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Title: Merrillite and Apatite as Recorders of Planetary Magmatic Processes

(On the article **"Volatile abundances of coexisting merrillite and apatite in the martian meteorite Shergotty: Implications for merrillite in hydrous magmas."**) by Francis McCubbin, Charles Shearer, Paul Burger, Erik Hauri, Jianhua Wang, Stephen Elardo, and James Papike

Brad Jolliff, Washington University in St. Louis, Campus Box 1169, One Brookings Drive, St. Louis, MO 63130, e-mail: blj@wustl.edu

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Abstract

Merrillite, $Ca_{18}(Ca,[])Mg_2(PO_4)_{14}$ - $Ca_{18}Na_2Mg_2(PO_4)_{14}$ - $Ca_{16}REE_2(Mg,Fe)_2(PO_4)_{14}$ 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 H-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. (2015) [ref to journal issue] 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.

Main Text

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. (2015) 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 planetary recorder 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 (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. 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 DTM using carefully prepared apatite and other standards (McCubbin et al., 2015). Complete analyses are essential to evaluate the stoichiometric constraints.

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 were, 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 H- and O-fugacity of the melts from which they formed. In the highlight 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 multidimensional space that includes the various coupled substitutions affected by the balance of H^+ and the Na-site vacancy.

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

John Hughes jmhughes@uvm.edu

Francis McCubbin francis.mccubbin@gmail.com

Charles Shearer cshearer@unm.edu

James Papike jpapike@unm.edu

Jeremy Boyce jwboyce@alum.mit.edu