI-67-2-85.7</td>
<td>2.60</td>
<td>1.76317</td>
<td>0.18634</td>
<td>0.02515</td>
<td>0.43131</td>
<td>1.6334</td>
<td>0.20922</td>
</tr>
<tr>
<td>KI-81-2-88.6</td>
<td>2.37</td>
<td>2.28269</td>
<td>0.20036</td>
<td>0.20036</td>
<td>0.53280</td>
<td>2.0177</td>
<td>0.14720</td>
</tr>
</tbody>
</table>
The purpose of sealing and digesting the samples in carious tubes was to ensure that the powder, acid + spike solution equilibrate. The Re and PGE elements were extracted from the sample into the acid + spike solution. After digestion the Osmium Separation Procedures (OSP) was performed. The digested powders and blanks were put into centrifuge tubes containing carbon tetrachloride (CCl₄) and centrifuged. After centrifuging the tubes containing CCl₄ and aqua regia; Os was attracted to the CCl₄ while Re & the remaining PGE remained in the aqua regia.

The denser CCl₄ is extracted from the centrifuge tubes and put into Teflon vessels containing hydrobromic acid (HBr), where the HBr reduced the Os and stabilize it. The aqua regia was placed to the side for later use. After the Os was completely reduced, it was transferred from the CCl₄ to the HBr. The CCl₄ is removed and disposed of while the HBr is dried down under a heat lamp. The Os can now be purified further by Osmium Micro-Distillation (OMD).

In OMD a small amount of HBr is added to the Os which is then transferred to the center of a conical Teflon vessel cap and dried down under the heat lamp. After the HBr on the cap is dried, HBr is added the tip of the Teflon conical vessel and dichromate is added to the Os on the cap. The conical Teflon vessel is inverted, screwed onto the cap, wrapped in aluminum foil, and heated to ~80°C in a heat block (Figure 14). The purpose of having the conical vessel inverted is to have the HBr on the top of the Teflon conical vessel, so when the Os evaporates from the dichromate and rises, it is trapped in the small amount of HBr. After heating overnight in a heat block, the caps are unscrewed from the conical vessels, the caps are rinsed, and the conical vessels containing the HBr are dried under a heat lamp. The Os is now ready for loading into the mass spectrometer.

*Figure 14. Inverted conical vessels wrapped in aluminum foil and heated in a heat block during Osmium Micro-Distillation.*
The Re and remaining PGE in the aqua regia is dried down, diluted with low molarity HNO₃, centrifuged to remove residual sludge, and then eluted onto an anion exchange column (Figure 15). In dilute HCl or HNO₃, these elements will stick to the anion resin, whereas most other rock components will not and wash through the column. Rhenium & PGE are washed off the columns with high molarity HNO₃ and HCl. The Teflon vessels containing the Re, Ru, Pt, Ir, and Pd are dried under a heat lamp and then analyzed with an Inductively-Couple Plasma Mass Spectrometer (ICP-MS).

Mass Spectrometer

A mass spectrometer is an instrument used to measure isotope abundances by sending ions through a magnetic field. The ions are separated on the basis of their masses and then the relative intensities of the different isotopes are measured and the isotopic ratios for each rock can be measured. Determining the isotope ratio is important because the ratio values are used in the isotope dilution equation to solve for the concentration of a particular element.

Measuring the relative intensities of the Os isotopes is done with the Thermal Ionization Mass Spectrometer (TIMS) (Figure 16a). The first step is to clean the filaments by removing used Pt ribbons from posts and filing the sides of the filaments’ posts; this step eliminates cross sample contamination in the mass spectrometer. New Pt ribbons were attached to the sides of the posts by using copper electrode in a welding machine. Next the ribbons and their filaments are degassed in a degassing machine to get rid of any contamination on the filament posts and on the ribbon. The ribbons and filaments were allowed to cool over night and then the samples were loaded onto the ribbons. To do this the filaments have to be screwed into the filament holder and placed on the degassing machine. The Os sample from the chemical separation is placed on the
ribbon in HBr, dried, then Ba(OH)$_2$ is added. Once the ribbon is dry the filament can then be
loaded into the mass spectrometer for analysis. Rhenium, Ru, Ir, Pt, and Pd were analyzed with
the ICP-MS (Figure 16b). An ICP-MS has the same basic functions as a TIMS, but do not
require the use of filaments and filament ribbons. The elements are in 0.8M HNO$_3$ solution.

Figure 16. (a) Thermal Ionization Mass Spectrometer. (b) Inductively-Couple Plasma Mass
Spectrometer

*Isotope Dilution*

Isotope dilution is a process where a known amount of an isotopically enriched ‘spike’ is added
to a sample. The measured isotopic composition of the mix can be used to calculate the
concentration of the element. For an example the isotope dilution equation is given below where
the number of atoms of $^{185}$Re and $^{187}$Re, in the spike, and the isotope ratio are the knowns. The
only component not known is the concentration of Re in the sample. Rearranging the equation to
solve for X, the concentration of Re.

*Isotope Dilution Equation*

\[
\left( \frac{^{185}\text{Re}}{^{187}\text{Re}} \right)_{\text{MIX}} = \left( \frac{\text{# Atoms of Isotope } ^{185}\text{Re}}{\text{# Atoms of Isotope } ^{187}\text{Re}} \right)_{\text{SPIKE}} + \left( \frac{\text{# Atoms of Isotope } ^{185}\text{Re}}{\text{# Atoms of Isotope } ^{187}\text{Re}} \right)_{\text{SAMPLE}}
\]

*The Knowns*

\[
\left( \text{# Atoms of } ^{185}\text{Re} \right)_{\text{SPIKE}} = \frac{(\text{weight of spike}) \times (\text{concentration of Re in spike}) \times (\text{Atom}\% \ ^{185}\text{Re})_{\text{SPIKE}} \times (\text{Avagadro's #})}{(\text{Atomic wt. of Re})_{\text{SPIKE}}}
\]
\[
\text{(\# Atoms of } ^{187}\text{Re})_{\text{SPIKE}} = \frac{\text{(weight of spike)} \times (\text{concentration of Re in spike}) \times (\text{Atom}\% \ ^{187}\text{Re})_{\text{SPIKE}} \times (\text{Avagadro's #})}{(\text{Atomic wt. of Re})_{\text{SPIKE}}}
\]

\[
\text{(\# Atoms of } ^{185}\text{Re})_{\text{SAMPLE}} = \frac{(\text{Avagadro's #}) \times (\text{Atom}\% \ ^{185}\text{Re}) \times (\text{weight of sample})}{(\text{Atomic wt. of Re})_{\text{SAMPLE}}}
\]

\[
\text{(\# Atoms of } ^{187}\text{Re})_{\text{SAMPLE}} = \frac{(\text{Avagadro's #}) \times (\text{Atom}\% \ ^{187}\text{Re}) \times (\text{weight of sample})}{(\text{Atomic wt. of Re})_{\text{SAMPLE}}}
\]

**Rearrange to Solve for X**

\[
X = \left[ \frac{\left( \frac{^{185}\text{Re}}{^{187}\text{Re}} \right)_{\text{MIX}} \times \left( \text{(\# Atoms of Isotope } ^{187}\text{Re})_{\text{SPIKE}} \right) - \left( \text{(\# Atoms of Isotope } ^{185}\text{Re})_{\text{SPIKE}} \right)}{\left( \text{(\# Atoms of Isotope } ^{185}\text{Re})_{\text{SAMPLE}} - \left( \frac{^{185}\text{Re}}{^{187}\text{Re}} \right)_{\text{MIX}} \times \left( \text{(\# Atoms of Isotope } ^{187}\text{Re})_{\text{SAMPLE}} \right) \right)} \right]
\]

**Uncertainties**

**The Blanks**

An isotope dilution measurement could be undependable due to the “blank”. The “blank” is the amount of contamination of natural elements which could end up as part of the final measurement of a particular element. In this project the “blank” consist of natural Re and PGE which reside in the glassware, Teflon-ware, or acids used in the elemental separation chemistry; and contamination could be residual metals (e.g. Pt) from the drills used to extract the rocks.

For this study certain steps were taken to reduce the amount of “blank” during elemental separation. The blanks were subtracted from the final measurement for a rock. For example, the Teflon used for the chemistry procedures can be “cleaned” by soaking them in highly concentrated acids because Re and PGE and any other element or contamination are soluble in HCl and HNO\text{3} and the surfaces of the core samples can be sandpapered until they are smooth.

**Review of Uncertainties**

The uncertainties 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 will be applied to final cited concentration. Below are the uncertainty calculations which will be applied for all the elements in each rock, but for an example, the Os uncertainties for samples Iki-22 and KI-81-1-169 are calculated.
**Uncertainty of Sample and Spike Weights**

The uncertainty introduced by weighing sample and spikes is ~±0.00004g, meaning each time the sample and spike is weighed the fifth significant figure changes back and forth between two numbers, while the previous four significant figures stay stationary. The weight uncertainties are calculated by dividing the balance uncertainty by the sample and spike weights, yielding the fractional uncertainty of the sample and spike weights; moving the decimal to the right two places gives the uncertainty percentage (Table 5).

Table 5. The weight uncertainty calculations for Osmium in cores Iki-22 and KI-81-1-169.

<table>
<thead>
<tr>
<th></th>
<th>Iki-22</th>
<th>KI-81-1-169</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample wt</td>
<td>2.01862 ± .00004 g</td>
<td>1.96035 ± .00004 g</td>
</tr>
<tr>
<td>Sample wt uncertainty %</td>
<td>.002%</td>
<td>.002%</td>
</tr>
<tr>
<td>Spike wt</td>
<td>0.03458 ± .00004 g</td>
<td>0.03826 ± .00004 g</td>
</tr>
<tr>
<td>Spike wt uncertainty %</td>
<td>.12%</td>
<td>.10%</td>
</tr>
</tbody>
</table>

**Isotope Ratio Uncertainty**

The isotope ratio of \(^{190}\text{Os} / ^{192}\text{Os}\) and the uncertainty of the measured relative intensities of the isotopes are given in the TIMS results. The ratio uncertainty is calculated by dividing the relative intensity uncertainty by the isotope ratio and moving the decimal place to the right two places to get the uncertainty percentage (Table 6). The isotope ratio uncertainties for Re and the remaining PGE will be multiplied by two, because the isotope ratio uncertainties are two sigma (95% probability).

Table 6. The isotope ratio uncertainty calculations for Osmium in cores Iki-22 and KI-81-1-169.

<table>
<thead>
<tr>
<th>Isotope Ratio</th>
<th>Iki-22</th>
<th>KI-81-1-169</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{190}\text{Os} / ^{192}\text{Os})</td>
<td>1.5144 ± .0008</td>
<td>1.589 ± .0005</td>
</tr>
<tr>
<td>Uncertainty %</td>
<td>.053%</td>
<td>.031%</td>
</tr>
</tbody>
</table>

**Blank Corrections**

Overall three blanks were measured they are 0.00745ng, 0.0103ng, and 0.00088ng. The average Os blank was calculated by taking the average of the three blanks yielding the total Os blank uncertainty 0.00088 ± 0.0015ng (8.8 ± 1.5pg).
Os Concentration

The isotope dilution calculations for Iki-22 and KI-81-1-169 are 1.2276ng and 1.2490ng (Os quantity), and to find the true Os quantity, which has no contamination of natural elements, the Os blank is subtracted from the Os quantity in a method called Os blank correction (Table 6).

\[
1.2276_{\text{Os quantity}} - 0.0074_{\text{Os blank}} = 1.2201_{\text{ng}}
\]

Table 7 also lists all the uncertainties previously discussed; and the blank uncertainty is the largest uncertainty and therefore will control the Os concentration calculations. To find the Os concentration in the samples, the Os blank corrected is divided by the sample weight and then the blank uncertainty is multiplied by the Os concentration and divided by a hundred to get the uncertainty of the Os concentration in ng/g.

\[
\frac{1.2201}{2.01862} = 0.6044 \text{ (Os con.)}
\]

\[
\frac{(0.123) \times (0.6044)}{100} = 0.00073 \text{ (Os conc. unc.)}
\]

Table 7. Lists the blank correction, Isotope ratio, sample weight, and blank uncertainties; Spike weight uncertainty is the largest value and is therefore applied to calculating the uncertainty of the Osmium concentrations.

