

Phosphate minerals of some granitic rocks and associated quartz veins from northern and central Portugal

Fosfáty granitických hornin a je doprovázejících křemenných žil ze severního a středního Portugalska.

(7 text-figs, 6 tabs)

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Phosphate minerals are common in northern and central Portuguese granitic rocks. Childrenite, eosphorite and intermediate compositions in this solid-solution series occur in muscovite granites at Paredes da Beira and Penamacor-Monsanto, muscovite-biotite granites at Penamacor-Monsanto and in aplite veins at Vidago. The compositions of childrenite and eosphorite are similar in each of these localities. Gormanite occurs in a muscovite granite at Segura. Triphylite is altered to strengite in the muscovite granite at Paredes da Beira, and to manganoo vivianite from $(\text{Fe}_{2.1}\text{Mn}_{0.1}\text{Mg}_{0.3})$ to $(\text{Fe}_{1.9}\text{Mn}_{0.9}\text{Mg}_{0.2})$, blue ludlamite, phosphoferrite and mitridatite in Vidago aplite. Green ludlamite and brushite were also found in aplite at this locality. Montebrasite and natromontebrasite were found in Li-aplite-pegmatite veins from Gonçalo and Segura. Mimetite with As/P ratio of 1.04 and a kintoreite-like phase are alteration products of galena in quartz veins at Segura.

Key words: triphylite, vivianite, childrenite, eosphorite, brushite, phosphoferrite, ludlamite, mitridatite, strengite, perloffite, montebrasite, natromontebrasite, gormanite, mimetite, kintoreite.

Introduction

Hercynian granitic pegmatites and quartz veins from the territory of Portugal are world-famous for some of their mineral occurrences in general, and of phosphates in particular. The granitic pegmatites at Mangualde, hydrothermal tungsten-tin quartz veins at Panasqueira and weathered outcrops of uraninite veins at Sabugal yielded significant contributions to the understanding of these important accessory phases (Fron del 1951, Isaacs et al. 1979, Dunn et al. 1988, Cossato et al. 1989, Grice et al. 1990) and they also expanded the mineralogical system by the species jahnsite $\text{CaMnMn}_2\text{Fe}^{3+}_2(\text{PO}_4)_4(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, panasqueirite $\text{CaMg}(\text{PO}_4)(\text{OH}, \text{F})$, rittmannite $(\text{Mn}^{2+}, \text{Ca})\text{Mn}^{2+}(\text{Fe}^{3+}, \text{Mn}^{2+})_2(\text{Al}, \text{Fe}^{3+})_2(\text{PO}_4)_4(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, sabugalite $\text{HAl}(\text{UO}_2)_2(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$, thadeuite $(\text{Ca}, \text{Mn}^{2+})(\text{Mg}, \text{Fe}^{2+}, \text{Mn}^{2+})_3(\text{PO}_4)_2(\text{OH}, \text{F})_2$ and zodacite $\text{Ca}_2\text{MnFe}^{3+}_4(\text{PO}_4)_8(\text{OH})_4 \cdot 12\text{H}_2\text{O}$. However, all the phosphate-bearing pegmatites and hydrothermal quartz veins examined so far are located in central Portugal. In the present paper, we report on phosphate occurrences in northern Portugal (site for the projected Vidago dam and Paredes da Beira) and other localities in central Portugal (Gonçalo, Penamacor-Monsanto and Segura) (Fig. 1).

Localities and paragenetic relationships

The studied phosphate minerals occur in granitic, plutonic rocks, granitic pegmatites and associated quartz veins from five selected Portuguese localities (Fig. 1). The granitic rocks are peraluminous, S-type and Hercynian in age (Silva – Neiva 1990, Neiva – Campos 1992, Ramos 1998, Antunes 1999).

Vidago

At the site for the projected Vidago dam across the Tamega river, northern Portugal, Hercynian aplite veins intruded Silurian schists and metagraywackes. Phosphate samples from boreholes were studied. The aplite contains quartz, microcline, albite, muscovite, schorl, zircon, apatite, other phosphates and siderite.

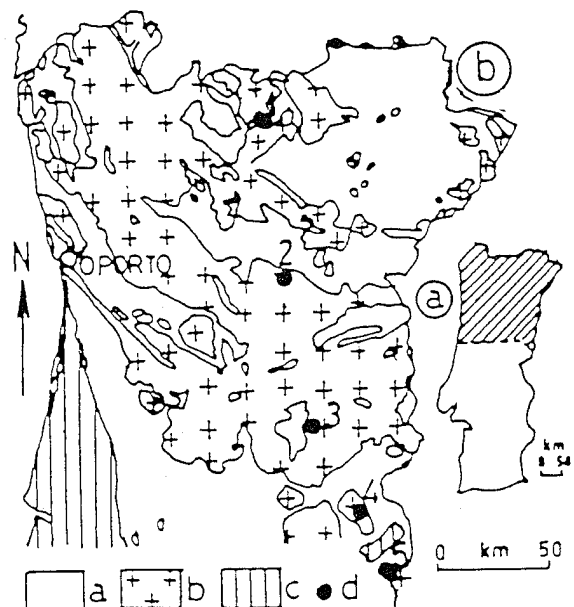
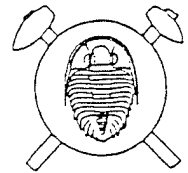


Fig. 1a. Location of Fig. 1b on the map of Portugal. b. Location of the areas chosen to study the phosphate minerals. a. Cambrian metamorphic complexes, Paleozoic, some igneous and ultrabasic rocks; b. Hercynian granitic rocks; c. Mesozoic and Cenozoic sedimentary rocks; d. the areas selected – 1: site for the projected Vidago dam, 2: Paredes da Beira, 3: Gonçalo, 4: Penamacor-Monsanto, 5: Segura.



Primary colorless triphylite occurs in euhedral crystals ranging from 80 x 30 μm up to 300 x 200 μm . It is rarely rimmed and penetrated along fractures by vivianite (Fig. 2), pleochroic from blue to brownish. This mineral (100 x 60 μm) also penetrates between quartz and albite. Other triphylite crystals are locally rimmed by ludlamite, pleochroic from blue to colorless, which



Fig. 2. Triphylite (t) from the Vidago aplite altered to vivianite (v) along fractures, in plane polarized light (x 25).

also surrounds muscovite and penetrates silicate minerals. Siderite also surrounds some triphylite crystals.

