

Crystal chemistry and nomenclature of the triphylite group of phosphates

Hatert, F.^{1*}, Lyalina, L.M.² and Selivanova, E.A.²

¹ Laboratory of Mineralogy, University of Liège B18, 4000 Liège, Belgium (fhatert@uliege.be)

² Geological Institute, Kola Science Center of the Russian Academy of Sciences, Apatity, 184209, Russia

Minerals of the triphylite group are phosphates that occur as primary phases in some rare-element granitic pegmatites. Their olivine-type crystal structure (space group *Pbnm*) is characterized by two chains of edge-sharing octahedra parallel to the *c* axis: the first chain is constituted by the *M1* octahedra occupied by Li, Na, or vacancies, and the second chain is formed by the *M2* sites occupied by Fe, Mn, and Mg [1]. The occupancy of the *M1* position varies from 0 to 1 in Li-bearing species, and it approaches 1 in Na-bearing species. The structural formula of triphylite-type phosphates is $M1M2TO_4$, where *T* corresponds to P^{5+} in tetrahedral coordination [1]. The cation ordering between *M1* and *M2*, first defined for natrophilite [2], is the main crystal-chemical difference between triphylite-type phosphates and silicates of the forsterite-fayalite series, in which Fe and Mg are disordered over the two sites.

Oxidation of Fe^{2+} to Fe^{3+} and of Mn^{2+} to Mn^{3+} produces Li-vacancies at the *M1* sites, which are necessary to maintain charge balance. This process is responsible for the so-called "Quensel-Mason" oxidation sequence, in which triphylite ($LiFe^{2+}PO_4$) and lithiophilite ($LiMn^{2+}PO_4$) progressively transform into heterosite ($Fe^{3+}PO_4$) and purpurite ($Mn^{3+}PO_4$) [3]. The alignment of the *M1* octahedra along the *c* axis explains why the [001] direction becomes an easy and fast pathway for Li/Na leaching during the oxidation, or for Li/Na absorption when conditions lead to the reduction of Fe and Mn. This is the principle widely used Li-ion batteries based on olivine-type phosphates [4].

Based on new crystal-chemical data on natural samples [5], we present an IMA-CNMNC-accepted scheme for the classification and nomenclature of the triphylite group of minerals [6]. Besides the Li-bearing species of the triphylite-lithiophilite and heterosite-purpurite solid solutions, the group also contains the Na-bearing phosphates natrophilite ($NaMn^{2+}PO_4$) and karenwebberite ($NaFe^{2+}PO_4$) [7], as well as the Li-Mg-bearing phosphate simferite which has been redefined as $LiMgPO_4$. Ferrisicklerite and sicklerite correspond to intermediate phases in the triphylite-heterosite and lithiophilite-purpurite solid solutions, respectively. As a consequence, and according to the CNMNC dominant-constituent rule [8], they were discredited. A new mineral oxidation sequence is also defined, which modifies the traditional "Quensel-Mason" sequence by taking into account the different oxidation capacities of iron and manganese.

References:

- [1] Losey A et al. (2004) *Can Mineral* 42: 1105-1115
- [2] Moore P B (1972) *Am Mineral* 57: 1333-1344
- [3] Quensel P (1937) *Geol Fören Stockholm Förhand* 59, 77-96.
- [4] Yakubovich O et al. (2020) *Minerals* 10(6): 524
- [5] Hatert F et al. (2012) *Can Mineral* 50: 843-854
- [6] Lyalina L et al. (2023) *Eur J Mineral* 35: 427-437
- [7] Vignola P et al. (2013) *Am Mineral* 98: 767-772
- [8] Hatert F & Burke E A J (2008) *Can Mineral* 46: 717-728