<table>
<thead>
<tr>
<th></th>
<th>Iki-22</th>
<th>KI-81-1-169</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO (wt %)</td>
<td>19.52</td>
<td>26.87</td>
</tr>
<tr>
<td>Os (quantity)</td>
<td>1.2276 ng</td>
<td>1.2490 ng</td>
</tr>
<tr>
<td>Os blank</td>
<td>0.0074 ng</td>
<td>0.0074 ng</td>
</tr>
<tr>
<td>Os (blank corrected)</td>
<td>1.2201 ng</td>
<td>1.2415 ng</td>
</tr>
<tr>
<td>Blank unc.</td>
<td>0.123%</td>
<td>0.121%</td>
</tr>
<tr>
<td>Ratio unc.</td>
<td>0.053%</td>
<td>0.031%</td>
</tr>
<tr>
<td>Sample wt unc.</td>
<td>0.002%</td>
<td>0.002%</td>
</tr>
<tr>
<td>Spike wt unc.</td>
<td>0.116%</td>
<td>0.105%</td>
</tr>
<tr>
<td>Os concentration</td>
<td>0.6044 ± 0.00073 ng/g</td>
<td>0.6333 ± 0.00076 ng/g</td>
</tr>
</tbody>
</table>
Results

The MgO content and concentrations measured for Re and the PGE are listed in table 8 and then plotted on separate graphs (Figure 17). On each graph the Residual ($R^2$) value is included to indicate how well the data points fit on the linear regression line. Osmium and Ru concentrations range from 0.0006 to 1.06 ppb and 0.0034 to 2.01 ppb respectively. Plotted on a graph with variation in MgO wt. %, Os and Ru behave as highly compatible elements with positive correlations. Regressions for both elements have relatively high residual ($R^2$) values of 0.865 (Ru) and 0.858 (Os), indicating a good linear correlation. Iridium concentrations were measured between 0.0003 to 0.76 ppb and graphed; Ir does not correlate as well as Os and Ru with a low $R^2$ of 0.41.

Re has low concentrations (0.030 - 2.0) and a poor correlation to changes in MgO wt. %, with an $R^2$ of 0.32. Palladium concentrations ranges 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).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MgO (wt. %)</th>
<th>Os (ppb)</th>
<th>Ir (ppb)</th>
<th>Ru (ppb)</th>
<th>Pt (ppb)</th>
<th>Pd (ppb)</th>
<th>Re (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI-81-1-169.9</td>
<td>26.87</td>
<td>0.6333</td>
<td>0.3312</td>
<td>1.958</td>
<td>1.401</td>
<td>1.962</td>
<td>0.1511</td>
</tr>
<tr>
<td>KI-81-1-239.9</td>
<td>26.55</td>
<td>0.9669</td>
<td>0.4801</td>
<td>1.613</td>
<td>10.43</td>
<td>0.2474</td>
<td>0.03041</td>
</tr>
<tr>
<td>KI-67-3-6.8</td>
<td>25.83</td>
<td>1.065</td>
<td>0.3807</td>
<td>1.482</td>
<td>1.151</td>
<td>1.351</td>
<td>0.4186</td>
</tr>
<tr>
<td>KI-81-1-210.0</td>
<td>24.5</td>
<td>0.8207</td>
<td>0.7508</td>
<td>2.012</td>
<td>1.921</td>
<td>0.3490</td>
<td>0.03901</td>
</tr>
<tr>
<td>Iki-22</td>
<td>19.52</td>
<td>0.6044</td>
<td>0.3927</td>
<td>1.301</td>
<td>5.564</td>
<td>1.526</td>
<td>0.2247</td>
</tr>
<tr>
<td>KI-79-3-150.4</td>
<td>13.5</td>
<td>0.4343</td>
<td>0.5196</td>
<td>0.6264</td>
<td>3.102</td>
<td>2.463</td>
<td>0.2269</td>
</tr>
<tr>
<td>KI-67-3-27.5</td>
<td>12</td>
<td>0.2224</td>
<td>0.2668</td>
<td>0.5171</td>
<td>2.394</td>
<td>2.626</td>
<td>0.4306</td>
</tr>
<tr>
<td>KI-75-1-139.3</td>
<td>11.7</td>
<td>0.2403</td>
<td>0.7639</td>
<td>1.412</td>
<td>1.636</td>
<td>0.2868</td>
<td>0.06889</td>
</tr>
<tr>
<td>KI-67-3-39.0</td>
<td>10.73</td>
<td>0.1725</td>
<td>0.2252</td>
<td>0.4530</td>
<td>3.533</td>
<td>5.812</td>
<td>0.2985</td>
</tr>
<tr>
<td>IKI-58</td>
<td>8.08</td>
<td>0.05603</td>
<td>0.1651</td>
<td>0.4017</td>
<td>2.285</td>
<td>2.083</td>
<td>0.4141</td>
</tr>
<tr>
<td>KI-67-3-81</td>
<td>7.73</td>
<td>0.09690</td>
<td>0.1227</td>
<td>0.1588</td>
<td>2.360</td>
<td>3.169</td>
<td>0.2120</td>
</tr>
<tr>
<td>KI-75-1-121.5</td>
<td>7.5</td>
<td>0.02664</td>
<td>0.2127</td>
<td>0.2408</td>
<td>1.582</td>
<td>1.239</td>
<td>0.1873</td>
</tr>
<tr>
<td>KI-75-1-75.2</td>
<td>5.77</td>
<td>0.01044</td>
<td>0.0065</td>
<td>0.04781</td>
<td>2.620</td>
<td>3.605</td>
<td>0.9308</td>
</tr>
<tr>
<td>KI-67-2-85.7</td>
<td>2.6</td>
<td>0.1050</td>
<td>0.1170</td>
<td>0.1037</td>
<td>5.180</td>
<td>3.883</td>
<td>0.6261</td>
</tr>
<tr>
<td>KI-81-2-88.6</td>
<td>2.37</td>
<td>0.0006</td>
<td>0.0003</td>
<td>0.0034</td>
<td>3.924</td>
<td>3.125</td>
<td>2.0293</td>
</tr>
</tbody>
</table>

Table 8. Measured Re, Ir, Os, Pd, Pt, and Ru concentrations (ppb) in KILL cores of various MgO
Figure 17. Plots of MgO (wt. %) versus Re, Os, Ir, Pt, and Ru concentrations (in ppb).
Table 9. Iridium. The blank correction, Isotope ratio, sample weight, and blank uncertainties; the largest uncertainty (in red) is applied to calculating the uncertainty of the Iridium concentrations (in blue).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MgO Content wt.%</th>
<th>Ir (quantity) ng</th>
<th>Ir Blank ng</th>
<th>Ir (blank corrected) ng</th>
<th>Blank Unc. %</th>
<th>Ratio Unc. %</th>
<th>Sample wt Unc. %</th>
<th>Spike wt Unc. %</th>
<th>Ir Concentration (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI-81-1-169.9</td>
<td>26.87</td>
<td>0.5080</td>
<td>0.00155</td>
<td>0.6492</td>
<td>0.14</td>
<td>0.14</td>
<td>0.0020</td>
<td>0.55</td>
<td>0.3311±0.0018</td>
</tr>
<tr>
<td>KI-81-1-239.9</td>
<td>26.55</td>
<td>0.8399</td>
<td>0.00155</td>
<td>0.8384</td>
<td>0.070</td>
<td>0.17</td>
<td>0.0023</td>
<td>0.10</td>
<td>0.4801±0.0008</td>
</tr>
<tr>
<td>KI-67-3-6.8</td>
<td>25.83</td>
<td>0.6787</td>
<td>0.0003</td>
<td>0.6784</td>
<td>0.090</td>
<td>0.66</td>
<td>0.0022</td>
<td>0.10</td>
<td>0.3807±0.0025</td>
</tr>
<tr>
<td>KI-81-1-210.0</td>
<td>24.50</td>
<td>1.5135</td>
<td>0.00155</td>
<td>1.5120</td>
<td>0.040</td>
<td>0.15</td>
<td>0.0020</td>
<td>0.080</td>
<td>0.7508±0.0011</td>
</tr>
<tr>
<td>Iki-22</td>
<td>19.52</td>
<td>0.7942</td>
<td>0.00155</td>
<td>0.7927</td>
<td>0.080</td>
<td>0.060</td>
<td>0.0020</td>
<td>0.55</td>
<td>0.3927±0.0021</td>
</tr>
<tr>
<td>KI-79-3-150.4</td>
<td>13.50</td>
<td>1.1262</td>
<td>0.0003</td>
<td>1.1259</td>
<td>0.060</td>
<td>0.14</td>
<td>0.0018</td>
<td>0.090</td>
<td>0.5196±0.0007</td>
</tr>
<tr>
<td>KI-67-3-27.5</td>
<td>12</td>
<td>0.4800</td>
<td>0.0003</td>
<td>0.4797</td>
<td>0.13</td>
<td>0.52</td>
<td>0.0022</td>
<td>0.909</td>
<td>0.2668±0.0013</td>
</tr>
<tr>
<td>KI-75-1-139.3</td>
<td>11.7</td>
<td>1.3436</td>
<td>0.00155</td>
<td>1.3421</td>
<td>0.050</td>
<td>0.10</td>
<td>0.0023</td>
<td>0.11</td>
<td>0.7639±0.0008</td>
</tr>
<tr>
<td>KI-67-3-39.0</td>
<td>10.73</td>
<td>0.4575</td>
<td>0.0003</td>
<td>0.4572</td>
<td>0.14</td>
<td>0.47</td>
<td>0.0020</td>
<td>0.090</td>
<td>0.2252±0.0010</td>
</tr>
<tr>
<td>IKI-58</td>
<td>8.08</td>
<td>0.2955</td>
<td>0.0003</td>
<td>0.2940</td>
<td>0.21</td>
<td>0.15</td>
<td>0.0022</td>
<td>0.19</td>
<td>0.1651±0.0003</td>
</tr>
<tr>
<td>KI-67-3-81</td>
<td>7.73</td>
<td>0.2510</td>
<td>0.0003</td>
<td>0.2507</td>
<td>0.25</td>
<td>1.36</td>
<td>0.0020</td>
<td>0.18</td>
<td>0.1227±0.0016</td>
</tr>
<tr>
<td>KI-75-1-121.5</td>
<td>7.5</td>
<td>0.3764</td>
<td>0.00155</td>
<td>0.3749</td>
<td>0.17</td>
<td>0.15</td>
<td>0.0023</td>
<td>0.19</td>
<td>0.2127±0.0004</td>
</tr>
<tr>
<td>KI-75-1-75.2</td>
<td>5.77</td>
<td>0.0152</td>
<td>0.0003</td>
<td>0.0149</td>
<td>4.20</td>
<td>2.06</td>
<td>0.0017</td>
<td>0.18</td>
<td>0.0065±0.0002</td>
</tr>
<tr>
<td>KI-67-2-85.7</td>
<td>2.6</td>
<td>0.2078</td>
<td>0.00155</td>
<td>0.2062</td>
<td>0.30</td>
<td>0.22</td>
<td>0.0023</td>
<td>0.19</td>
<td>0.1170±0.0003</td>
</tr>
<tr>
<td>KI-81-2-88.6</td>
<td>2.37</td>
<td>0.0010</td>
<td>0.0003</td>
<td>0.0007</td>
<td>83.97</td>
<td>8.70</td>
<td>0.0018</td>
<td>0.27</td>
<td>0.0003±0.0002</td>
</tr>
</tbody>
</table>

