

Phosphate associations in the granitic pegmatites: the relevant significance of these accessory minerals

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Owing to their flexible crystallochemical properties, and to their ability to form complex mineral parageneses, phosphate minerals constitute accessory minerals sensitive to the different evolution stages of the granitic pegmatites.

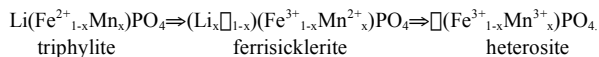
A review of the literature shows us that numerous authors already had this conviction. P. Quensel and B. Mason are certainly among the pioneers, when they investigated in details the phosphate minerals of the Varuträsk pegmatite, Sweden.

The significance of the phosphate minerals will be envisaged in the following stages of the pegmatites.

The first one is the “primary” stage or the magmatic stage. Occurrence of phosphates in a pegmatite involves various and valuable informations about the geochemical properties of the rest-magma: the presence of triphylite, $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$, and the Li content (Varlamoff, 1958-1959), the F/OH ratio in the amblygonite-montebasite solid solution, $\text{LiAlPO}_4(\text{F},\text{OH})$, and the F content of the pegmatitic melt (London *et al.*, 2001), the P content of the melt (Roda *et al.*, 2004). Moreover, the degree of fractionation of the pegmatites can be also derived from the evolution of the Fe/Mn ratio in the triphylite-lithiophilite series, or in the zwieselite-triplite series, $(\text{Fe},\text{Mn},\text{Mg})\text{PO}_4\text{F}$. The evolution of this ratio can be parallelized with its behaviour in other Fe – Mn-bearing accessory minerals (columbo-tantalite minerals, the almandine-spessartine series).

The metasomatic stage deeply influences the phosphate parageneses. The role of Na is particularly prevailing. Formation of alluaudite in the Fe-Mn phosphates, and formation of lacroixite, NaAlPO_4F , in the Al-rich phosphate associations are absolutely remarkable. Relations between lacroixite and brazilianite, $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4$, will be briefly discussed.

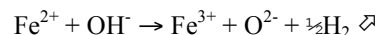
A tricky problem concerns the Quensel – Mason’s sequence, corresponding to the topotactic transformation of triphylite into ferriscklerite, after into heterosite,



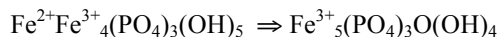
This sequence is famous, frequent, and poorly known. It represents a progressive oxidation of Fe, and of Mn, concomitant to a Li-leaching. The Fe/Mn ratio is preserved. Oxidation of Fe and concomitant leaching of Na is also known in the minerals of the alluaudite-group.

The influence of the hydroxylation stage, the hydrothermal alteration of low temperature, is also prominent. At the beginning of this transformation stage, it seems that a paragenesis huréaulite, $(\text{Mn},\text{Fe})_5(\text{PO}_4)_2(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ – barbosalite, $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2$ – tavorite, $\text{LiFe}(\text{PO}_4)\text{OH}$, is

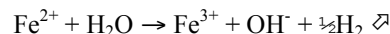
formed, and the Fe/Mn ration of the whole assemblage is virtually identical than of the parent triphylite. During this stage, it seems that the role of Ca is also relevant. These transformations affect both the Fe-Mn phosphates and the Al-rich phosphates. We observe formation of Ca-rich zones within alluaudite of metasomatic origin, formation of a fluorapatite rim, development of the jahnsite-group minerals. In the Al-rich phosphates associations, we observe the formation of bertossaite, $\text{Li}_2\text{CaAl}_4(\text{PO}_4)_4(\text{OH})_4$. The relative abundance of Ca-rich secondary phosphates seems to be in close relationship with the degree of fractionation of the pegmatite. Other oxidation processes of Fe may also be detected, occurring during the late hydrothermal stage. Owing to crystal structure refinements, Moore (1982) described the auto-oxidation process, preserving both the crystal structure and the Fe/Mn ratio, according to the reaction



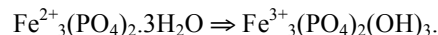
e.g. during oxidation of rockbridgeite,



or to the reaction



e.g. during transformation of phosphoferrite into kryzhanovskite,



When the temperature is decreasing, the behaviour of Fe and Mn tends to become more and more independent. Roughly, Mn forms oxides or hydroxides, whereas Fe, mainly Fe^{3+} , is still engaged in phosphate minerals.

The weathering also produces complex and interesting phosphate associations. These associations are strongly influenced by the geochemical character of the previous transformations of the primary phosphates. Moreover, the nature of the climate seems to be very determinative in the development of some phosphate mineral species: vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, or phosphosiderite, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. The pH variations during pedogenesis also play a role in the crystallization, of variscite, $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$, or wavellite, $\text{Al}_3(\text{PO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$.

Since the presidential address of Fisher (1958), little progress has been made. The revenge of the pegmatite phosphates is evident but their problems are far from being solved.

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