

Crystal chemistry of merrillite in martian basalts and its significance to interpreting basalt petrogenesis.

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Introduction: The phosphates apatite and “merrillite-whitlockite” are common accessory minerals found in terrestrial and extraterrestrial magmatic rocks. They often occur as late-stage crystallization products of magmas, and their occurrence and composition reflect characteristics of that residual magma. For example, P to halogen ratio of the residual melt may influence the phosphate mineral assemblage. The crystal chemistry of terrestrial and lunar “merrillite-whitlockite” has been discussed in detail in numerous studies [e.g. 1-6]. Shearer et al. [6] illustrated the role of phosphate crystal chemistry in dictating the behavior of Eu. Here, we examine the variation in chemistry of “merrillite-whitlockite” from a variety of martian basalts, compare them to similar phosphates in lunar basalts, and decipher the petrogenetic significance of their crystal chemistry.

Analytical Approach: The major and minor elements (P, Ca, Si, Ti, Fe, Mn, Mg, Sr, Na, Y, Ce, S, F, and Cl) in merrillites from a suite of basaltic shergottites (Los Angeles, QUE 94201, NWA 2986, LAR 06319, Shergotty, EETA 79001, NWA 1183, Zagami, 998, Dar al Ghani, 476) and lherzolites (ALHA 77005, 30) were examined using electron probe microanalysis (EPMA). These measurements were collected on the JEOL JXA 8200 electron microprobe at the Institute of Meteoritics, Dept. of Earth and Planetary Sciences at the University of New Mexico. Samples were initially characterized using a combination of back-scattered electron imaging (BSE) and wavelength-dispersive mapping (WDS) to locate potential analysis points. Quantitative analyses were collected using an accelerating voltage of 15 kV, and a beam current of 20 nA. The spot was slightly defocused to 3 microns, and Na, Cl, and F were measured early in the analysis to mitigate the effects of volatilization/migration of these elements during analysis. Standardization was achieved using a combination of in-house and Taylor Company EPMA mineralogical standards.

Discussion:

Merrillite or Whitlockite in martian basalts?: Jolliff et al. [3,4] and Hughes et al. [5] confirmed that merrillite rather than whitlockite occurred in lunar basalts. This occurrence of merrillite was partially attributed to the “dry” character of lunar basalts [3-5]. Hydrogen analyses of phosphates from selected martian basalts (i.e., QUE 94201, Shergotty) indicate that they are merrillite (i.e., <200 ppm H₂O [7]), and that the relationship between the occurrence of merrillite, OH in associated apatite, and water content of the basalt is not straightforward [7].

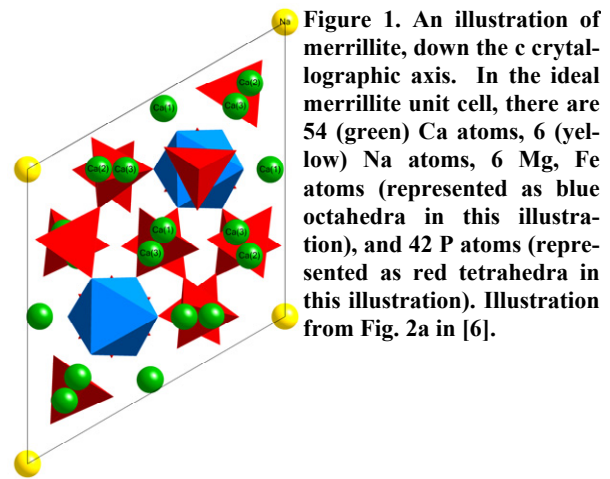


Figure 1. An illustration of merrillite, down the c crystallographic axis. In the ideal merrillite unit cell, there are 54 (green) Ca atoms, 6 (yellow) Na atoms, 6 Mg, Fe atoms (represented as blue octahedra in this illustration), and 42 P atoms (represented as red tetrahedra in this illustration). Illustration from Fig. 2a in [6].

General crystal chemistry of merrillite: In the merrillite structure (Fig. 1) there are 54 Ca polyhedra (shown as green atoms in figure), 6 partially occupied Na polyhedra (shown as yellow atoms in figure), 6 Mg, Fe octahedra, and 42 P tetrahedra per unit cell. No two P tetrahedra share a corner. Every tetrahedron shares corner(s) with Ca polyhedra and sometimes Na polyhedra and Mg, Fe octahedra. Every Ca-polyhedron shares all corners with tetrahedra (i.e., every Ca polyhedron is linked to 8 tetrahedra). Every Na polyhedra (6-coordinated) is linked to 6 tetrahedra. Figure 2 illustrates the relationship between ionic radii and cations that occupy each site in merrillite.

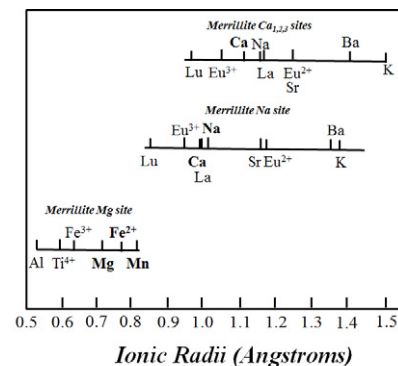


Figure 2. Cations typically found in merrillite, grouped by relevant crystallographic sites. Illustration from Fig. 2b in [6].