Irregular yellowish brown crystals of eosphorite up to 3.2 x 2.6 mm are locally rimmed by colorless brushite. Phosphoferrite occurs in irregular green crystals (3 x 2 mm). Very rare irregular crystals (200 x 100 μm) of brown to greenish brown perloffite were also found.

In other samples, bright green to apple green ludlamite and greenish-brown mitridatite occur in veinlets of 1.3 x 0.02 mm cutting the silicate minerals, mainly plagioclase, but mitridatite rarely surrounds muscovite.

Paredes da Beira - Penedono

At Paredes da Beira - Penedono, northern Portugal, several two-mica granites and a few bodies of muscovite granite intrude a Cambrian schist-metagraywacke complex. The medium-grained, locally porphyritic, muscovite granite contains quartz, microcline, albite, muscovite, rare bi-

otite, tourmaline, apatite, zircon, ilmenite, rutile and rare monazite (Silva - Neiva 1990). Locally, this granite contains other phosphates besides apatite. Euhedral greenish gray to gray crystals of triphylite ranging from 1.5 x 1.1 mm to 2.2 x 1.0 mm are locally rimmed by brown childrenite, but others are rimmed by violet strengite. Irregular crystals of childrenite (0.24 x 0.18 mm) also occur.

Gonçalo

At Gonçalo, central Portugal, Hercynian subhorizontal granitic aplite-pegmatite veins, up to 3.5 m thick, intrude a Cambrian schist-metagraywacke complex, two-mica granites and muscovite granites. Three types of aplite-pegmatite veins were distinguished (Ramos 1998). 1) Stanniferous veins occur at a relatively lower level, are of beige colour, unzoned, non-layered, and contain quartz (2-5 cm up to 15-20 cm diameter), K-feldspar (up to 50 x 15 cm), albite (2 x 1 cm), muscovite (1 mm - 1 cm), cassiterite (1 mm - 1 cm), amblygonite, zinnwaldite, rare montebrasite, lepidolite, topaz, beryl, cassiterite, manganocolumbite, tourmaline, zircon, monazite and rutile. They were exploited for tin. 2) The Li-rich veins occur at a higher level, are layered and locally zoned, of pinkish lilac colour due to abundant purple lepidolite, some pale pink petalite and rare spodumene. They also contain quartz (up to 5 x 5 cm, but rarely up to 15 x 10 cm), K-feldspar (2 x 1 cm, up to 15 x 10 cm), albite (up to 3 x 1 cm), muscovite, zinnwaldite, lepidolite, petalite (up to 2 x 3 cm), apatite, montebrasite, natromontebrasite, topaz, beryl, cassiterite, manganocolumbite-manganotantalite, microlite, tourmaline, zircon, monazite and rutile. They are finer-grained, more complex, evolved, richer in Na, Mn, Li, Rb, Sr, Nb, Ta and poorer in Si, K, Fe, Be and Sn than the stanniferous veins. 3) The mixed aplite-pegmatite veins are located between the stanniferous veins and Li-rich veins, and have an intermediate composition.

Montebrasite occurs in the three types of aplite-pegmatite veins, but natromontebrasite was only found in the Li-rich aplite-pegmatite veins. These two phosphates occur in the early zones of pegmatite crystallization, are contemporaneous with K-feldspar, surrounded by albite and corroded by lepidolite, albite and quartz. Montebrasite and natromontebrasite occur mainly in subhedral single crystals, ranging from 50 μm to 1 cm, commonly twinned, but also with montebrasite/natromontebrasite cores and natromontebrasite/montebrasite outer parts.

Penamacor-Monsanto

At Penamacor-Monsanto, central Portugal, a Hercynian zoned granite pluton intrudes the Cambrian schist-metagraywacke complex. The granite consists mainly of a coarse- to medium-grained porphyritic biotite-muscovite granite (GI) at the border and a coarse-grained porphyritic muscovite-biotite granite (GII) in the core. However minor medium-grained porphyritic biotite-muscovite granite (GIII) occurs in an intermediate zone between the

other two granites and it evolves into a muscovite-biotite granite (GIIIFr) which locally surrounds GI (Neiva – Campos 1992).

Unaltered granites are rare and most outcrops display hydrothermal alteration. The altered granites contain quartz, kaolinized micropertitic microcline, albite (locally microclinized), biotite locally replaced by muscovite, chlorite, andalusite partially altered into muscovite, sillimanite, apatite, monazite, zircon, ilmenite, rutile and later subhedral or radial muscovite replacing feldspars. The most altered granites (GIIIFrb and GIIIC) do not contain biotite, but they also have cassiterite, abundant phosphates and rare sulphides (Neiva – Campos 1993). Primary phosphates are not preserved. Childrenite and eosphorite are the most common secondary phosphates, and strengite was only found in one of the least altered granites (Table 1).

Childrenite and eosphorite occur as anhedral yellowish brown crystals ranging from 60 x 50 μm to 1.8 x 0.4 mm and in white veinlets cutting all other minerals. Childrenite contains inclusions of apatite. Rare zoned crystals with a core of childrenite and a rim of eosphorite were locally found.

Segura

At Segura, central Portugal, a Hercynian two-mica granite, muscovite granite, granodiorite porphyry and Li-bearing granitic aplite-pegmatite veins containing cassiterite and lepidolite intrude the Cambrian schist-metagraywacke complex. Aplite veins intrude this complex and granites, whereas quartz veins with cassiterite and wolframite intersect the schist-metagraywacke complex. Quartz veins with barite, galena and sphalerite intersect this complex and the muscovite granite.

The muscovite granite contains quartz, microcline, albite, muscovite, rare biotite, hydroxylapatite, fluorapatite, zircon, rutile and gormanite. Gormanite occurs in anhedral crystals, of average dimensions of 500 x 100

μm . It is pleochroic from blue to bluish green and is surrounded by quartz crystals.

The Li-bearing granitic pegmatites contain quartz, microcline, albite, muscovite, apatite, montebrasite, natromontebrasite, topaz, lepidolite, cassiterite, columbite, zircon and rutile (Antunes 1999). Montebrasite and natromontebrasite are associated with montebrasite/natromontebrasite cores and natromontebrasite/montebrasite outer parts. They are subhedral, 3 x 2 mm in size, and partially replaced by muscovite.

