

CRYSTAL-CHEMISTRY OF A NEAR END-MEMBER TRIPLITE, $Mn^{2+}_2(PO_4)_F$, FROM CODERA VALLEY (SONDRIO PROVINCE, CENTRAL ALPS, ITALY)

P. Vignola¹, G. Gatta², F. Hatert³, A. Guastoni⁴, D. Bersani⁵

¹ CNR, Istituto per la dinamica dei processi ambientali, via Mario Bianco 9, 20131 Milano, Italy

² Dipartimento di Scienze della Terra, Università degli Studi di Milano, via Botticelli 23, 20133 Milano, Italy

³ Laboratoire de Minéralogie, Dépt de Géologie, Université de Liège, Bâtiment B18, Sart Tilman, B-4000 Liège, Belgium.

⁴ Dipartimento di Mineralogia e Petrologia, Università di Padova, Corso Garibaldi 3735137 Padova, Italy

⁵ Dipartimento di Fisica, Università di Parma, Viale G.P. Usberti 7/a, 43124 Parma, Italy

Phosphate minerals of the solid solution series triplite-zwieselite-magnotriplite, respectively $Mn^{2+}_2(PO_4)_F$, $Fe^{2+}_2(PO_4)_F$ and $(Mg,Fe^{2+},Mn^{2+},Ca)_2(PO_4)_F$, are primary phosphates commonly found in complex granitic pegmatites. These phosphates usually occur in fluorine-rich Lithium-Cesium-Tantalum (LCT)-type dikes, even as gigantic masses up to 4 meters in diameter (Simmons *et al.* 2003). Triplite was discovered more than two centuries ago by Vauquelin (1802) at Limoges, Chanteloube, Haute-Vienne, France and described as "phosphate natif de fer mélangé de manganèse". Some years later, Hausmann (1813) named "triplite" this new phosphate mineral. In the following two centuries, occurrences of phosphate minerals belonging to the triplite-zwieselite-magnotriplite and triplite-triploidite solid solutions were described in a significantly high number of granitic pegmatites (among the most famous:

Stoneham and Auburn, Maine; Branchville, Connecticut; 7U7 Ranch and Mt Loma, Arizona; Mica Lode and School Section, Colorado; San Luis and Salado, Argentina; Varuträsk, Sweden; Zwiesel and Hagendorf, Germany; Fregeneda and Cañada, Spain; Mangualde, Portugal; Alto do Ligonha, Mozambique; Tsaobismund and Okatjimukuju, Namibia; Olary Block, South Australia). Chemical analyses of triplite summarized in the paper of Heinrich (1951), along with those reported by other authors, show rather variable Mn:Fe:Mg ratios with different compositions belonging to the solid solution triplite-zwieselite-magnotriplite. Particularly interesting is the F/OH-substitution, which appears to have a rather continuous variation in the solid-solution triplite-triploidite (Figure 1).

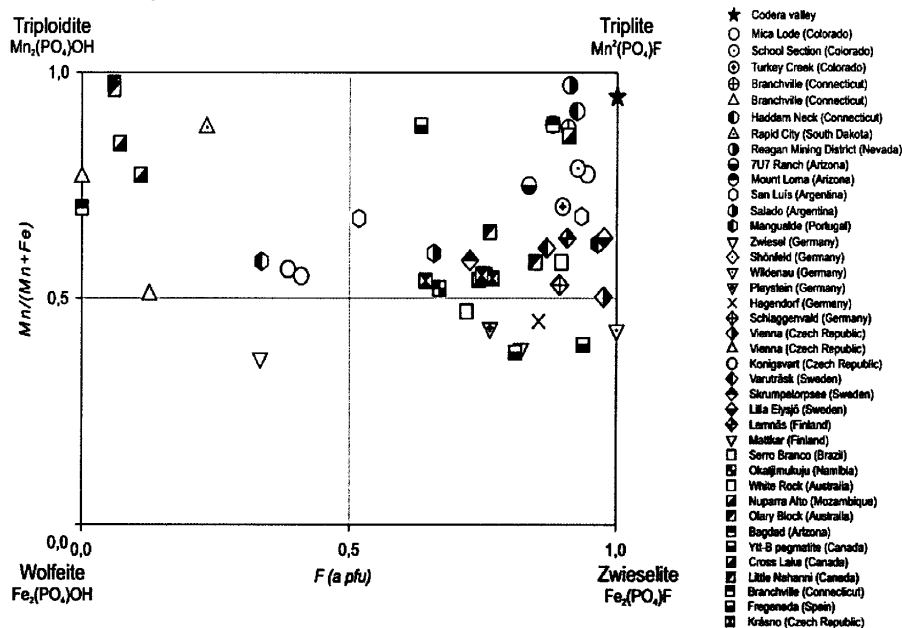


Fig. 1: Diagram F versus Mn/(Mn+Fe) representing the chemical compositions of triplite, triploidite, wolfeite and zwieselite found in the literature and based on our experimental findings.