Table 10. Osmium. The blank correction, Isotope ratio, sample weight, and blank uncertainties; the largest uncertainty (in red) is applied to calculating the uncertainty of the Osmium concentrations (in blue).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MgO Content wt.%</th>
<th>Os (quantity) ng</th>
<th>Os Blank ng</th>
<th>Os (blank corrected) ng</th>
<th>Blank Unc. %</th>
<th>Ratio Unc. %</th>
<th>Sample wt Unc. %</th>
<th>Spike wt Unc. %</th>
<th>Os Concentration (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI-81-1-169.9</td>
<td>26.87</td>
<td>1.2190</td>
<td>0.00745</td>
<td>1.2415</td>
<td>0.12</td>
<td>0.031</td>
<td>0.0020</td>
<td>0.10</td>
<td>0.6333±0.00076</td>
</tr>
<tr>
<td>KI-81-1-239.9</td>
<td>26.55</td>
<td>1.6973</td>
<td>0.0088</td>
<td>1.6885</td>
<td>0.090</td>
<td>1.14</td>
<td>0.0023</td>
<td>0.010</td>
<td>0.9669±0.01102</td>
</tr>
<tr>
<td>KI-67-3-6.8</td>
<td>25.83</td>
<td>1.9092</td>
<td>0.0103</td>
<td>1.8989</td>
<td>0.080</td>
<td>2.25</td>
<td>0.0022</td>
<td>0.010</td>
<td>1.065±0.2398</td>
</tr>
<tr>
<td>KI-81-1-210.0</td>
<td>24.50</td>
<td>1.6616</td>
<td>0.0088</td>
<td>1.6528</td>
<td>0.090</td>
<td>1.35</td>
<td>0.0020</td>
<td>0.010</td>
<td>0.8207±0.01108</td>
</tr>
<tr>
<td>Iki-22</td>
<td>19.52</td>
<td>1.2276</td>
<td>0.00745</td>
<td>1.2201</td>
<td>0.12</td>
<td>0.053</td>
<td>0.0020</td>
<td>0.12</td>
<td>0.6044±0.00073</td>
</tr>
<tr>
<td>KI-79-3-150.4</td>
<td>13.50</td>
<td>0.9515</td>
<td>0.0103</td>
<td>0.9412</td>
<td>0.16</td>
<td>3.08</td>
<td>0.0018</td>
<td>0.040</td>
<td>0.4343±0.00069</td>
</tr>
<tr>
<td>KI-67-3-27.5</td>
<td>12</td>
<td>0.4101</td>
<td>0.0103</td>
<td>0.3998</td>
<td>0.38</td>
<td>1.54</td>
<td>0.0022</td>
<td>0.030</td>
<td>0.2224±0.00342</td>
</tr>
<tr>
<td>KI-75-1-139.3</td>
<td>11.7</td>
<td>0.4309</td>
<td>0.0088</td>
<td>0.4221</td>
<td>0.36</td>
<td>1.90</td>
<td>0.0023</td>
<td>0.030</td>
<td>0.2403±0.00457</td>
</tr>
<tr>
<td>KI-67-3-39.0</td>
<td>10.73</td>
<td>0.3604</td>
<td>0.0103</td>
<td>0.3501</td>
<td>0.43</td>
<td>3.62</td>
<td>0.0020</td>
<td>0.020</td>
<td>0.1725±0.00624</td>
</tr>
<tr>
<td>IKI-58</td>
<td>8.08</td>
<td>0.1086</td>
<td>0.0088</td>
<td>0.0998</td>
<td>1.50</td>
<td>4.32</td>
<td>0.0022</td>
<td>0.010</td>
<td>0.0560±0.000242</td>
</tr>
<tr>
<td>KI-67-3-81</td>
<td>7.73</td>
<td>0.2083</td>
<td>0.0103</td>
<td>0.1980</td>
<td>0.76</td>
<td>3.16</td>
<td>0.0020</td>
<td>0.010</td>
<td>0.0969±0.00306</td>
</tr>
<tr>
<td>KI-75-1-121.5</td>
<td>7.5</td>
<td>0.0358</td>
<td>0.0088</td>
<td>0.0470</td>
<td>3.19</td>
<td>3.41</td>
<td>0.0023</td>
<td>0.020</td>
<td>0.0266±0.00085</td>
</tr>
<tr>
<td>KI-75-1-75.2</td>
<td>5.77</td>
<td>0.0344</td>
<td>0.0103</td>
<td>0.0241</td>
<td>6.24</td>
<td>7.31</td>
<td>0.0017</td>
<td>0.010</td>
<td>0.0104±0.0006</td>
</tr>
<tr>
<td>KI-67-2-85.7</td>
<td>2.6</td>
<td>0.1940</td>
<td>0.0088</td>
<td>0.1852</td>
<td>0.81</td>
<td>7.31</td>
<td>0.0023</td>
<td>0.020</td>
<td>0.105±0.00768</td>
</tr>
<tr>
<td>KI-81-2-88.6</td>
<td>2.37</td>
<td>0.0117</td>
<td>0.0103</td>
<td>0.0014</td>
<td>103.98</td>
<td>3.09</td>
<td>0.0018</td>
<td>0.020</td>
<td>0.0006±0.00062</td>
</tr>
</tbody>
</table>
Table 11. Palladium. The blank correction, Isotope ratio, sample weight, and blank uncertainties; the largest uncertainty (in red) is applied to calculating the uncertainty of the Palladium concentrations (in blue).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MgO Content wt.%</th>
<th>Pd (quantity) ng</th>
<th>Pd Blank ng</th>
<th>Pd (blank corrected) ng</th>
<th>Blank Unc. %</th>
<th>Ratio Unc. %</th>
<th>Sample wt Unc. %</th>
<th>Spike wt Unc. %</th>
<th>Pd Concentration (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI-81-1-169.9</td>
<td>26.87</td>
<td>3.9216</td>
<td>0.075</td>
<td>3.8466</td>
<td>2.6</td>
<td>0.13</td>
<td>0.0020</td>
<td>0.55</td>
<td>1.962±0.05102</td>
</tr>
<tr>
<td>KI-81-1-239.9</td>
<td>26.55</td>
<td>0.6020</td>
<td>0.170</td>
<td>0.4320</td>
<td>23.6</td>
<td>0.12</td>
<td>0.0023</td>
<td>0.10</td>
<td>0.2474±0.05839</td>
</tr>
<tr>
<td>KI-67-3-6.8</td>
<td>25.83</td>
<td>2.6857</td>
<td>0.278</td>
<td>2.4074</td>
<td>4.2</td>
<td>0.15</td>
<td>0.0022</td>
<td>0.10</td>
<td>1.351±0.05675</td>
</tr>
<tr>
<td>KI-81-1-210.0</td>
<td>24.50</td>
<td>0.8728</td>
<td>0.170</td>
<td>0.7028</td>
<td>14.5</td>
<td>0.45</td>
<td>0.0020</td>
<td>0.080</td>
<td>0.3490±0.05061</td>
</tr>
<tr>
<td>KI-79-3-150.4</td>
<td>13.50</td>
<td>5.6156</td>
<td>0.278</td>
<td>5.3373</td>
<td>1.9</td>
<td>0.070</td>
<td>0.0018</td>
<td>0.090</td>
<td>2.463±0.04680</td>
</tr>
<tr>
<td>KI-67-27.5</td>
<td>12</td>
<td>4.9992</td>
<td>0.278</td>
<td>4.7210</td>
<td>2.2</td>
<td>0.070</td>
<td>0.0022</td>
<td>0.090</td>
<td>2.626±0.05777</td>
</tr>
<tr>
<td>KI-75-1-139.3</td>
<td>11.7</td>
<td>0.6738</td>
<td>0.170</td>
<td>0.5038</td>
<td>20.2</td>
<td>0.33</td>
<td>0.0023</td>
<td>0.11</td>
<td>0.2868±0.05793</td>
</tr>
<tr>
<td>KI-67-3-39.0</td>
<td>10.73</td>
<td>12.0776</td>
<td>0.278</td>
<td>11.7993</td>
<td>0.90</td>
<td>0.060</td>
<td>0.0020</td>
<td>0.090</td>
<td>5.811±0.05231</td>
</tr>
<tr>
<td>KI-67-3-81</td>
<td>7.73</td>
<td>6.7522</td>
<td>0.278</td>
<td>6.4739</td>
<td>1.6</td>
<td>0.060</td>
<td>0.0022</td>
<td>0.19</td>
<td>3.169±0.05070</td>
</tr>
<tr>
<td>KI-75-1-121.5</td>
<td>7.5</td>
<td>2.3550</td>
<td>0.170</td>
<td>2.1850</td>
<td>4.7</td>
<td>0.070</td>
<td>0.0023</td>
<td>0.19</td>
<td>1.239±0.05826</td>
</tr>
<tr>
<td>KI-75-1-75.2</td>
<td>5.77</td>
<td>8.5865</td>
<td>0.278</td>
<td>8.3082</td>
<td>1.2</td>
<td>0.070</td>
<td>0.0017</td>
<td>0.18</td>
<td>3.605±0.04326</td>
</tr>
<tr>
<td>KI-67-2-85.7</td>
<td>2.6</td>
<td>7.0170</td>
<td>0.170</td>
<td>6.8470</td>
<td>1.5</td>
<td>0.070</td>
<td>0.0023</td>
<td>0.19</td>
<td>3.883±0.05825</td>
</tr>
<tr>
<td>KI-81-2-88.6</td>
<td>2.37</td>
<td>7.4115</td>
<td>0.278</td>
<td>7.1332</td>
<td>1.4</td>
<td>0.070</td>
<td>0.0018</td>
<td>0.27</td>
<td>3.124±0.04375</td>
</tr>
</tbody>
</table>

