Zr AND Nb DISTRIBUTION COEFFICIENTS: FURTHER CONSTRAINTS ON THE GENESIS OF HIGH-Ti MARE BASALTS AND KREEP. I.S. McCallum, Department of Geological Sciences, University of Washington, Seattle, Washington 98195 and M.P. Charette, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125

Introduction: In high-Ti mare basalts and KREEP materials Duncan et al. (1,2) have observed significant variations in the ratios between trace elements (K, Ba, Zr, Y, Nb) commonly considered to be incompatible. Perturbations of these ratios from lunar average values are interpreted by these authors to indicate (1) A-11 and A-17 high-Ti mare basalts were derived by extensive partial melting of an ilmenite rich cumulate which formed during the initial differentiation of the moon. (2) KREEP-rich materials have been derived from a source region which has geochemical characteristics complementary to the source regions of the high-Ti mare basalts, (3) fractionation of ilmenite during formation of the source regions may be the cause of the observed variations. To test these hypotheses, we are measuring the crystal/liquid distribution coefficients of Zr, Nb, Y, Hf and Ta between Fe-Ti oxides, pyroxenes, plagioclases and coexisting silicate melt. In this paper we present data on the distribution coefficients of Zr and Nb.

Experimental: Experiments were carried out on a synthetic analog of high-Ti mare basalt 75035. Charges were doped with 0.5, 1.0, 1.5, and 2.0 wt.% ZrO₂ and Nb₂O₅, and isothermal runs were carried out at 1128°C, 1113°C and 1105°C using the Pt loop method. Charges were cooled from above the liquidus to the run temperature at 15°C per minute. Runs were from 72 to 80 hours durations and the oxygen fugacity was controlled by gas mixing (CO₂/H₂) at approximately IW × 10⁻⁰.₅. Phase compositions were determined by microprobe analysis. Results are shown in Figs. 1-3.

Results: Armalcolite is the liquidus phase for all compositions. Ilmenite becomes stable between 1135°C and 1130°C and armalcolite is resorbed. Plagioclase and clinopyroxene crystallize between 1128°C and 1113°C. Ilmenite, armalcolite and plagioclase are compositionally homogeneous in all runs while clinopyroxene is slightly zoned in the 1105°C runs. At 1128°C and 1113°C glass is homogeneous while in runs at 1105°C glass adjacent to Fe-Ti oxides is slightly depleted or enriched in the trace element.

In Figs. 1-3, the data are fitted by straight lines each line being labeled with its corresponding equation. Error bars are 1σ. DZr is given by the slope and in almost all cases the best-fit line passes close to the origin suggesting that a simple proportionality is obeyed at all concentrations. D,Zr (ilm/liquid) is constant and appears to be independent of the level of doping temperature and melt composition. The value of 0.28 is similar to that estimated by Palme and Wlotzka (3). D values for the other crystal/liquid pairs are listed below. Armalcolite concentrates Zr and Nb much more effectively than does ilmenite. Of particular significance is the fact that DNb (ilm/liquid) = 3 × D,Zr (ilm/liquid) since it implies that fractionation of ilmenite or the presence of ilmenite as a residual phase in the source region can result in large variations in Zr/Nb in silicate melts. On the other hand, since D,Zr (cpx/liquid) > DNb (cpx/liquid), fractionation of clinopyroxene would result in
ZR AND NB DISTRIBUTION COEFFICIENTS

I.S. McCallum

variations in Zr/Nb of the opposite sense. Plagioclase excludes Zr and Nb.

