SYNTHESIS OF IRON- AND SODIUM-BEARING WHITLOCKITE FOR INTERPRETATION OF EXTRATERRESTRIAL PHOSPHATE MINERALS. C. T. Adcock[1], E. M. Hausrath[1], and M. Ren[1], [1]University of Nevada, Las Vegas, Department of Geoscience, 4505 S. Maryland Pkwy., Las Vegas, Nevada, 89154. Christopher.Adcock@unlv.edu

Introduction: Phosphorus-bearing minerals are of particular interest in both terrestrial and extraterrestrial studies. Phosphorus likely played a critical role in the origin of life on our planet, and all currently known life requires phosphorus as a nutrient [1]. Phosphorus-bearing minerals also occur in extraterrestrial materials, including martian and lunar meteorites, and are important as indicators of potential habitability (astrobiology), volatile budgets, and late stage magma evolution in parent bodies [2-7]. Specifically for Mars, a planet with 10 times more phosphorus than Earth [8, 9], phosphorus minerals have been used to investigate past aqueous environments, weathering, the overall water budget history of the planet, and the potential for life to have arisen there [10-14].

Presently, our only known samples of planetary bodies are in the form of meteorites or lunar samples. In martian meteorites and lunar materials most of the phosphorus is held in the phosphate minerals merrillite ($Ca_9(Na,Fe,Mg)(PO_4)_7$) and chlorapatite ($Ca_5(PO_4)_3Cl$) [15, 16]. Therefore, these minerals have been the focus of numerous martian and lunar studies. Merrillite is of particular interest, in part, because it is generally an extraterrestrial mineral and is common among phosphate phases in many extraterrestrial materials. In fact, merrillite is the dominant phosphate phase in Shergottite meteorites [15].

Although generally an extraterrestrial mineral, merrillite (or a merrillite-like phase) has been identified in terrestrial mantle xenoliths [17]. The mineral also forms a solid-solution with whitlockite ($Ca_9(Fe,Mg)(PO_3OH)(PO_4)_6$) where it occurs in minor amounts (~5% or less) [18]. Whitlockite is a rare phosphate mineral which has not been confirmed in extraterrestrial materials [6]. These two endmember minerals are similar in structure and are distinguished mainly by the presence of H^+ in whitlockite and the absence of H^+ in merrillite. The relative paucity of whitlockite in extraterrestrial materials (and vice versa) suggests the minerals may hold clues to important differences between Earth and other bodies such as Mars. However, this also means that samples of natural merrillite for study can be difficult to obtain.

Merrillite can be synthesized from the mineral whitlockite by heating to >1000 °C [18-20]. Although whitlockite is relatively rare, methods have been developed to synthesize the mineral hydrothermally and synthetic whitlockite has been routinely used to produce merrillite for planetary studies [e.g. 18-20].

Among the challenges of using synthetic whitlockite to produce merrillite is synthesizing whitlockite with cation chemistry similar to natural extraterrestrial merrillite. The easiest form of whitlockite to synthesize is the Mg-endmember (i.e. $(Ca_9(Mg)(PO_3OH)(PO_4)_6)$. However, extraterrestrial merrillite also includes Fe^{2+} and Na^+. We have previously synthesized Fe-bearing whitlockite by hydrothermal methods [20]. Until recently, terrestrial whitlockite was not thought to contain significant Na^+ (<0.5 wt.% as Na_2O) [e.g. 18, 21, 22], as the "Na-site", open in merrillite, is occupied by H^+ in whitlockite [16]. However, whitlockite with higher Na^+ content has since been documented (up to 1.0 wt% as Na_2O) [23]. In previous work, we were able to incorporate both Fe^{2+} and Na^+ into synthesized whitlockite in concentrations similar to terrestrial whitlockite and some of the more Na-poor lunar merrillite [24]. However, with the exception of lunar merrillite, extraterrestrial merrillite (including martian) generally has higher Na^+ content (~1 - 3 wt%) [e.g. 6, 16, 21]. In this ongoing research we are continuing to increase both Fe^{2+} and Na^+ content in synthesized whitlockite (for merrillite synthesis) to reach cation chemistry comparable to that found in martian and other meteoritic merrillite.

Methods: Whitlockite syntheses were based on methods of [18, 20, 24]. Solutions of $MgNO_3 \cdot 6H_2O$, FeS, and $Ca_5(PO_4)_7OH$ were created with 18.2 MΩ water in a Parr acid digestion vessel. A Na^+ cation source was introduced into solution in predetermined Na/Mg molar ratios. The solution was mixed and the pH adjusted using H_3PO_4 to pH <2.8. The vessel was sealed and incubated at 240 °C for 7 days.

After incubation, vessels were quick cooled in a water bath. Synthesized material from the vessels was inspected by optical microscopy to identify whitlockite and any other phases present (typically monetite, hydroxyapatite, and metallic opaques or oxides). Synthesized whitlockite from each experiment was then mounted in epoxy mounts, prepared, and analyzed for chemistry by Electron Microprobe (EMP) at the UNLV Electron Microprobe and Imaging Lab (EMiL).

