

Phosphates from Piona granitic pegmatites (Central Southern Alps, Italy)

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ABSTRACT

Primary and hydrothermal phosphate associations found in some dikes belonging to the Late Triassic Piona pegmatite swarm have been studied. Three primary phosphate associations characterize the LCT, Rare-Element, beryl-columbite-phosphates pegmatites, embedded in high-grade metamorphic basement of Southern Alps. High to low temperature hydrothermal alteration characterizes the late stage phosphates crystallization.

Keywords: LCT granitic pegmatites, phosphates, graftonite-beusite, triphylite, ferrowyllieite, Piona.

GEOLOGICAL SETTING

The Piona pegmatite swarm is embedded into the high-grade metapelites (sillimanite-, garnet-bearing gneiss) of the Dervio-Olgiasca Zone (DOZ) which belongs to the crystalline basement of the Central Southern Alps. The DOZ represents a segment of upper to middle continental crust, originated after Variscan intermediate pressure amphibolite facies metamorphism and exhumated during the Alpine orogenesis (di Paola & Spalla, 2000). From Norian to Liassic (223-186 Ma, Bertotti et al., 1993) the south Alpine basement was involved in the continental rifting concluded with the creation of the Adriatic passive continental margin (Sanders et al., 1996; Bertotti et al., 1999). The crustal thinning was accompanied by high temperature thermal conditions at relative low pressure (di Paola & Spalla, 2000) with extended magmatic activity (Bertotti et al., 1999). The temperature increase in the DOZ registered a peak of 600-720°C at a pressure of 4.5-5.5 Kbar (Diella et al., 1992). This high temperature event started around 240 Ma ago. The emplacement and crystallization of Piona pegmatites may be marked by the muscovite closing temperature for Rb/Sr ($550 \pm 50^\circ\text{C}$) in a time ranging between 229 ± 7 Ma and 208 ± 4 Ma (Sanders et al., 1996). Anatectic origin for the granitic melt is proposed by Sanders et al. (1996) through high Al content and large amount of carbon (CO₂ and CH₄) found in the primary fluid inclusions.

The pegmatite swarm is composed of about 30 dykes, 10 of which are larger than 5 m and longer than 10 m. The granitic nature of melt is established by the primary mineralogical composition: quartz+albite±K-feldspar±muscovite. Common accessories are: garnet (almandine-spessartine), schorlite, apatite and, where present, beryl, phosphates and chrysoberyl. Columbite-group minerals, microlite, and cassiterite were found in the most evolved pegmatites. The dikes are lens-shaped and zoned with general sharp contacts with the country rock (transition zones with the hosting gneiss, enriched in mica, garnet and tourmaline, are rarely present). Those dikes are unfolded with light brittle deformation. Phosphates are almost common accessories of the three dikes named Malpensata, Luna and Sommafiume.

THE PHOSPHATE-BEARING DIKES

The phosphate-bearing pegmatites show an asymmetrical zoned structure composed by 4 main

units: 1) fine grained pegmatite with coarse garnet+tourmaline layers; 2) wall zone (graphic albite+quartz) with muscovite and tourmaline; 3) megacryst plagioclase zone (blocky albite) with tourmaline and beryl; 4) quartz core. Phosphates (in elongated masses), columbite-group minerals, cassiterite, microlite together with beryl are hosted into the megacryst plagioclase zone or at the contact between this last and the quartz core.

Phosphates structure and chemical composition

Back-scattered electron images of polished and thin sections evidenced a prevailing lamellar structure of phosphate masses while granular textures are uncommon and usually confined to the rim. The contact with the hosting pegmatite is frequently highlighted by a F-, Cl-rich hydroxylapatite rim.



FIGURE 1. Back-scattered electron image of association II, Malpensata dike. (ground mass=beusite, very light-grey grains=arrojadite, medium-grey lamellae=wolfeite, medium-grey masses at the bottom=heterosite).

Exceptionally a mono-crystalline mass of alluaudite up to 25 cm in length was found at the Malpensata dyke. Chemical data show three different associations of primary phosphates: I) graftonite + sarcopside + triphylite, II) beusite + triphylite ± arrojadite and III) alluaudite ± beusite ± arrojadite. Graftonite composition

vary from Ca- and Fe-rich in association I to Ca-poor and Mn-rich one (beusite) in association II (Tab. 1). In accordance with previous authors (Hurlbut, 1965; Wise & Černý, 1990; Smeds *et al.*, 1998; Černý *et al.*, 1998) the relative abundances together with the textural relationships and chemical features of the primary associations I and II can be considered as an exsolution product from a high temperature Ca-, Mg- and Li-rich graffonite-like parent. Association III is characterized by the large occurrence of alkalis and aluminium bearing phosphates (mainly alluaudite) associated with beusite. Association III was found in close relation with the most evolved paragenesis of Malpensata dike (cassiterite, microlite and U-rich microlite, ferrotapiolite - ferrotantalite, manganocolumbite and Hf - rich zircon) typical of some localized portions of the inner blocky albite zone. These chemical and paragenetic features suggest to consider this primary phosphate association as the most evolved one.

