

WYLLIEITE REACTION CORONAS ON SCORZALITE IN PEGMATITE DYKES - SERRA DE ARGÁ (PORTUGAL)

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ABSTRACT

In the region of Serra de Argá (Northern Portugal) pegmatite dykes with approximately 50 cm thick and 2 m long, affected by Variscan deformation, contain scorzalite that is partially replaced by wyllieite reaction coronas.

Mineral composition of the dykes consists of quartz, albite, potassium feldspar and muscovite. Accessory minerals include andalusite, Mn-rich fluorapatite, columbite-(Fe), gahnite, uraninite, montebrasite and brazilianite (Dias, 2012).

Scorzalite occur as disseminated bluish to greenish single crystals up to 3 mm in size. Inclusions of muscovite, gahnite and montebrasite (?) were identified. Scorzalite often displays complex alteration patterns corresponding to the development of brownish to black Al-Fe-Mn rich products (gormanite or childrenite-eosphorite?). Other breakdown products include associations of crandallite-goyazite and variscite. Scorzalite electron-microprobe analysis showed the following average composition: $(\text{Fe}^{2+}_{0.90}\text{Mg}_{0.05}\text{Ca}_{0.07}\text{Mn}_{0.02}\text{Zn}_{0.0-0.01})_{-0.95-1.01}\text{Al}_{2.0-2.1}(\text{PO}_4)_2(\text{OH})_2$.

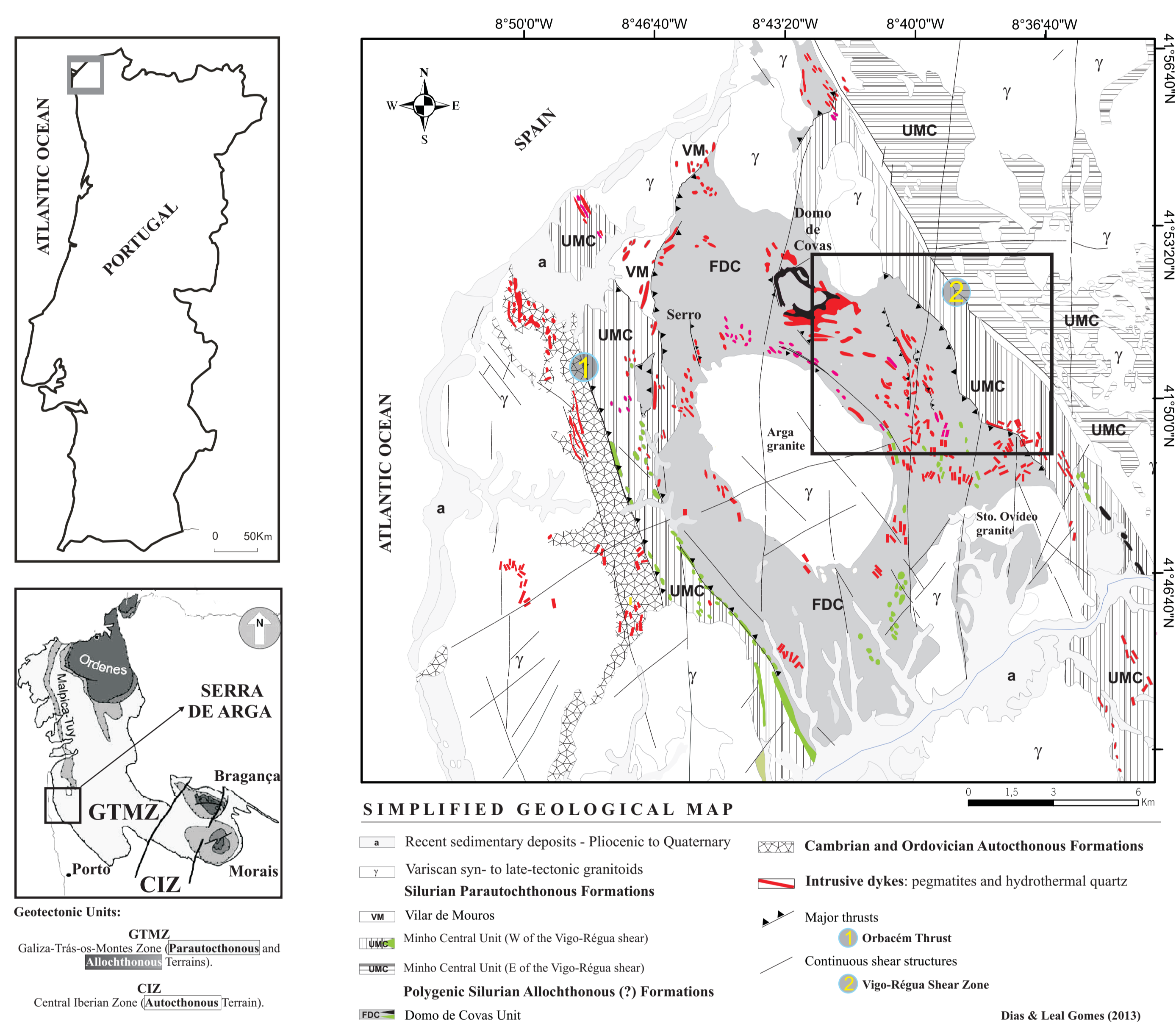
Wyllieite forms light blue corona-like overgrowths around primary scorzalite and also penetrate along fracture fillings of the scorzalite crystals, as revealed by transmitted light microscopy and EMP study. Electron-microprobe analysis provided $\text{P}_2\text{O}_5 = 45.5-47.2$; $\text{Al}_2\text{O}_3 = 8-8.6$, $\text{MnO} = 15.2-16.3$, $\text{FeO} = 23.5-24.6$, $\text{MgO} = 0.44-0.54$; $\text{Na}_2\text{O} = 4.2-5.3$ wt. %. The resulting formula, calculated on the basis of 12 O, is $(\text{Na}_{0.64-0.79}\text{Ca}_{0.02-0.03}\text{Mn}_{0.30-0.39})_{-1.01-1.22}(\text{Mn}_{0.60-0.71}\text{Fe}^{2+}_{0.29-0.40})_{-1}(\text{Fe}^{2+}_{0.27-0.61}\text{Fe}^{3+}_{0.34-0.67}\text{Mg}_{0.05-0.06})_{-1}(\text{Al}_{0.72-0.77}\text{Fe}^{3+}_{0.23-0.28})_{-1}(\text{PO}_4)_3$. Some of these compositions correspond to wyllieite, while oxidized grains correspond to rosemeryite (Hatert *et al.*, 2006).

