REE crystal chemistry of phosphates in extraterrestrial basalts at different oxygen fugacities. Direct determination of europium valence state in merrillite-whitlockite.

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Introduction: The REE crystal chemistry of terrestrial and extraterrestrial merrillite-whitlockite has been discussed in detail in numerous studies [e.g. 1-5]. The REE abundances in merrillite-whitlockite are substantially higher than any other phase in extraterrestrial basalts. Although generally low in modal abundance (<<1% to ~4%), they often carry greater than 90% of a rocks REE. The REE patterns of these phosphates are generally fairly flat to LREE enriched with small (Eu*/Eu=1.5) (martian basalts) to very large (Eu*/Eu=50) negative Eu anomalies (lunar lithologies with high KREEP) [i.e. 3-4]. The scale of these anomalies is potentially a product of numerous processes: bulk basaltic melt composition, f_{O2}, phases that crystallized prior to the phosphate, and the overall behavior of Eu in the merrillite-whitlockite structure. As only total Eu and not the individual valence state of Eu are commonly determined, the role of each of these factors is relatively unknown. The effect of f_{O2} on the relative proportions of divalent and trivalent Eu has proven to be a useful tool for estimating f_{O2} in a variety of magmatic systems. This dependence of the ratio Eu^{2+}/Eu^{3+} on f_{O2} can be illustrated by the reaction: $Eu^{3+} + 1/2O^{2-} \rightarrow Eu^{2+} + 1/4O_2$. The concept of using Eu valence as a quantitative oxybarometer was initially demonstrated by [6]. Here, we directly determine the Eu^{3+}/Eu^{2+} in natural merrillite-whitlockite for the following purposes: (1) to measure the Eu^{3+}/Eu^{2+} in extraterrestrial merrillite-whitlockite using XANES, (2) to unravel the crystal chemical behavior of Eu^{3+} and Eu^{2+} in these phosphates, and (3) to evaluate its potential in preserving the magmatic f_{O2} record in the late-stages of basalt crystallization.

Analytical Approach: Merrillite-whitlockite were selected for this study because (1) they are common in many extraterrestrial basalts, (2) their REE abundance commonly makes up a large portion of the REE budget for extraterrestrial basalts and thereby makes their analysis possible using XANES and (3) they crystallize late in the history of most basalts, potentially providing a record of late-stage f_{O2}. The sample suite used in this study was selected from a variety of merrillite-whitlockite-bearing assemblages from the Moon, Mars, and Earth. They represent a very wide range of f_{O2} from IW-1 to approximately QFM+1. Phosphates in these samples were imaged, mapped, and analyzed for major and minor elements using a JEOL JXA 8200

EMP. Trace element concentrations (REEs) were determined using a Cameca IMS 4f ion probe. The ion probe analyses involved repeated cycles of peak counting on the isotopes of the REE. Absolute concentrations of the trace elements were calculated using the empirical relationship between measured peak/$^{42}Ca^+$ ratios normalized to known CaO content and elemental abundance in the standards.

XANES analyses were performed with the GeoSoilEnviroCARS X-ray microprobe at the Advanced Photon Source (APS), Argonne National Laboratory, Illinois, using techniques described by Sutton et al. [7]. The microprobe consisted of an APS undulator X-ray source, an Oxford Instruments WDX-600 wavelength dispersive detector with a LiF200 crystal, and both sealed and flow proportional counters. The X-ray microprobe was used to determine Eu^{3+}/Eu^{2+} in the phosphates with a ~2 μm spatial resolution using the XANES technique. In this method, the intensity of Eu $L\alpha$ fluorescence X-rays is monitored as the energy of the incident X-radiation is scanned through the Eu LIII absorption edge (~6977 eV) with high-energy resolution (<1 eV). The XANES spectra for Eu^{2+} and Eu^{3+} have distinct resonance peaks separated by ~8 eV, at 6975.5 and 6983.4 eV, respectively, which are attributed to electron transitions between $2p_{3/2}$ and $5d$ electronic states. The proportions of the two species were determined from the relative intensities of these peaks after calibration with the end-member standards, $Eu^{2+}TiO_3$ and $Eu^{3+}_2O_3$, which were measured as powders in transmission mode. The XANES data reduction procedure was analogous to that used by [8]. The XANES spectra were first normalized to an intensity of zero well below the absorption edge, and to unity well above the edge. The intensities of the peaks were then defined to be the areas of two fitted Gaussians after subtraction of the main absorption edge (arctangent function) using the XANES analysis software package Athena [8]. The area ratio of the end-member spectra was determined to be 2.01 (Eu^{3+}/Eu^{2+}), and this correction factor was applied to the Eu^{2+} peak areas in determining the Eu^{3+}/Eu^{2+} abundance ratios for the unknowns. The estimated precision of the Eu valence determinations is ~0.03 (1σ).

