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Highlights and Breakthroughs

Merrillite and apatite as recorders of planetary magmatic processes

Brad Jolliff[1,*]

[1]Department of Earth and Planetary Sciences Washington University in St. Louis, Campus Box 1169, One Brookings Drive, St. Louis, Missouri 63130, U.S.A.

Abstract: Merrillite, $Ca_{18}(Ca,\square)Mg_2(PO_4)_{14}$–$Ca_{18}Na_2Mg_2(PO_4)_{14}$–$Ca_{16}REE_2(Mg,Fe)_2(PO_4)_{14}$ occurs as a primary phosphate along with apatite, in lunar and martian rocks, and in meteorites. It is nominally anhydrous, but attempts to directly measure H in this mineral have not previously been reported. Because of the occurrence on Earth of whitlockite, $Ca_{18}(Mg,Fe^{2+})_2(PO_4)_{12}[HPO_4]_2$, and the apparent incorporation in whitlockite of a merrillite component, the lack of a whitlockite component in extraterrestrial merrillite could be taken as an indicator of low hydrogen fugacity, and this implication has been applied to lunar merrillite. On the other hand, for martian rocks, where magmatic OH or H_2O contents were likely higher, apatite accordingly contains higher OH contents, yet coexists with anhydrous, Na-rich merrillite. With direct measurements by SIMS, McCubbin et al. (2014), which is in the July issue of *American Mineralogist* (p. 1347–1354), show that Shergotty merrillite is anhydrous and infer that the high *T* of crystallization of Shergotty precluded incorporation of a whitlockite component. The mineral pair apatite-merrillite in extraterrestrial rocks constitutes a powerful pair for recording magmatic conditions; however, as McCubbin et al. show, the implications of these minerals and their compositions must be interpreted in light of careful and complete analyses and crystal chemical constraints. **Keywords:** Merrillite, apatite, shergotty, planetary materials

The use of mineral assemblages and crystal chemistry as recorders of the conditions of magmas and magmatic fractionation has been a focus of research by J.J. Papike, C.K. Shearer, their students, and coworkers over the past several decades, especially with regard to the major planetary suites of terrestrial, lunar, and martian basalts and other rocks (e.g., Papike et al. 2005; Shearer et al. 2011). McCubbin et al. (2014) contribute to this body of work through their analysis of martian primary phosphates, apatite, and merrillite. Merrillite, in particular, holds great potential as a unique recorder of planetary magmatic compositions and conditions because it [or its terrestrial brethren whitlockite (Hughes et al. 2006, 2008) and bobdownsite (Tait et al. 2011)] occurs in all of the planetary suites, but with different and distinctive compositions in each planetary suite (Jolliff et al. 2006).

The key to unlocking this information has been the careful analysis of both apatite and merrillite using a combined electron- and ion-microprobe approach to determine directly the F, Cl, and OH contents, as well as REE and other significant substituents, on the same mineral grains. The measurement of F and other beam-sensitive elements with the electron microprobe must be done with a time-dependent measurement, and careful stoichiometric constraints must be taken into account. Concentrations of F, Cl, OH, and other potential anions were measured with the Cameca 6f ion microprobe at the Department of Terrestrial Magnetism (DTM) using carefully prepared apatite and other standards (McCubbin et al. 2014). Complete analyses are essential to evaluate the stoichiometric constraints. In merrillite with significant REE concentrations, as in the case of lunar merrillite, a complete suite of REE must be analyzed (or the abundant ones analyzed and others interpolated) and included in the EPMA corrections and stoichiometric calculations. The same holds true for apatite that contains significant REE concentrations.

McCubbin and coworkers, and others (e.g., Boyce et al. 2010) have shown that apatite is a sensitive indicator of magmatic OH and halogen contents, and that previous inferences about completely anhydrous lunar magmas are, in fact, not correct (e.g., McCubbin et al. 2010). Merrillite, however, which can form a solid solution with whitlockite (Hughes et al. 2006, 2008), might also—in its composition—reflect magmatic volatiles, making coexisting apatite-merrillite pairs powerful indicators of hydrogen fugacity and oxygen fugacity of the melts from which they formed. In the highlighted article, McCubbin et al. show, through careful analysis of coexisting pairs of apatite and merrillite in the martian meteorite, Shergotty, that essentially anhydrous merrillite can coexist with OH-bearing apatite. Thus the occurrence in extraterrestrial materials (lunar, martian, meteoritic) of merrillite and not whitlockite is most likely best understood as a function of crystallization temperature and thermal stability of H in merrillite-whitlockite species. This finding begs the question of what the phase diagram for these two minerals looks like in multi-dimensional space that includes the various coupled substitutions affected by the balance of H^+ and the Na-site vacancy, especially the trivalent REE, which substitute for Ca, requiring a corresponding charge balance.

Minerals observed in the context of rocks in which they occur are keys to understanding the rocks, the manner in which the

* E-mail: blj@levee.wustl.edu

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rocks crystallized or were altered, and the processes and interior workings of parent bodies where they formed. The potential information to be gained from careful analysis of the structures and compositions of minerals underscores the importance of capable in-situ mineralogical analysis instruments for planetary exploration as well as an emphasis on the collection and return of samples from other planets to Earth for detailed study in the best terrestrial laboratories.

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