Crystal chemistry of martian merrillite: Mg#

The Mg# ($\{[Mg_{\text{atomic}}] / ([Mg_{\text{atomic}}] + [Fe_{\text{atomic}}])\} * 100$) of the martian merrillites thus far analyzed ranges from approximately 10 to 90 (Fig. 3). Hess et al. [8] and Jolliff et al. [4] pointed out that merrillite should have a higher Mg# than either coexisting melt, silicate (i.e. pyroxene) or apatite. Jolliff et al. [4] postulated that the difference in Mg# between merrillite and apatite was

due primarily to differences in the size of the site accommodating the Mg^{2+} and Fe^{2+} rather than the crystallization sequence of the two phosphates. The variation of Mg# among the martian merrillites is closely related to the Mg# of bulk rock and associated silicates.

Mg# and Na: Sodium in merrillite exhibits a strong positive correlation to Mg# (Fig. 3). This relationship may seem counterintuitive, but it likely reflects the crystallization relationship between plagioclase and merrillite. The high-Na merrillite (i.e. NWA 1183, DaG 476) are associated with basalts with compositions (Al_2O_3 , Na_2O), mineral proportions (i.e. plagioclase) and textures that suggest that plagioclase hits the liquidus later than basalts with low-Na merrillite (i.e. QUE 94201). Jolliff et al. [3] does not observe a similar relationship in merrillites from the Moon. This can be attributed to differences in the charge balancing relationships to accommodate Na in the merrillite structure. Jolliff et al. [3] demonstrated that the substantial concentration of REE in lunar merrillites are accommodated in the merrillite structure with vacancies in the Ca and Na polyhedra. In martian merrillite, in which the REE are significantly lower, vacancies in the Na polyhedral are not driven by the REE substitution.

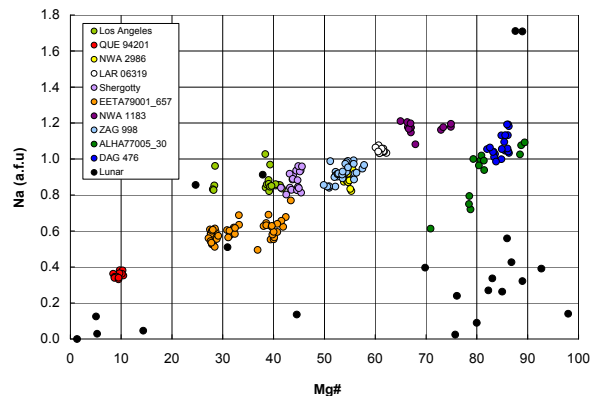


Figure 3. Na vs. Mg# in martian and lunar merrillite [3].

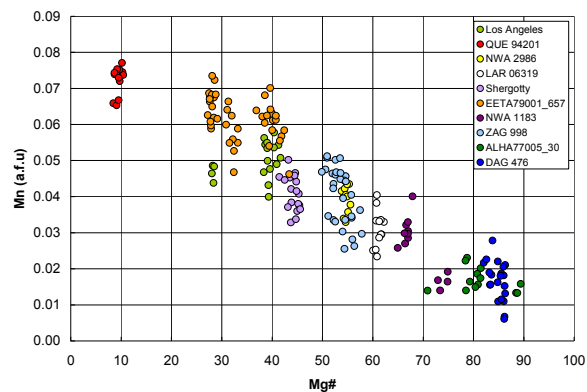
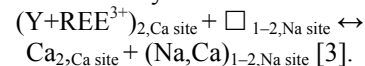


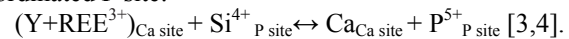
Figure 4. Mn vs. Mg# in martian merrillite.

Mg# and Mn: Manganese in the merrillite increases with decreasing Mg# and Na. This systematic variation does not reflect the bulk MnO in these martian basalts in that the variation in MnO is limited (MnO wt.% = 0.41 – 0.50). This variation may provide an index for the crystallization history of merrillite.

REE: Jolliff et al. [3,4] demonstrated that trivalent REE substitute into the main 8-coordinated Ca sites in merrillite (referred to as Ca_1 , Ca_2 , and Ca_3 , with a total of 18 sites per 56 O atoms). Charge balance for the substitution of trivalent REE is compensated through coupled substitution involving both the Ca sites and the irregular octahedrally coordinated Na site:



Another coupled substitution that has been proposed to compensate for trivalent REE into merrillite involves the substitution of Si^{4+} for P^{5+} in the tetrahedrally coordinated P site:



Within the context of these petrogenetic models, the REE pattern of the merrillite reflects the whole-rock isotopic and chemical characteristics of the martian basalts. Merrillites in “depleted” basalts have LREE depleted patterns whereas merrillites from the enriched martian basalts have relatively flat patterns. This is a relatively straightforward way of distinguishing among different martian basalts. The extent of the Eu anomaly is not completely reliant on the fO_2 of the martian basalts [6].

Conclusions: The major element chemistry of merrillite is driven by numerous variables that include melt composition, timing of crystallization relative to plagioclase, and crystal chemical behavior of the Mg-, Na-, and Ca-sites. Differences observed in martian versus lunar merrillites are controlled by the nature of coupled substitutions (i.e. REE). The REE reflect a slightly different variable; REE pattern shapes of the merrillite most likely fingerprint the nature of the mantle source from which the martian basalt was derived.

References: [1] Gopal and Calvo (1972) Nature Physical Science, 237, 30–32. [2] Dowty (1977) Earth Planet Sci. Lett. 35, 347–351. [3] Jolliff et al. (1993) GCA 57, 4069–4094. [4] Jolliff et al. (2006) Am. Mineral. 91, 1583–1595. [5] Hughes et al. (2006) Am. Mineral. 91, 1547–1595. [6] Shearer et al. (2011) Am. Mineral. 96, 1418–1421. [7] McCubbin et al. (2012) in review. [8] Hess et al. (1990) LPSC XXI, abs. 1258.