Quartz veins contain apatite, muscovite, chlorite, cobaltite, pyrite, sphalerite, chalcocopyrite, barite, galena, anglesite, mimetite, kintoreite and limonite. Mimetite and kintoreite are anhedral, white, they occur in veinlets along fractures as a replacement of galena and are associated with anglesite.

Experimental

The various phosphate minerals have been identified by their optical properties in transmitted light and by electron-microprobe analyses (Table 1). They were analyzed on a Cameca Camebax electron-microprobe at the Geological and Mining Institute, S. Mamede de Infesta, Portugal. Analyses were conducted at an accelerating voltage of 15 kV and a beam current of 20 nA. Standards include apatite (PK α), wollastonite (CaK α), Fe₂O₃ (FeK α), MnTiO₃ (MnL α), MgO (MgK α), Al₂O₃ (AlK α), albite (NaK α), LiF (FK α), vanadinite (ClK α), barite (SK α), galena (PbM α), pure (CuK α) and arsenopyrite (AsL α). Each element was counted for 20 seconds. ZAF corrections were applied.

Chemical composition of the phosphates

Triphylite

Triphylite LiFe²⁺PO₄ and lithiophilite LiMn²⁺PO₄ are end-members of a solid-solution series, the natural mem-

Table 1. List of the identified phosphate minerals in some granitic rocks and associated quartz veins from northern and central Portugal

Locality	Rock type	Phosphate minerals	
		Primary	Secondary
Vidago	aplite veins	triphylite	vivianite, blue ludlamite, phosphoferrite, eosphorite, brushite, perloffite, green ludlamite, mitridatite
Paredes da Beira	muscovite granite	triphylite	childrenite, strengite
Gonçalo	aplite-pegmatite veins	montebrasite natromontebrasite	
Penamacor-Monsanto	granites GIIIIa GIIIIFra GIIIIFrb GIIIIc		strengite childrenite, eosphorite childrenite childrenite, eosphorite
Segura	muscovite granite Li-bearing pegmatite barite-galena-sphalerite quartz veins	montebrasite natromontebrasite	gormanite mimetite, kintoreite

a, b, c – increasing degree of hydrothermal alteration. GIIIIa, GIIIIFra – medium-grained porphyritic muscovite-biotite granites; GIIIIFrb – medium-to coarse-grained muscovite-biotite granite; GIIIIc – medium to coarse-grained porphyritic muscovite granite.

bers of which cover virtually the whole range of possible compositions (Gaines et al. 1997). Samples from Vidago and Paredes da Beira (Table 2) show significant difference in Fe/Mn. This ratio changes in dependence on the temperature of crystallization, Mn normally increasing with decreasing temperature (e. g. Keller et al. 1994, Fransolet et al. 1997). However, Fe/Mn also significantly depends on its initial value in the bulk composition of the parent system, and on the presence or absence of competing phases. Thus assigning a difference in temperature of crystallization between our two localities is not an easy task, despite the very substantial compositional difference between the two triphylite occurrences. Nevertheless, the much more advanced degree of fractionation at Vidago (Fig. 3) is beyond dispute, whatever may be the reason.

Vivianite

Electron-microprobe analysis of the blue to brownish phosphate which surrounds the Vidago triphylite yielded a composition (Fig. 2, Table 2, 1a) which gives a simple integral stoichiometry of the main components $(\text{Fe}^{2+}_{1.94}\text{Mn}_{0.86}\text{Mg}_{0.18})_{\Sigma 2.98}(\text{PO}_4)_2$. Remainder to 100 wt %, over and above the anhydrous components is equal to

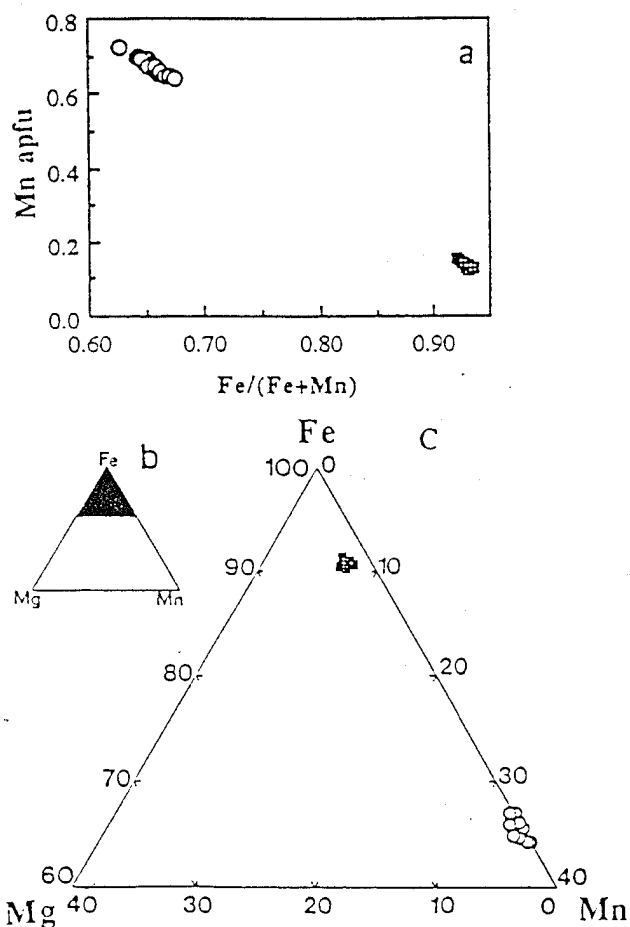


Fig. 3. Compositions of triphylite from Vidago aplite and Paredes da Beira muscovite granite. a: Mn - Fe/(Fe+Mn) diagram; b, c: Fe - Mn - Mg diagrams, with b showing the location of c. Symbols: ○ - Vidago, ■ - Paredes da Beira.

