3D electron diffraction of tranquillityite from the Martian shergottite Northwest Africa 856: is its elusive crystal structure one step closer to being finally solved?

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Tranquillityite, currently defined as $Fe^{2+}{}_8Zr_2Ti_3Si_3O_{24}$, is a rare silicate first discovered in returned samples from the Apollo 11 mission (Lovering et al., 1971) and subsequently found in meteorites from the Moon and Mars (e.g., Leroux & Cordier, 2006) and as an accessory phase in terrestrial mafic rocks (Rasmussen et al., 2012). Since its discovery more than fifty years ago, its low degree of crystallinity has hindered the determination of its crystal structure. Preliminary crystallographic studies indicated a hexagonal lattice with a = 11.69(05) Å and c = 22.25(10) Å (Lovering et al., 1971). Subsequently, it was discovered that lunar tranquillityite is metamict due to radiation damage by uranium occurring in traces in its structure. Experimental attempts to recrystallize tranquillityite showed a fluorite-related face-centered cubic (FCC) cell with a = 4.85(3) Å (Gatehouse et al., 1977). In-zone electron diffraction by transmission electron microscope (TEM) on preserved crystalline domains in terrestrial tranquillityite showed strong reflections consistent with this FCC cell, but also weaker reflections suggesting a superstructure with both a lower symmetry and a larger unit cell (Rasmussen et al., 2012). Until now, this crystal structure remains elusive.

In this work, we performed wavelength-dispersive X-ray spectroscopy (WDS) by electron probe microanalyzer, electron back-scattered diffraction (EBSD) by scanning electron microscope, focused ion beam, energy-dispersive X-ray spectroscopy and 3D electron diffraction (3DED) by TEM on tranquillityite grains from the Martian shergottite Northwest Africa 856 in order to shed light on its real crystal-chemical features. WDS analyses give the empirical formula (normalized on the basis of 24 oxygen atoms per formula unit): $Fe_{7.70}Mg_{0.54}Ca_{0.17}Mn_{0.11}Zr_{0.97}Nb_{0.03}Ti_{3.19}Al_{0.19}Si_{3.40}O_{24}$. 3D reconstruction of the reciprocal space of tranquillityite can be indexed on a body-centered orthorhombic cell with a = 6.560(10) Å, b = 7.038(11) Å, c = 18.780(29) Å. This cell is consistent with the supercell observed by Rasmussen et al. (2012). Preliminary attempts to solve and refine its crystal structure in the space group *Imma* also show that the cations are packed in distorted face-centered cubes with an average edge of about 4.77 Å in length, similar to the cell parameter of the FCC cell found by previous studies. Despite the great improvement in the structural characterization of tranquillityite, some open issues remain: 1) a good, yet non-perfect match between EBSD and 3DED data; 2) a rather high residual after the structure refinement; 3) the occurrence of very weak reflections suggesting an even larger cell (also observed in the diffraction pattern by Rasmussen et al., 2012). Further analyses will be performed in order to solve this half-century crystallographic enigma.

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