SOLAR SYSTEM ACTINIDE ABUNDANCES: I. LABORATORY PARTITIONING BETWEEN
WHITLOCKITE, DIOPSIDIC CLINOPYROXENE AND ANHYDROUS MELT. T. Benjamin, R.
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Experimental determination of the geochemical behavior of Pu-U-Th is es-
ternal for the application of measured actinide abundances in lunar/meteoritic
materials to the problems of a) the time dependence of r-process nucleosyn-
thesis prior to the formation of the solar system (1), b) calculating consistent
relative ages from $^{244}$Pu/$^{238}$U, $^{129}$I/$^{127}$I, and initial $^{87}$Sr/$^{86}$Sr, and c) under-
standing why large numbers of igneous rocks have the solar system Th/U ratio
of 3.8, and what processes yield rocks with fractionated Th/U ratios.

Whitlockite, $\text{Ca}_3(\text{PO}_4)_2$ and diopsidic clinopyroxene are synthesized at 1
atm and 20 Kbar from a composition (2 $\text{Ca}_2\text{Si}_2\text{O}_6+\text{NaAl}_2\text{Si}_2\text{O}_6+\text{CaAl}_2\text{Si}_2\text{O}_6$) mixed
with 25 wt.% and 15 wt.% $\text{Ca}_3(\text{PO}_4)_2$ respectively, and spiked to concentrations
of ~10ppm $^{239}\text{Pu}$ or ~20ppm $^{235}\text{U} + \sim 50$ppm $^{230}\text{Th}$. Crystal-melt partition coef-
ficients (D) are measured by particle track radiography: $^{230}\text{Th}$ by alpha de-
tection using cellulose acetate detectors, $^{239}\text{Pu}$ and $^{235}\text{U}$ by detection of neu-
tron induced fission fragments with muscovite detectors. The 20 Kbar experi-
ments are buffered to $f_{O_2} \sim 10^{-9}$ (at 1380°C) with graphite capsules sealed in
Pt. Runs at 1 atm pressure are buffered with Co-CoO ($f_{O_2} \sim 10^{-9}$ at 1270°C) or
unbuffered in sealed Pt capsules ($f_{O_2}$=air). The thermal history of each run
consists of heating to a superliquidus temperature, for times of 1-16 hours,
linear cooling (2-200 deg/hr) to a subliquidus temperature, (~1380°C at 20
Kbar; ~1300 at 1 atm) for times of 0-8 hr, followed by quenching. The thermal
history is chosen to produce relatively large (50µm) crystals, required due to
the finite range of the particles analyzed. Table 1 contains a complete set
of 20 Kbar partition coefficients and some 1 atm Th and U whitlockite values
for comparison. Each entry is the average of crystals from an independent run.
The actinides show negligible diffusion in the crystalline phases; however D
values from the average track densities of zoned crystals can be corrected (by
amounts ranging from 0-50%) to the true (i.e. solid-melt interface) values (ref
2, equation 14) using an amount of crystallization calculated by mass balance
from the measured compositions of the starting materials and final product
phases. However, for consistency, Table 1 lists only uncorrected values. It
is probably not possible to prove rigorously that crystal-melt interface equi-
librium was attained; however we propose that most disequilibrium effects would
not be reproducible from run to run or upon variation of experimental condi-
tions. Consequently, we have invested considerable time in evaluating our ana-
lytical errors in order that reproducibility can be quantitatively assessed.
We apply four consistency tests for equilibrium: (a) reproducibility of D
within and between runs; (b) reproducibility of minor element D (Table 2); (c)
results independent of cooling rate; (d) no actinide zoning in glass at the
crystal interface. Overall, our whitlockite data satisfy these criteria for
cooling rates varying over 2 orders of magnitude, with the possible exception
of D (Si) for 20 Kbar whitlockite in Table 2. The very low D (cpx) for U and
Th are hard to measure and one run gives ~0.005 for both elements, about 2
times the remaining values. Even 0.002 may still be an upper limit, but for
any geochemical application, such low values can be considered to be 0.

Although it is impossible to independently vary pressure, temperature and

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degree of crystallization, Table 1 indicates that the changes in conditions between the 1 atm and 20 Kbar runs produce relatively small changes in partitioning. Free energy data for actinide oxides indicate that all elements should be predominately tetravalent at fO₂=10⁻⁹, but U should be oxidized to the +6 state in air. Thus, as expected D (Th-whit) is unchanged between fO₂=10⁻⁹ and air. Somewhat surprisingly D (U-whit) shows only a small change. Relative to the 20 Kbar value, D (Pu-whit) changes by a factor of 7-8, probably indicating that at fO₂=10⁻⁹, Pu is primarily +3 reflecting strong stabilization of lower valence states in silicate melts e.g. due to nonideality as proposed by Boynton (3). The large (factor of 400) increase in the Pu⁴⁺/Pu³⁺ activity ratio between fO₂=10⁻⁹ and air implies that 0.58 can be assigned to D (Pu⁴⁺) for whitlockite. Tentatively we take 4.6 as D (Pu³⁺), although this assignment is less certain (zoning correction will lower this to ~3-3.5). Fig. 1 shows the resulting D patterns with our tentative valence assignments indicated. Under lunar/meteoritic conditions Pu will almost certainly be trivalent and have larger D values for phosphates and clinopyroxenes than U or Th, assuming U remains tetravalent. However if the phosphate content of the residual source material for an igneous rock is ≥0.1%, then fractionation of Pu from U and Th during partial melting would be difficult, given the low D (Pu) for clinopyroxene in Table 1. However, effects of melt and pyroxene composition are probably quite important, and the values in Table 1 apply to phosphate-rich melts. Preliminary results for D (Th) and D (U) for clinopyroxene in a phosphate-free melt are 0.026 and 0.016, ten times higher than the values of Table 1. This is still effectively 0 for U and Th as far as partial melting is concerned, thus our data provide support for the widely-accepted hypothesis that heat flow measurements provide the total U content of a planet. However, an equivalent composition-correlated enrichment for Pu would make Dcpx(Pu) large enough to be systematically depleted in igneous melts compared to U and Th. Late stage fractional crystallization involving partial crystallization of phosphates can easily fractionate all actinides. The best solar system actinide abundance ratios probably can be obtained from chondritic components which have not been subjected to igneous processes and which have otherwise no evidence for refractory lithophile element fractionation. Fig. 2 compares our diopside data with those for the rare earths from both laboratory studies (4) and natural phenocryst/matrix (5). For comparison the ionic radius positions of Pu⁴⁺ and U⁴⁺, where no data exist, are indicated. Our data provide some support for the coherence of Pu³⁺ and light rare earths, particularly Pr (3) or Nd (6); however variations of a factor of 2 are still possible, which are very serious for chronological applications.

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1. Pu-U-Th Partition Coefficients (uncorrected for zoning)

\[
P = 20 \text{ kbar} \quad P = 1 \text{ atm, whit/liq}
\]

- \( \text{whit/liq} \)
- \( \text{whit/liq} \)
- \( \text{fo}_2 = \text{air} \)

\[
\begin{array}{cccc}
\text{Th} & 0.0026 \pm 6 & 1.18 \pm 8 & 1.42 \pm 10 \\
0.0020 \pm 6 & 1.08 \pm 7 & 1.31 \pm 9 & 1.41 \pm 10 \\
0.0053 \pm 7 & 1.19 \pm 8 & & \\
0.0016 \pm 12 & & & \\
\text{U} & 0.0016 \pm 9 & 0.58 \pm 4 & 0.48 \pm 4 \\
0.0047 \pm 11 & 0.60 \pm 4 & 0.58 \pm 4 & 0.35 \pm 2 \\
0.0016 \pm 1 & 0.46 \pm 4 & 0.43 \pm 4 & \\
\text{Pu} & 0.138 \pm 5 & 4.6 \pm 3 & - & 0.58 \pm 4 \\
0.083 \pm 6 & 4.6 \pm 6 & & \\
0.124 \pm 2 & & & \\
\end{array}
\]

[Errors apply to last significant figure(s)]

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Table 2. Minor element crystal/liquid partition coefficients

<table>
<thead>
<tr>
<th>Element</th>
<th>Crystal (1 atm)</th>
<th>Crystal (20 kbar)</th>
<th>Clinopyroxene (20 kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na (10^-3)</td>
<td>Mg (10^-3)</td>
<td>Si (10^-3)</td>
</tr>
<tr>
<td>Th</td>
<td>0.18 \pm 0.03</td>
<td>0.44 \pm 0.02</td>
<td>5.1 \pm 0.3</td>
</tr>
<tr>
<td>U</td>
<td>0.15 \pm 0.04</td>
<td>0.44 \pm 0.02</td>
<td>5.9 \pm 0.5</td>
</tr>
<tr>
<td>Pu</td>
<td>0.16 \pm 0.03</td>
<td>0.46 \pm 0.03</td>
<td>6.1 \pm 0.7</td>
</tr>
<tr>
<td></td>
<td>0.13 \pm 0.02</td>
<td>0.47 \pm 0.02</td>
<td>5.8 \pm 0.4</td>
</tr>
</tbody>
</table>

*Each entry represents separate run and is based on analysis of at least 2 crystals; errors are inter-crystal standard deviations and are usually consistent with microprobe analytical precision.

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