

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

JOHN M. HUGHES,^{1,*} BRADLEY L. JOLLIFF,² AND JOHN RAKOVAN¹

¹Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.

²Department of Earth and Planetary Sciences and the McDonnell Center for Space Sciences, Washington University, St. Louis, Missouri 63130, U.S.A.

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 *R3c* by X-ray diffraction methods; the high-quality structure refinements yielded $R < 0.019$. Whitlockite, ideally $\text{Ca}_{18}\text{Mg}_2(\text{PO}_4)_{12}[\text{PO}_3(\text{OH})]_2$ and merrillite, ideally $\text{Ca}_{18}\text{Na}_2\text{Mg}_2(\text{PO}_4)_{14}$, 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 $[(\text{Mg},\text{Fe})(\text{PO}_4)_6]^{16-}$ 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 $[\text{Ca}_{19}(\text{PO}_4)_2]^{32+}$, and in whitlockite, the terrestrial phase in which hydrogen is accommodated, the interstitial unit has the formula $[\text{Ca}_{18}(\text{PO}_3[\text{OH}])_2]^{32+}$, yielding the charge-balancing relationship $[\text{H}_{(\text{whit})} \leftrightarrow \text{Ca}_{0.5(\text{merr})}]_2$. 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