

THE ORIGIN OF WHITLOCKITE: IMPLICATIONS FOR THE EVOLUTION OF THE LUNAR HIGHLANDS Clive R. Neal* & Lawrence A. Taylor, Dept. of Earth Sciences, University of Tennessee, Knoxville, TN 37996. * Now at: Dept. of Earth Sciences, University of Notre Dame, Notre Dame, IN 46556

Rare-earth-element-rich whitlockite has been described from alkali anorthosites [1-4], ferroan anorthosites (e.g., [5]), Mg-Suite anorthosites [4,6], the alkali gabbro-norite suite from Apollo 16 (e.g., [6,7]), and the Apollo 15 quartz monzonite (e.g., [8]), as well as in the mesostases of mare basalts (e.g., [9,10]). All LREE are present between 13,000 and 36,000 times chondritic abundances, whereas the HREE are between 4,000 and 18,000 times chondritic levels (Fig. 1). There is controversy as to the exact nature of whitlockite formation, but it is evident that whitlockite has crystallized from an evolved silicate melt [11].

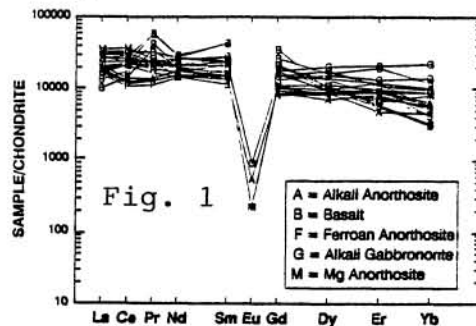
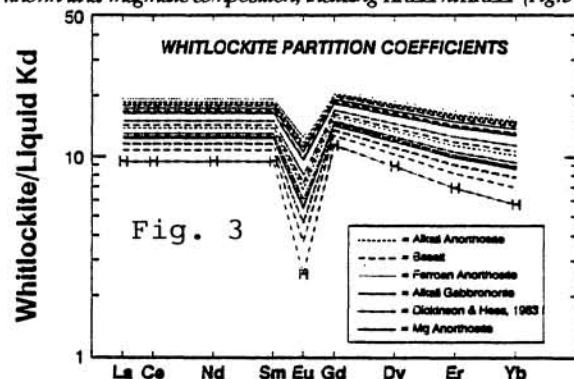


Fig. 1. The total REE concentration for each whitlockite was calculated by extrapolation. We assumed that the REE profile for whitlockite/liquid Kds presented by Dickinson and Hess [12] was correct and that the Kds for La, Ce, Nd, and Sm were the same. In this way, we have been able to estimate whitlockite/liquid REE Kd values (Fig. 3) for each whitlockite composition (Fig. 1). As such, equilibrium liquid REE profiles (Fig. 4) have been calculated for each whitlockite shown in Fig. 1. The LREE abundances in these equilibrium liquids range from approximately 600 to 3000 times chondritic levels. Eu abundances have only been accurately determined for 3 whitlockites [15] and demonstrated that the whitlockites (Fig. 1) and the corresponding equilibrium liquids (Fig. 4) possess large negative Eu anomalies. Generally, all equilibrium liquids exhibit LREE-enriched profiles, with negative correlations for both the LREE and HREE, although some exhibit relatively flat HREE profiles (Fig. 3). These whitlockite equilibrium liquids generally contain REE abundances which are higher than any known lunar magmatic composition, including KREEP or KREEP (Fig. 5).

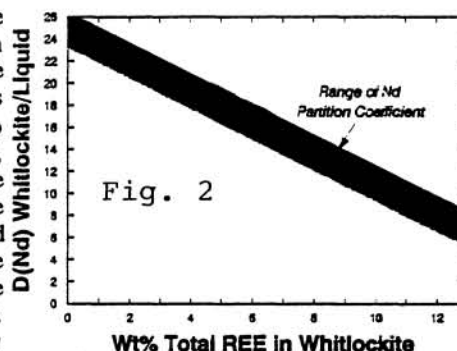


Therefore, if whitlockite in the lunar highlands formed from the *in-situ* crystallization of intercumulus liquid, similar mineral assemblages to those in the basaltic mesostases would be expected. This is not the case, as whitlockite is commonly found in isolation (e.g., [2,6,18]), or associated with apatite (e.g., [7]), or apatite and pyroxene [3].

