EXPERIMENTAL STUDY INTO THE STABILITY OF WHITLOCKITE AND HYDROXYLAPATITE IN BASALTIC MAGMAS
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Introduction: Apatite $(Ca_5(PO_4)_3(F,Cl,OH))$, merrillite $(Ca_{18}Na_2Mg_2(PO_4)_{14})$, and whitlockite $(Ca_9(Mg,Fe^{2+})(PO_4)_6[PO_3(OH)])$ are the primary phosphate minerals found in most planetary materials including rocks from Earth, Moon, Mars, and asteroids [1–2]. For many years, the terms merrillite and whitlockite have been used interchangeably in the meteorite literature. Much of the confusion regarding the relationship between terrestrial and extraterrestrial "whitlockite" is based on the presence or absence of hydrogen in the mineral structure. Whitlockite has approximately 8500 ppm H_2O, and the term "merrillite" has been adopted to identify the hydrogen-free form of whitlockite [2]. The atomic structures of merrillite and whitlockite were examined in detail by Hughes et al. [3–4]. On Earth, whitlockite has been found in rocks from evolved pegmatitic systems [2–4] and in some mantle rocks [e.g., 5]. Furthermore, terrestrial whitlockite has been shown to have some merrillite component [4]. For the meteoritic and lunar materials that have been investigated, merrillite appears to be far more common than whitlockite, and it has been proposed that the whitlockite component is unique to terrestrial samples [4]. There are some reports of "whitlockite" in the meteorite literature; however, these may represent misidentifications of merrillite because there have been no reports of extraterrestrial whitlockite that have been verified through crystal structural studies or analyzed for their H contents. Hughes et al. [3] reported the atomic arrangement of lunar merrillite and demonstrated that the phase is similar to meteoritic merrillite and, predictably, devoid of hydrogen. In a follow-up study, Hughes et al. [4] reported the atomic arrangements of two natural samples of whitlockite, one synthetic whitlockite, and samples of synthetic whitlockite that were heated at 500 °C or 1050 °C for 24 h. The crystal chemistry and crystal structures of the phases were compared, and it was discovered that the latter treatment resulted in the dehydrogenation of whitlockite to form merrillite.

The presence of merrillite vs. whitlockite was widely thought to serve as an indication that magmas were anhydrous [e.g., 6–7]. However, McCubbin et al., [8] determined that merrillite in the martian meteorite Shergotty had no discernible whitlockite component despite its coexistence with OH-rich apatite. Consequently, McCubbin et al., [8] speculated that the absence of a whitlockite component in Shergotty merrillite and other planetary merrillites may be a consequence of the limited thermal stability of H in

whitlockite (stable only at T <1050 °C), which would prohibit merrillite-whitlockite solid-solution at high temperatures. In the present study, we have aimed to test this hypothesis experimentally by examining the stability of whitlockite in basaltic magmas at 1.2 GPa and a temperature range of 1000–1300 °C.

Experimental Methods: A powdered mix was synthesized based on the QUE 94201 composition, and this powdered mix was packed into a Mo^0 capsule with natural whitlockite crystals from Big Fish River, Yukon Canada. Next, the capsule was loaded into a salt-pyrex cell using the same cell assembly reported by McCubbin et al. [9]. The assembled cell was then placed within a 1.27 cm (diameter) Depths of the Earth piston-cylinder apparatus (using the piston-out method) and pressurized immediately. Next, the temperature was raised to a melting temperature of 1400 °C. After melting for 30 minutes, the temperature was dropped as quickly as possible (typically ~500 C/min) to the desired crystallization temperature of 1000–1300 °C and left to crystallize for 18–40 hours. The temperature of each experiment was controlled by a W_5Re_{95}-$W_{26}Re_{74}$ (Type C) thermocouple. At the end of each experiment, the run was rapidly quenched by shutting off the power to the system and slowly decompressed.

Analytical Methods: Experimental charges were cast in epoxy and subsequently ground and polished for analysis by electron probe microanalysis (EPMA). EPMA was conducted on a JEOL JXA 8200 electron microprobe equipped with 5 wavelength dispersive spectrometers in the Institute of Meteoritics at the University of New Mexico using the same procedures as those described in [9].

The epoxy-mounted samples were subsequently extracted and mounted in indium for analysis by NanoSIMS at NASA JSC. The ion probe was run in multicollection mode and the isotopic analyses of apatite, merrillite, and glass were measured in 'isotope mode'. Negative secondary ions of ^{16}OH, ^{18}O, and ^{56}CaO were collected simultaneously with electron multipliers. A Cs+ primary beam of ~150 pA was rastered over ~64 µm2 areas and an electronic gate was used. Well characterized phosphate and glass standards with a range of H_2O contents were used to calibrate H_2O abundances. The background H_2O measured on nominally anhydrous San Carlos olivine and a dry glass standard of QUE 94201 bulk composition was ~40 ppm.

