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Fundamental difference between synthetic powder and natural or synthetic single-crystal 1*M* micas: Geometric homo-octahedral vs. geometric meso-octahedral sheets

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ABSTRACT

Based on powder X-ray diffraction (pXRD) measurements of many mica solid solution series of synthetic powder samples (between Mg, Co, Ni, and Fe end-members, with different degrees of oxidation, vacancy, and Al/Si contents, and including an OH/F substitution series; 75 samples indexed as 1*M* polytype, space group *C*2/*m*) and on 175 previously published structural refinements of 1*M* micas (refined in space group *C*2/*m*) comprising 37 synthetic and 138 natural single-crystal samples, we show that the relation

$$(c/a)\cos\beta^* = 1/3$$

between the *a*, *c*, and β monoclinic lattice parameters (β* = 180E – β), holds exactly (within experimental error) for all the synthetic powder samples whereas it does not hold in general for the natural or synthetic single crystal samples. This relation is not imposed by the *C*2/*m* space group. It is predicted to hold for geometric homo-octahedral sheets (having equal M1 and M2 site bond-lengths) and predicted not to hold in general for geometric meso-octahedral sheets (having unequal M1 and M2 site bond lengths). We conclude that synthetic powder samples (usually having particle diameters in the range 0.1–20 μm) are geometric homo-octahedral whereas single crystals (typical size of $0.05 \times 0.05 \times 0.01$ mm or larger) are geometric meso-octahedral, with either M1 > M2 (most common, 153 samples out of 175) or M1 < M2. The geometric meso-octahedral character of the single crystals is corroborated by several parameters of the structure refinements. The synthetic powders presumably appear not to have had the time to equilibrate into a minimal free energy state, possibly because average diffusion hoping times occurring in those syntheses (compared to synthesis times) are larger than under synthesis conditions that lead to single-crystals (e.g., fluxing agents used in single-crystal syntheses, geological conditions of natural samples), whereas all the single crystal samples have to some extent exploited the free energy advantage of sorting smaller and larger cations into distinct crystallographic sites in a geometric meso-octahedral sheet structure. These results suggest further experimental work in which the conditions for and kinetics of octahedral M1/M2 chemical ordering could be studied.