$7\text{H}_2\text{O}$. Such water content corresponds to that of switzerite $(\text{Mn} > \text{Fe}^{3+})_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ (Zanazzi et al. 1986, White et al. 1986). The only other similar phosphate is vivianite, $\text{Fe}^{2+}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, which however, has $8\text{H}_2\text{O}$ and is not known to contain substantial Mn in any of its occurrences. However, X-ray diffraction study by M. A. Cooper, University of Manitoba, confirmed the structural identity with vivianite, which must have lost a part of its water content during the analysis. Besides this triphylite-related occurrence, a phosphate with the composition $(\text{Fe}^{2+}_{2.45}\text{Mn}_{0.39}\text{Mg}_{0.48})_{\Sigma 3.32}(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ (Table 2, 1b) was also found penetrating between quartz and albite. It is mainly richer in Fe and poorer in Mn than the previous composition. Figure 4 shows a negative correlation between Fe and Mn which indicates the dominant substitution $\text{Fe} \leftrightarrow \text{Mn}$.

Eosphorite-childrenite

Eosphorite $\text{Mn}^{2+}\text{Al}(\text{PO}_4)(\text{OH})_2 \cdot \text{H}_2\text{O}$ and childrenite $\text{Fe}^{2+}\text{Al}(\text{PO}_4)(\text{OH})_2 \cdot \text{H}_2\text{O}$ form a solid solution series. The childrenite in the muscovite granite from Paredes da Beira and altered muscovite-biotite granite GIIIFrb from Penamacor-Monsanto have a similar range in composition (Table 3, Fig. 5a, b). Childrenite is more Mn-rich in altered granites GIIIC and GIIIFra from Penamacor-Monsanto. Altered granite GIIIFra also contains Fe-rich eosphorite, and the eosphorite has a wide range in composition in altered granite GIIIC. However, the most Mn-rich eosphorite occurs in the aplite from Vidago.

Brushite

Brushite yields chemical compositions very close to its theoretical formula, with negligible Fe, Mn and Mg sub-

Table 2. Results of electron-microprobe analyses of some phosphate minerals of granitic rocks from northern Portugal

	Triphylite		Vivianite					
	1	σ	2	σ	1a	σ	1b	σ
P_2O_5	45.92	0.32	46.12	1.12	29.32	0.18	28.87	0.49
FeO	29.44	0.60	40.65	0.95	29.35	1.27	35.84	1.08
MnO	15.27	0.50	3.02	0.16	12.77	0.89	5.68	1.27
MgO	0.06	0.10	0.56	0.10	1.52	0.39	3.97	0.56
CaO	0.01	0.03	0.01	0.01	-	-	-	-
Li_2O^*	9.58	0.05	9.59	0.15	-	-	-	-
total	100.28		99.95		73.46		74.36	
P	2.018	0.006	2.024	0.025	2.000		2.000	0.097
Fe^{2+}	1.278	0.027	1.763	0.059	1.944	0.090	2.453	0.087
Mn	0.672	0.022	0.133	0.010	0.857	0.053	0.394	0.070
Mg	0.005	0.007	0.043	0.007	0.179	0.047	0.484	0.226
Ca	0.001	0.002	0.001	0.001	-	-	-	-
Li	2.000		2.000		-	-	-	-
Fe/Mn	1.90	0.09	13.16	0.82	2.27		6.54	1.57
n	13		11		12		10	

1 - aplite from Vidago; 2 - muscovite granite from Paredes da Beira. Atomic contents for triphylite normalized to 8 oxygen atoms; a - calculated by charge-balancing for 8 oxygen atoms and a fixed content of 2 lithium atoms. Atomic contents for vivianite calculated on the basis of 2P. - not detected; n - number of analyses

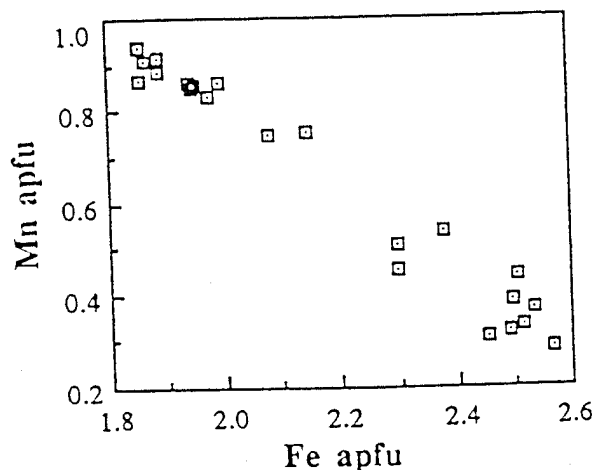


Fig. 4. The correlation between Fe and Mn in vivianite from Vidago aplite.

stituting for Ca (Table 3 and Fig. 5b). Remainder to 100 wt %, over and above the anhydrous components, is equal to H₂ and 3.87H₂O (Table 3).

Phosphoferrite and ludlamite

Phosphoferrite and ludlamite are similar in chemical composition, but they differ in their water contents, structure and symmetry: phosphoferrite (Fe²⁺,Mn²⁺)₃(PO₄)₂ · 3H₂O is orthorhombic whereas ludlamite (Fe²⁺,Mg,Mn)₃(PO₄)₂ · 4H₂O is monoclinic. They were both found at Vidago; their compositions give empirical formulas, normalized to 2P, of (Fe_{1.83}Mn_{0.86}Mg_{0.18})_{Σ2.87}(PO₄)₂ · 3.05H₂O for phosphoferrite and (Fe_{1.88}Mn_{0.34}Mg_{0.70})_{Σ2.92}(PO₄)₂ · 3.94H₂O for blue ludlamite in samples containing triphylite, and (Fe_{2.67}Mn_{0.14}Ca_{0.08}Mg_{0.05})_{Σ2.94}(PO₄)₂ · 3.76H₂O for green ludlamite in samples without triphylite. Ludlamite mainly rimming triphylite has higher Mg, Mn+Mg and lower Fe/Mn, Fe/Mg and Fe/(Fe+Mn+Mg) values than ludlamite lacking direct relationship to triphylite (Fig. 6 and Table 4). Phosphoferrite has a value of Fe/(Fe+Mn+Mg) ratio similar to that of blue ludlamite