Such unusual previously undescribed scorzalite breakdown was caused by post-magmatic, Na bearing fluids interacting with the pegmatite. Na could have become available by feldspar breakdown. Both albite and K-feldspar occur in the matrix and reflect distinct high phosphorous contents. K-feldspar contains up to 3.6 wt% of P_2O_5 and coexisting albite up to 1.98 wt%. Distribution of P between Fk and Ab ($\text{P}_{\text{Fk/Ab}}$) is 1.8. Textural relationships indicate albitization of the K-feldspar.

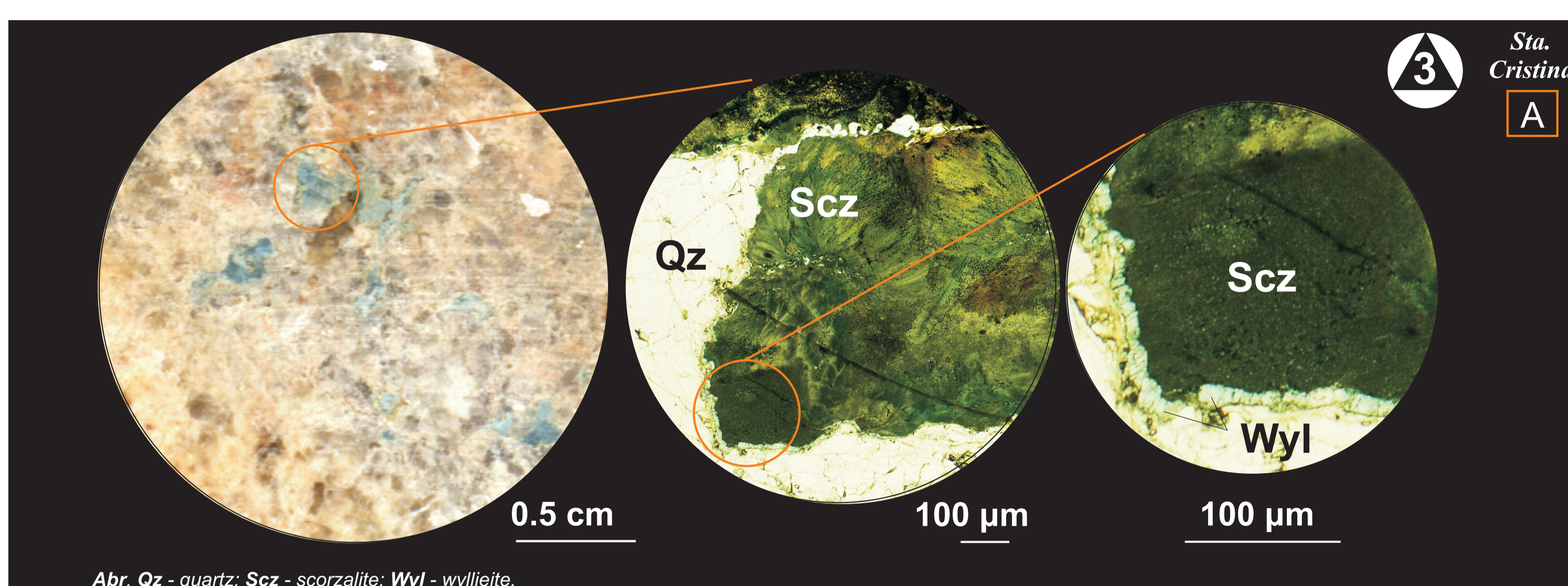
According to (Hatert *et al.*, 2006), wyllieite could have formed at temperatures lower than 400°C, considering a pressure of 0.1 Kbar. These estimates are within the considered field for scorzalite collapse (475-560°C, 1-3 Kbar) (Schmid-Beurmann *et al.*, 2000).