TABLE 1. Selected analyses of primary phosphates (gft=graffonite, sar=sarcopside, tph=triphylite, beu=beusite, allu=alluaudite, arj=arrojadite).

| sample | association I | | | | association II | | | association III | | |
|---|---------------|------------|------------|------------|----------------|-----------|------------|-----------------|-----------|--|
| | Luna | | Luna | | Sommafiume | | | Malpensata | | |
| | P1D gft | P1D sar | P2A gft | P2A tph | P5 beu | P5 tph | P3 allu | P3 beu | P3 arj | |
| SiO ₂ (wt%) | 0.02 | 0.02 | 0.03 | 0.06 | 0.02 | 0.05 | 0.07 | 0.02 | 0.05 | |
| P ₂ O ₅ | 42.08 | 41.04 | 40.87 | 45.86 | 42.15 | 47.89 | 44.96 | 41.90 | 39.32 | |
| Fe ₂ O ₃ [†] | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 24.15 | 0.00 | 1.98 | |
| Mn ₂ O ₃ [†] | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.18 | |
| Al ₂ O ₃ | 0.01 | 0.01 | 0.02 | 0.00 | 0.01 | 0.05 | 6.33 | 0.01 | 2.14 | |
| FeO | 31.42 | 49.17 | 32.66 | 36.79 | 28.57 | 31.62 | 0.14 | 24.12 | 27.50 | |
| MnO | 8.93 | 4.05 | 10.33 | 2.94 | 22.38 | 9.00 | 16.64 | 23.65 | 14.79 | |
| CaO | 13.18 | 0.14 | 13.55 | 0.08 | 6.14 | 0.08 | 0.81 | 7.43 | 1.98 | |
| MgO | 1.23 | 3.51 | 1.16 | 4.32 | 0.42 | 1.67 | 0.26 | 0.07 | 0.18 | |
| ZnO | 0.13 | 0.02 | 0.22 | 0.04 | 0.19 | 0.01 | 0.11 | 0.80 | 0.43 | |
| Na ₂ O | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 7.67 | 0.00 | 6.69 | |
| K ₂ O | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.01 | 0.01 | 1.52 | |
| Li ₂ O [†] | 0.68 | 0.00 | 0.00 | 9.51 | 0.65 | 10.74 | 0.00 | 0.83 | 0.42 | |
| Total | 97.69 | 97.97 | 98.84 | 99.60 | 100.52 | 101.13 | 101.14 | 98.84 | 97.19 | |
| Structural formulae on the basis of: | | | | | | | | | | |
| | 8 O | | 8 O | | 4 O | | 8 O | | 4 O | |
| Si | 0.001 | 0.001 | 0.002 | 0.002 | 0.001 | 0.001 | 0.005 | 0.001 | 0.019 | |
| P | 2.030 | 2.031 | 1.990 | 0.995 | 2.028 | 1.015 | 2.909 | 2.037 | 11.985 | |
| Fe ³⁺ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1.389 | 0.000 | 0.536 | |
| Mn ³⁺ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.049 | |
| Al | 0.000 | 0.001 | 0.001 | 0.000 | 0.000 | 0.001 | 0.285 | 0.000 | 0.454 | |
| Fe ²⁺ | 1.497 | 2.403 | 1.571 | 0.788 | 1.358 | 0.662 | 0.009 | 1.158 | 8.282 | |
| Mn ²⁺ | 0.431 | 0.201 | 0.503 | 0.064 | 1.078 | 0.191 | 1.077 | 1.150 | 4.511 | |
| Ca | 0.805 | 0.009 | 0.835 | 0.002 | 0.374 | 0.002 | 0.066 | 0.457 | 0.763 | |
| Mg | 0.105 | 0.306 | 0.099 | 0.165 | 0.035 | 0.062 | 0.029 | 0.006 | 0.097 | |
| Zn | 0.006 | 0.001 | 0.009 | 0.001 | 0.008 | 0.000 | 0.006 | 0.034 | 0.115 | |
| Na | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1.138 | 0.000 | 4.676 | |
| K | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 | 0.698 | |
| Li | 0.156 | 0.000 | 0.000 | 0.980 | 0.147 | 1.081 | 0.000 | 0.192 | 0.613 | |
| Σ M | 3.001 | 2.920 | 3.019 | 2.000 | 3.000 | 2.000 | 4.001 | 3.000 | 20.793 | |

* calculated assuming stoichiometry

Ferrisicklerite, heterosite and wolfeite commonly replace triphylite lamellae as high temperature hydrothermal products. Low temperature hydrothermal products are represented mainly by kryzhanovskite and jahnsite-(CaMnFe) in oxidizing conditions and by vivianite and phosphoferrite in non-oxidizing ones. Some minor secondary, low temperature, phosphates such as jahnsite-(CaMnMn), beraunite, withmoreite, messelite, rockbridgeite, strunzite, fairfieldite, switzerite-metaswitzerite and vivianite are present as spongy masses or micro-crystals clothing hydrothermal cavities.

CONCLUSION

- The granitic mineralogical composition and the association of accessories, especially the presence of conspicuous amount of phosphates and beryl together with columbite-group minerals, indicate that Piona pegmatite swarm belongs to the Rare-Element LCT family, beryl-columbite-phosphate subtype, in the classification of Černý (Černý & Ercit, 2005).
- Chemical data and field observations suggest a zoned distribution of primary phosphate masses, particularly in the most evolved Malpensata dike.
- High temperature hydrothermal alteration of triphylite is marked by a progressive lithium leaching and the formation of ferrisicklerite, heterosite and wolfeite.
- The most abundant low temperature hydrothermal products (kryzhanovskite and jahnsite) show a progressive hydration as main process with minor Ca metasomatism in oxidizing conditions.

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