

IRON, TITANIUM, AND MAGNESIUM ISOTOPIC COMPOSITIONS OF LUNAR ILMENITE-BEARING CUMULATES. K. B. Prissel¹, M. J. Krawczynski¹, ¹Department of Earth and Planetary Sciences, Washington University in St. Louis, Campus Box 1169, 1 Brookings Drive, St. Louis, MO 63130-4899, k.b.williams@wustl.edu

Introduction: The lunar mantle is heterogeneous and the mantle source regions for the mare basalts are thought to be dominated by products and chemical gradients related to the crystallization of a lunar magma ocean (LMO). In general, there are three important compositional components that comprise the mare basalt sources: ultramafic cumulates, high-titanium ilmenite-bearing cumulates, and KREEP. High-precision, non-traditional stable isotope analyses of lunar samples have recently provided new compositional constraints for the petrologic history of the Moon and lunar volcanism. Resolvable differences in iron, titanium, and magnesium isotopic compositions exist between the low-Ti and high-Ti mare basalts [1-4].

Ilmenite, an Fe- and Ti-rich mineral, has been hypothesized as the main control for the Fe and Ti isotopic compositions observed in lunar mare basalts. Using combined Fe, Ti, and Mg isotopic compositions of mare basalts, we present new calculations for the isotopic composition of the ilmenite cumulates incorporated into mare basalt sources. We then integrate mineral-melt isotopic fractionations with LMO crystallization models based on recent experimental studies in order to determine whether an ilmenite bearing cumulate with the required isotopic composition can be produced.

Mare basalt source mixing model: We have developed a three-component mixing model to deconvolve the compositions of mare basalts. The three components are defined as (1) partial melt of ultramafic cumulates, (2) high-Ti, ilmenite-bearing cumulates, and (3) KREEP. The ultramafic composition is taken as Apollo 15 C Green Glass from [8]. For the high-Ti cumulates, our model uses the component composition

defined in [9]. For the KREEP component, we use the composition of KREEP basalt 15386 from [10]. This KREEP basalt has been used to approximate the KREEP component in previous mare basalt mixing models (e.g., [11]). For samples 70017, 70215, 75075, and 15016, we have calculated the proportion of each component needed to recreate the bulk major element composition of the sample [12] by non-linear least squares in logratio space [13].

Mare basalt isotopic compositions are a function of their deep mantle sources and shallow petrogenetic processes. For the models described here, we have assumed that the mare basalt source has the isotopic composition of the mare basalt (Table 1). However, processes such as fractional crystallization or partial melting may also influence the resulting elemental and isotopic compositions. Additionally, our mixing models have used KREEP basalt as an endmember composition. However, it is important to note that the KREEP basalt itself is a mixture of components that may not be equally distributed throughout the mare basalt sources.

Isotopic composition of the ilmenite-bearing cumulate component. In order to determine the isotopic composition of the ilmenite bearing cumulate, we have calculated an isotopic mass balance for each mare basalt sample assuming the following equation:

$$(X_{UM}^i \delta_{UM}^i) + (X_{IBC}^i \delta_{IBC}^i) + (X_{KP}^i \delta_{KP}^i) = \delta_{sample}^i$$

where δ^i represents the isotopic compositions, and X represents the mass fraction of element i for a given component (UM = ultramafic component, IBC = ilmenite-bearing cumulates, KP = KREEP) calculated from

Sample	Sample Type	$\delta^{49}\text{Ti}$ (‰)	95% CI	$\delta^{26}\text{Mg}$ (‰)	95% CI	$\delta^{56}\text{Fe}$ (‰)	95% CI
70017	High-Ti basalt	0.015	0.011	-0.250	0.030	0.205	0.029
70215	High-Ti basalt	0.033	0.015	-0.374	0.001	0.171	0.028
				-0.240	0.030		
75075	High-Ti basalt	0.018	0.014	-0.694	0.016	0.217	0.030
				-0.220	0.010		
15016	Low-Ti basalt	-0.008	0.019	-0.090	0.020	0.067	0.029
15386	KREEP basalt	-	-	-0.349	0.038	0.140	0.058

Table 1. Isotopic compositions for mare basalt samples with multiple isotopic measurements. Fe data from [14-16]. Ti data from [2]. Mg data from [3,4].

the composition and estimated proportion of each source component. Because olivine and orthopyroxene will not fractionate isotopes to a measurable extent during equilibrium crystallization or melting (e.g., [17,18]), the ultramafic component can be approximated as having bulk Moon isotopic composition. Thus, we have assigned the bulk silicate Moon isotopic compositions for Fe [18], Ti [2], Mg [3] as the isotopic compositions of the ultramafic component. We have assigned the Fe and Mg isotopic compositions of 15386 (Table 1) to the KREEP component. For the Ti isotopic composition of the KREEP component, we have assigned the Ti isotopic composition of a KREEP-rich impact melt breccia ($\delta^{49}\text{Ti} = 0.33\%$, [19]). The isotopic compositions of the ilmenite-bearing cumulates are calculated using:

$$\delta_{IBC}^i = (\delta_{sample}^i - X_{UM}^i \delta_{UM}^i - X_{KP}^i \delta_{KP}^i) / X_{IBC}^i$$

Lunar magma ocean crystallization model: Experimental studies have determined that ilmenite begins crystallizing near 88-98% LMO solidification [20-22]. Determining the isotopic composition of the ilmenite crystallizing from the LMO requires knowledge of 1) the isotopic evolution of the melt through ~90% LMO crystallization, and 2) the ilmenite mineral-melt isotopic fractionation.

