LABORATORY STUDIES OF Pu-U-Th FRACTIONATION
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Understanding the chemical behavior of Pu under meteoritic/lunar conditions is important because (A) chemical fractionation of Pu-U-Th invalidates the use of meteoritic actinide abundances to infer the time-dependence of r-process nucleosynthesis in the galaxy prior to the formation of the solar system (1) and (B) it has not been possible to calculate consistent relative ages for meteorites based on \(^{244}\text{Pu}/^{238}\text{U}, \text{ } ^{129}\text{I}/^{127}\text{I}\) and initial Sr data (2), and the effects of Pu/U fractionation must be understood before these discrepancies can be resolved. Lunar rock \(^{244}\text{Pu}\) data are still more complex. The simplifying assumption of no meteoritic Pu-U-Th fractionation, which was made in the classical Pu literature, is now known to be untrue (3,4). Because Pu no longer exists in nature, laboratory experiments are the only way to study Pu chemistry relative to Th and U.

Experimental. We have studied crystal/melt partitioning from phosphate-diopside-feldspar starting compositions. Small adjustments in bulk composition are made to produce clinopyroxene, whitlockite, fluorapatite, or chlorapatite as the liquidus phase. Spikes of \(^{239}\text{Pu}\) or \(^{235}\text{Pu} + ^{230}\text{Th}\) are added at 10-50 ppm levels and the partition coefficients are measured by particle track radiography using induced fission tracks for U and Pu and alpha tracks for Th. Our spatial resolution is comparable to the fission or alpha ranges, so relatively large crystals must be grown (\(\geq 5\text{mm}\)). Initial studies have been at 20 kbar pressure because larger crystals could be more readily grown than at 1 atm. (We interpret this as due to lower melt viscosity accompanying the higher liquidus temperature). Samples were cooled at 0.5-3°C/min from 50-100°C below the liquidus. Recently, we have grown adequate crystals at 1 atm using cooling rates of 1-2°C/hr, but only a few data from these runs are available. The 20 kbar runs were made in graphite crucibles, corresponding to the same \(\text{O}_2\) fugacity at 1 atm. To produce the same \(\text{O}_2\) fugacity at 1 atm, we have used Co/CoO solid buffers with the buffer and sample sealed in Pt. Although we do not yet have a complete set of data, our most recent 20 kbar graphite crucible runs have also been inside sealed Pt capsules, as the initial unsealed runs revealed detectable amounts of \(\text{H}_2\text{O}\) in the melt and variable F/Cl ratios in the apatites.

Results. The 20 kbar crystal/liquid partition coefficients (K) given in Table 1 distinguish between the sealed and unsealed capsule runs. Changes in the melt concentration during crystallization produce detectable actinide zoning in larger crystals because diffusion in the crystalline phases is negligible (5). Assuming equilibrium at the crystal/melt interface, the measured average, partition coefficient can be corrected to the interface (true) value if the amount of crystallization is known from microprobe analyses. Because the fraction of melt crystallized is kept small, these corrections are usually \(\sim 10-20\%\), in the sense of increasing small (<1) K values and decreasing large (>1) values.

The most striking qualitative feature of the data in Table 1 is that the actinides are readily fractionated in our experiments. Secondly, relatively small variations in experimental conditions appear to be important.

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ference in the K (whit/liq) for Pu may reflect the presence of H₂O in the melt in the unsealed capsule run; however, within errors, the K (cpx/liq) for Pu is the same in sealed and unsealed capsules. Also, we have not yet established that our results reflect equilibrium partitioning. Partition coefficients less than 0.1 are difficult to measure because of the effect of finite track ranges producing gradients into the crystal from the surrounding glass; thus the lower K (cpx/liq) for U and Th from the sealed runs are better values since they apply to larger grains.

Table 1 shows that Pu is always fractionated into the crystals more than Th, whereas U is always excluded from the crystals relative to Pu and Th. The three actinides are preferentially incorporated into whitlockite relative to apatite and clinopyroxene. Whitlockite has the largest and diopsidic-clino-

pyroxene the smallest Ca structural site, but the systematics do not reflect the ionic size sequence for tetravalent actinide cations (Pu<Th).

The 1 atmosphere U partition coefficient, K (whit/liq) = 0.54, is similar to the 20 kbar results. For Th, at 1 atm for a run with H₂O in the melt, K (whit/liq) = 2. At our O₂ fugacity all the actinides are expected to be in the +4 state. To compare the effects of a valence state change, K (whit/liq) was measured to be 0.27 for U in air, where the valence state is +6, compared to 0.54 for the Co/CoO buffer. This suggests that the effect of valence state change is far less important for U partitioning than the analogous valence state change for Eu.

Discussion. Our results are still too preliminary and incomplete to draw any final conclusions or to use in igneous differentiation models, but some tentative qualitative comparisons with meteorite results are interesting. Our apatite/whitlockite crystal-crystal partition coefficient for U (0.2) is drastically different from the analogous U concentration ratios, 6-25, measured in equilibrated chondrites (3,6). The meteoritic apatites are chlorapatite, and runs comparing pure fluoro- and chlorapatite are now in progress, but in general the reason for this large difference is not understood.

Aluminous clinopyroxenes are grown (6-9% Al₂O₃) in our 20 kbar runs; consequently it seems fair to compare our results with the aluminous pyroxenes found in Angra Dos Reis (4). However, as Table 2 shows, the whit/cpx crystal-crystal partition coefficients are similar for Pu, but the laboratory value is much higher for U. It may be that, compared to Pu, U partitioning into clinopyroxene is enhanced by the presence of FeO and TiO₂. The apparent difference in the behavior of U and Pu may also indicate that the laboratory K (cpx/liq) for Pu is too high. If our K (whit/liq) are applicable, and if Angra Dos Reis is regarded as a cumulate rock, then the liquid from which Angra Dos Reis whitlockite crystallized must have had a highly fractionated Pu/U ratio (0.003 - .004) compared to that found in the meteorite. In general the ease with which Pu-U-Th can be fractionated in our laboratory experiments suggests that Pu measurements on meteorites, such as Angra Dos Reis, that are formed by igneous processes must be used cautiously in inferring the solar system Pu/U ratio.
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Table 1  Pu-U-Th Crystal/Liquid Partition Coefficients at 20 Kbar

<table>
<thead>
<tr>
<th></th>
<th>Whit/liq</th>
<th>Ap/liq</th>
<th>Cpx/liq</th>
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</thead>
<tbody>
<tr>
<td>Pu</td>
<td>4.7 ±0.2</td>
<td>-</td>
<td>0.145 ±0.009</td>
</tr>
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<td>2.6 ±0.1</td>
<td>1.3 ±0.2</td>
<td>0.14 ±0.03</td>
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<tr>
<td>U</td>
<td>0.58±0.4</td>
<td>-</td>
<td>0.0047±0.0007</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>0.074±.006</td>
<td>0.011±0.003</td>
</tr>
<tr>
<td>Th</td>
<td>-</td>
<td>0.59 ±0.06</td>
<td>0.042±0.006</td>
</tr>
</tbody>
</table>

(a) uncorrected for fraction crystallized; (b) run in unsealed capsules

Table 2  Whitlockite/Cpx Partition Coefficients

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Angra Dos Reis (4)</th>
<th>Expt.</th>
<th>Angra Dos Reis (4)</th>
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<tr>
<td>Pu</td>
<td>24(a)</td>
<td>18</td>
<td>U</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>120(a)</td>
</tr>
</tbody>
</table>

(a) Using estimated corrections for fraction crystallized.

References.