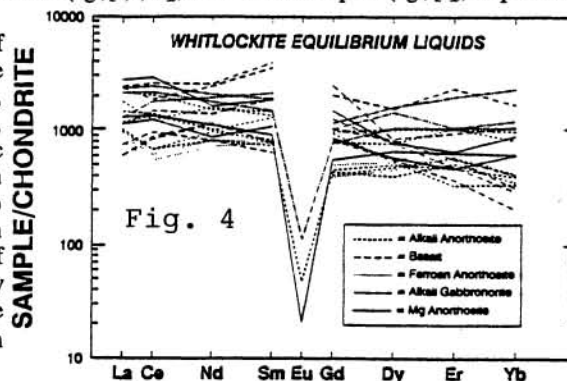
Analysis of basaltic mesostases demonstrates that in this case, the process of silicate liquid immiscibility (SLI) is fundamental to the crystallization of whitlockite. The process of SLI produces a high-silica (acidic) and a high-Fe (basic) melt. The elements Si, Al, K, Rb, Cs, and Na are preferentially partitioned into the acidic immiscible melt, whereas Ti, Cr, Fe, Mn, REE, P, Ca, Th, U, Zr, F, and Cl are partitioned into the basic immiscible melt [19-21]. Therefore, the basic immiscible melt will contain high abundances of the REE. In order to try and produce a melt with high REE abundances to crystallize whitlockite, the REE abundances of the basic immiscible melts have been calculated from the three KREEP compositions (Fig. 5) using the liquid/liquid Kds of Watson [21]. These two-liquid REE Kds compare well with those reported for pre-SLI, low P_2O_5 systems by Ryerson and Hess [22]. As seen in Figs. 4 & 5, the whitlockite equilibrium liquids are more akin to these basic immiscible melts calculated from KREEP or KREEP compositions.

WHITLOCKITE/LIQUID REE Kds - In order to evaluate the REE composition of the melt from which whitlockite crystallized, accurate REE partition coefficients (Kds) must be known. Dickinson and Hess [12] reported whitlockite partition coefficients for Ce (9.5), Sm (9.5), Eu (2.6), Gd (11.4), and Yb (5.8), and McKay et al. [13] reported Kds for Nd and Sm. Although the REE in whitlockite are present in the wt% level, the experimental results of McKay et al. [13] indicated that there was no unexpected deviation from Henry's Law behavior, and that experimental coefficients may be safely extrapolated to natural concentrations.

McKay et al. [13] and McKay [14] demonstrated that the Kd for a particular REE in whitlockite is dependent upon total REE concentration. Also, this study confirmed that the Kd for Nd and Sm were approximately the same, as concluded by Dickinson and Hess [12]. In order to obtain whitlockite Kds, we have used the rationale of McKay et al. [13]. In Figure 2, the variation of Nd Kd with total REE concentration in whitlockite is presented. We have determined the Nd Kd for each of the whitlockites in



PARAGENESIS OF LUNAR WHITLOCKITE - The presence of whitlockite in the basaltic mesostases suggests extreme fractional crystallization of a basaltic magma is required. In these basalts, whitlockite is commonly found in association with ilmenite, fayalite, silica (cristobalite), and K-rich glass. While basic and acidic glasses are not present, the assemblage fayalite-ilmenite-phosphate-cristobalite is consistent with the crystallization of a basic immiscible glass. Taylor et al. [16] reported the presence of such a mesostasis assemblage in basalt 12063,9 and concluded that the modal proportions of fayalite and cristobalite represented the crystallized equivalents of a ferropyroxenitic or basic immiscible melt. Viscosity differences between acidic and basic immiscible melts (~30,000 versus 11 poise, respectively - [17]) indicates that crystallization of the basic immiscible melt will be more readily achieved than that of the acidic equivalent. The relatively fast cooling of the lunar basalts at the surface means we only see this in a microcosm. At depth, the cooling would be slower allowing for more extensive mesostasis (and whitlockite) crystallization and possible separation of the immiscible



GEOLOGICAL SETTING - The basic immiscible melt derived from KREEP/urKREEP by the process of SLI is the only liquid which contains high enough REE abundances to produce observed whitlockite compositions. In the case of basaltic mesostases, the residual magma must approach a KREEPy composition which undergoes SLI to form whitlockite with the appropriate REE abundances. However, the lack of the required mesostasis assemblage in highland rocks demonstrates that the inter-cumulus liquid was not responsible for the observed whitlockites.