We have developed a model that tracks the isotopic composition of minerals precipitating from the LMO and the residual LMO liquid. We have modeled the isotopic compositional evolution during near-fractional crystallization sequences of bulk Moon compositions using several experimental models [20-23]. For each experimental crystallization sequence, the published synthetic mineral and glass compositions determine the mineral-melt major element partitioning. The initial isotopic compositions for the LMO models are the bulk silicate Moon isotopic compositions used for the ultramafic component in our mixing model.

Mineral-melt fractionation factors. We have modeled isotopic compositions of the melt and each mineral phase during LMO crystallization by assigning mineral-melt isotopic fractionations for each element (Fe [6, 17, 18], Ti [2], Mg [24]). The bulk isotopic composition of the instantaneous solid at a given crystallization step is calculated by mass balance using the concentration of the element and isotopic composition in each mineral phase crystallized. The isotopic composition of the remaining liquid at each crystallization step is determined by subtracting the instantaneous solid that crystallized, accounting for the fraction of each element removed.

Results: Using the component proportions calculated by major element mass balance, we have determined the isotopic compositions of the ilmenite-bearing

cumulates. Results from the isotopic source mixing models for the mare basalts indicate that the ilmenite-bearing cumulate would have the isotopic composition $\delta^{56}\text{Fe} = +0.05$ to $+0.26\%$, $\delta^{49}\text{Ti} = -0.08$ to -0.014% , and $\delta^{26}\text{Mg} = -0.15$ to $+1.0\%$.

Toward the end of LMO crystallization, the effect of ilmenite fractionation on the isotopic composition of the residual melt increases. Our LMO models indicate that the first ilmenites to crystallize would have Ti isotopic composition $\delta^{49}\text{Ti} = -0.112\%$ and fractionation of Ti isotopes by ilmenite crystallization can result in ilmenite with $\delta^{49}\text{Ti} = +0.3\%$ toward the end of LMO crystallization. Similarly, the modeled isotopic compositions of ilmenites crystallizing during LMO solidification match the range Mg isotopic compositions estimated for the ilmenite-bearing cumulate.

There are currently two hypotheses for the role of ilmenite in generating the iron isotopic compositions of the mare basalts. One hypothesis is that ilmenite is isotopically heavier than the melt from which it crystallizes, and thus increased incorporation of ilmenite cumulates would produce heavier basalt compositions [4,5]. Alternatively, experimental studies indicate ilmenite would be lighter than the melt from which it crystallizes [6,7]. In this hypothesis, ilmenite fractionation drives the melt (and subsequently crystallizing ilmenite) toward heavier isotopic compositions. The Fe isotopic compositions for the ilmenite bearing cumulate can be modeled using a light fractionation, producing progressively heavier ilmenite as the LMO solidifies.

References: [1] Dauphas et al. (2017) *RiMG*, 82, 415-510. [2] Millet et al. (2016) *EPSL*, 449, 197-205. [3] Sedaghatpour et al. (2013). [4] Sedaghatpour & Jacobsen (2019) *PNAS*, 116 (1), 73-78. [5] Wang et al. (2015) *EPSL*, 430, 202-208. [6] Williams et al. (2016) 47th *LPSC*, 2779. [7] Sossi & O'Neill (2017) *GCA*, 196, 121-143. [8] Delano (1986) *JGR*, 91, D201-213. [9] Brown & Grove (2015) *GCA*, 171, 201-215. [10] Vaniman & Papike (1980) *Proc. Conf. Lunar Highlands Crust*, 271-337. [11] Neal et al. (1988) *Proc. 18th LPSC*, 139-153. [12] Meyer (2012) *Lunar Sample Compendium*. [13] Krawczynski & Olive (2011) *AGU Fall Meeting*. [14] Liu et al. (2010) *GCA*, 74, 6249-6262. [15] Weyer et al. (2005) *EPSL*, 240, 251-264. [16] Poirasson et al. (2004) *EPSL*, 223, 253-266. [17] Prissel et al. (2018) *GCA*, 238, 580-598. [18] Sossi & Moynier (2017) *EPSL*, 471, 125-135. [19] Greber et al. (2017) *GCA*, 213, 534-552. [20] Lin et al. (2017) *Nature Geoscience*, 10, 14-18. [21] Rapp & Draper (2018) *MaPS*, 1-24. [22] Charlier et al. (2018) *GCA*, 234, 50-69. [23] Elardo et al. (2011) *GCA*, 75, 3024-3045. [24] Chen et al. (2018) *EPSL*, 487, 74-83.

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