1. GEOLOGICAL SETTING OF SERRA DE ARGÁ PEGMATITES

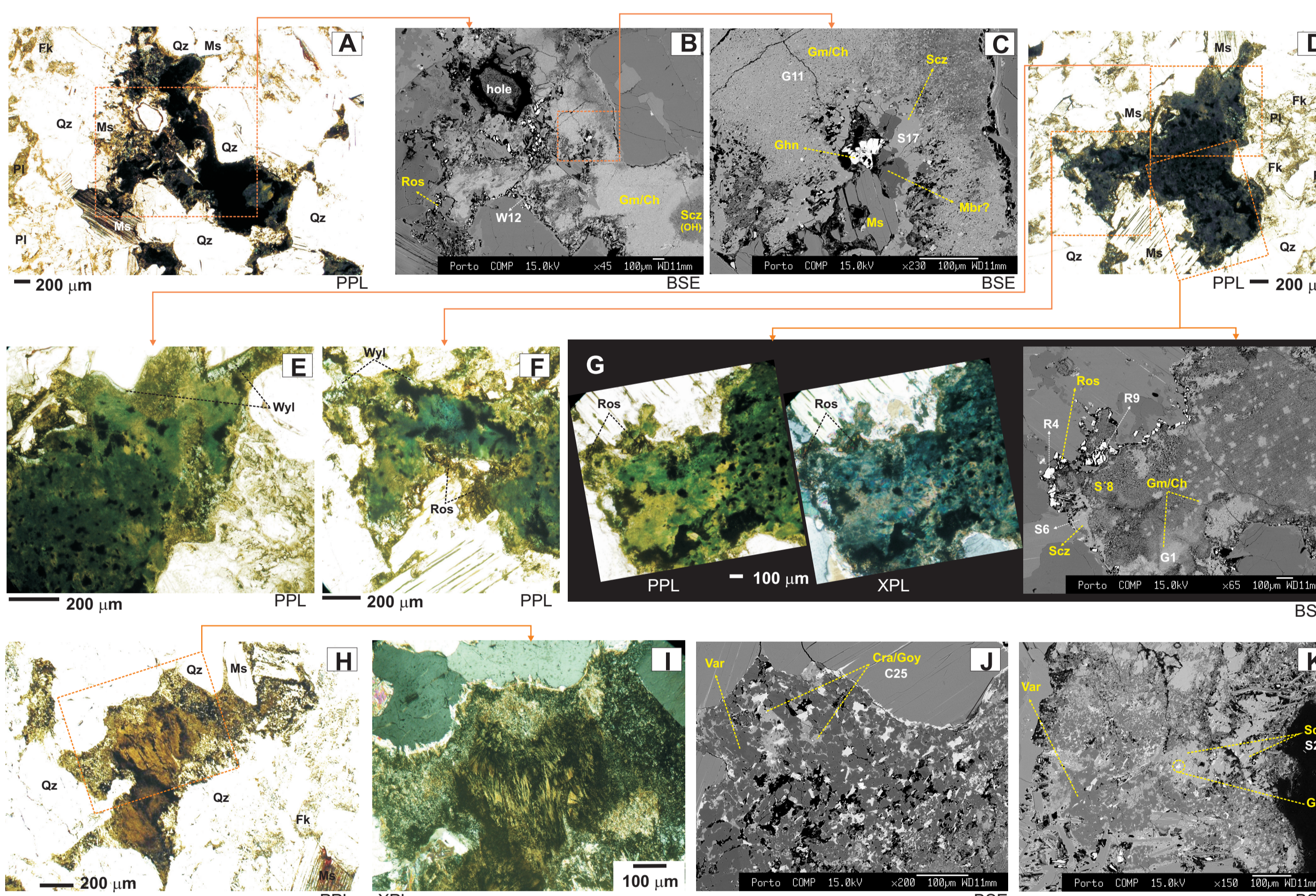
The Serra de Argá pegmatite field consists of a swarm of granite-related apatite-pegmatite sills and dykes (Leal Gomes, 1994) and earlier highly peraluminous anatectic pegmatites (Dias, 2012), mostly emplaced in metasedimentary and metacoolite-siliciclastic Silurian series (Minho Central and Domo de Covas Units). The first group, developed around the Argá granite plutone (S-type peraluminous granite, ± 318 Ma), comprises evolved Li-bearing pegmatites with a layered structure, belonging to the beryl, petalite, lepidolite and elbaite subtypes of the rare-element class; the pegmatites are mineralized with cassiterite and Nb-Ta oxides. The anatectic pegmatites consist of thin stroma and vein-like irregular bodies, derived from low-degree hydrated partial melts in conditions of intermediate P-T (2.9-4.2 kbar, 650-710 °C). The composition is significantly enriched in muscovite and andalusite (or albite) and depleted in potassium feldspar. They are characterized by a more or less simple structure although an internal zonation is commonly observed and inward fractionation is noticeable. A classification as theyssal or muscovite types is proposed, although a remarkable feature is the occurrence of tantalum rutile, ferrocolumbite and tapiolite in some of the vein deposits.



3. SCORZALITE-WYLLIEITE INTERGROWTHS



The polished specimen is of a fine-grained portion of a pegmatite dyke from Santa Cristina type locality (see Fig. 2), consisting essentially of quartz, plagioclase, potassium feldspar and muscovite in a subhedral granular texture. Scorzalite crystals ranging in size from 0.1-3mm are scattered throughout the rock and may be recognized by their deep blue color. The photomicrographs show PPL views of one scorzalite crystal surrounded by a 0.02-0.05 mm wide rim of wyllieite.