Table 12. Platinum. The blank correction, Isotope ratio, sample weight, and blank uncertainties; the largest uncertainty (in red) is applied to calculating the uncertainty of the Platinum concentrations (in blue).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MgO Content wt.%</th>
<th>Pt (quantity) ng</th>
<th>Pt Blank ng</th>
<th>Pt (blank corrected) ng</th>
<th>Blank Unc. %</th>
<th>Ratio Unc. %</th>
<th>Sample wt Unc. %</th>
<th>Spike wt Unc. %</th>
<th>Pt Concentration (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI-81-1-169.9</td>
<td>26.87</td>
<td>3.1377</td>
<td>0.39</td>
<td>2.7477</td>
<td>1.25</td>
<td>0.12</td>
<td>0.0020</td>
<td>0.55</td>
<td>1.401±0.01752</td>
</tr>
<tr>
<td>KI-81-1-239.9</td>
<td>26.55</td>
<td>18.6204</td>
<td>0.39</td>
<td>18.2304</td>
<td>0.19</td>
<td>0.070</td>
<td>0.0023</td>
<td>0.10</td>
<td>10.43±0.01984</td>
</tr>
<tr>
<td>KI-67-3-6.8</td>
<td>25.83</td>
<td>2.5188</td>
<td>0.47</td>
<td>2.0512</td>
<td>1.68</td>
<td>0.22</td>
<td>0.0022</td>
<td>0.10</td>
<td>1.151±0.01934</td>
</tr>
<tr>
<td>KI-81-1-210.0</td>
<td>24.50</td>
<td>4.2591</td>
<td>0.39</td>
<td>3.8691</td>
<td>0.89</td>
<td>0.23</td>
<td>0.0020</td>
<td>0.080</td>
<td>1.921±0.01710</td>
</tr>
<tr>
<td>KI-67-3-81</td>
<td>19.52</td>
<td>11.6231</td>
<td>0.39</td>
<td>11.2331</td>
<td>0.31</td>
<td>0.14</td>
<td>0.0020</td>
<td>0.55</td>
<td>5.564±0.03061</td>
</tr>
<tr>
<td>KI-79-3-150.4</td>
<td>13.50</td>
<td>7.189</td>
<td>0.47</td>
<td>6.7222</td>
<td>0.51</td>
<td>0.080</td>
<td>0.0018</td>
<td>0.090</td>
<td>3.102±0.01582</td>
</tr>
<tr>
<td>KI-67-27.5</td>
<td>12</td>
<td>4.771</td>
<td>0.47</td>
<td>4.3044</td>
<td>0.80</td>
<td>0.12</td>
<td>0.0022</td>
<td>0.090</td>
<td>2.394±0.01915</td>
</tr>
<tr>
<td>KI-75-1-139.3</td>
<td>11.7</td>
<td>3.2655</td>
<td>0.39</td>
<td>2.8755</td>
<td>1.20</td>
<td>0.16</td>
<td>0.0023</td>
<td>0.11</td>
<td>1.636±0.01964</td>
</tr>
<tr>
<td>KI-67-3-39.0</td>
<td>10.73</td>
<td>7.640</td>
<td>0.47</td>
<td>7.1731</td>
<td>0.48</td>
<td>0.090</td>
<td>0.0020</td>
<td>0.090</td>
<td>3.533±0.01696</td>
</tr>
<tr>
<td>KI-58</td>
<td>8.08</td>
<td>4.4596</td>
<td>0.39</td>
<td>4.0696</td>
<td>0.85</td>
<td>0.31</td>
<td>0.0022</td>
<td>0.19</td>
<td>2.285±0.01943</td>
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<tr>
<td>KI-67-3-81</td>
<td>7.73</td>
<td>5.287</td>
<td>0.47</td>
<td>4.8205</td>
<td>0.71</td>
<td>0.15</td>
<td>0.0020</td>
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<td>3.1794</td>
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<td>0.0023</td>
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<td>1.582±0.01946</td>
</tr>
<tr>
<td>KI-75-1-75.2</td>
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<td>6.504</td>
<td>0.47</td>
<td>6.0371</td>
<td>0.57</td>
<td>0.090</td>
<td>0.0017</td>
<td>0.18</td>
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</tr>
<tr>
<td>KI-67-2-85.7</td>
<td>2.6</td>
<td>9.5237</td>
<td>0.39</td>
<td>9.1337</td>
<td>0.38</td>
<td>0.070</td>
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<td>0.19</td>
<td>5.180±0.01969</td>
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<tr>
<td>KI-81-2-88.6</td>
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<td>9.424</td>
<td>0.47</td>
<td>8.9569</td>
<td>0.38</td>
<td>0.090</td>
<td>0.0018</td>
<td>0.27</td>
<td>3.924±0.01491</td>
</tr>
</tbody>
</table>
Table 13. Ruthenium. The blank correction, Isotope ratio, sample weight, and blank uncertainties; the largest uncertainty (in red) is applied to calculating the uncertainty of the Ruthenium concentrations (in blue).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MgO Content wt.%</th>
<th>Ru (quantity) ng</th>
<th>Ru Blank ng</th>
<th>Ru (blank corrected) ng</th>
<th>Blank Unc. %</th>
<th>Ratio Unc. %</th>
<th>Sample wt Unc. %</th>
<th>Spike wt Unc. %</th>
<th>Ru Concentration (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI-81-1-169.9</td>
<td>26.87</td>
<td>3.8399</td>
<td>0.00025</td>
<td>3.8396</td>
<td>0.17</td>
<td>0.090</td>
<td>0.0020</td>
<td>0.55</td>
<td>1.958±0.01077</td>
</tr>
<tr>
<td>KI-81-1-239.9</td>
<td>26.55</td>
<td>2.8173</td>
<td>0.00025</td>
<td>2.8171</td>
<td>0.24</td>
<td>0.31</td>
<td>0.0023</td>
<td>0.10</td>
<td>1.613±0.00500</td>
</tr>
<tr>
<td>KI-67-3-6.8</td>
<td>25.83</td>
<td>2.6558</td>
<td>0.0137</td>
<td>2.6421</td>
<td>0.25</td>
<td>0.66</td>
<td>0.0022</td>
<td>0.10</td>
<td>1.482±0.00979</td>
</tr>
<tr>
<td>KI-81-1-210.0</td>
<td>24.50</td>
<td>4.0534</td>
<td>0.00025</td>
<td>4.0532</td>
<td>0.17</td>
<td>0.13</td>
<td>0.0020</td>
<td>0.080</td>
<td>2.012±0.00342</td>
</tr>
<tr>
<td>KI-67-3-7.5</td>
<td>12</td>
<td>0.9434</td>
<td>0.0137</td>
<td>0.9297</td>
<td>0.72</td>
<td>0.52</td>
<td>0.0022</td>
<td>0.090</td>
<td>0.5171±0.00372</td>
</tr>
<tr>
<td>KI-79-3-150.4</td>
<td>13.50</td>
<td>1.3771</td>
<td>0.00025</td>
<td>1.3575</td>
<td>0.50</td>
<td>0.14</td>
<td>0.0018</td>
<td>0.090</td>
<td>0.6264±0.00313</td>
</tr>
<tr>
<td>KI-67-3-27.5</td>
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<td>0.9434</td>
<td>0.0137</td>
<td>0.9297</td>
<td>0.72</td>
<td>0.52</td>
<td>0.0022</td>
<td>0.090</td>
<td>0.5171±0.00372</td>
</tr>
<tr>
<td>KI-75-1-139.3</td>
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<td>2.4823</td>
<td>0.00025</td>
<td>2.4820</td>
<td>0.27</td>
<td>2263.1</td>
<td>0.0023</td>
<td>0.11</td>
<td>1.412±0.00388</td>
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<tr>
<td>KI-67-3-39.0</td>
<td>10.73</td>
<td>0.9333</td>
<td>0.0137</td>
<td>0.9196</td>
<td>0.73</td>
<td>0.47</td>
<td>0.0020</td>
<td>0.090</td>
<td>0.4530±0.00331</td>
</tr>
<tr>
<td>IKI-58</td>
<td>8.08</td>
<td>0.7155</td>
<td>0.00025</td>
<td>0.7152</td>
<td>0.94</td>
<td>1.21</td>
<td>0.0022</td>
<td>0.19</td>
<td>0.4017±0.00486</td>
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<tr>
<td>KI-67-3-81</td>
<td>7.73</td>
<td>0.3381</td>
<td>0.0137</td>
<td>0.3244</td>
<td>2.07</td>
<td>1.36</td>
<td>0.0020</td>
<td>0.18</td>
<td>0.1538±0.00329</td>
</tr>
<tr>
<td>KI-81-2-88.6</td>
<td>2.37</td>
<td>0.0214</td>
<td>0.0137</td>
<td>0.0077</td>
<td>87.09</td>
<td>8.70</td>
<td>0.0018</td>
<td>0.27</td>
<td>0.0034±0.00296</td>
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</table>

Table 14. Rhenium. The blank correction, Isotope ratio, sample weight, and blank uncertainties; the largest uncertainty (in red) is applied to calculating the uncertainty of the Rhenium concentrations (in blue).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MgO Content wt.%</th>
<th>Re (quantity) ng</th>
<th>Re Blank ng</th>
<th>Re (blank corrected) ng</th>
<th>Blank Unc. %</th>
<th>Ratio Unc. %</th>
<th>Sample wt Unc. %</th>
<th>Spike wt Unc. %</th>
<th>Re Concentration (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI-81-1-169.9</td>
<td>26.87</td>
<td>0.2972</td>
<td>0.00011</td>
<td>0.2961</td>
<td>1.69</td>
<td>0.12</td>
<td>0.0020</td>
<td>0.10</td>
<td>0.1511±0.00255</td>
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<tr>
<td>KI-81-1-239.9</td>
<td>26.55</td>
<td>0.0641</td>
<td>0.011</td>
<td>0.0531</td>
<td>9.42</td>
<td>0.24</td>
<td>0.0023</td>
<td>0.010</td>
<td>0.03041±0.00286</td>
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<tr>
<td>KI-67-3-6.8</td>
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<td>0.7466</td>
<td>0.0007</td>
<td>0.7459</td>
<td>0.67</td>
<td>0.12</td>
<td>0.0022</td>
<td>0.010</td>
<td>0.4186±0.00280</td>
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<tr>
<td>KI-81-1-210.0</td>
<td>24.50</td>
<td>0.0896</td>
<td>0.011</td>
<td>0.0786</td>
<td>6.36</td>
<td>0.17</td>
<td>0.0020</td>
<td>0.010</td>
<td>0.03901±0.00248</td>
</tr>
<tr>
<td>IKI-22</td>
<td>19.52</td>
<td>0.4547</td>
<td>0.00011</td>
<td>0.4536</td>
<td>1.10</td>
<td>0.10</td>
<td>0.0020</td>
<td>0.12</td>
<td>0.2247±0.00247</td>
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<td>KI-79-3-150.4</td>
<td>13.50</td>
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<td>0.0007</td>
<td>0.4916</td>
<td>1.02</td>
<td>0.090</td>
<td>0.0018</td>
<td>0.010</td>
<td>0.2269±0.00231</td>
</tr>
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<td>0.7747</td>
<td>0.0007</td>
<td>0.7740</td>
<td>0.65</td>
<td>0.13</td>
<td>0.0022</td>
<td>0.010</td>
<td>0.4306±0.00280</td>
</tr>
<tr>
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<td>11.7</td>
<td>0.1320</td>
<td>0.011</td>
<td>0.1210</td>
<td>4.13</td>
<td>0.15</td>
<td>0.0023</td>
<td>0.010</td>
<td>0.06889±0.00285</td>
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<tr>
<td>KI-67-3-39.0</td>
<td>10.73</td>
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<td>0.6061</td>
<td>0.82</td>
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<td>0.010</td>
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<td>0.7374</td>
<td>0.68</td>
<td>0.030</td>
<td>0.0022</td>
<td>0.010</td>
<td>0.4141±0.00282</td>
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<td>0.4337</td>
<td>0.0007</td>
<td>0.4330</td>
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<td>7.5</td>
<td>0.3412</td>
<td>0.011</td>
<td>0.3302</td>
<td>1.51</td>
<td>0.050</td>
<td>0.0023</td>
<td>0.010</td>
<td>0.1873±0.00283</td>
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<td>7.57</td>
<td>2.1456</td>
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<td>2.1449</td>
<td>0.23</td>
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<td>0.0017</td>
<td>0.010</td>
<td>0.9308±0.00214</td>
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<td>1.1038</td>
<td>0.45</td>
<td>0.030</td>
<td>0.0023</td>
<td>0.010</td>
<td>0.6261±0.00282</td>
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<tr>
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<td>4.6329</td>
<td>0.0007</td>
<td>4.6322</td>
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<td>0.090</td>
<td>0.0018</td>
<td>0.010</td>
<td>2.029±0.00223</td>
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</table>
Discussion

 Supporting the Hypothesis

The MgO plots for Os and Ru show that the hypothesis for these elements is supported. It was hypothesized that Os and Ru are compatible. The compatible elements would display a positive slope which is associated with well-suited elements; as the melt crystallizes from high MgO content to low, the concentration of the compatible element will decrease.

Due to the poor correlation of Re, Pd, Pt, and Ir in the graphs, the hypothesis that Re, Pd, and Pt are incompatible and Ir is compatible is not well supported. Therefore it can be deduced that Re, Pd, Pt, and Ir are being controlled by an additional phase other than olivine during fractional crystallization of the Kilauea Iki lava lake; and the low abundances of Re is perhaps a result of degassing of Re during the eruption of the Kilauea volcano.

Additional Phases

Rhenium and the PGE are sulfur loving (chalcophile) elements and there is a possibility that sulfur and chromite are the additional phases controlling Pd, Pt, and Ir during fractional crystallization of the lava lake. Chromite is an oxide is found as inclusions in the olivine phenocrysts in cores from the 1959 eruption. Sulfides are rarely found in Kilauea basalts, but it is reportedly found as inclusions or associated with ilmenite and titanomagnetite separates from differentiated rift lava (Helz 1983, Desborough 1968). Sulfides are also found in interstitial liquid in Alae Lava Lake (Helz 1983, Skinner 1969). The Kilauea summit lavas are the first known occurrences of sulfide in Kilauean basalts (Helz 1983). Sulfide occurs in olivine as one phase in swarms of inclusions (Helz 1983). For a sulfide to be stable as a separate phase a combination of necessary conditions must take place. These special requirements (e.g., temperature, silicate melt composition, and sulfur and oxygen fugacities) are discussed in greater detail in Helz 1983.