The crystal structure of this primary phosphate was first solved by Waldrop (1969) on a sample from Mica Lode, Freemont County, Colorado. The

chemical composition of such a sample was previously reported by Heinrich (1951): $(Mn_{0.95}, Fe_{0.27}, Mg_{0.69}, Ca_{0.08})_{\Sigma 1.99}(PO_4)(F_{0.91}, OH_{0.03})_{\Sigma 0.94}$

The crystal structure of triplite was refined by Waldrop in the space group $I2/a$ with the following unit-cell constants: $a=12.065(1)$, $b=6.454(1)$, $c=9.937(1)$ Å and $\beta=107.093(6)$ °. The structure is composed by isolated PO_4 tetrahedra joined on the vertices to distorted MO_4F_2 octahedra. The octahedra M(1) and M(2) are linked into chains by shared edges. The chains of M(1) octahedra are parallel to [010], those of M(2) parallel to [100]. According to the structure model of Waldrop (1969), fluorine is distributed between two mutually exclusive sites, with partial site occupancy, only ~0.62 Å apart. Waldrop (1969) reported that, in the sample from Mica Lode, Mn and Fe appear to be disordered in the two octahedral sites.

During a field survey in Codera valley (Novate Mezzola, Sondrio province, northern Italy), one of the authors (A.G.) found some masses of triplite up to 5 mm, hosted in a granitic pegmatite dike, and in close association with fluorapatite, Mn-rich elbaite and Mn-oxides. In thin section, triplite occurs in rounded masses deeply fractured; fractures are sharp and filled by Mn oxides. Under polarized light, the mineral is colorless, pleochroism is absent, and no evidence of alteration was detected. Triplite from Codera valley is biaxial (+) with a very high relief and anomalous interference colors up to first-order red. Tiny grains of fluorapatite occur inside the triplite masses, mainly located along fractures. Phosphate masses, hosted by feldspar, are rimmed by poly-granular quartz and albite lamellae. Electron-microprobe chemical analyses in wavelength dispersive mode revealed a composition very close to the end-member, and with the following empirical formula $(Mn^{2+}_{1.75}Fe^{2+}_{0.10}Ca_{0.10}Mg_{0.01})_{\Sigma 1.96}(PO_4)F_{1.00}$. The almost total absence of OH^- is confirmed by Raman spectroscopy. The presence of a very small Raman band ascribable to the OH^- stretching modes, at 3498 cm^{-1} , is visible only when using the 473.1 nm laser line (the most sensitive one to OH^- groups). This weak OH^- band is also visible at 3485 cm^{-1} on the infrared spectrum of triplite from Codera. The single-crystal structure refinement confirms the general model previously described by Waldrop (1969) for a natural triplite and by Rea & Kostiner (1972) for a synthetic $Mn_2(PO_4)F$ compound. The main difference with the structure model reported by Waldrop (1969) concerns the F site. Our data led to one independent F site with full site occupancy, whereas Waldrop (1969) reported two mutually

exclusive F sites with partial site occupancy, being only ~0.62 Å apart, with unusually high anisotropic displacement parameters if compared to the other O sites. In her comparative study of the crystal structure of triplite and triploidite (i.e. $(Mn,Fe)_2PO_4(OH)$), Waldrop (1970) considered the analogy of the split of the F site in two subsites in triplite (mutually exclusive) and that of the OH^- sites in triploidite. However, in the latter, the split leads to an ordered distribution with distinct OH^- sites with full occupancy and a doubling of the cell volume ($a = 12.366$, $b = 13.276$, $c = 9.943$ Å, $\beta = 108.23^\circ$, space group $P2_1/a$). Such a configuration appears to be ascribable to the proton-metal repulsion. Despite Waldrop (1970) not considering the possibility of a solid solution along the triplite-triploidite join, as the different F/OH environments make the structure non-isotypic, the chemical composition of triplites and triploidites reported in the literature appear to show a potential F/OH substitution. Likely, the structure of triplite can preserve its metrics and symmetry (i.e. $a = 12.109$, $b = 6.516$, $c = 10.117$ Å, $\beta = 106.16^\circ$, space group $I2/a$) even with a modest F/OH substitution. Such a behaviour was observed in several F/OH-bearing minerals, in which the end-members of the solid solution have different symmetry [e.g. topaz: $Al_2SiO_4(F,OH)_2$]. The chemical analysis of the sample of triplite used by Waldrop (1969) was performed by Henrich (1951), and appeared to contain only a modest amount of hydroxyl [i.e. $(Mn_{0.95}, Fe_{0.27}, Mg_{0.69}, Ca_{0.08})_{\Sigma 1.99}(PO_4)(F_{0.91}, OH_{0.03})_{\Sigma 0.94}$]. In their structure refinement of the synthetic $Mn_2F(PO_4)$ compound, Rea and Kostiner (1972) found only one F site, according to our experimental findings.

References:

- Hausmann, J.F.L. (1813) *Handbuch der Mineralogie*. 1st edition, 3 volumes, Göttingen, 3, 1079.
- Henrich, E.W. (1951) Mineralogy of triplite. *American Mineralogist*, 36, 256-271.
- Rea, J.R. and Kostiner, E. (1972) The crystal structure of manganese fluorophosphates, $Mn_2(PO_4)F$. *Acta Crystallographica*, B28, 2525-2529.
- Simmons, W.B., Webber, K.L., Falster, A.U. & Nizamoff J.W. (2003) *Pegmatology: pegmatite mineralogy, petrology & petrogenesis*. Rubellite Press, New Orleans.
- Vauquelin, L.N. (1802) Phosphate natif de fer melangé de manganèse. *Journal des Mines*, 11, 295.
- Waldrop, L. (1969) The crystal structure of triplite, $(Mn,Fe)_2FPO_4$. *Zeitschrift für Kristallographie*, 130, 1-14.
- Waldrop, L. (1970) The crystal structure of triploidite and its relation to the structures of other minerals of the triplite-triploidite group. *Zeitschrift für Kristallographie*, 131, 1-20.