The photomicrographs were made from a thin section of the sample illustrated above and show PPL, XPL and BSE views of scorzalite crystals. A-C: a section of irregularly shaped scorzalite which has been replaced by gormanite or childrenite-eosphorite (brownish to black in PPL) show inclusions of muscovite, gahnite ($\text{Zn}_{10}\text{Fe}_{10}\text{Mn}_{10}\text{Al}_{10}\text{O}_{10}$) and montebrasite (?). The brownish yellow color around the margin of scorzalite is a narrow mantle of rosemeryite which is also clearly identified in the BSE view. D: another scorzalite crystal less altered to gormanite showing a deep blue absorption color and a corona of wyllieite and rosemeryite (developed indiscriminately between scorzalite and the various groundmass minerals). E-G: High magnification views of parts of the field of view shown in fig. D. In the first view (E) the brownish yellow color of rosemeryite serve to distinguish it from the wyllieite which shows a light blue absorption color and high relief. In the second view (F) wyllieite appears to form an inner mantle surrounded by rosemeryite. Photograph G shows scorzalite relics and a predominant slightly more hydrated and Mn-rich scorzalite blue to greenish in color (Scz-OH). The dark patches which are lighter in the BSE view are mainly of gormanite/childrenite-eosphorite. The narrow brown rim is of rosemeryite, with anomalous interference colors in the XPL view. H-K: scorzalite crystals altered to aggregates of variscite and crandallite. Scorzalite relics can be recognized and wyllieite-rosemeryite coronas are absent.