Results: In total, we conducted 7 successful experiments (Table 1), although QUEYKN_003 has not

yet been analyzed by NanoSIMS. All of the experimental charges consisted of at least one phosphate phase and quenched silicate melt, and 5 of the experiments resulted in two phosphates and melt (Figure 1). Apatite was present in all experimental run products with the exception of QUEYKN_005, and merrillite was present in all experimental run products with the exception of QUEYKN_002. H_2O abundances of quenched melt (glass), apatite, and merrillite from each experiment were determined by NanoSIMS and reported in Table 1. The melt water abundances ranged from 1.18–3.29 wt.% H_2O. The experiment with the lowest water abundance had merrillite only with no apatite. The experiment that had apatite only corresponded to a melt water content of 3.14 wt.% H_2O. All of the apatite was hydroxylapatite with 82–100% of the apatite X-site occupied by OH^-. Furthermore, all of the merrillites had substantial whitlockite components, ranging from 22–41% whitlockite.

Table 1. Summary of crystallization temperatures of each experiment and average H_2O abundances of melt, apatite, and merrillite. n.a. = not analyzed, and - = not present

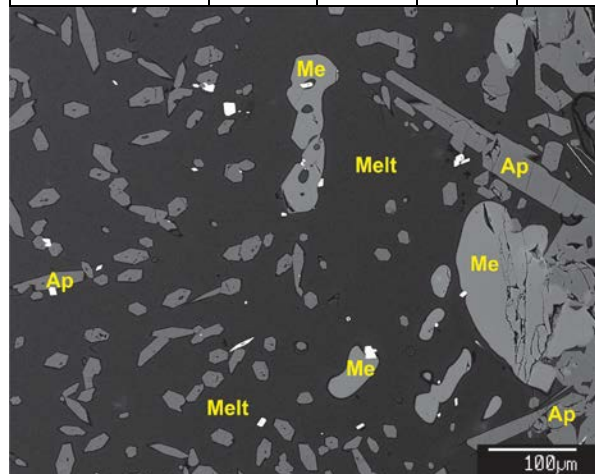| Sample	T (°C)	Melt	Ap	Me
QUEYKN_001	1300	2.34	1.56	0.27
QUEYKN_002	1250	3.14	1.84	-
QUEYKN_003	1200	n.a.	n.a.	n.a.
QUEYKN_004	1150	2.71	1.46	0.28
QUEYKN_005	1100	1.18	-	0.28
QUEYKN_006	1050	3.00	1.60	0.19
QUEYKN_007	1000	3.29	1.68	0.35

Figure 1. Back-scattered electron image of experimental run product QUEYKN_003, with apatite (Ap), merrillite (Me), and melt (Melt).

Discussion: The experimental results indicate that hydroxylapatite and merrillite can coexist in H_2O-rich magmas, consistent with the presence of OH-bearing apatites in numerous planetary materials that coexist with merrillite [e.g., 1]. Importantly, however, a whitlockite component is present in the merrillite up to at least 1300 °C at a pressure of 1.2 GPa. This observation indicates that the upper limit on the thermal stability of a whitlockite component in merrillite, determined to be 1050 °C in low-pressure hydrothermal systems [4], is not applicable at higher pressure and/or silicate melt systems with H_2O abundances in excess of 1.18 wt.% H_2O. Consequently, the thermal instability of whitlockite, alone, cannot explain the coexistence of OH-bearing apatite and anhydrous merrillite in planetary materials as suggested by [8]. Additional studies on the apatite-melt-merrillite systematics at lower pressures that are relevant to the crystallization of martian, lunar, and asteroidal basalts are needed to better understand the factors that control the coexistence of OH-bearing apatite and nearly anhydrous merrillite.

Alternatively, the presence of a whitlockite component could result from incomplete dehydrogenation of whitlockite starting materials. Consequently, we plan to run additional experiments that use synthetic merrillite seeds to test whether they become hydrated during the course of an experiment.

Notably, the only experiment that did not have apatite was also the experiment with the lowest melt H_2O abundance. Although this represents only a single data point, we speculate that the stability of hydroxylapatite in basaltic melt at 1.2 GPa may require a melt with 1.18–2.34 wt.% H_2O before hydroxylapatite is stable. Consequently, the maximum mineral-melt D value to stabilize hydroxylapatite is within the range of 1.5 and 0.76 at 1.2 GPa over the temperature range of 1100–1300 °C.

Conclusions: Apatite and merrillite can coexist in magmas with 2.34–3.29 wt.% H_2O. However, all the merrillite produced in the present study exhibit between 22 and 41% of a whitlockite component, which could be attributed to either the elevated pressure and/or elevated H_2O abundances in our experiments. Additional experiments are needed to understand the coexistence of nearly anhydrous merrillite and OH-bearing apatite in many planetary materials.

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