Results: In all syntheses, optical microscopy confirmed crystal morphologies consistent with whitlockite. The amount of impurities or additional phases in syntheses were similar to Mg-endmember syntheses [20]. However, yields of whitlockite from Fe/Na experiments were generally lower. EMP analyses of the synthetic whitlockite confirmed stoichiometries consistent with whitlockite (Table 1) as well as incorporation of Na^+ and Fe^{2+} in variable amounts (Table 1). Increases in the Na:Mg molar ratio in the experiments appear to enhance Na^+ incorporation in a roughly predictable manner (Figure 1). The addition of FeS to the experiment also appears to enhance Na^+ incorporation.

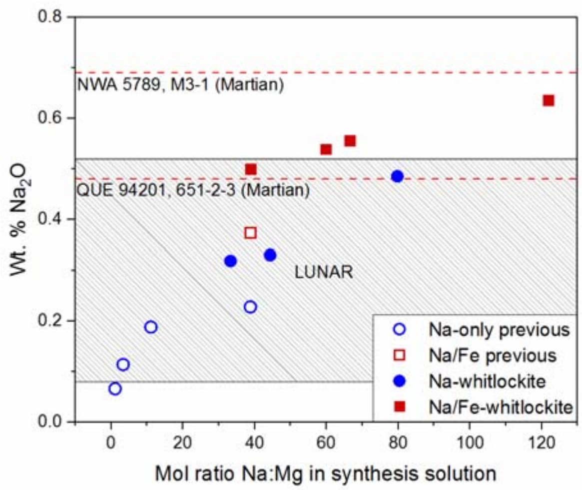

Figure 1. Wt. % of Na_2O incorporated into synthetic whitlockite vs. Na:Mg molar ratios in synthesis solutions. Hollow symbols are from [24]. Shaded area represents typical Na_2O content of lunar merrillite based on ±1 standard deviation from the average of analyses compiled in [16, 22, 26]. Dashed lines represent concentrations for specific martian meteroites Northwest Africa 5789 (NWA 5789) and Queen Alexandra Range 94201 (QUE 94201) analyzed by [25]. Top of typical martian range as determined above is ~1.8 wt.% [6, 16, 21, 23, 25].

Discussion and Ongoing Work: Whitlockite Na^+ contents from our experiments are higher than our previous work and now cover the range of most lunar samples. Content is also similar to the lower Na^+ content of merrillite found in some meteorites like martian meteorites Northwest Africa 5789 and Queen Alexandra Range 94201 [25]. In syntheses that included Fe^{2+}, the Fe content was similar to that of merrillite in select lunar samples (e.g. 14161, sub-samples 7350 and 7233) [16]. In addition, Fe^{2+} concentrations were similar to or exceeded that of merrillite in meteorites such as Allegan (H5 chondrite) or Forksville (L6 chondrite), and approached the content of martian meteorite Allan Hills 84001 [16, 21, 25].

Very high Na:Mg molar ratios were required for significant Na^+ incorporation (Figure 1). Incorporation of Fe^{2+} also appears to enhance the Na^+ concentration in the synthesized whitlockite, something suggested, but not confirmed in our previous work [24].

Future work includes experiments to achieve Mg^{2+}, Fe^{2+}, and Na^+ whitlockite contents similar to a broader range of martian and other meteoritic merrillite. We will also plan to synthesize Mars-relevant merrillite from the produced whitlockite. The ability to economically and quickly synthesize chemically closer analog of an extraterrestrial mineral will reduce the need to use natural extraterrestrial merrillite, an otherwise limited resource.

Table 1. Stoichiometries based on EMP analyses

ID	Stoichiometry
EXT 17	$Ca_{8.95}Mg_{0.94}\mathbf{Na_{0.02}}(PO_3OH)(PO_4)_{6.02}$
EXT 18	$Ca_{8.94}Mg_{0.96}\mathbf{Na_{0.04}}(PO_3OH)(PO_4)_{6.02}$
EXT 19	$Ca_{8.87}Mg_{0.92}\mathbf{Na_{0.07}}(PO_3OH)(PO_4)_{6.06}$
EXT 20	$Ca_{8.81}Mg_{0.92}\mathbf{Na_{0.08}}(PO_3OH)(PO4)_{6.08}$
EXT 21	$Ca_{8.90}Mg_{0.91}Fe_{0.03}\mathbf{Na_{0.13}}(PO_3OH)(PO_4)_{6.01}$
EXT 41	$Ca_{8.86}Mg_{0.95}\mathbf{Na_{0.11}}(PO_3OH)(PO_4)_{6.02}$
EXT 42	$Ca_{8.96}Mg_{0.97}\mathbf{Na_{0.11}}(PO_3OH)(PO_4)_{5.96}$
EXT 43	$Ca_{8.85}Mg_{0.96}\mathbf{Na_{0.16}}(PO_3OH)(PO_4)_{6.00}$
EXT 44	$Ca_{8.88}Mg_{0.96}Fe_{0.02}\mathbf{Na_{0.17}}(PO_3OH)(PO_4)_{5.84}$
EXT 45	$Ca_{8.89}Mg_{0.95}Fe_{0.02}\mathbf{Na_{0.18}}(PO_3OH)(PO_4)_{5.90}$
EXT 46	$Ca_{8.79}Mg_{0.95}Fe_{0.02}\mathbf{Na_{0.19}}(PO_3OH)(PO_4)_{5.86}$
EXT 47	$Ca_{8.87}Mg_{0.95}Fe_{0.06}\mathbf{Na_{0.22}}(PO_3OH)(PO_4)_{5.87}$

Note: Bold ID's are from the current work. Others are from [24].

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