Through the use of the ICP-MS ID technique, Re and PGE were examined in the komatiitic basalt lava lake in the Vetreny belt (Baltic shield) and it was found that Ru, Ir, Pt, and Pd are compatible with chromite, while Pt and Pd compatibility are moderate compared to Ru and Ir (Puchtel el al., 2001) (Figure 18). Therefore the speculation of chromite being the controlling
phase in the Kilauea Iki lava lake is plausible. Chromium data, however, are not available for the Iki samples to test this hypothesis.

Degassing of Rhenium

There have been proposals that the low and variable Re concentrations in Ocean Island Basalts (OIB) is due to outgassing during volcanic events (Norman et al., 2004; Bennett et al., 2000). For instance Re loss during magmatic out-gassing was examined in greater detail through comparing metal abundances and sulfur contents in a suite of basaltic degassed and un-degassed glasses from Ko’olau and Moloka’i volcanoes, Hawaii (Norman et al., 2004). Rhenium concentrations in the un-degassed glasses (1.2 – 1.5 ppb) were higher than those measured in the degassed glasses (0.24 – 0.87).

Figure 18. Variation diagrams of PGE (ppb) vs. Cr (ppm) for the komatiitic basalt lava lake rocks and mineral separates. (From: Puchtel et al., 2001)
The KILL cores used in for this project are OIB, therefore the assumption that degassing of Re during the eruption of Kilauea can be a reason for the poor correlation of Re. This presumption is further supported by the investigation of Re concentrations in sub-aerial tholeiites from Kilauea and Mauna Kea (Bennett et al., 2000) through the use of the isotope dilution method and sample dissolution. The Re abundances were relatively low and the Cu/Re ratios were high, most likely due to Re loss upon eruption or during degassing of shallow magma chambers (Figure 19).

![Figure 19](image-url)

Figure 19. Many Hawaiian lavas including all the submarine erupted picrites show Cu/Re ratios similar to the mantle value over a wide range of melting fractions as indicated by the Sm/Nd ratios. The exceptions, with high Cu/Re ratios and low Re concentrations, include some subaerial Kilauea flows and subaerial Mauna Kea lavas from HDSP (Hawaii Scientific Drilling Project). The may be indicative of Re loss by degassing upon eruption or during storage in shallow magma chambers. (From: Bennett et al., 2000)

**Estimates of bulk distribution coefficients**

Bulk distribution coefficients were estimated for Ru, Re, and Os by calculating model liquid and solid 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 concentrations obtained for sample KI-79-3-150.4, a rock with MgO similar to the estimated parental melt and using the equations below, where \( C_L \) and \( C_S \) are the concentrations of the liquid and solid, \( C_o \) is the concentration of the trace element in the whole system (starting concentration of the parental melt), \( F \) is the fraction of liquid, and \( D \) is the Bulk Distribution Coefficient.

\[
C_L = C_o \times F^{(D-1)}
\]
The values used for $C_o$ are the concentrations of Os (0.43ng/g), Re (0.21ng/g), and Ru (0.63ng/g) in sample KI-79-3-150.4 (~14 MgO wt. %). F is a variable representing the fraction of melt in the system (e.g. 100 to 1 percent melt). Estimated D-values were varied until the concentrations of the liquids and solids correlated well with the trend for the Iki data. For example, the starting concentration for Os is 0.43ng/g; therefore the concentration of Os at 100 percent melt should be ~0.43ng/g. Once there is a good correlation between bulk-D and fraction of liquid, the concentrations of Os relative to Re concentrations were plotted (Figure 20a-b).

Figure 20. (a) Bulk distribution coefficients for Os and Re. (b) Bulk distribution coefficients for Re and Ru.

Figure 20a illustrates Re as an incompatible element with a bulk-D value of 0.45, where its concentration is higher in the liquid phase than in the solid phase. Os is a compatible element with a bulk-D value of 2.5. As a compatible element its concentration is higher in the solid phase than in the liquid phase. Ru is a compatible element ($D = 3.0$) and therefore behaves similar to Os. As the lava lake crystallized Ru may take the place of a major element in available
sites in the crystal structure of olivine, rather than remaining in the melt. As a result, the concentration of Ru is greater in the solid phase than in the liquid phase (Figure 20b). For contrast and comparison, Brenan et al., (2005) diagram (Figure 5) reported data for Ru at high oxygen fugacities (-2 to -5) as a compatible element and Re at lower fugacities as a incompatible element.

Conclusions
Concentrations of Re and PGE were measured in borehole cores from the Kilauea Iki lava lake. Osmium (0.0006 – 1.06 ppb) and Ru (0.0034 – 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 – 0.7 ppb), Pd (0.24 – 5.8 ppb), Pt (1.15 – 10.4 ppb), and Re (0.030 – 2.0 ppb) have limited correlation to changes in MgO wt. %, 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 (2.5), Re (0.45), and Ru (3.0) were estimated by calculating the $C_L$ and $C_S$ on a spreadsheet and plugging in different values for $D$ into the equations until a match with the Iki data was achieved.

Acknowledgments — I wish to thank Dr. Rosalind T. Helz from the USGS for providing the cores and thin-sections for this experiment, as well as acting as a consultant; providing additional information on the rocks and thin-sections. Thanks also go to Dr. Igor S. Puchtel for guidance in the University of Maryland’s geochemistry clean laboratories, with the chemical separation methods and application, and direction with making and preparing mass spectrometer filaments and filament ribbons; and for guidance with the Thermal Ionization and Inductively-Couple Plasma Mass Spectrometers. Thanks to Dr. Roberta L. Rudnick for the use of her digital camera and microscope to photograph thin-sections. Thank you to Dr. Philip A. Candela for the crash course in oxygen and sulfur fugacities. Special thanks is due to Dr. Richard J. Walker for taking the role as my thesis advisor, mentor, and teacher; for constantly being available to help in the laboratories, with my scientific writing skills, for coaching me in how to use the TIMS and ICP-
MS, and for his patience. I would also like to thank Dr. Walker for encouraging me to participate in the American Geophysical Union meeting.

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## Appendix A

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<tr>
<th>Name</th>
<th>Symbol</th>
<th>Atomic wt</th>
<th>Atomic #</th>
<th>Group #</th>
<th>Period #</th>
<th>Block</th>
<th>Colour</th>
<th>Classification</th>
<th># naturally occurring Isotopes</th>
<th>Isotopes</th>
</tr>
</thead>
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<td>Os</td>
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<td>Pt</td>
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<td>Metallic</td>
<td>7</td>
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</tr>
</tbody>
</table>

...
Appendix B

Isotope Dilution Equations

Isotope Dilution Equation

\[
\left( \frac{^{185}\text{Re}}{^{187}\text{Re}} \right)_{\text{MIX}} = \left( \frac{\text{# Atoms of Isotope}^{185}\text{Re}}{\text{# Atoms of Isotope}^{187}\text{Re}} \right)_{\text{SPIKE}} + \left( \frac{\text{# Atoms of Isotope}^{185}\text{Re}}{\text{# Atoms of Isotope}^{187}\text{Re}} \right)_{\text{SAMPLE}}
\]

The Knowns

(\text{# Atoms of}^{185}\text{Re})_{\text{SPIKE}} = \frac{\text{(weight of spike)} \times \text{(concentration of Re in spike)} \times (\text{Atom}\%^{185}\text{Re})_{\text{SPIKE}} \times (\text{Avagadro's #})}{\text{(Atomic wt. of Re)}_{\text{SPIKE}}}

(\text{# Atoms of}^{187}\text{Re})_{\text{SPIKE}} = \frac{\text{(weight of spike)} \times \text{(concentration of Re in spike)} \times (\text{Atom}\%^{187}\text{Re})_{\text{SPIKE}} \times (\text{Avagadro's #})}{\text{(Atomic wt. of Re)}_{\text{SPIKE}}}

(\text{# Atoms of}^{185}\text{Re})_{\text{SAMPLE}} = \frac{(\text{Avagadro's #}) \times (\text{Atom}\%^{185}\text{Re}) \times (\text{weight of sample})}{(\text{Atomic wt. of Re})_{\text{SAMPLE}}}

(\text{# Atoms of}^{187}\text{Re})_{\text{SAMPLE}} = \frac{(\text{Avagadro's #}) \times (\text{Atom}\%^{187}\text{Re}) \times (\text{weight of sample})}{(\text{Atomic wt. of Re})_{\text{SAMPLE}}}

Rearrange to Solve for X

X = \left[ \left( \frac{^{185}\text{Re}}{^{187}\text{Re}} \right)_{\text{MIX}} \times \left( \frac{\text{# Atoms of Isotope}^{185}\text{Re}}{\text{# Atoms of Isotope}^{187}\text{Re}} \right)_{\text{SPIKE}} \right] - \left( \frac{\text{# Atoms of Isotope}^{185}\text{Re}}{\text{# Atoms of Isotope}^{187}\text{Re}} \right)_{\text{SPIKE}}

\left( \frac{\text{# Atoms of Isotope}^{185}\text{Re}}{\text{# Atoms of Isotope}^{187}\text{Re}} \right)_{\text{SAMPLE}} = \left[ \left( \frac{^{185}\text{Re}}{^{187}\text{Re}} \right)_{\text{MIX}} \times \left( \frac{\text{# Atoms of Isotope}^{185}\text{Re}}{\text{# Atoms of Isotope}^{187}\text{Re}} \right)_{\text{SPIKE}} \right] - \left( \frac{\text{# Atoms of Isotope}^{185}\text{Re}}{\text{# Atoms of Isotope}^{187}\text{Re}} \right)_{\text{SPIKE}}
Analytical Method Appendix C

I. Prepare Powders
   A. Sand paper drilled or sawn surfaces of rocks until surfaces are contaminant free.
   B. Jaw-crusher
      1. clean area, Jaw-crusher, and tray (Fig. 1)
         a. Make sure nothing is in the machine and tray which could contaminate your sample.
         b. Clean everything between each sample.
      2. Tightly screw in knob (located in the front of the machine).
      3. place tray into slot
         a. Catches the crushed rock.
      4. Turn on machine and drop a piece of rock between plates and collect crushed rock in tray.
   C. Disk Mill
      1. Clean area and equipment (Fig. 2).
      2. Turn knob counterclockwise before locking the disk mill, allowing space between the two disks.
      3. Put crushed rock on top of a piece of paper with crease in the middle.
      4. Turn on disk mill and turn knob clockwise until you hear the two disks rub against each other.
      5. Pour crushed rock into machine. Once the sample goes through, turn knob counterclockwise until disks no longer touch.
      6. Turn off disk mill and pour powder onto creased paper and collect it in a clean bottle (Fig. 3).
         a. Make sure to throw away creased paper and use a new sheet for each sample.

II. Re-Os-highly siderophile elements (PGE) chemical separation.
   A. Re-Os-PGE preparation.
      1. Required materials.
         a. (10) carius tubes
         b. (20) 15ml round bottom Teflon vials
         c. (10) 5ml conical bottom Teflon vials
d. Funnels
e. Transfer pipetters
f. Centrifuge tubes
g. Biorad columns
h. 100-200 mesh anion resin
i. HCL (concentrated, 1M)
j. HNO₃ (concentrated, 0.8M, 6M)
k. HBr (concentrated)
l. Milli-Q water
m. (2) 5ml pipetter tips for adjustable pipetter
n. 10-200 µl pipetter tips for adjustable pipetter
o. 2000 ml beaker
p. Protective eyewear
q. Lab coat
r. gloves

2. Cleaning Carius Tubes.

a. Wearing goggles, lab coat, and gloves are required.
b. Rinse low blank pyrex tubes with building distilled water.
   i. Low blank pyrex tubes will be used in this study.
c. Place tubes in mixture of 50% aqua rega (25% HNO₃ to 25% HCl) and 50% Milli-Q water.
   i. Mix acids and water under a hood.
   ii. Make sure acid fills the interior of each tube to clean all surface areas.
d. Cover beaker with glass watch glass and gently boil (bubbles slowly forming and rising from the bottom of the beaker). Check beaker frequently until a stable temperature is reached. Let beaker boil for at least 12 hours (Fig. 4).
   i. For large beakers set hot plate dial 65-70.
   ii. For small beakers set hot plate dial 40-50.
e. Allow beaker to cool overnight. Remove tubes using the Teflon puller to raise the tubes above the level of the acid. As you remove the tubes, gently invert and shake the acid out of the interior of the tube back into the bath (Fig. 5).
   i. Double gloving is required.
Place cleaned tubes in a clean tray with building distilled water (Fig. 6a).