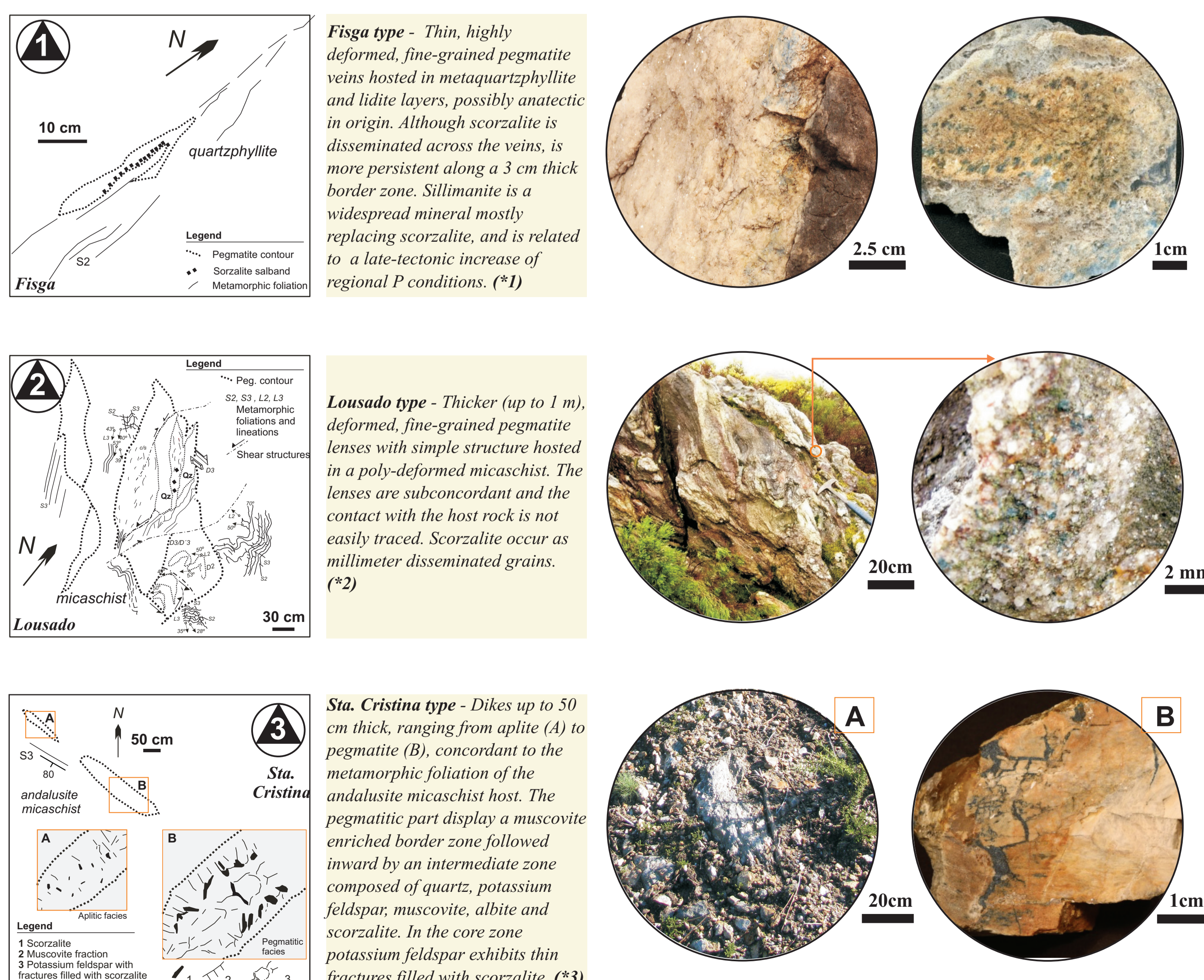
4. SELECTED COMPOSITIONS - ELECTRON MICROPROBE ANALYSIS

| wt. % | WYLLIEITE - ROSEMARYITE | | | SCORZALITE | | | OTHER PHOSPHATES | | | |
|--------------------------------|-------------------------|--------|--------|------------|-------|-------|------------------|-------|--------|-------|
| | W7 | W12 | W13 | R9 | R4 | S6 | S23 | S'8 | G11 | C25 |
| TiO ₂ | 0.02 | - | - | - | 0.02 | - | 0.008 | - | 0.0057 | - |
| Al ₂ O ₃ | 8.07 | 8.59 | 8.41 | 8.29 | 8.43 | 30.61 | 30.63 | 28.10 | 25.72 | 31.99 |
| FeO | 24.64 | 23.88 | 23.49 | 23.81 | 24.12 | 19.38 | 19.04 | 21.51 | 22.86 | 1.11 |
| MnO | 16.16 | 16.43 | 16.27 | 15.92 | 15.20 | 0.43 | 0.37 | 2.80 | 5.42 | 0.15 |
| MgO | 0.52 | 0.47 | 0.51 | 0.54 | 0.44 | 0.57 | 0.80 | 0.42 | 0.24 | 0.008 |
| CaO | 0.22 | 0.28 | 0.34 | 0.28 | 0.35 | - | 0.03 | 0.07 | 0.09 | 7.99 |