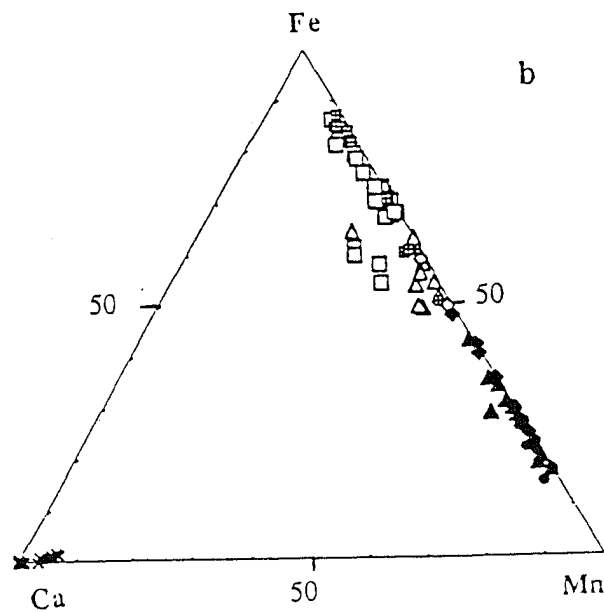
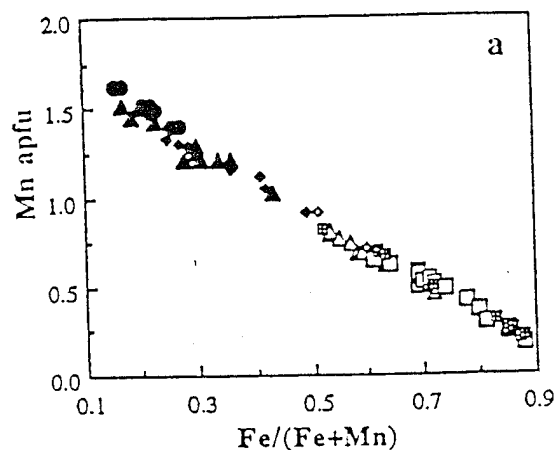


Fig. 5a, b, c. Compositions of eosphorite and childrenite from granitic rocks at Vidago, Paredes da Beira and Penamacor-Monsanto: b. also includes composition of brushite from Vidago aplite. a: Mn - Fe/(Fe+Mn) diagram; b: Fe - Mn - Ca diagram. Symbols: - eosphorite: ● - aplite from Vidago, ◆ - altered muscovite-biotite granite GIIIFra and ▲ - altered muscovite granite GIIIC from Penamacor-Monsanto; childrenite: ■ - muscovite granite from Paredes da Beira; ◇ - GIIIFra, □ - altered muscovite-biotite granite GIIIFrb and △ - GIIIC from Penamacor-Monsanto; × - brushite from Vidago aplite.

Table 3. Results of electron-microprobe analyses of some phosphate minerals of granitic rocks from northern and central Portugal

	Eosphorite						Childrenite						Brushite		
	1	σ	3a	σ	3c	σ	2	σ	3a	3b	σ	3c	σ	1	σ
P ₂ O ₅	31.15	0.36	32.55	0.37	31.59	0.93	31.66	0.86	32.53	32.26	1.19	32.94	0.70	41.10	0.46
FeO	6.60	1.13	10.33	2.59	8.07	2.33	31.13	3.83	16.33	20.27	1.64	16.24	1.35	0.25	0.23
MnO	23.43	1.16	19.17	2.42	20.87	2.23	6.89	3.68	13.13	7.58	1.93	11.65	1.95	0.98	1.00
MgO	0.41	0.26	0.20	0.13	0.27	0.22	0.51	0.41	0.76	0.57	0.53	0.27	0.31	0.05	0.08
CaO	0.19	0.23	0.10	0.07	0.26	0.26	0.39	0.18	0.26	0.68	0.86	0.83	0.73	32.19	1.52
Al ₂ O ₃	23.13	0.30	22.49	0.39	22.80	0.59	22.97	1.17	22.37	22.26	0.84	22.43	1.31	-	-
Total	84.91		84.84		83.86		93.55		85.38	83.62		84.41		74.57	
P	2.000		2.000		2.000		2.000		2.000	2.000		2.000		2.000	
Fe ²⁺	0.419	0.069	0.627	0.158	0.504	0.148	1.318	0.232	0.992	1.271	0.115	0.974	0.095	0.012	0.012
Mn	1.505	0.082	1.178	0.147	1.321	0.150	0.435	0.237	0.308	0.470	0.118	0.707	0.112	0.048	0.049
Mg	0.046	0.029	0.022	0.014	0.030	0.025	0.057	0.044	0.082	0.062	0.058	0.029	0.033	0.004	0.007
Ca	0.015	0.019	0.008	0.005	0.021	0.020	0.031	0.014	0.020	0.053	0.066	0.064	0.058	1.982	0.079
Al	2.067	0.038	1.923	0.041	2.009	0.043	2.020	0.133	1.914	1.921	0.113	1.900	0.083	-	-
n	9		8		17		12		2	25		9		23	

1-aplite from Vidago; 2-muscovite granite from Paredes da Beira. 3-hydrothermally altered granites from Penamacor-Monsanto: a-GIIIFra, b-GIIIFrb; c-GIIIC (see Table 1). Atomic contents calculated on the basis of 2 P. - not detected; n-number of analyses.

related to triphylite, but distinct by lower Fe/(Fe+Mn+Mg) and Fe/Mn values than green ludlamite not associated with triphylite (Table 4).

Mitridatite

Mitridatite is a hydrated CaFe^{3+} -phosphate which forms a substitution series with its Mn^{3+} -dominant analog, robertsite (Moore 1974). At Vidago, mitridatite yields the formula $\text{Ca}_{3.33}(\text{H}_2\text{O})_6(\text{Fe}^{3+}_{8.30}\text{Mn}^{3+}_{0.22})_{\Sigma 9.02}(\text{PO}_4)_9\text{O}_6 \cdot 3.17\text{H}_2\text{O}$ (Table 4) based on the structure refined by Moore-Araki (1977). This formula indicates the presence of only a negligible proportion of the robertsite end member.

Strengite

Strengite $\text{Fe}^{3+}\text{PO}_4 \cdot 2\text{H}_2\text{O}$ forms a complete isomorphic series with its aluminous analog, variscite $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$. Strengite from both localities reported here, Penamacor-Monsanto and Paredes da Beira, is very close to the end-member composition, as Al is virtually absent; however the Paredes da Beira strengite does contain a small percentage of Mn_2O_3 (Table 4, Fig. 7). A manganian end-member is not known, but some Mn^{3+} may substitute for Fe^{3+} .

Perloffite

Perloffite $\text{Ba}(\text{Mn}^{2+}, \text{Fe}^{2+})_2\text{Fe}^{3+}_2(\text{PO}_4)_3(\text{OH})_3$ is the Fe^{3+} analog of bjarebyite (Kampf 1977). Electron-microprobe analyses of Vidago perloffite yield a composition (Ta-

ble 4) which leads to an average formula of $(\text{Ba}_{0.73}\text{Ca}_{0.16})_{\Sigma 0.89}(\text{Mg}_{0.14}\text{Mn}_{1.02}\text{Fe}_{0.93})_{\Sigma 2.09}(\text{Al}_{0.66}\text{Fe}^{3+}_{1.34})_2[(\text{PO}_4)_{2.50}(\text{SiO}_4)_{0.50}]_{\Sigma 3}(\text{OH})_{3.13}$. The remainder to 100 wt % over and above the anhydrous components gave calculated OH content.

Montebrasite

The amblygonite-montebrasite solid-solution series has two end-members, amblygonite $\text{LiAl}(\text{PO}_4)\text{F}$ and montebrasite $\text{LiAl}(\text{PO}_4)(\text{OH})$, but it varies from amb_0 to amb_{92} (Greiner - Bloss 1987). Na may substitute for Li to produce natromontebrasite $(\text{Na}, \text{Li})\text{Al}(\text{PO}_4)(\text{OH}, \text{F})$ which occurs in four localities around the world (Gaines et al. 1997). Compositions of montebrasite and natromontebrasite from aplite-pegmatite veins at Gonçalo and Segura were determined by electron-microprobe and normalized to 1P (Table 5). They show some deficiency in Al, which is attributed to slight alteration. Montebrasite and natromontebrasite from Segura are richer in F, up to 4.5 wt %, than those from the other locality (Table 5).

At Gonçalo, montebrasite from Li-rich aplite-pegmatite veins has a wider range in composition than the montebrasite from stanniferous aplite-pegmatite veins (Table 5). There is a complete solid solution between montebrasite and natromontebrasite in the Li-rich aplite-pegmatite veins at Gonçalo. Montebrasite from Li-bearing pegmatite at Segura has a composition close to the composition of montebrasite from Li-rich aplite-pegmatite veins at Gonçalo.

Table 4. Results of electron-microprobe analyses of some secondary phosphate minerals of granitic rocks from northern and central Portugal.

	Phosphoferrite		Ludlamite				Mitridatite		Strengite			Perloffite		
	1	σ	1a	σ	1b	σ	1	σ	2	3	σ	1	σ	
P ₂ O ₅	35.79	0.73	34.67	0.61	34.01	0.61	34.52	0.12	35.94	0.66	35.12	0.56	26.55	1.92
SiO ₂	-	-	-	-	-	-	-	-	-	-	-	-	4.45	1.83
Fe ₂ O ₃	-	-	-	-	-	-	37.95	0.15	42.25	1.14	43.85	0.85	-	-
Al ₂ O ₃	-	-	-	-	-	-	-	-	-	0.03	0.06	-	5.06	0.45
FeO	33.14	0.72	38.10	1.35	45.92	1.35	-	-	-	-	-	-	24.27	0.89
Mn ₂ O ₃	-	-	-	-	-	-	0.94	0.25	2.49	0.49	0.42	0.04	-	-
MnO	15.39	0.39	7.13	0.88	2.31	0.88	-	-	-	-	-	-	10.35	0.53
MgO	1.81	0.32	2.85	0.57	0.44	0.57	-	-	0.80	0.44	0.35	0.07	0.82	0.19
CaO	-	-	0.03	0.61	1.07	0.61	17.66	0.38	0.06	0.05	1.60	0.13	1.36	0.32
BaO	-	-	-	-	-	-	-	-	-	-	-	-	16.61	1.24
H ₂ O	13.87	0.71	17.22	0.94	16.25	0.94	8.93	0.15	18.46	0.56	18.63	0.56	8.43	0.55
Total	100.00		100.00		100.00		100.00		100.00		100.00		100.00	
P	2.000		2.000		2.000		9.000		1.000		1.000		2.504	0.196
Si	-		-		-		-		-		-		0.496	0.196
Fe ³⁺	-		-		-		8.793	0.032	1.046	0.045	1.110	0.037	1.336	0.051
Al ³⁺	-		-		-		-		-		0.001		0.664	0.051
Mn ³⁺	-		-		-		0.222	0.057	0.062	0.013	0.011	0.001	-	-
Fe ²⁺	1.829	0.075	2.171	0.114	2.667	0.125	-		-		-		0.925	0.109
Mn ²⁺	0.860	0.021	0.411	0.125	0.136	0.051	-		-		-		1.023	0.049
Mg	0.178	0.028	0.239	0.133	0.045	0.059	-		0.039	0.021	0.017	0.003	0.136	0.030
Ca	-		0.003	0.003	0.080	0.046	5.827	0.144	0.002	0.002	0.057	0.007	0.163	0.040
Ba	-		-		-		-		-		-		0.725	0.062
OH	-		-		-		-		-		-		3.130	0.209
H ₂ O	3.053	0.213	3.912	0.294	3.764	0.254	9.170	0.151	2.023	0.060	2.090	0.065	-	-
n	8		6		11		6		7		7		14	

1- Vidago; 2- Paredes da Beira; 3- Penamacor-Monsanto. Atomic contents calculated on the basis of 2 P for phosphoferrite and ludlamite, 9 P for mitridatite, 1 P for strengite, P+Si=3 and Al+Fe³⁺=2 for perloffite. Calculated Fe₂O₃ 15.94±0.53 and FeO 9.93±1.10 wt % for perloffite. Ludlamite: 1a from a sample containing triphylite, 1b from another sample containing mitridatite. - not detected; n - number of analyses.