Results:
The major elements, REE, and Eu^{3+}/Eu^{2+} were determined for merrillite-whitlockite derived from sam-

ples from a variety of planetary environments that exhibit strikingly different f_{O_2} (IW-1 to approximately QFM+1). These samples included a mare basalt (15058), KREEP basalt clast (15386), a "depleted" shergottite (QUE 94201), "enriched" olivine-phyric and pyroxene-phyric shergottites (LAR 06319, Los Angeles, NWA 2896), and a terrestrial pegmatite (Tip Top). The Eu in all merrillite was dominated by Eu^{3+} with the average Eu valence ranging from 2.89 to 3.00 (Figure 1).
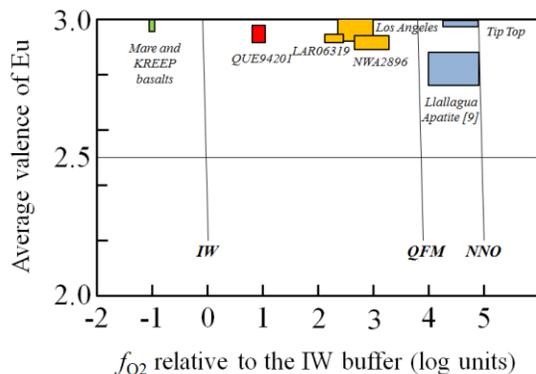

Fig. 1. Variation in average Eu valence versus oxygen fugacity. Green=Moon, Red and Orange=Mars, Blue=Earth.

Discussion:

REE and Eu in merrillite-whitlockite: Jolliff et al. [3,4] demonstrated that trivalent REE substitute into the main 8-coordinated Ca sites in merrillite (referred to as Ca1, Ca2, and Ca3 sites which occur as 18 sites per 56 O atoms). Charge balance for the substitution of trivalent REE is compensated through coupled substitution involving both the Ca sites and the irregular octahedrally coordinated Na site: $(Y+REE^{3+})_{2,Ca\ site} + \square_{1-2,Na\ site} \leftrightarrow Ca_{2,Ca\ site} + (Na,Ca)_{1-2,Na\ site}$ [3]. Another coupled substitution that has been proposed to compensate for trivalent REE into merrillite involves the substitution of Si^{4+} for P^{5+} in the tetrahedrally coordinated P site: $(Y+REE^{3+})_{Ca\ site} + Si^{4+}_{P\ site} \leftrightarrow Ca_{Ca\ site} + P^{5+}_{P\ site}$ [3,4]. Eu^{2+} should also be able to substitute into the 8-fold coordinated Ca site but without any charge compensation. However, our direct measurements of Eu^{2+}/Eu^{3+} suggests that the higher charged, smaller REEs are preferred into the Ca site rather than the slightly larger, divalent cations such as Eu^{2+} (Figure 2). This indicates that merrillite crystal chemistry plays an extremely important role in partitioning of the various valence states of Eu into its structure. This has direct implications for both extrapolated and measured distribution coefficients (D) for merrillite. Most D's for merrillite suggest that D^{Eu} for merrillite are significantly lower than D^{REE} for adjacent REEs. For example, the compilation of D^{REE} for merrillite indicates $D^{Sm\ or\ Gd}$ ranges from 2 to 10 times that of D^{Eu} [3]. This cannot be cor-

rect based on our results. The D^{Eu} must approximate the $D^{Sm\ or\ Gd}$. The Eu anomaly commonly observed in merrillite most likely reflects the effect of phases that precede it during the crystallization of the basalt and not f_{O_2} directly. Therefore, care must be taken in deriving Eu melt compositions from Eu anomalies in merrillite.
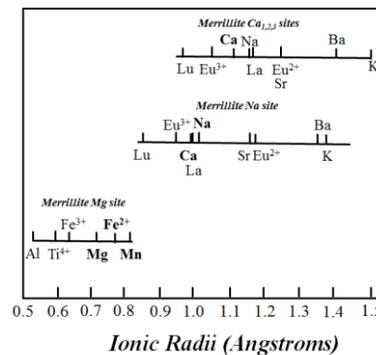

Fig. 2. Ionic radii for cations occupying merrillite sites. Cations noted in bold are the dominant cations in the site.

Relationship between Eu in apatite versus merrillite-whitlockite: In most compilations of D^{REE} apatite and merrillite, the D for merrillite is significantly higher by at least an order of magnitude [3]. However, our valence state data compared to the previous measurements of Eu^{3+}/Eu^{2+} in Llallagua apatite [9] suggests that while the Ca sites in the apatite are not as accepting of REE compared to merrillite, the proportion of Eu^{3+} to Eu^{2+} is lower (Fig. 1). This may be a result of the occurrence of 9-fold coordinated Ca sites in apatite.

Merrillite-whitlockite Eu valence oxybarometer: It was initially our intent to examine the relationship between f_{O_2} and the Eu^{3+}/Eu^{2+} as a potential oxybarometer in basaltic magmas at temperatures just above the solidus. It is very clear from our results, that due to the preference of merrillite for Eu^{3+} relative to Eu^{2+}, such a relationship does not exist. However, as suggested above, the Eu^{3+}/Eu^{2+} in apatite may be more sensitive to f_{O_2}. However, these measurements at the Eu concentration levels in most natural extraterrestrial apatite (Eu=1-10 ppm) currently cannot be made by XANES.

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