| Na ₂ O | 4.98 | 5.20 | 5.31 | 4.69 | 4.24 | 0.008 | - | 0.04 | 0.21 | 0.01 |
| K ₂ O | 0.02 | 0.02 | 0.00 | 0.01 | 0.03 | 0.061 | - | 0.01 | 0.03 | 0.06 |
| BaO | 0.08 | 0.12 | 0.01 | 0.11 | - | 0.061 | 0.13 | - | 0.02 | 0.77 |
| ZnO | - | - | - | - | 0.09 | 0.04 | 0.33 | 0.06 | 0.06 | - |
| F | 0.15 | 0.08 | - | 0.15 | 0.07 | - | - | 0.04 | - | 0.35 |
| Cl | 0.01 | 0.00 | - | - | - | - | - | 0.01 | 0.00 | 0.01 |
| Cr ₂ O ₃ | 0.07 | - | 0.02 | 0.06 | - | - | 0.01 | 0.04 | 0.08 | 0.01 |
| P ₂ O ₅ | 46.56 | 46.30 | 45.93 | 47.18 | 45.46 | 41.16 | 41.7 | 39.15 | 33.4 | 30.26 |
| Y ₂ O ₃ | - | - | - | 0.04 | - | 0.02 | - | - | - | - |
| SrO | 0.10 | - | - | 0.04 | 0.03 | - | 0.006 | 0.03 | 0.03 | 6.97 |
| SO ₂ | - | 0.04 | 0.05 | - | - | - | 0.05 | 0.06 | 0.002 | - |
| As ₂ O ₅ | - | 0.04 | - | 0.04 | - | - | - | - | 0.01 | - |
| Total | 101.59 | 101.44 | 100.35 | 101.17 | 98.47 | 92.33 | 93.11 | 92.32 | 88.18 | 79.53 |