Rinse each tube 3 times (inside and out) with Milli-Q water.

Place tubes in a clean large beaker filled with Milli-Q water. Place beaker on a hotplate. Gently boil overnight.

Place inverted tubes in a hood on plastic wrap and dry completely (Fig. 6b).

Wrap dry tubes in plastic wrap and put into storage box.

3. Cleaning Teflon Vessels
   a. Wearing goggles, lab coat, and gloves is required.
   b. Place round and conical bottom Teflon vessels in a 2000 ml beaker containing a mixture of 50% Milli-Q water, 25% HCl, 25% HNO₃.
      i. Mix under a hood.
      ii. Put them into beaker individually to ensure total submergence to clean all surface area.
   c. Set hot plate on 55 dial.
   d. Place beaker on hot plate for 12 hours or over night (Fig. 7).
   e. After boiling let beaker cool for several hours.
   f. Decant acid into another clean beaker.
   g. Rinse clean Teflon and beaker with Milli-Q water.
   h. Rinse clean Teflon and beaker (individually) with Milli-Q water.
      i. Make sure all surfaces are rinsed repeatedly.
   i. Put Teflon in a beaker filled with Milli-Q water. Place beaker on a hot plate on a low dial setting for 3 hours.
      i. Repeat twice.
   j. Place inverted Teflon in laminar flow hood on plastic wrap to dry (Fig. 8).
      i. Remove from hood as soon as dry.
   k. Store clean Teflon into zip-lock bags or clean box.

4. Cleaning Transfer Pipetters and Pipetter Tips
   a. Pipetter and pipetter tips are always kept clean in the clean lab and are stored in acid filled (dilute HCl) bottles.
b. Pipetter and pipetter tips used in chemistry experiment should be removed from acid prior to starting work.

c. Once removed from acid, the tips should be rinsed inside and out at least 3 times with Milli-Q water.

d. To rinse out the inside of the pipetters fill a clean beaker with Milli-Q water and use the pipetters to suck in the water, shake it to rinse the inside completely, and then expel the water into another beaker.
   i. Do this 3 times.

e. Once chemistry work is done, place pipetters and pipetter tips back into the dilute HCl beaker.

B. Re-Os-HSE chemistry

1. Introduction of Sample and Spikes to Carius Tubes

a. Fill a bucket with crushed ice. Label four cleaned carius tubes and the cap and bottom of four cleaned 15ml round bottom Teflon vessels (1, 2, 3, and 4) with Lumocolor Permanent marker pens. Bury the carius tubes in the ice bath (Fig. 9a & b).

b. Weigh the aluminum foil and sample.
   i. Want 2 grams of sample

c. Place sample into carius tube by using a Teflon funnel (Fig. 10).
   i. Use a separate piece of aluminum foil for each sample.

d. Add appropriate amounts of spikes to Teflon vessels (Fig. 11).

e. Add spike into carius tubes using Teflon funnels.
   i. Spike in vessel 1 goes into carius tube 1; spike in vessel 2 goes into carius tube 2, etc.
f. Add 3.5 ml of concentrated distilled HCl to Teflon vessels (1, 2, 3, and 4).
g. Add HCl in Teflon vessel 1 to carius tube 1 using Teflon funnel, and so forth (vessel 2 to carius tube 2, etc.).
   i. Rinse any residual powder present in funnel top with HCl.
h. Cover the openings of carius tubes with laboratory film (Figure 12).
i. Let mix freeze.
j. Add 5 ml of concentrated nitric acid (HNO₃) to Teflon vessels (1, 2, 3, and 4).
k. Add HNO₃ in Teflon vessel 1 to carius tube 1 using Teflon funnel, and so forth (HNO₃ in vessel 2 goes into carius tube 2, etc.)
   i. Rinse any residual powder present in funnel top with HNO₃.
l. Let mix freeze. Rinse the funnel with a few drops of Milli-Q water.
m. Remove funnels from carius tubes and dispose into trash can.

2. Sealing Carius Tubes
   a. Transfer carius tubes + samples to the mineral separation laboratory.
   b. Clamp the carius tube in holder. Using propane torch for Pyrex tubes, heat central portion of neck until it closes (Figure 13a & b).
      i. Take care not to pull upward to form a capillary.
   c. Turn OFF gases and clean-up room before leaving.
      Cooled glass detritus must go in the glass disposal box.
   d. Allow carius tubes to cool for 15 minutes.
   e. Wrap tubes in aluminum foil and label which carius tube is which (1, 2, 3, or 4)
   f. Place each wrapped carius tube into a metal jacket (Fig. 14a). Each jacket should be LIGHTLY screwed.
g. Turn oven onto 240° and place each metal jacket inside (Fig. 14b). Allow tubes to cook for a few days.

3. Osmium Separation Procedures
   a. Take metal jackets out of oven and allow them to cool off.
   b. Rinse and clean 15ml round bottom Teflon vessels used for weighting spikes with Milli-Q water and kimwipes. Cover the top edges of the Teflon vessels with Teflon thread seal tape (Fig. 15)
      i. This will prevent any Os evaporating.
   c. Place all four Teflon vessels under the hood.
   d. Remove four 60ml and two 15ml centrifuge tubes from acid bath. Rinse three times with Milli-Q water (Fig. 16). When dry label the four 60ml centrifuge tubes with sample numbers (1, 2, 3, and 4) and label the two 15ml centrifuge tubes 1 and 2. Put all centrifuge tubes in a centrifuge rack and place them and bottles of HBr and CCl₄ under the hood (Fig. 17)
   e. Label two 5ml pipette tips (previously cleaned) “acid” and “solvent”. Label one transfer pipette for each sample with sample numbers (1, 2, 3, and 4). Put all six under the hood.
   f. Working under a hood and wearing gloves; put 3ml of carbon tetrachloride (CCl₄) into each centrifuge tubes using the same 5ml pipette tip for all 4 Teflon vessels. Disregard the CCl₄ pipette tip, and get a new one.
   g. Under the hood put 4ml of concentrated distilled hydrobromic acid (HBr) into each Teflon vessel using the new 5ml pipette tip (Fig 17)
h. Fill a bucket with ice and return to mineral separation room. Remove the four carius tubes from the metal jackets, take off the aluminum foil, shake the contents, and clean the exterior of the carius tubes with Milli-Q water.

i. Using a (scratcher?) scratch a straight line halfway around the top part of each carius tube and submerge them into the ice bucket. After 15 minutes clamp the carius tube in holder. Using propane torch for Pyrex tubes heat the tip of a glass wand and then press the hot tip to the carius tube where you scratched it. Repeat for the other 3 carius tubes.
   i. The heat from the glass wand tip will cause the carius tube to crack along the scratched line.

j. Turn OFF gases and clean-up room before leaving. Cooled glass detritus must go in the glass disposal box. Return to clean lab with carius tubes in bucket.

k. Put on vinyl gloves and put a large empty beaker under hood.

l. Unscrew the top off of the 15ml centrifuge tube #1. Holding carius tube #1 away from you under the hood, press on the top part of the tube where it is cracked. The top of the tube should pop off easily. Disregard the top into the empty beaker.

m. Pour contents in carius tube #1 into 15ml centrifuge tube #1. Disregard the carius tube into the large beaker (Fig. 18a). Squirt 6N HNO₃ into carius tube to wash down any content clinging to the insides of the tube and pour into 15ml centrifuge tube #1 (Fig. 18b).
   i. DO NOT let the tip of the 6N HNO₃ bottle touch the carius tube.

n. Screw back on the top of the 15ml centrifuge tube #1.

o. Repeat steps l-n for carius tube #2 and 15ml centrifuge tube #2.

p. Shake each sealed centrifuge tube for 1-2 minutes and then centrifuge them on high for 15 minutes (Fig. 19)
q. Repeat steps l-n for carius tubes # 3-4 but pour contents into 60ml centrifuge tubes # 3 and 4. Shake them for 1-2 minutes.

r. Take 15ml centrifuge tubes 1 and 2 from the centrifuge machine. Pour contents from 15ml centrifuge tube #1 to 60ml centrifuge tube #1. Do the same for contents in 15ml centrifuge tube #2 but into 60ml centrifuge tube #2.

s. Shake all four 60ml centrifuge tubes and the centrifuge them for 2 minutes. Return centrifuge tubes back to hood after centrifuging them.

t. Using transfer pipette, slowly draw out the CCl₄ from bottom of the 60ml centrifuge tube #1 and transfer to the HBr in Teflon vessels #1 (Fig. 20). Do the same for the others (60ml centrifuge tube #2 to Teflon vessel #2, etc.).

   i. Make sure NOT to transfer any of the aqueous phase to the HBr. To be on the safe side, you can rinse off the outsides of the transfer pipette with Mill-Q water before transferring.

u. REPEAT steps s-t again ONE more time by adding another 2ml of CCl₄ to each centrifuge tube, shake them, and centrifuge again on high for 3 minutes.

v. REPEAT steps s-t again ONE more time by adding 2ml of CCl₄ to each centrifuge tube, shake them, and centrifuge again on high for 3 minutes.

w. Rinse pipette tips and save for later.

x. Re-label Teflon vessels by adding Os to each cap and sides. This is the CCl₄ containing the Osmium isotopes (Fig. 21).

y. Take out another four clean 15ml round bottom Teflon vessels and label them 1, 2, 3, and 4. Pour contents in 60ml centrifuge tube #1 into Teflon vessel #1; 60ml centrifuge tube #2 into Teflon vessel #2; etc. and cap them. These Teflon vessels are filled with the aqueous solution containing Re and the other PGEs.

z. Place Teflon vessels #1, 2, 3, and 4 on a hot plate (two at a time) at 85°C for 2-3 hours or overnight (Fig. 22). Place Teflon vessels Os1, Os2, Os3, and Os4 in heat block.

aa. Clean the 15ml and 60ml centrifuge tubes and caps with Milli-Q water. Let them dry in hood.
bb. Remove Teflon vessels Os1, Os2, Os3, and Os4 from heat block. Pour contents in Teflon vessel Os1 into cleaned 60ml centrifuge tube #1. Do the same for the others (Teflon vessel Os2 into 60ml centrifuge tube #2, etc.). Centrifuge tubes for 3 minutes.

c. Extract the HBr (the lighter and clearer liquid on top) from 60ml centrifuge #1 and transfer to Teflon vessel Os1. Do the same for the others (60ml centrifuge tube #2 to Teflon vessel Os2, etc.)

i. The Os is no longer part of the CCl4 but is in the HBr.

dd. Pour the CCl4 (the darker liquid at the bottom of the centrifuge tube) into a waste bottle for disposal.

e. Place Teflon vessels Os1, Os2, Os3, and Os4 with HBr under heat lamp and dry.

4. Osmium Micro-distillation

a. Label four cleaned conical bottom Teflon vessels (cap and bottom) for each sample (Os1, Os2, Os3, and Os4) and wrap top edges with Teflon thread seal tape.

b. Clean area under hood and place down plastic wrap. Cut out four thin strips and square shape pieces of aluminum foil.

c. Using a 50-200 µL pipette tip, add 15 µL of concentrated HBr to the bottom of the 15ml round bottom Teflon vessel Os1. Using the tip, mix the HBr and Os together and then transfer the mix onto the center of a flat cap from the 5ml conical bottom Teflon vessel Os1 (Fig 23).

i. Repeat step c for all the samples (15ml Teflon vessel Os2 to 5mL conical Teflon cap Os2, etc.)

ii. Use separate pipette tip for each sample.

d. Place cap under heat lamp and dry down completely (~40 minutes).

e. AFTER Os + HBr mix has dried down turn on heat block to 70°C. Add 19µL of concentrated HBr to the tip of the 5ml conical bottom Teflon vessels Os1, Os2, Os3, and Os4. Tap cap to get all HBr into the bottom.

f. Add 43 µL of dichromate to flat cap where sample dried down.

i. DO NOT touch the tip of pipette to the sample.

g. Carefully and quickly (don’t let the HBr to fall into sample) invert conical Teflon vessel over cap and screw cap onto vessel.

h. Wrap Teflon vessel in aluminum foil, leaving the tip with HBr uncovered, and place it inverted on heat block for 2-3 hours (Fig 24).
i. Carefully remove Teflon vessel from hotplate and carefully remove aluminum foil.

j. Gently unscrew Teflon cap and check the residue. If it looks green as is or looks green after adding a little Milli-Q water, there was insufficient Cr⁺³ for oxidizing the Os; therefore add more dichromate and redistill. If residue looks red and dissolves into yellow liquid when water is added, the cap can be rinsed out and dried.

k. Screw cap back onto vessel. It is best to let HBr sit for several hours to make sure all Os is reduced. The HBr can then be evaporated under a heat lamp.

l. The sample is now ready for loading into mass spectrometer.

5. Anion Exchange Column Procedures for Rhenium and Platinum-Group Elements

a. Add 10 ml of to the 0.8M HNO₃ in Teflon vessels 1, 2, 3, and 4. Screw cap back on and place vessels onto hot plate over night.

b. Take out four 10mL Teflon columns from acid bath, rinse with Milli-Q water 3×, and dry under the hood. Label them (1,2, 3, and 4) and put into column stand and place catch cups under each column.

c. Pour the contents in Teflon vessels 1, 2, 3, and 4 into centrifuge tubes, centrifuge the samples, and place to the side for later.

d. Fill Teflon vessels 1, 2, 3, and 4 halfway (7.50 ml) with Quartz distill HNO₃. screw back on cap and place onto hotplate for cleaning.

e. Reduced Column Chemistry for Re and HSE (after Os extraction)

   i. Fill columns with 1.6 ml of resin (AG ¹ × 8 100-200 mesh, cleaned for PGE)

   ii. Clean with 10 ml Milli-Q water (Fig. 25a)

   iii. Clean with 10 ml 8N HNO₃ (2×)

       1) Make sure to use the Quartz distilled acid

   iv. Clean with 2 ml Milli-Q water

   v. Clean with quartz distilled HCl

   vi. Equilibrate with 2 ml 0.8N HNO₃ (2×)

   vii. Load centrifuged samples (liquid only) into columns.

       1) Throw centrifuge tubes into the trash.

   viii. Elute 5 ml 0.8N HNO₃

   ix. Elute with 2 ml 0.8N HNO₃ (2×)

   x. Elute with 5ml 1M HCl

   xi. Elute with 2ml of 0.8M HNO₃

       1) Use Teflon distilled acid.

   xii. Remove catch cups and dispose the waste in the appropriate waste container.
xiii. Replace the catch cups with four new Teflon vessels (labeled Re1, Re2, Re3, and Re4) under the columns
   1) Collect 10 ml 6N HNO₃ into Teflon vessels (Fig 25b)
   2) Place under heat lamp to dry down.

xiv. Remove the Teflon vessels 1, 2, 3, and 4 from hotplate. Pour the quartz distill HNO₃ into the appropriate waste container. Place the Teflon vessels (relabeled Ru, Pt, and Ir) under the columns.
   1) Collect 15 ml 13.5N HNO₃ into Teflon vessels
   2) Place under heat lamp to dry down.

xv. Place four new Teflon vessels (labeled Pd1, Pd2, Pd3, and Pd4) under columns
   1) Elute 1 ml H₂O
   2) Collect 15 ml 10N HCl
   3) Place under heat lamp to dry down.

f. AFTER samples have dried and you can see visible residue on the bottom of the Teflon vessels, re-cleaning the samples with 0.25ml anion exchange columns is imperative. Re-clean samples as follows:
   i. Dissolve all the samples in 2ml of 6M HNO₃ and place on hotplate to dissolve for an hour.
   ii. Mix sample Re1, Ru1, Ir1, Pt1, and Pd1 together in one of the Teflon vessels marked for sample 1 (e.g. Re1). Do the same for all the other samples; mix Re2, Ru2, Ir2, Pt2, and Pd2 together in a Teflon vessel marked for sample 2 (e.g. Re2).
   iii. Placed the mixed samples under a heat lamp to dry down.
   iv. Dissolve the samples in 2ml of 0.8M HNO₃ and place on hotplate.
   v. Take four 0.25ml Teflon columns out of the acid bath. Rinse with Milli-Q water.
   vi. Place some quartz wool (the size of the tip a pinkie finger) inside each column. Using a glass stirring rod push the quartz wool down to the bottom of the column. DO NOT pack down or force the wool down, it will slow down the rate of rinsing.
   vii. Fill the columns with 0.25ml of resin (AG 1× 8 100-200 mesh, cleaned for PGE). Be careful

g. Cleaning up
   i. Wrap the columns tightly in plastic wrap and disregard into the trash can.
III. Mass Spectrometer

A. Filament Preparation

1. Clean filaments (Fig 25a) by removing all old Pt ribbons and file down the posts of the filaments with a filer to make the post surfaces smooth (Fig 26b).

![Figure 26](image)

2. File down copper electrodes and place them into welding machine (Fig 27a).

3. Screw filaments into ribbon loader. Load the Pt ribbon into the ribbon loader and using the straight edge of a razor, bend the edges of ribbon upward to the insides of the filament posts (Fig 27b).

4. Use wedge machine to fasten ribbon onto the filament posts (Fig 27c).

5. Load filaments onto degassing machine, two at a time for at least 10 minutes (Fig 27d). While filaments are degassing prepare the next two filaments for degassing.

6. Put degassed filaments into a storage box and let sit overnight.

B. Loading Sample/Blank onto Ribbon

1. Screw filament onto the filament holder (make sure it is not too tight, but tight enough for the filament not to fall out). DO NOT touch the ribbon.

2. Place filament and holder onto the degassing machine and turn it on.

3. Using a pipetter add 1.1 μL of HBr to conical Teflon vessel Os1 in order to dissolve the sample completely.

4. Using the same pipette tip, load sample onto filament ribbon

   a. Hold pipetter at an angle to the side and hold onto the top of the pipette tip with your other hand to keep the tip steady.

5. Turn on the degassing machine. Press RESET. Make sure that machine is on its lowest setting. Flip on the LEFT or RIGHT switch (depending on which side the filament is on), and wait for it to dry (~5 minutes).
6. On laboratory film paper, put a small drop (1.1 μL) of barium hydroxide (Ba(OH)₂) onto the film. Spread 0.7 μL of Ba(OH)₂ onto the filament ribbon.

7. Turn up the degassing machine’s setting a little over 0.5 and the Ba(OH)₂ should turn white and then clear as you continue to increase the setting.

8. Once dried load the filament into TIMS.

C. Loading Filament into TIMS (Fig 28)

1. Make sure the beam valve is closed; filament power supply and high voltage power supply are OFF.
2. close the source valve and turn the RED safety arm on vacuum gauge all the way to the right (clockwise).
3. make sure the rough pump is off (down position on switch)
4. open N₂ tank.
5. open N₂ bleed valve.
6. open needle valve.
7. loosen the 2 bolts holding the filament block with the hex tool.
8. Put in new filament block; lightly tighten in place with hex head bolt; reconnect the filament leads. Make sure that the filament leads do not touch each other and push the leads about ½ way onto the connections.
9. replace faceplate and bolts.
10. turn on the rough pump (up position)
11. Turn the thermocouple switch to ‘R’. if system tips, press the reset button on the left side of the control panel.
12. close the needle valve when the pressure reads 5⁻¹⁰
13. Turn off the rough pump and turn the thermocouple switch to ‘F’.
14. Turn off the ion gauge filament; then open the source valve.
15. Move the red reset arm on the vacuum gauge back to approximately 500 millitorr.
16. Wait a minute or two, then turn ion gauge filament on.
17. add liquid nitrogen (LN₂) when the pressure reads 10⁻⁶ millitorrs. Always check to make sure there is no water in the cold finger before adding the LN₂.
18. if running Os or Re open O₂ tank with black knob until pressure >0. Re-tighten black knob. Bleed in O₂ to add approximately 1 × 10⁻⁷ millitorrs to vacuum.
19. ready to analyze sample.
Thin-Sections Descriptions Appendix D

Sample KI-79-1R1-167.8

**Plagioclase**

**PPL:**
- Color: Colorless
- Relief: low
- Pleochroism: none
- Shape: subhedral (elongated)
- Size: <0.75mm- 1mm
- Cleavage Traces: none

**XPL:**
- Birefringence: 1st order gray, white
- Twinning habit(s): Simple, Albite and Pericline twins
- Extinction Habit: inclined
- Alteration: zoning

**Olivine**

**PPL:**
- Color: light brown
- Relief: high
- Pleochroism: none
- Shape: anhedral
- Size: 0.5mm–0.15 mm
- Cleavage Traces: none

**XPL:**
- Birefringence: 2nd order blue, pink
- Twinning habits(s): none
- Extinction habit: reverse zoning. As the stage is turned, the mineral does not go extinct everywhere at the same time. Instead it goes extinct from exterior to interior.
- Alteration: zoned

**Pyroxene**

**PPL:**
- Color: light brown
- Relief: moderate-high
- Pleochroism: none
- Shape: subhedral
- Size: 0.75mm-2mm
- Cleavage Traces: yes

**XPL:**
- Birefringence: 1st order orange, red, and pink.
- Twinning habits(s): none
- Extinction habit: zoned
- Alteration: colorless, opaque, & light brown

**Matrix**

**PPL:**
- Color: colorless, opaque, & light brown

**XPL:**
- Birefringence: isometric, 1st order gray & orange-isch

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**Summary**

Over All Proportions: Matrix 85%
Pyroxene 7%
Olivine 3%

Ooze sample
Olivines have a light brown color due to small inclusions in the crystal.

Rock Name: **Basalt**
Sample iki-58

Olivine

**PPL:**
- Color: colorless – light brown
- Relief: high
- Pleochroism: none
- Shape: sub-euhedral
- Size: 0.16mm-0.5mm
- Cleavage Traces: none

**XPL:**
- Birefringence: 2nd order blue, pink, yellow, and green
- Twinning habit(s): parallel extinction
- Extinction Habit: reverse zoning
- Alteration: reverse zoning
- Any other outstanding feature: (1) resorption rims (2) Olivine shows reverse zoning: as the stage is turned, the mineral does not go extinct everywhere at the same time. Instead it goes extinct from exterior to interior.

Glass

**PPL:**
- Color: light brown

**XPL:**
- Birefringence: isometric

Summary

Over all Proportions
- Olivine 20%
- Glass 80%

Olivine grains have opaque inclusions.
This rock is an eruption sample.
Rock Name **Volcanic Glass**
Sample Iki-22 (S-5)

Olivine

**PPL**
- Color: colorless
- Relief: high
- Pleochroism: none
- Shape: sub-euhedral
- Size: 0.5mm-2mm
- Cleavage Traces: none

**XPL**
- Birefringence: 2nd order pink, blue, and green
- Twinning habit(s): none
- Extinction Habit: parallel extinction
- Alteration: washed color. As if there has been weathering, but this confuses me because KILL is a closed system.

Any other outstanding feature: (1) resorption rims in the fractures of the olivine grains. (2) opaque inclusions in the olivine grains.

