

EXPERIMENTAL STUDY INTO THE STABILITY OF WHITLOCKITE IN BASALTIC MAGMAS

F. M. McCubbin¹, J. J. Barnes¹, P. Srinivasan², E. S. Whitson², K. E. Vander Kaaden³, and J. W. Boyce¹, ¹NASA Johnson Space Center, Mailcode XI2, 2101 NASA Parkway, Houston, TX 77058, USA. ²Institute of Meteoritics, Department of Earth & Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA. ³Jacobs Technology/JETS, NASA Johnson Space Center, Mailcode XI2, 2101 NASA Parkway, Houston, TX 77058, USA.

Introduction: Apatite $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$, merrillite $\text{Ca}_{18}\text{Na}_2\text{Mg}_2(\text{PO}_4)_{14}$, and whitlockite $\text{Ca}_9(\text{Mg},\text{Fe}^{2+})(\text{PO}_4)_6[\text{PO}_3(\text{OH})]$ 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 likely 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 and 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., (2014) 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.

Experiments: 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 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 $\text{W}_3\text{Re}_{95}\text{-W}_{26}\text{Re}_{74}$ (Type C) thermocouple. At the end of each experiment, the run was rapidly quenched by shutting off the power to the system.

Results/discussion: All of the run products were analyzed by electron probe microanalysis (EPMA), and we plan to analyze the run products by secondary ion mass spectrometry (SIMS) prior to the presentation of this work. Most of the run products contain at least two phosphate minerals and a melt phase, and the lower temperature experiments below 1100 °C also included additional mineral phases (e.g., silica, ilmenite, pyroxene, and plagioclase). We were able to identify one of the phosphate minerals in the experiments as hydroxylapatite based on EPMA data, and the other phosphate phase is either merrillite or whitlockite, SIMS data is required to distinguish between the two phases. Consequently, analysis of our run products by SIMS should provide a direct test of the magmatic stability of whitlockite in basaltic magmas.

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