# PHOSPHATE MINERAL ASSOCIATIONS IN THE CEMA PEGMATITE (SAN LUIS PROVINCE, ARGENTINA): PARAGENESIS, CHEMISTRY AND SIGNIFICANCE IN THE PEGMATITE EVOLUTION

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## ABSTRACT

Fe-Mn phosphates nodules are common in the border core unit of the Cema pegmatite (San Luis range, Argentina). Two different complex phosphates associations have been distinguished in these nodules. One of them is lithiophilite-sicklerite-rich (LS), with varulite and hureaulite as the main secondary products, Fe/(Fe+Mn) values in the range 0.37-0.39, and MgO contents always below 1 wt%. The other association is sicklerite-beusite-qingheiite-rich (SBQ), with varulite and joosteite as the main replacement products, higher Fe/(Fe+Mn) values, between 0.46-0.48, and also higher MgO values, up to 2.14 wt%. According to the mineralogical and chemical data, a higher temperature of crystallization is proposed for the SBQ association in relation to the LS one. On the other hand, the important Mn enrichment observed in these phosphates, in a pegmatite that is not extremely fractionated, could be explained as a result of the previous crystallization of other Fe-(Mg-Mn)-rich minerals, such as almandine and schorl, in the border and external zones of this pegmatite. The crystallization of these silicates would have strongly depleted the activity of Fe in the remaining pegmatite melt.

**Keywords:** fluid inclusion, $^{40}Ar/^{39}Ar$ dating, Moslavačka Gora

## INTRODUCTION

Pegmatites are common in the northeastern part of the San Luis range (Argentina). Many of these bodies are enriched in phosphorus, frequently showing phosphates nodules where complex associations occur. Such is the case of the P-Li-Be-B-bearing Cema pegmatite, located at 32º34´52" S and 65º24´51" W, in the Libertador General San Martín Department. This pegmatite belongs to the Conlara pegmatite field, situated in the northern part of the Eastern Pampean Ranges of San Luis (Galliski, 1994). The crystalline basement in this part of the range is composed by eopaleozoic rocks belonging to the Conlara Metamorphic Complex (Sims et al. 1997), composed dominantly by gneisses and pelitic schists.

During the Ordovician, these rocks were intruded by S-type granites and the associated pegmatitic bodies. In the case of the Cema pegmatite, it mainly intrudes into gray-colored mica schists, and also partly into a dioritic lens in its NW part.

In this study the phosphates associations of the Cema pegmatite are described, taking into account their textural features and chemistry. Moreover, an interpretation of the role played by these phosphates in the internal evolution of the pegmatite is given, discussing the possible influence of other Fe-(Mg-Mn)-bearing minerals occurring in this body.

## GENERAL GEOLOGY OF THE PEGMATITE

The Cema pegmatite is a discordant body, with a NS strike, dipping 52° to the SW. It has an irregular shape, with a length of 100 m and a thickness difficult to estimate, as only the upper part of the pegmatite crops out. Taking into account the thicknesses of the different structural units, the whole pegmatite may show just a few meters between the contacts. The Cema body presents a complex inner zonation, with an asymmetric development. The following zones have been recognized: border zone, external zone, intermediate zone and core zone, in addition to a border core unit and two replacement units. The presence of Fe-(Mg-Mn) rich silicates as tourmaline (schorl) and garnet (almandine) in the border and in the external zones is remarkable. It is also noteworthy that spodumene crystals, up to 40 cm in length, constitute one of the main minerals in the quartz-core zone. The phosphates occurring in the Cema pegmatite are associated with the border core unit, where they appear together with subhedral beryl crystals, up to 10 cm in size. Phosphates occur as yellowish ellipsoidal masses, 0.1 to 1 m in size, inside the quartz. Finally, two different replacement units have been distinguished in the Cema pegmatite. The first one is albite rich, and could be related to an episode of Na-metasomatism, after the primary crystallization of the pegmatite, already in a sub-solidus stage; whereas the second one, muscovite-rich, could have developed during a hydrothermal greissenification stage, presumably at a lower temperature.

## DATA COLLECTION AND ANALYSES

The studied phosphate samples were collected from the walls of the open pit, from different nodules. Mineral identification was carried out by a combination of petrographic, powder X-ray diffraction, and electron microprobe techniques. Chemical analyses were performed at the Université Paul Sabatier (Toulouse, France), with a Camebax SX 50 electron microprobe. The operating conditions were: voltage of 15 kV and a beam current of 20 nA for all elements. The standards used for the phosphates are: CaF2 for F, albite for Na, andradite for Fe, Ca and Si, graftonite for Mn and P, titanite for Ti, olivine for Mg, and ZnS for Zn.

## PETROGRAPHY AND CHEMISTRY OF PHOSPHATES

Up to now more than twenty different phosphate minerals have been identified in the Cema pegmatite (Table 1). It is remarkable that, in general, these phosphates are mostly Mn-rich, with lower contents in Fe, and relatively high Mg contents for some of them. Many of the identified phosphates correspond to late/secondary phases, however, some primary and/or early secondary phosphates also occur, such as lithiophilite, beusite,

triploidite, qingheiite, dickinsonite, sicklerite, joosteite and varulite.

Two different phosphate associations may be distinguished in Cema. In one of them colourless lithiophilite is abundant, being frequently pseudomorphosed partially by orange-yellowish sicklerite and/or deep yellow varulite. Strongly pleochroic hureaulite and rockbridgeite are also common alteration products of lithiophilite, together with very dark lipscombite. In the second association lithiophilite has not been detected up to now, and sicklerite seems to be a primary phase. It occurs with a granoblastic texture, together with colourless beusite and olive green qingheiite. Sicklerite is partially pseudomorphosed by deep yellow varulite, whereas black joosteite is another replacement product, occurring frequently in some triple points between the sicklerite crystals.

