ZIRCON/MELT PARTITION COEFFICIENTS FOR THE RARE-EARTH ELEMENTS IN EVOLVED ROCKS: THE USEFULNESS OF ACCESSORY MINERALS IN PETROGENETIC STUDIES ON THE EARTH AND MOON

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Zircon is a key accessory phase in understanding the evolution of evolved rocks, particularly granites, syenites, alkali basalts, and kimberlites (a terrestrial equivalent of KREEP?) of the Earth [1]. Lunar zircons commonly occur as loose grains in soils and breccias and "sawdust", but are rarely found in situ in a rock [2]. It is likely that lunar zircon did not become a liquidus phase until late in the fractionation of its parent melt. In such cases, analyses of zircons and calculation of their evolved parent compositions could provide invaluable clues regarding the compositions of some of the last crystallizing liquids on the Moon.

Analyses of the trace-element chemistry of lunar zircons are rare. Only three lunar zircon REE analyses have been reported (Fig. 1[3,4]). Hinton and Meyer [3] have published the REE pattern of a zircon, which contains a positive Ce anomaly, from sample 14321,1613. They have suggested that this anomaly reflects relatively oxidizing micro-environments on the Moon which led to the stabilization of Ce in the +4 valence state. Snyder et al. [4] have reported a pair of zircon REE analyses which do not indicate a positive Ce anomaly. The lack of any Ce anomaly for lunar zircon is expected, as conditions on the Moon are much more reducing than those on the Earth. Furthermore, Schreiber et al. [5] have indicated that Ce should not be stabilized in a magma which contains Fe (as it will reduce the Ce to the 3+ valence state and itself become oxidized to the 3+ state). Lunar rocks contain an appreciable amount of Fe and most of it in the +2 valence state. Therefore, we would not expect Ce to be stabilized in typical lunar magmas.

The definition of the mineral/melt partition coefficient can be rearranged to give the relation, \( C_S/k_D = C_L \), where \( C_S \) = concentration in the solid or mineral, \( C_L \) = concentration in the liquid or melt, and \( k_D \) is the mineral/melt partition coefficient. Using published mineral/melt \( k_D \)s, it is possible to calculate liquid compositions which could have been in equilibrium with these zircons. However, as Hinton and Upton [1] have pointed out, using average \( k_D \)s from the literature [6] can be misleading. For their partitioning studies, early workers used bulk zircon samples (as opposed to single zircons) which likely contained trace amounts of REE-rich inclusions or alteration products. Therefore, partition coefficients for the LREE were artificially high. Hinton and Upton [1] suggested a group of partition coefficients which are consistent with a power-law dependence on the ionic radii of the elements. As such, the REE partition-coefficient pattern decreases monotonically from Lu through La. However, for terrestrial rocks, they suggested a Ce partition coefficient that is an order of magnitude higher than the power law dependence calculations. For lunar conditions, we suggest the use of the zircon/melt partition coefficients given by Hinton and Upton [1] (Table 8, column 3), with the exception of Ce (where we prefer a value of 0.04, instead of 0.4).

Despite the uncertainties in partition coefficients, REE liquid compositions calculated here are similar in pattern to lunar granites [7], and are approximately a factor of 8 lower in the HREE and a factor of 4-5 lower in the LREE (Fig. 2). These lunar zircons may have fractionated from unusual late-stage liquids, as indicated by their spatial association with proposed immiscible melt glasses [4]. These immiscible melts were generated by silicate liquid immiscibility (SLI) of an evolved basaltic liquid. During SLI, two complementary liquids are produced: one rich in Fe, Ti, P, and REE (REEP-fraction of Neal and Taylor [8]) and the other rich in K, Na, and Si (K-fraction, i.e., granitic). The post-SLI fractional crystallization and differentiation of these immiscible liquids has not been studied in detail.
Lunar zircons could have precipitated from a liquid which underwent fractionation from one of these immiscible liquids. However, it is not likely that these zircons precipitated from the REEP-fraction of SLI. The REEP-fraction (or basic portion) of SLI contains the largest proportion of Zr, REE, and P of the two complementary SLI liquids. But, due to the likely crystallization of Zr-bearing ilmenite [8], the REEP-fraction will not readily become saturated with respect to zircon -- i.e., zircon is not an expected phase in the REEP-fraction.

It is postulated that these lunar zircons fractionated from the K-fraction (i.e., granitic portion; similar to felsite 73255, [9]) of SLI. This postulate is supported by the observation that many lunar zircons are associated with granite. Lunar granites generally consist of K-feldspar, quartz, and a phosphate (and/or some other REE-enriched phase). The REE are totally incompatible with quartz and are only weakly partitioned into K-feldspar (REE kD's ≤ 0.04, except for Eu). Therefore, the bulk distribution coefficient of a fractionating assemblage, containing K-feldspar, quartz, and a phosphate, is dominated by the partitioning behavior of the phosphate (or other REE-rich accessory minerals). Assuming the phosphate as the sole contributor to the bulk distribution coefficient, we can calculate the percentage of this phosphate in the assemblage using the Rayleigh fractionation equation (rearranged), $D_0 = [(\ln C_L/C_D)/(\ln F) + 1]$, where $F$ = fraction of liquid remaining [percentage of crystallization = 100*(1-F)]. $D_0$ = bulk distribution coefficient (as per [10]). $C_D$ = concentration in the original liquid, and $C_L$ = concentration in the residual liquid, and the definition of the bulk distribution coefficient, $D_0 = X*k_D$. Then, $X$, the fraction of phosphate, is calculated by: $X = [(\ln C_L/C_D + \ln F)/(k_D*\ln F)]$. In order to generate the REE pattern for liquid in equilibrium with lunar zircon, 5-10 wt.% whitlockite (or approximately 15-25%apatite) would be required in the fractionation assemblage [for ≥ 95% fractional crystallization (F=0.05); smaller degrees of fractionation would require a larger proportion of whitlockite and/or apatite in the fractionation assemblage]. No rock containing such a high proportion of whitlockite has yet been found on the Moon. If, instead, fractionation of some other REE-rich phase was responsible for lowering the REE abundances in the equilibrium liquid, then a proportionately smaller amount of the mineral would be required in the fractionation assemblage. For instance, yttrobetafite (a Ca-Ti-Nb-Y oxide [11]) is also found in lunar granophyres and may contain 2-3x the REE abundances of whitlockite [3]. Assuming the mineral/melt partition coefficients for the REE are 2-3x larger for yttrobetafite than for whitlockite, only 3-5% yttrobetafite would be required in the fractionation assemblage. Still, this is a rather large proportion of such a rare accessory phase. Before trace-element analyses in accessory phases such as zircon, whitlockite, and yttrobetafite can be used effectively to model late-stage igneous processes, a thorough experimental study of partitioning at low oxygen fugacities in evolved (KREEPy) melt compositions must be undertaken.

There is obvious need for additional experimentation pertinent to the REEP-fraction and K-fraction of SLI. It is likely that both immiscible melts will undergo further fractional crystallization. But, what is the crystallization sequence? To what degree will these melts actually fractionate? Will the REEP-fraction be capable of metasomatizing portions of the lunar crust as proposed by Neal and Taylor [8]? All are questions which are important to lunar petrogenesis and which need further evaluation.