Recommended values of distribution coefficients

\[ Dc/l \]

<table>
<thead>
<tr>
<th></th>
<th>ilm.</th>
<th>armal.</th>
<th>cpx.</th>
<th>rutile</th>
<th>plag.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Dc/Zr )</td>
<td>0.28</td>
<td>1.17</td>
<td>0.12</td>
<td>-</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>( Dc/Nb )</td>
<td>0.81</td>
<td>1.41</td>
<td>0.02</td>
<td>15.6</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Discussion: A. Mare basalts. \( Ba(K)/Zr, Ba(K)/Nb \) and \( Zr/Nb \) ratios in A-12 and A-15 basalts (2,4) are similar to average lunar crustal values indicating that \( Ba, K, Zr, \) and \( Nb \) are behaving largely as incompatible elements regardless of the details of the petrogenesis of these basalt suites. On the other hand, the low values (relative to lunar average values) of these same ratios in high-Ti mare basalts indicate a two-stage origin involving partial melting of an ilmenite-rich cumulate (2). While a two-stage origin for mare basalts is now widely accepted (5), the presence of ilmenite as a residual phase in the source regions is more controversial (6,7).

Models of the fractional crystallization of bulk moon compositions show ilmenite to be a stable phase during the latter stages of crystallization. On the basis of the distribution coefficients discussed above, it can be inferred: (1) the first ilmenite-rich cumulate to form will have low \( Zr/Nb \) values and relatively low \( Ba(K)/Zr \) and \( Ba(K)/Nb \) values, assuming \( Ba \) and \( K \) behave essentially as incompatible elements during fractional crystallization, (2) with continued fractional crystallization, \( Zr/Nb \) will increase in the residual melt and later-formed ilmenite-bearing cumulates will show higher \( Zr/Nb \) values. For incipient equilibrium partial melting of such cumulates \( (F=0) \), the melt will have relatively high \( Zr/Nb \) approaching average lunar values. As \( F \) increases, \( Zr/Nb \) decreases until at the point when all the ilmenite has melted, \( Zr/Nb \) in the melt will be essentially the same as \( Zr/Nb \) in the residuum. On the basis of this analysis we conclude that A-11 (low \( K \)) and A-17 high-Ti mare basalts have been generated by substantial degrees of partial melting of a pre-formed ilmenite-rich cumulate. The relatively high values of \( Ba(K)/Zr \) and \( Zr/Nb \) in A-11 (high \( K \)) basalts are consistent with an origin for this suite by a much smaller degree of partial melting of a similar ilmenite-rich cumulate. However, initial \( ^{87}Sr/^{86}Sr \) values in A-11 (high \( K \)) basalts indicate that a different source region was involved in their genesis. This ilmenite-bearing source region formed at a somewhat later stage during the fractional crystallization of the lunar magma ocean. The above conclusions may have to be modified if (1) clinopyroxene is a significant phase in the source regions and (2) the \( \frac{D_{Zr}}{D_{Nb}} \) ratio of 5-10, as determined experimentally, is valid. These \( D \)'s are strongly composition dependent and evaluation of the role of clinopyroxene must await explicit determination of this dependence.

B. KREEP: KREEP rocks show interelement ratios, e.g., \( Ba(K)/Zr \) and \( Ba(K)/Y \) complementary to those in high-Ti mare basalts. \( Zr/Nb \) are in the range of average lunar values and \( Ti/Zr \) ratios are extremely low (1). The hypothesis that KREEP melt formed in a single stage process as a late-stage residual melt from the fractional crystallization of the magma ocean is particularly amenable to testing by our data.

Continued fractional crystallization of ilmenite from the magma ocean will have the following effects: (1) The \( Zr/Nb \) ratio will increase in the residual
ZR AND NB DISTRIBUTION COEFFICIENTS

I. S. McCallum

Melt as more ilmenite is removed and will approach average lunar values, (2) Ba(K)/Zr and Ba(K)/Nb will increase rapidly in the residual melt, (3) Ti/Zr will decrease markedly in the residual melt since \( D_{T_i/Zr} \geq 1 \), for all compositions, (4) the rate of increase of Fe/Fe+Mg will be lower if significant quantities of ilmenite are removed, (5) concentrations of incompatible LIL elements will increase. The combined effect is to produce residual melts with many of the geochemical characteristics of KREEP. However, it must be pointed out that this model requires KREEP melts to be saturated with ilmenite at low pressure and this has not yet been demonstrated.

References: