

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 (Czech summary)

(7 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 manganian vivianite from $(\text{Fe}_{2.4}\text{Mn}_{0.4}\text{Mg}_{0.5})$ 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. Montebasite and natromontebasite 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, montebasite, natromontebasite, 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 $\text{CaMnMn}_2\text{Fe}^{3+}_2(\text{PO}_4)_4(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, panasqueiraite $\text{CaMg}(\text{PO}_4)(\text{OH}, \text{F})$, rittmannite $(\text{Mn}^{2+}, \text{Ca})\text{Mn}^{2+}(\text{Fe}^{2+}, \text{Mn}^{2+})_2(\text{Al}, \text{Fe}^{3+})_2(\text{PO}_4)_4(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, sabugalite $\text{HAl}(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$, 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 $\text{Ca}_4\text{MnFe}^{3+}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 12\text{H}_2\text{O}$. 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.

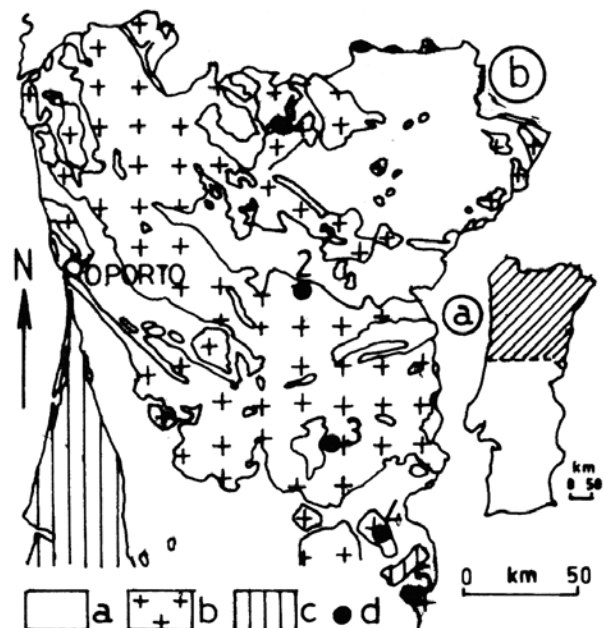


Fig. 1 a – location of Fig. 1b on the map of Portugal; 1b – Location of the areas chosen to study the phosphate minerals; a – Cambrian metamorphic complexes, Paleozoic, some igneous and ultrabasic rocks; b – Hercynian granitic rocks; c – Mesozoic and Cenozoic sedimentary rocks; d – the areas selected: 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 $80 \times 30 \mu\text{m}$ up to $300 \times 200 \mu\text{m}$. It is rarely rimmed and penetrated along fractures by vivianite (Fig. 2), pleochroic from blue to brownish. This mineral ($100 \times 60 \mu\text{m}$) also penetrates between quartz and albite. Other triphylite crystals are locally rimmed by ludlamite, pleochroic from blue to colorless, which

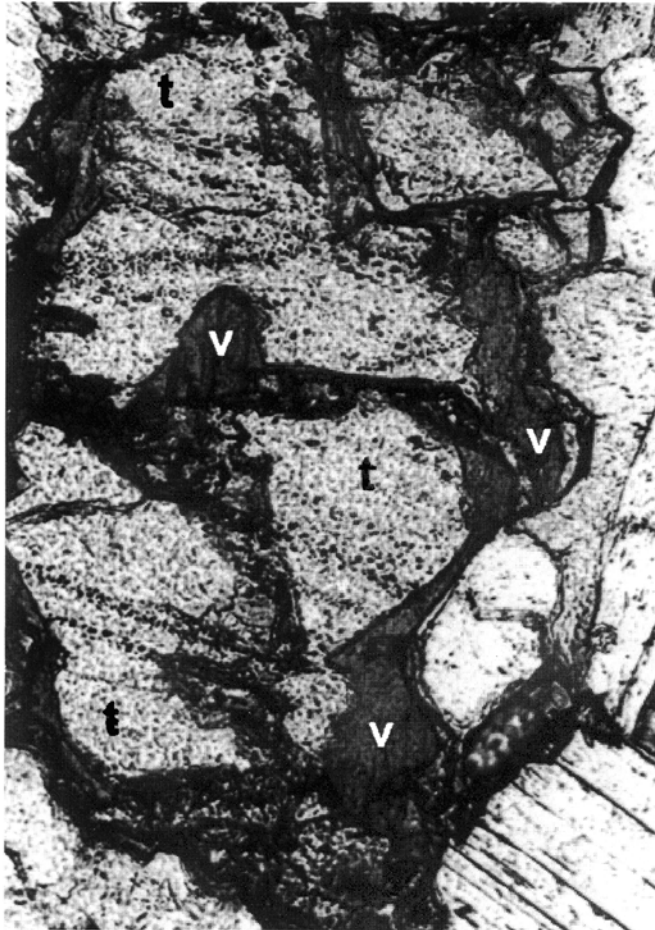


Fig. 2 Triphylite (t) from the Vidago aplite altered to vivianite (v) along fractures, in plane polarized light (x25).

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

Irregular yellowish brown crystals of eosphorite up to $3.2 \times 2.6 \text{ mm}$ are locally rimmed by colorless brushite. Phosphoferrite occurs in irregular green crystals ($3 \times 2 \text{ mm}$). Very rare irregular crystals ($200 \times 100 \mu\text{m}$) 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 $1.3 \times 0.02 \text{ mm}$ 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 biotite, 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 $1.5 \times 1.1 \text{ mm}$ to $2.2 \times 1.0 \text{ mm}$ are locally rimmed by brown childrenite, but others are rimmed by violet strengite. Irregular crystals of childrenite ($0.24 \times 0.18 \text{ mm}$) 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 $50 \times 15 \text{ cm}$), albite ($2 \times 1 \text{ cm}$), muscovite (1 mm–1 cm), cassiterite (1 mm–1 cm), amblygonite, zinnwaldite, rare montebbrasite, 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 $5 \times 5 \text{ cm}$, but rarely up to $15 \times 10 \text{ cm}$), K-feldspar ($2 \times 1 \text{ cm}$, up to $15 \times 10 \text{ cm}$), albite (up to $3 \times 1 \text{ cm}$), muscovite, zinnwaldite, lepidolite, petalite (up to $2 \times 3 \text{ cm}$), apatite, montebbrasite, natromontebbrasite, 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.

Montebbrasite occurs in the three types of aplite-pegmatite veins, but natromontebbrasite 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. Montebbrasite and natromontebbrasite occur mainly in subhedral single crystals, ranging from $50 \mu\text{m}$ to 1 cm, commonly twinned, but also with montebbrasite/natromontebbrasite cores and natromontebbrasite/montebbrasite 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, and 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, montebbrasite, natromontebbrasite, topaz, lepidolite, cassiterite, columbite, zircon and rutile (Antunes 1999). Montebbrasite and natromontebbrasite are associated with montebbrasite/natromontebbrasite cores and natromontebbrasite/montebbrasite 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, chalcopyrite, 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 Cu (CuK α) and arsenopyrite (AsL α). Each element was counted for 20 seconds. ZAF corrections were applied.

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	montebbrasite natromontebbrasite	
Penamacor-Monsanto	granites GIIIa GIIIFra GIIIFrb GIIIC		strengite childrenite, eosphorite childrenite childrenite, eosphorite
Segura	muscovite granite Li-bearing pegmatite barite-galena-sphalerite quartz veins	montebbrasite natromontebbrasite	gormanite mimetite, kintoreite

a, b, c – increasing degree of hydrothermal alteration; GIIIa, GIIIFra – medium-grained porphyritic muscovite-biotite granites; GIIIFrb – medium-to coarse-grained muscovite-biotite granite; GIIIC – medium to coarse-grained porphyritic muscovite granite.

Chemical composition of the phosphates

Triphylite

Triphylite $\text{LiFe}^{2+}\text{PO}_4$ and lithiophilite $\text{LiMn}^{2+}\text{PO}_4$ are end-members of a solid-solution series, the natural members 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.

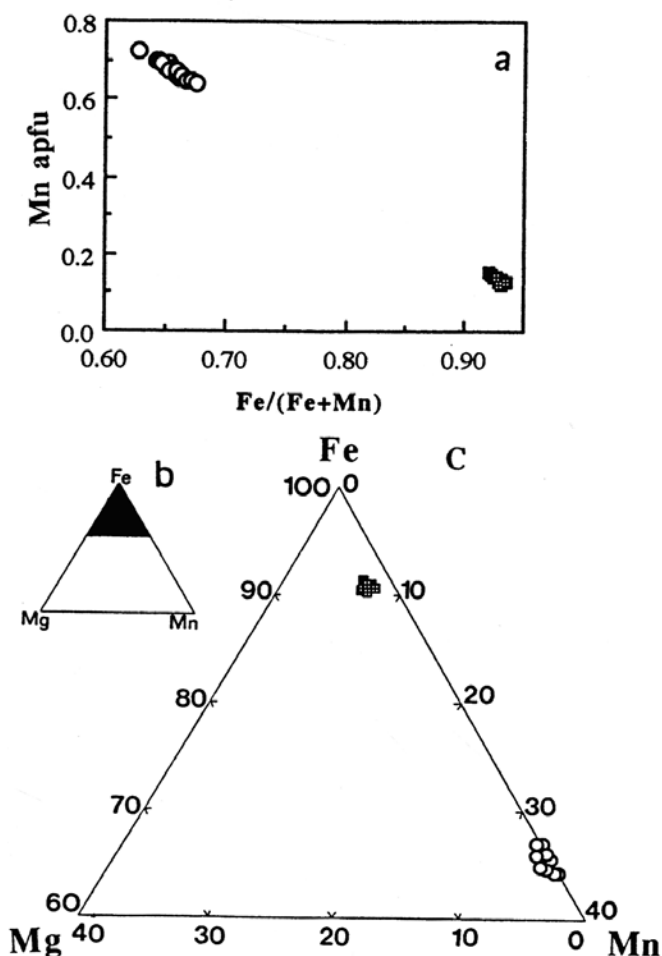


Fig. 3 Compositions of triphylite from Vidago aplite and Paredes da Beira muscovite granite: a – Mn-Fe/(Fe+Mn) diagram; b, c – Fe-Mn-Mg diagrams, with b showing the location of c. Symbols: ○ – Vidago, □ – Paredes da Beira.

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 $7\text{H}_2\text{O}$. 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 $\text{Fe} \rightleftharpoons \text{Mn}$.

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-Mon-

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	29.82	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^a	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	0.058	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	18		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.

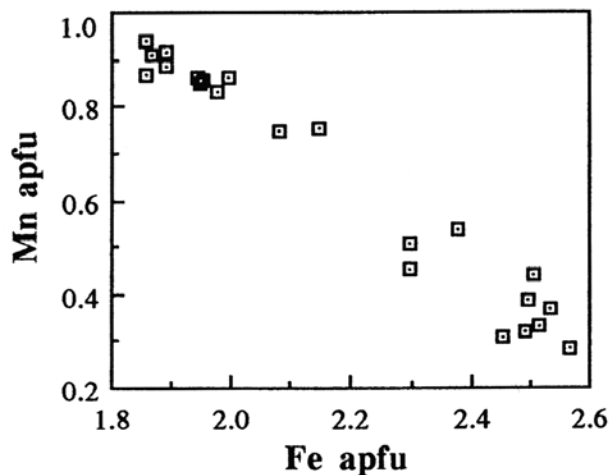


Fig. 4 The correlation between Fe and Mn in vivianite from Vidago aplite.

santo. 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 substituting for Ca (Table 3 and Fig. 5b). Remainder to 100 wt. %, over and above the anhydrous components, is equal to H_2 and $3.87H_2O$ (Table 3).

Phosphoferrite and ludlamite

Phosphoferrite and ludlamite are similar in chemical composition, but they differ in their water contents, structure and symmetry: phosphoferrite $(Fe^{2+}, Mn^{2+})_3(PO_4)_2 \cdot 3H_2O$ is orthorhombic whereas ludlamite $(Fe^{2+}, Mg, Mn)_3(PO_4)_2 \cdot 4H_2O$ is monoclinic. They were both found at Vidago; their compositions give empirical formulas, normalized to 2P, of $(Fe_{1.83}Mn_{0.86}Mg_{0.18})_{\Sigma 2.87}(PO_4)_2 \cdot 3.05H_2O$ for phosphoferrite and $(Fe_{1.88}Mn_{0.34}Mg_{0.70})_{\Sigma 2.92}(PO_4)_2 \cdot 3.94H_2O$ for blue ludlamite in samples containing triphylite, and $(Fe_{2.67}Mn_{0.14}Ca_{0.08}Mg_{0.05})_{\Sigma 2.94}(PO_4)_2 \cdot 3.76H_2O$ 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 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, robert-

site (Moore 1974). At Vidago, mitridatite yields the formula $Ca_{5.83}(H_2O)_6(Fe^{3+}_{8.80}Mn^{3+}_{0.22})_{\Sigma 9.02}(PO_4)_9O_6 \cdot 3.17H_2O$ (Table 4) based on the structure refined by Moore – Arai (1977). This formula indicates the presence of only a negligible proportion of the robertsite end member.

Strengite

Strengite $Fe^{3+}PO_4 \cdot 2H_2O$ forms a complete isomorphic series with its aluminous analog, variscite $AlPO_4 \cdot 2H_2O$. 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 percent-

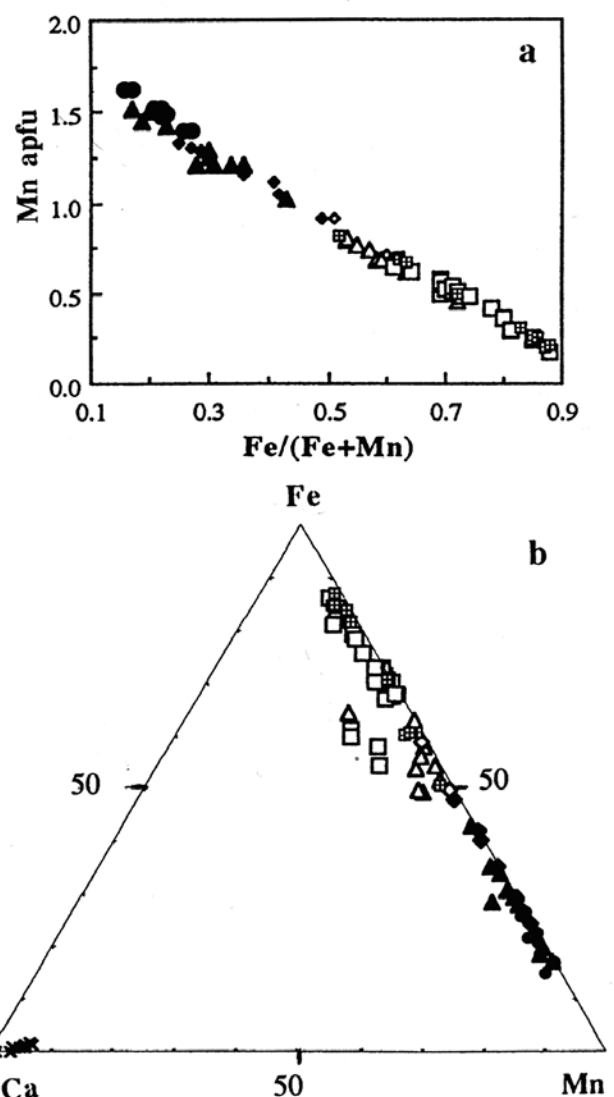


Fig. 5 a, b, c – Compositions of eosphorite and childrenite from granitic rocks at Vidago, Paredes da Beira and Penamacor-Monsanto; b – also includes composition of brushite from Vidago aplite; a – Mn-Fe/(Fe+Mn) diagram; b – Fe-Mn-Ca diagram; Symbols: eosphorite: ● – aplite from Vidago, ◆ – altered muscovite-biotite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

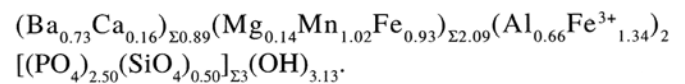
	Eosphorite						Childrenite						Brushite		
	1	σ	3a	σ	3c	σ	2	σ	3a	3b	σ	3c	σ	1	σ
P ₂ O ₅	31.15	0.36	32.55	0.37	31.59	0.98	31.66	0.86	32.53	32.26	1.19	32.94	0.70	41.10	0.46
FeO	6.60	1.13	10.33	2.59	8.07	2.38	31.13	3.83	16.33	20.27	1.64	16.24	1.35	0.25	0.23
MnO	23.43	1.16	19.17	2.42	20.87	2.23	6.89	3.68	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	22.48	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	0.808	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 – GIIFra, b – GIIFrb, c – GIIFc (see Table 1). Atomic contents calculated on the basis of 2 P; “–” – not detected; n – number of analyses.

age of Mn₂O₃ (Table 4, Fig. 7). A manganian end-member is not known, but some Mn³⁺ may substitute for Fe³⁺.

Perloffite

Perloffite Ba(Mn²⁺,Fe²⁺)₂Fe³⁺₂(PO₄)₃(OH)₃ is the Fe³⁺ analog of bjarebyite (Kampf 1977). Electron-microprobe analyses of Vidago perloffite yield a composition (Table 4) which leads to an average formula of



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 LiAl(PO₄)F and monte-

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	σ	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	–	–	–	–	–	–	10.85	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	0.18	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	0.289	0.138	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±0.58 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.

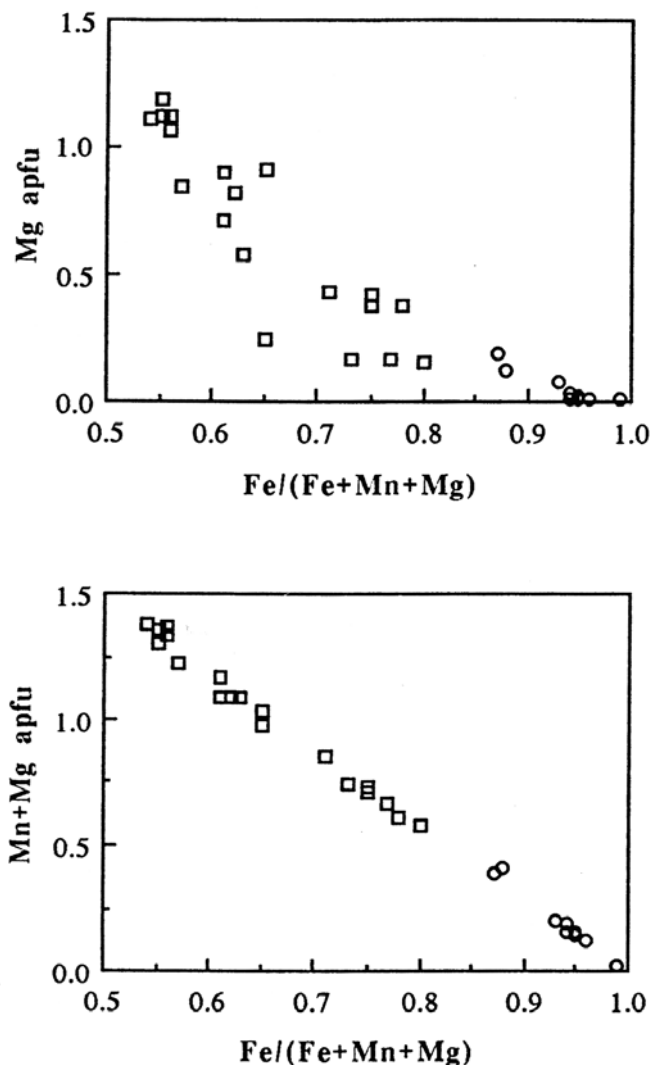


Fig. 6 Compositions of ludlamite from Vidago aplite. Symbols from samples: □ – containing triphylite, ○ – without triphylite.

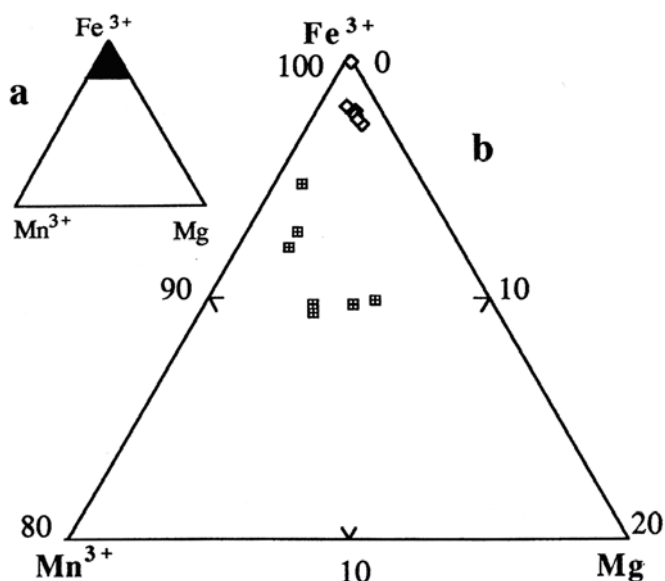


Fig. 7 Compositions of strengite from muscovite granite at Paredes da Beira and from the muscovite-biotite granite GIIIa at Penamacor-Monsanto. Symbols: ▣ – Paredes da Beira, ◇ – Penamacor-Monsanto.

Table 5 Compositions of montebbrasite and natromontebbrasite from aplite-pegmatite veins from northern and central Portugal.

	Montebbrasite			Natromontebbrasite			
	1	2	σ	1	2	σ	
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		90.28		96.63	94.83
Al	0.922	0.950	0.036	0.947	0.085	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.

brasilite LiAl(PO₄)(OH), but it varies from amb₀ to amb₉₂ (Greiner – Bloss 1987). Na may substitute for Li to produce natromontebbrasite (Na, Li)Al(PO₄)(OH,F) which occurs in four localities around the world (Gaines et al. 1997). Compositions of montebbrasite and natromontebbrasite 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. Montebbrasite and natromontebbrasite from Segura are richer in F, up to 4.5 wt. %, than those from the other locality (Table 5).

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

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 ba-

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	38.46	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		–	
FeO	22.67	1.19	As ₂ O ₃	11.86	0.66		–	
MnO	1.46	0.24	SO ₃	–		1.31	0.68	
MgO	0.81	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	88.88		CuO	–		0.07	0.05	
			Cl	3.07	0.04			
			Total	100.20			84.78	
			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	0.028	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.

sis 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 Pb₅(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.

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, PbFe₃(PO₄)₂(OH,H₂O)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 KAl₃(SO₄)₂(OH)₆ and jarosite KFe³⁺₃(SO₄)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 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, efoforit 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_{2,4-1,9}Mn_{0,4-0,9}Mg_{0,5-0,2}), modrým ludlamitem, fosferitem a mitridatitem. Zelený ludlamit a brushit byly také nalezeny na této lokalitě. Montebrazit a natromontebrazit byly zjištěny na Li-aplit-pegmatitových žilách z lokalit Gonoalo a Segura. Mimetezit s As/P 1,04 a kintoreitu podobná fáze jsou produkty alterace galenitu z křemenných žil na lokalitě Segura.