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The crystal chemistry of whitlockite and merrillite and the dehydrogenation of whitlockite to merrillite

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ABSTRACT

The atomic arrangements of two natural samples of whitlockite, a synthetic whitlockite specimen, a synthetic whitlockite specimen heated at 500 °C, and a synthetic merrillite specimen (formed through dehydrogenation of synthetic whitlockite by heating at 1050 °C for 24 h) have been determined in space group *R*3*c* by X-ray diffraction methods; the high-quality structure refinements yielded $R < 0.019$. Whitlockite, ideally $Ca_{18}Mg_2(PO_4)_{12}[PO_3(OH)]_2$ and merrillite, ideally $Ca_{18}Na_2Mg_2(PO_4)_{14}$, are similar phases that differ by the lack of hydrogen and the concomitant addition of charge-balancing sodium (or calcium) in merrillite. The atomic arrangements of whitlockite and merrillite contain a structural unit consisting of a $[(Mg,Fe)(PO_4)_6]_2^{16-}$ complex anion that forms a "bracelet-and-pinwheel" arrangement. The central octahedral cation and the six coordinating phosphate tetrahedra form a pinwheel, and in whitlockite and merrillite the pinwheels are not polymerized; the structural units are linked by interstitial complexes. In unsubstituted merrillite (assuming no Na or REE substituents for Ca), the interstitial complex has a formula of $[Ca_{19}(PO_4)_2]^{32+}$, and in whitlockite, the terrestrial phase in which hydrogen is accommodated, the interstitial unit has the formula $[Ca_{18}(PO_3[OH])_2]^{32+}$, yielding the charge-balancing relationship $[H_{(whit)} \leftrightarrow Ca_{0.5(merr)}]_2$. Whitlockite and merrillite are perhaps the only phases that form a solid solution with terrestrial and extra-terrestrial end-members that differ by structural adjustments that result from the accommodation of hydrogen in the terrestrial phase. The results of the study also suggest that in terrestrial samples of whitlockite, a merrillite component of the solid solution is common, but that extraterrestrial samples of merrillite are devoid of any whitlockite component.

Keywords: Whitlockite, merrillite, structures, dehydrogenation