Glass

**PPL**
- Color: light brown

**XPL**
- Birefringence: isometric

Summary
- Over all Proportions: Glass 75%  
  Olivine 25%

Eruption sample
Rock name
Sample KI-67-3-39.0

Pyroxene

**PPL**
- Color: light brown
- Relief: moderate-high
- Pleochroism: none
- Shape: sub-anhedral
- Size: 05.mm-2mm
- Cleavage Traces: multi directional

**XPL**
- Birefringence: 1st order orange and redish-pink, tan, gray
- Twinning habit(s): none
- Extinction Habit: ~90° extinction angle
- Alteration: yes
- Any other outstanding feature: (1) ooze squeezing through the fractures of the pyroxenes.

Olivine

**PPL**
- Color: colorless
- Relief: high
- Pleochroism: none
- Shape: sub - euhedral
- Size: 1mm-1.25mm
- Cleavage Traces: none

**XPL**
- Birefringence: 2nd order green, blue, and yellow
- Twinning habits(s): none
- Extinction habit: parallel extinction
- Alteration: none
- Any other outstanding feature: (1) opaque inclusions in the olivine grains. (2) Faint planar extinction in one of the minerals observed, but over all parallel extinction.

Matrix

**PPL**
- Color: light brown color, colorless, opaque spots

**XPL**
- Birefringence: 1st order gray, black, brown, red-ish orange. 2nd order pink and blue.
- Twinning habits(s): twinning is noticeable.

**Summary**

**Over all Proportions**
- Matrix 65%
- Olivine 15%
- Pyroxene 20%

**Ooze sample**
- Large Olivine phenocrysts with opaque inclusions

**Rock Name** Basalt
Sample KI-79-3-158.0

Pyroxene

**PPL**
- Color: light brown
- Relief: high
- Pleochroism: none
- Shape: sub-anhedral
- Size: 0.5mm-1.5mm
- Cleavage Traces: multidirectional

**XPL**
- Birefringence: 1st order orange, brown, tan
- Twinning habit(s): none
- Extinction Habit: zoning
- Alteration: zoning

Plagioclase

**PPL**
- Color: colorless
- Relief: low
- Pleochroism: none
- Shape: euhedral (elongated)
- Size: 1mm-3.25mm
- Cleavage Traces: none

**XPL**
- Birefringence: 1st order gray, white, and black
- Twinning habit(s): albite, combined albite and Carlsbad, and polysynthetic twins
- Extinction habit: inclined
- Alteration: zoning
- Any other outstanding feature:

Olivine

**PPL**
- Color: colorless
- Relief: high
- Pleochroism: none
- Shape: anhedral
- Size: 0.5mm – 3mm
- Cleavage Traces: none

**XPL**
- Birefringence: 2nd order blue, green, and pink
- Twinning habit(s): none

Glass

**PPL**
- Color: light brown

**XPL**
- Birefringence: isotropic

Summary

Over all Proportions
- Pyroxene 60%
- Plagioclase 30%
- Glass 5%
- Olivine 5%

Sample is a segregation vein and an olivine poor ferrobasalt.
The pyroxenes and olivines are oikysts which are enclosing the plagioclase.

Rock Name **Basalt**
Sample KI-81-1-169.9

Olivine

**PPL**
- Color: colorless
- Relief: high
- Pleochroism: none
- Shape: sub-euhedral (some minerals show a six sided shape)
- Size: 1.5mm-3mm
- Cleavage Traces: none

**XPL**
- Birefringence: 2\(^{nd}\) order pink, yellow, blue, green, and purple.
- Twinning habit(s): none
- Extinction Habit: planar and parallel extinction
- Alteration: none
- Any other outstanding feature: opaque inclusions in the olivine grains

Plagioclase

**PPL**
- Color: colorless
- Relief: low
- Pleochroism: none
- Shape: anhedral
- Size: \(\leq 0.5\)mm
- Cleavage Traces: none

**XPL**
- Birefringence: 1\(^{st}\) order gray, white, and black
- Twinning habits(s): polysynthetic and simple twins
- Extinction habit: inclined
- Alteration: zoning

**Summary**

*Over all Proportions*

Olivine 70%
Plagioclase 30%

*Some olivine minerals are well rounded, while others have a six sided shape.*

**Rock Name** Porphyritic Basalt
Sample KI-75-1-121.5

Plagioclase

PPL
Color: colorless
Relief: low
Pleochroism: none
Shape: anhedral
Size: <0.5mm-2mm
Cleavage Traces: none

XPL
Birefringence: 1st order gray, white, and black
Twinning habit(s): albite twins
Extinction Habit: extinction angle ~90°
Alteration: zoning

Pyroxene

PPL
Color: light brown
Relief: high
Pleochroism: none
Shape: anhedral
Size: ~0.5mm
Cleavage Traces: linear and multidirectional

XPL
Birefringence: 1st order tan, orange, red-pink.
Twinning habit(s): none
Extinction habit: extinction angle ~90°
Alteration: none

Olivine

PPL
Color: lighter brown than the pyx
Relief: high
Pleochroism: none
Shape: anhedral
Size: ~0.3mm-.05mm
Cleavage Traces: none

XPL
Birefringence: 2nd order blue, green
Twinning habit(s): none
Extinction habit: parallel extinction
Alteration: none

Matrix

PPL
Color: light brown
Relief: low, moderate, and high in some spots
Pleochroism: none
Shape: anhedral
Size: <0.5mm
Cleavage Traces: multi-directional

XPL
Birefringence: 1st order and 2nd order interference colors
Twinning habit(s): none
Extinction habit: none
Alteration: none

Summary
Based on interference colors I believe that the tiny (< 0.5mm) individual grains are pyroxenes and olivines. Because they are so small it is hard to observe them and place them into their own unique
category, therefore I am going to put the smaller grains into the matrix category; making the composition of the matrix to be composed of olivine, pyroxene, and plagioclase (I can see some twinning in the matrix).

Over all Proportions  
Plagioclase 60%  
Matrix 40%

Rock Name  
Basalt

<table>
<thead>
<tr>
<th>Sample KI-67-3-8.2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pyroxene</strong></td>
</tr>
<tr>
<td><strong>PPL</strong></td>
</tr>
<tr>
<td>Color: light brown</td>
</tr>
<tr>
<td>Relief: high</td>
</tr>
<tr>
<td>Pleochroism: none</td>
</tr>
<tr>
<td>Shape: subhedral</td>
</tr>
<tr>
<td>Size: 1.5mm-3.5mm</td>
</tr>
<tr>
<td>Cleavage Traces: linear cleavage</td>
</tr>
<tr>
<td><strong>XPL</strong></td>
</tr>
<tr>
<td>Birefringence: 1&lt;sup&gt;st&lt;/sup&gt; order orange and red</td>
</tr>
<tr>
<td>Twinning habit(s): none</td>
</tr>
<tr>
<td>Extinction Habit: extinction angle ~90°</td>
</tr>
<tr>
<td>Alteration: none</td>
</tr>
</tbody>
</table>

| **Olivine**         |
| **PPL**             |
| Color: lighter brown than the pyx |
| Relief: high        |
| Pleochroism: none   |
| Shape: subhedral    |
| Size: 0.5mm-3mm ≥    |
| Cleavage Traces: none |
| **XPL**             |
| Birefringence: 2<sup>nd</sup> order yellow, blue, pink |
| Twinning habit(s): none |
| Extinction habit: parallel extinction |
| Alteration: resorption rims |

| **Plagioclase**     |
| **PPL**             |
| Color: colorless    |
| Relief: low         |
| Pleochroism: none   |
| Shape: euhedral (elongated) |
| **XPL**             |
| Birefringence: 1<sup>st</sup> order gray and white |
| Twinning habit(s): simple and polysynthetic twins |
| Extinction habit: inclined |
| Alteration: zoning |

| **Matrix**          |
| **PPL**             |
| Color: light brown, black opaque spots, and colorless |
| XPL (2× Objective)  |
| XPL (2× Objective)  |
Twinning habit(s): Twinning is noticeable

Summary

<table>
<thead>
<tr>
<th>Over all Proportions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyroxene 25%</td>
<td></td>
</tr>
<tr>
<td>Olivine 20%</td>
<td></td>
</tr>
<tr>
<td>Matrix+ Plagioclase</td>
<td>55%</td>
</tr>
</tbody>
</table>

Rock is an Ooze sample and the most differentiated.

Note: It was hard for me to distinguish between olivine and pyroxene because they each share the same characteristics. For example, the olivine in the picture for this sample is showing 2nd order colors and absorption rims, which is associated with Olivine minerals, BUT the same minerals are showing linear cleavages, which are associated with pyroxenes.

I am going to do deduce by using the Bowen’s Reaction Scale that the reason why so many of the olivine minerals are looking like the pyroxene minerals is because the olivine was half way turning into a pyroxene.

Rock Name Basalt

Sample KI-67-2-82.5

Plagioclase

PPL

Color: colorless
Relief: low
Pleochroism: none
Shape: euhedral (elongated)
Size: ≤ 1.5mm
Cleavage Traces: none

XPL

Birefringence: 1st order gray and white
Twinning habits(s): albite and Pericline twins
Extinction Habit: inclined
Alteration: zoning

Pyroxene

PPL

Color: light brown
Relief: high
Pleochroism: none
Shape: subhedral
Size: 0.5mm-1.5mm
Cleavage Traces: multi-directional

XPL

Birefringence: 1st order brown and orange
Twinning habits(s): none
Extinction habit: Some of the pyroxenes are showing extinction similar to bird’s eye, where the whole mineral does not go completely extinct with full rotation of stage. Therefore I am going to deduce that there was alteration.
Alteration: yes

Any other outstanding feature:
Olivine

**PPL**
- Color: light brown
- Relief: high
- Pleochroism: none
- Shape: subhedral
- Size: ≤ 1mm
- Cleavage Traces: none

**XPL**
- Birefringence: 2\textsuperscript{nd} order blue, pink, green
- Twinning habit(s): none
- Extinction habit: parallel extinction; extinction angle 90°-95°
- Alteration: resorption rims

**Matrix**

**PPL**
- Color: light brown, colorless, black opaque spots.

**XPL**
- Birefringence: 1\textsuperscript{st} order black and brown
- Twinning habit(s): twinning is noticeable in matrix

**Summary**

Over all Proportion
- Matrix + Plagioclase 90%
- Pyroxene 5%
- Olivine 5%

**Rock Name** Basalt/Ooze

Extinction Habit: symmetrical
Alteration: zoning
Any other outstanding feature: large number of plagioclase is zoning

**Pyroxene**

**PPL**
- Color: light brown
- Relief: high
- Pleochroism: none
- Shape: subhedral
- Size: 0.5mm-1.5mm
- Cleavage Traces: linear

**XPL**
- Birefringence: 1\textsuperscript{st} order gray, and white simple, albite, and Pericline twins
- Twinning habits(s): none

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**Sample KI-67-2-85.5**

**Plagioclase**

**PPL**
- Color: colorless
- Relief: low
- Pleochroism: none
- Shape: euhehedral (elongated)
- Size: 0.5mm-2mm
- Cleavage Traces: none

**XPL**
- Birefringence: 1\textsuperscript{st} order gray, and white simple, albite, and Pericline twins
- Twinning habit(s): none
Extinction habit: pyroxenes are showing a bird’s eye type of extinction, where it does not go completely extinct with rotation of the stage. Therefore I am going to deduce that there has been some kind of alteration.

Alteration: Yes

Any other outstanding feature: The pyroxenes are enclosing the plagioclase minerals, functioning as oikocrysts

Olivine

**PPL**
- Color: light brown
- Relief: high
- Pleochroism: none
- Shape: anhedral
- Size: ≤ 1mm
- Cleavage Traces: none

**XPL**
- Birefringence: 2nd order blue, yellow, green, purple.
- Twinning habits(s): none
- Extinction habit: parallel extinction
- Alteration: none
- Any other outstanding feature: olivine minerals appear to enclose the plagioclase minerals and are therefore functioning as oikocrysts.

Glass

**PPL**
- Color: brown

**XPL**
- Birefringence: isometric

**Summary**

*Over all Proportions*
- Glass 58%
- Pyroxene 10%
- Plagioclase 20%
- Olivine 2%

**Rock Name** Basalt/Ooze