PARTITIONING OF HAFNIUM AND ZIRCONIUM BETWEEN ILMENITE, ARMALCOLITE, PIGEONITE, AND HIGH-TI MARE BASALTIC MELT. G. McKay (SN4, NASA-JSC, Houston, TX 77058) and J. Wagstaff (Lockheed, 1830 NASA Rd. 1, Houston, TX 77258).

**Introduction.** Relative abundances of REE, Hf, and Zr have long been regarded important indicators of petrogenetic processes. Lu/Hf has assumed additional importance with the recent development of techniques for measuring Hf isotopic composition [e.g., 1,2]. Interpretation of Lu-Hf and Zr-Hf data has been hampered by the scarcity of crystal/liquid partitioning data for all three elements in the same sample. This situation has recently been improved by measurement of partition coefficients for phenocryst/matrix pairs [3]. However, partition coefficients are known to be sensitive to phase composition and intrinsic parameters such as temperature, pressure, and in some cases oxygen fugacity [e.g., 4-6]. To provide a self-consistent set of partition coefficients which are directly applicable to mare basalt petrogenesis, we are performing experimental determinations of Zr, Hf, and REE partition coefficients for near-liquidus mare basalt minerals. In addition to using the %-level doping technique, we are also performing experiments on samples doped with closer-to-natural concentrations of these elements. These low-concentration samples are being analyzed by isotope dilution by the Denver isotope group, and by high-sensitivity electron microprobe techniques at JSC. Preliminary Hf and Zr electron microprobe results for samples doped with ~1% Hf and for samples doped with 300-800ppm Zr, 50-100ppm Hf, and 50-200ppm of individual REE are reported here. Preliminary results from isotope dilution analysis of separated ilmenite and glass are reported elsewhere in this volume [7].

**Experiments and Results.** Starting materials were synthetic glasses of high-Ti mare basaltic composition doped as described above. Charges, suspended from Pt wire loops, were inserted in 1 atm gas mixing furnaces (log fO2 = IW + 0.5 to 1.5) at 1145°C (just below the liquidus for this composition), cooled slowly to 1120-1140°C, held for 1-4 days, and air quenched. Resulting crystals and glass were analyzed on the electron microprobe using long counting times and extreme care to accurately determine backgrounds. Resulting Hf and Zr distribution coefficients are shown in Table 1.

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**Table 1.** Crystal/liquid weight ratio partition coefficients for Hf and Zr. Uncertainties correspond to the last figure, and represent the larger of the standard deviation of replicate measurements, or the uncertainty contributed by x-ray counting statistics.

<table>
<thead>
<tr>
<th>Mineral:</th>
<th>Ilmenite</th>
<th>Armalcolite</th>
<th>Cr-spinel</th>
<th>Pigeonite (Wo7En65)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(Hf)(1):</td>
<td>0.41±2</td>
<td>1.45±2</td>
<td>0.08±1(2)</td>
<td>0.05±1</td>
</tr>
<tr>
<td>D(Zr)(3):</td>
<td>0.37±4</td>
<td>1.24±5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:** (1) Values measured for samples doped with ~1% Hf. Preliminary microprobe measurements for samples doped with ~100ppm Hf are 0.5±1 for ilmenite and 1.2±5 for armalcolite, where uncertainties are from counting statistics and do not include possible systematic errors in background measurement. (2) The value for spinel should be regarded as an upper limit, because the crystals were very small, and interference from adjacent glass is possible. (3) Preliminary values measured for samples doped with ~800ppm Zr. The possibility of systematic errors in background measurement has not yet been ruled out, but is not reflected in listed uncertainties.

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Comparison and Discussion. Ilmenite and armalcolite D(Zr) values from Table 1 are in good agreement (2-sigma) with 3-level doping results of MoCallum and Charette [8] for a similar composition (0.28 for ilmenite and 1.18 for armalcolite). Our new values for D(Hf) and D(Zr) are much lower (0.2x for Hf, 0.6x for Zr) than values measured by Fujimaki et al. [3] for phenocryst/matrix separates from kimberlite, and show less capacity for Zr/Hf fractionation. The large difference from kimberlite values is probably due to differences in temperature, pressure, oxidation conditions, and especially melt composition. Our D(Hf) value for ilmenite is less than that calculated from mare basalt mineral separates by Haskin and Korotev [9] using a closed system crystallization model. This disagreement is not surprising because their results represent an average D-value integrated over the entire basalt crystallization, including the later stages for which the highly evolved melt composition may significantly alter distribution coefficient values [e.g., Colson]. We believe our results are more appropriate for application to mare basalt petrogenesis.

Elsewhere in this volume we report partition coefficients for Zr, Hf, and HREE determined by isotopic dilution analysis of ilmenite and glass separated from experimental runs using the same starting composition and conditions as those used for the runs reported in this abstract [7]. Values determined from mineral separates are intermediate between values for ilmenite and armalcolite determined by microprobe. The most probable explanation is that the magnetically separated "ilmenite" fraction actually contained a significant proportion of armalcolite. We believed that we had found T-fO2 conditions under which this starting composition would crystallize only ilmenite. However, subsequent to analysis in Denver of the mineral separates from runs performed under these conditions, we found that some runs under the same conditions also grew armalcolite, probably in response to loss of small amounts of Fe to the Pt wire loops and the resulting increase in Ti/Fe.

Microprobe measurements of Lu distribution coefficients for ilmenite and pigeonite have not yet been completed. Irving et al. [10] reported D(Sm) values identical within uncertainty for coexisting ilmenite and armalcolite, so it is likely that D(Lu) will be nearly the same for both minerals. In this case, the values we report for separated "ilmenite" [7] will be nearly unaffected by the presence of armalcolite. This Lu value is in good agreement with that obtained by extrapolating Yb results of McKay and Weil [5], and indicates a strong capacity for ilmenite and armalcolite to fractionate Lu from Hf (D(Lu/Hf)=0.28 for ilmenite, 0.86 for armalcolite, assuming D(Lu) of 0.08 for both minerals). To the extent that HREE pigeonite distribution coefficients determined by McKay [11] for low-Ti mare basalts remain valid for hi-Ti compositions, pigeonite also has a strong capacity to fractionate Lu from Hf (D(Lu/Hf)=3), in a direction opposite to that for ilmenite.

Implications of the new ilmenite distribution coefficients for the mare basalt petrogenetic model of Fujimaki and Tatsumoto [12] are discussed by Fujimaki et al. [7]. Petrogenetic implications of the other new values are the subject of further investigation.