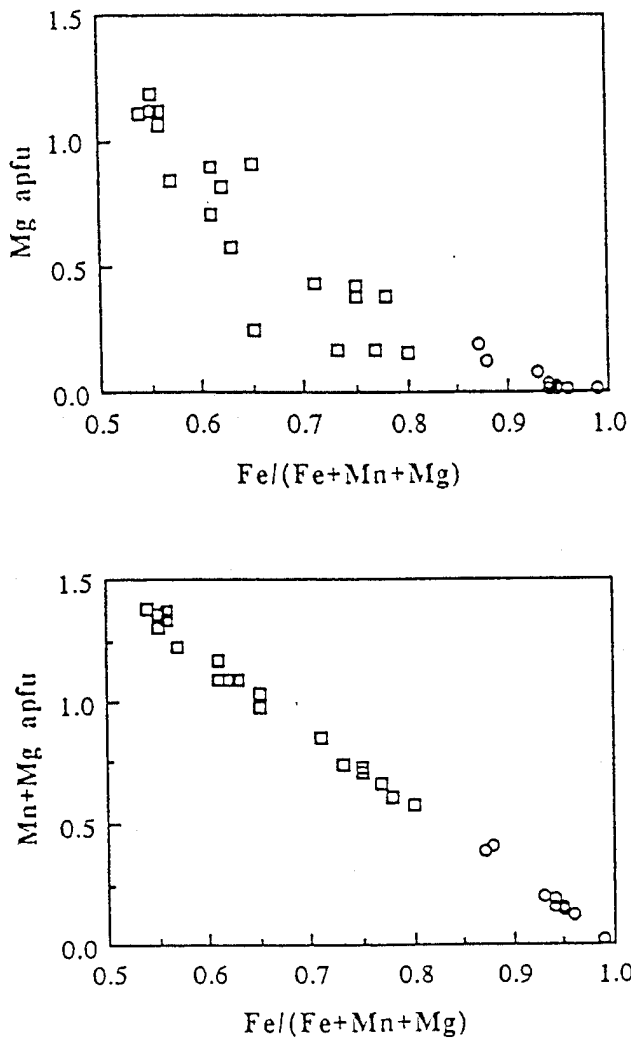


Fig. 6. Compositions of ludlamite from Vidago aplite. Symbols from samples:
 □ - containing triphylite, ○ - without triphylite.

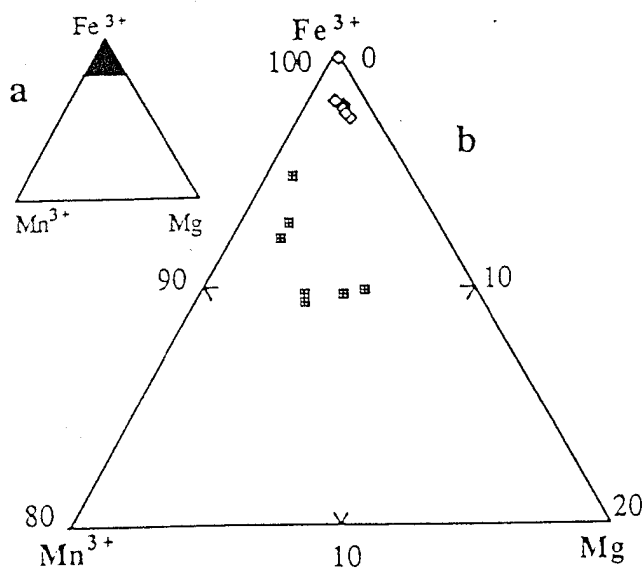


Fig. 7. Compositions of strengite from muscovite granite at Paredes da Beira and from the muscovite-biotite granite Gilla at Penamacor-Monsanto.
 Symbols: ■ - Paredes da Beira, ◇ - Penamacor-Monsanto.

Table 5. Compositions of montebasite and natromontebasite from aplite-pegmatite veins from northern and central Portugal

	Montebasite					Natromontebasite	
	1		σ	2		1	2
	a	b		b	σ	a	b
Al ₂ O ₃	35.43	35.07	0.94	34.16	0.71	33.80	33.29
FeO	0.02	0.03	0.03	0.03	0.03	0.04	0.04
MnO	0.02	0.06	0.10	-	-	0.04	-
MgO	0.05	0.03	0.03	-	-	0.04	-
CaO	0.05	0.06	0.03	-	-	0.06	-
Na ₂ O	0.05	3.65	3.68	4.25	4.59	13.00	10.85
P ₂ O ₅	53.53	51.40	1.60	50.22	1.89	49.65	48.02
F	-	-	-	2.79	1.64	-	4.54
	89.15	90.30		91.45		96.63	9.74
O≡F	-	-		1.18		-	1.91
Total	89.15	90.30		90.23		96.63	94.83
Al	0.922	0.950	0.036	0.947	0.035	0.948	0.965
Fe	-	0.001	0.001	0.001	0.001	0.001	0.001
Mn	-	0.001	0.001	-	-	0.001	-
Mg	0.002	0.001	0.001	-	-	0.001	-
Ca	0.001	0.002	0.001	-	-	0.002	-
Na	0.002	0.163	0.171	0.194	0.221	0.600	0.517
Li	0.998	0.837	0.171	0.806	0.221	0.400	0.483
P	1.000	1.000		1.000		1.000	1.000
F	-	-		0.208	0.129	-	0.353
OH	1.000	1.000		0.792	0.129	1.000	0.647
n	3	23		17		4	1

1- Gonçalo; 2- Segura; a - stanniferous aplite - pegmatite veins, b- Li-aplite-pegmatite veins. Cation contents normalized to 1 P.

Gormanite

A phosphate was found in the muscovite granite from Segura which gives on recalculation on either 19 oxygen equivalents, 4P or 4Al, atomic contents which come close to the stoichiometry of gormanite, Fe²⁺₃Al₄(PO₄)₄(OH)₆ · 2H₂O (Sturman et al. 1982), the ferrous counterpart of souzalite (Mg, Fe²⁺)₃(Al, Fe³⁺)₄(PO₄)₄(OH)₆ · 2H₂O (Moore 1970). The recalculation on the basis of 19 oxygen equivalents gives the best stoichiometry. However, Table 6 shows that Fe²⁺ plus related cations and Al are perceptibly lower than required by the ideal formula. Still, this approximation to gormanite is much better than to any others hydrous A²⁺-Al-phosphates.