A metasomatic model is proposed in order to account for the presence of whitlockite in the lunar highlands. Observations of metasomatized terrestrial rocks demonstrate that if only mild model metasomatism occurs, only one mineral is deposited (e.g., [23,24]). This is usually a hydrous mineral, either amphibole or phlogopite. However, Menzies and Wass [25] documented the occurrence of mantle xenoliths from south Australia, which had been modally metasomatized with apatite. These authors postulated that degassing of mantle CO_2 was responsible for causing apatite metasomatism.

In the lunar environment, we envisage a low-viscosity silicate melt as the metasomatic fluid, such as the basic liquid produced by SLI [17]. After SLI, the granitic melt ("K-Fraction") is extremely viscous (see above) and will be unable to migrate. Furthermore, this viscous melt will require slow cooling in order for crystals to form. Relative to the K-Fraction, the basic melt ("REEP-Fraction") will be able to flow and crystallize relatively easily. This difference in crystallizing abilities can be seen in the basaltic mesostases [16]. Neal and Taylor [17] proposed that the REEP-Fraction, from the immiscibility of urKREEP, metasomatized the lunar highlands, but that not all urKREEP underwent SLI. The viscosity differences between the K- and REEP-Fractions allowed their separation, and post-SLI crystal fractionation of ilmenite and fayalite reduced the density of the REEP-Fraction, promoting upward migration and metasomatism. Such a scenario accounts for the presence of only whitlockite in the highland cumulates. In addition, most highland rocks are high in other volatiles such as Cl [26]. We postulate that this is an additional REEP-Fraction component.

An apatite/whitlockite association in lunar highland cumulates was reported by Goodrich et al. [3], James et al. [7], and Marvin et al. [8]. Hess et al. [11] concluded that both whitlockite and apatite crystallized from highly evolved melts and that apatite crystallized after whitlockite, possibly in response to changing fluorine fugacities. We would propose that the apatite-whitlockite association is consistent with open system metasomatism by a REEP₂ melt. For example, when the two phosphates are in contact, whitlockite is commonly enclosed in apatite. As noted by Lindstrom et al. [15], Goodrich et al. [3], and Hess et al. [11], whitlockites contain more REE than apatites, but phosphate-liquid REE partitioning studies demonstrate that coexisting apatite and whitlockites should have identical REE contents [12,27]. We concur with Hess et al. [11] that whitlockite crystallized before apatite in these highland lithologies, probably because of low fluorine fugacities in the REEP₂ melt (the halogens appear to be preferentially partitioned into the basic immiscible melt - see above). If this metasomatic melt could no longer migrate, fluorine could build up, due to early whitlockite crystallization, which would then promote apatite crystallization. If the melt continued to migrate after whitlockite crystallization, discrete apatites and whitlockites would be produced. As whitlockite crystallized first, the REE abundances in the metasomatic melt will be severely reduced. Therefore, while the later crystallizing apatites would have similar REE liquid Kds to apatite, their REE contents will be lower.

CONCLUSIONS - The only liquid containing sufficient REE (and Ca and P) to account for lunar whitlockite compositions is the basic immiscible melt ("REEP-Fraction") produced from urKREEP/KREEP undergoing SLI. Even in basaltic mesostases, the process of SLI appears to be important in the paragenesis of whitlockite. The nature and composition of whitlockite in the lunar highlands is not consistent with crystallization of the inter-cumulus liquid, even if it did undergo SLI; the interstitial mineral assemblage in these rocks does not contain a sufficient number of phases. However, the interstitial mineral assemblage which is present is consistent with metasomatism by comparison with terrestrial equivalents, although the mineral compositions are different. No hydrous minerals are present on the Moon, so the metasomatic fluid is a low viscosity silicate melt, again consistent with the basic immiscible melt from urKREEP/KREEP. Post-SLI fractionation of ilmenite/fayalite from the REEP-Fraction reduces density and coupled with low viscosity, allows percolation of and metasomatism by this melt. Changing fluorine fugacities as this metasomatic melt evolves facilitates the eventual crystallization of apatite (after whitlockite). This apatite may form epitaxial overgrowths on the early whitlockite (if the metasomatic melt cannot migrate further) or form discrete apatites and whitlockites in the same rock, if percolation can continue. Because apatite crystallizes later than whitlockite, it will contain lower REE abundances due to the reduced level of REE in the metasomatic melt after whitlockite crystallization, even though apatite and whitlockite Kds are similar.

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