In addition to the textural relationships, chemical composition of phosphates also helps to establish the interrelationships between some of these phases. Fe/(Fe+Mn) is in general lower than 0.5 for the earliest phases, whereas for the latest phosphates this ratio shows broader values. In the lithiophilite-rich association this phosphate and its replacement products, sicklerite and varulite, show similar Fe/(Fe+Mn) ratios (0.37-0.39), and MgO values always lower than 1 wt.%. In the second association sicklerite shows higher Fe/(Fe+Mn) ratios (0.46-0.48) and contents in MgO up to 2.14 wt.%. In this association varulite and joosteite also inherit the Fe-Mn-Mg proportions of the preliminary phase.

## DISCUSSION

Taking into account the mineralogy and the chemistry of the different phases, the Li-P-B-Be-bearing Cema pegmatitic body may be classified as an intermediate to highly evolved pegmatite. Phosphates occurring in the border core unit indicate that P behaved as an incompatible element till intermediate stages of pegmatitic crystallization, when saturation in P was attained, as it is reported in other phosphate-bearing pegmatites (Roda et al., 1998, Roda et al., 2004). Two different phosphate associations may be distinguished in Cema: on one hand, the lithiophilite-rich association and, on the other hand, the sicklerite-beusite-qingheiite association. The former showing lower Fe/(Fe+Mn) ratios and Mg contents. Taking into account that usually these two values decrease as the pegmatite evolution degree increases, we could consider that the sicklerite-beusite-qingheiite association crystallized first when, on the other hand, the Li activity in the pegmatite melt was lower. At lower temperatures, and with higher Li activity in the melt, the lithiophilite-rich association would have formed.

Table 1. List of the identified phosphate minerals from the Cema pegmatite

| Mineral name | Formula | Association | |
|---|---|---|---|
| | | LS | SBQ |
| lithiophilite | $Li(Mn,Fe)PO_4$ | ++++ | o |
| sicklerite | $Li_{1-x}(Mn_{1-x},Fe^{3+}_{x})PO_4$ | ++++ | ++++ |
| beusite | $(Mn,Fe^{2+},Ca)_3(PO_4)_2$ | o | +++ |
| triploidite | $(Mn,Fe)_2(PO_4)OH$ | + | o |
| qingheiite | $Na_2(Mn,Mg,Fe^{2+})_2(Al,Fe^{3+})(PO_4)_3$ | + | ++ |
| varulite | $NaCaMn(Mn,Fe^{2+},Fe^{3+})_2(PO_4)_3$ | +++ | +++ |

| | | | |
|---|---|---|---|
| joosteite | $Mn^{2+}(Mn^{3+},Fe^{3+})(PO_4)O$ | o | ++ |
| apatite | $Ca_5(PO_4)_3(OH,F,Cl)$ | ++ | ++ |
| dickinsonite | $KNa_4Ca(Mn^{2+},Fe^{2+})_{14}Al(PO_4)_{12}(OH)_2$ | o | + |
| huréaulite | $Mn_5(PO_4)_2[PO_3(OH)]_2.4H_2O$ | +++ | o |
| eosphorite | $(Mn,Fe)Al(PO_4)(OH)_2.H_2O$ | o | + |
| rockbridgeite | $(Fe,Mn)^{2+}Fe^{3+}_4(PO_4)_3(OH)_5$ | ++ | o |
| jahnsite | $CaMn(Mg,Fe^{2+})_2Fe^{3+}_2(PO_4)_4(OH)_2.8H_2O$ | ++ | + |
| lipscombite | $(Fe^{2+}Mn)Fe^{3+}_2(PO_4)_2(OH)_2$ | + | o |
| gorman.-souzalite | $(Fe^{2+},Mg)_3(Al,Fe^{3+})_4(PO_4)_4(OH)_6.2H_2O$ | o | + |
| leucophosphite | $KFe_2(PO_4)_2(OH).2H_2O$ | + | o |
| phosphoferrite | $(Fe^{2+},Mn)_3(PO_4)_2.3H_2O$ | + | o |
| isoclasite | $Ca_2(PO_4)(OH).2H_2O$ | o | + |
| lazulite | $MgAl_2(PO_4)_2(OH)_2$ | o | + |
| reddingite | $Mn_3(PO_4)_2.3H_2O$ | + | o |
| pararobertsite | $Ca_2Mn^{3+}_3(PO_4)_3O_2.3H_2O$ | o | + |
| tavorite | $LiFe^{3+}(PO_4)(OH)$ | + | o |

LS: lithiophilite-sicklerite association; SBQ: sicklerite-beusite-qingheiite association. The abundance in each association is given as: ++++ = abundant, +++ = commonly present, ++ = rare, + = very rare, o = absent.

On the other hand, the extremely low values for the Fe/(Fe+Mn) ratio shown by most of the phosphates from Cema seem too low taking into account the mineralogy of the whole pegmatite, considered intermediate to highly evolved. The occurrence of other Fe-rich minerals, such as tourmaline (schorl) and garnet (almandine), both relatively abundant in the border and in the external zones of the pegmatite could be related with this Mn-enrichment, as it is reported for the Santa Ana pegmatite, farther south (Galliski et al., in press). The previous crystallization of these silicates could have depleted significantly the concentration in Fe in the pegmatitic melt, where usually the primary concentration of metal transition cations is low. This way, the primary growth of schorl and almandine would have strongly influenced the chemistry of phosphates in the Cema body, favouring relatively low Fe/(Fe+Mn) ratios in relation to the degree of evolution of the hosting pegmatite.

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