Mimetite

Mimetite from the sulphide-bearing quartz veins at Segura is an As-dominant phase but rich in phosphorus, thus deserving a place in our present review. Recalculated on the basis of 13 anions (Table 6), the mineral is very close to an intermediate 1:1 member of pyromorphite Pb₃(PO₄)₃Cl - mimetite Pb₅(AsO₄)₃Cl series, which shows complete miscibility (Baker 1966). However, intermediate members with substantial representation of both As and P are not abundant in natural occurrences, as a simultaneous geochemical supply of these elements is quite uncommon in any environment.

Table 6. Results of electron-microprobe analyses of some phosphates from muscovite granite and barite-galena-sphalerite quartz vein from Segura, central Portugal

Gormanite σ			Mimetite σ			Kintoreite σ		
P ₂ O ₅	33.46	0.58	P ₂ O ₅	7.09	0.24		19.95	0.59
Al ₂ O ₃	24.88	0.38	CaO	0.85	0.58		-	
Fe ₂ O ₃	22.67	1.19	As ₂ O ₃	11.86	0.66		-	
MnO	1.46	0.24	SO ₃	-			1.31	0.68
MgO	0.31	0.36	PbO	77.33	0.82		30.99	1.88
CaO	0.60	0.41	Fe ₂ O ₃	-			32.46	2.36
Total	83.33		CuO	-			0.07	0.05
			Cl	3.07	0.04			
			Total	100.20			84.73	
			O \equiv Cl	0.68				
			Total	99.52				
Mg	0.155	0.066	Pb	4.934	0.124	Pb	1.024	0.133
Fe ²⁺	2.444	0.154	Ca	0.216	0.142	Cu	0.006	0.004
Mn	0.160	0.023	P	1.423	0.045	Fe ³⁺	3.000	0.000
Ca	0.083	0.056	As	1.470	0.078	P	2.076	0.134
Al	3.779	0.027	Cl	1.232	0.022	S	0.121	0.067
P	4.197	0.017						
n	5			6			5	

Gormanite is from granite and the other phosphates are from quartz veins. Atomic contents calculated on the basis of 19 (O) for gormanite, 13 anions for mimetite and 3 Fe for kintoreite; (O)– oxygen atoms. n– number of analyses.

Kintoreite

A secondary phosphate mineral associated with anglesite and the above - described mimetite has an average composition, when normalized to 3Fe (Table 6), close to that of kintoreite, $PbFe_3(PO_4)_2(OH, H_2O)_6$, except the apparent discrepancy in the OH and H₂O contents. Kintoreite was described only very recently as a new mineral species (Ping et al. 1995), related to the alunite $KAl_3(SO_4)_2(OH)_6$ and jarosite $KFe^{3+}_3(SO_4)_2(OH)_6$ group (e. g. Scott 1987).

Discussion and conclusions

It is evident from the mineralogical, paragenetic and compositional relationships that several processes contributed to the formation of phosphates at the localities examined here.

Triphylite is the only primary phosphate, known from only two localities, with quite different values of Fe/Mn. Inferences concerning temperatures of formation are not feasible, as the different degrees of Fe-Mn fractionation could be rooted in the bulk chemistry of the parent rocks.

Alteration of triphylite could provide components for precipitation of secondary phases. At Vidago, vivianite and blue ludlamite are undoubtedly derived from triphylite, as probably is mitridatite (by analogy with most of its localities; e. g., Moore 1974, Galliski et al. 1998). Phosphoferrite has a similar value of the Fe/(Fe+Mn+Mg) ratio to that of blue ludlamite. So it may also be derived from triphylite. The parentage of the other secondary ferro-magnesian-magnesian phosphates is not clear, as they were found in isolation from triphylite and

in absence of other potentially primary phases. The origin of the Ca-rich brushite postdates that of eosphorite; brushite requires distinctly acidic conditions for its stabilization (Fiore – Laviano 1991). This and the usually low-temperature and late origin of mitridatite suggest that Ca became available for phosphate precipitation only in late stages of alteration processes.

On the other hand, strengite is undoubtedly an oxidation and leaching product of the Paredes da Beira triphylite, which it rims and surrounds. However the precursor of childrenite is unknown.

Unfortunately, the parentage and genetic conditions of the secondary phosphates in the Penamacor-Monsanto and Segura granites are beyond our reach, as they were found outside any relations to, and in the absence of any potential primary phase. However at Penamacor-Monsanto some eosphorite rims childrenite, indicating that hydrothermal fluids became richer in Mn in late stages. At Segura, however, oxidation of arsenopyrite and galena were essential for the formation of mimetite and the kintoreite-like phase, although the source of phosphorus is unknown.

Montebrasite and natromontebrasite were found in aplite-pegmatite veins from Gonçalo and Segura. The range of composition from Li-rich veins at Gonçalo is larger than at Segura; there is a complete solid solution between montebrasite and natromontebrasite.

We can conclude that the present data show a very good potential of the so far unexplored Portuguese granites, aplites pegmatites and associated hydrothermal products for finds of diversified assemblages of phosphate minerals, including rare and potentially new species.

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Fosfáty z granitických hornin a je doprovázejících křemenných žil ze severního a středního Portugalska.

Fosfáty jsou běžné v granitických horninách severního a středního Portugalska. Childrenit, eofosforit a jejich přechodné členy se vyskytují v muskovitických granitech z Paredes da Beira a Penamacor-Monsanto, v muskovit-biotitických granitech z Penamacor-Monsanto a v aplitových žilách na lokalitě Vidago. Jejich chemické složení je podobné na všech uvedených lokalitách. Gormanit se nachází v muskovitickém granitu na lokalitě Segura. Trifylin zatlačovaný strengitem je znám z muskovitických granitů v Paredes da Beira, ve Vidago aplitu je dále zatlačován manganatým vivianitem (Fe_{2-1,9}Mn_{0-0,9}Mg_{0,3-0,2}), modrým ludlamitem, fosfoferitem a mitridatitem. Zelený ludlamit a brushit byly také nalezeny na této lokalitě. Montebrazit a natromontebrazit byly zjištěny na Li-aplit-pegmatitových žilách z lokalit Gonçalo a Segura. Mimetezit s As/P 1,04 a kitoreitu podobná fáze jsou produkty alterace galenitu z křemenných žil na lokalitě Segura.