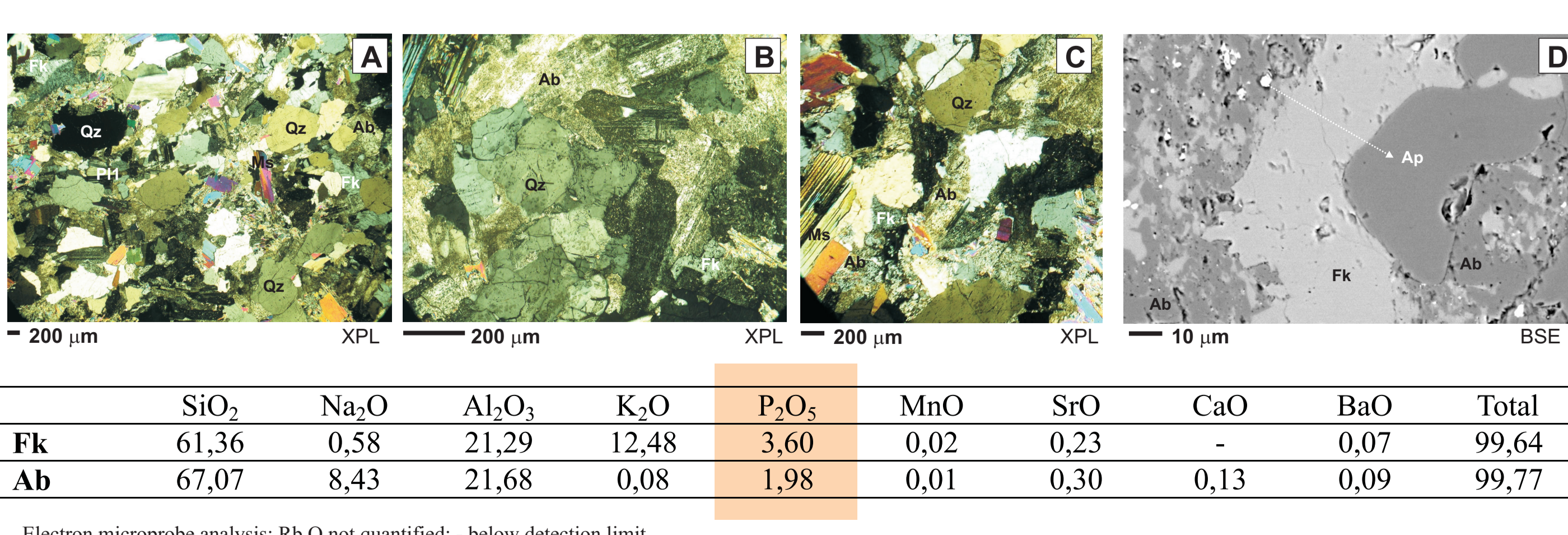
- Below detection limit. BSE images in Fig. 3 (B, C, G, J and K) indicate the spots chosen to perform the analyses.

2. SCORZALITE-BEARING PEGMATITES

Three types of scorzalite bearing pegmatites were identified:



5. CO-EXISTENT FELDSPARS - TEXTURES AND COMPOSITIONS



Electron microprobe analysis; Rb,O not quantified; - below detection limit.

The photomicrographs show the equigranular groundmass consisting of quartz, plagioclase, potassium feldspar and muscovite (A). Plagioclase feldspar and potassium feldspar are mostly subhedral and have slightly interdigitating boundaries. It appears that two generations of plagioclase are present: small subhedral to euhedral crystals showing multiple twinning (P1) and large subhedral crystals most easily identified by a turbid brownish appearance (Ab) resulting from very small inclusions of mica. The strong alteration of the plagioclase (B) is the first characteristic that enables to distinguish it from potassium feldspar, recognized here by the lack of alteration and sometimes the presence of simple twins (A). Evidence for potassium feldspar dissolution and replacement by albite + muscovite is shown in C. Apatite microinclusions are widely distributed within the albite and are clearly seen in the BSE view (D). The compositions of both albite and potassium feldspar are exceptionally rich in phosphorous.

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*1 and 2 - The composition of the veins is 45% quartz, 26% muscovite, 13% andalusite+sillimanite, 6% albite, accessory minerals (scorzalite, apatite, monazite, chrysoberyl, columbite-tantalite (?), and gahnite).

*3 - The composition of the apatite facies is: 41% quartz, 7.5% muscovite, 15.2% potassium feldspar, 29.6% albite, accessory minerals (scorzalite, wyllieite, rosemeryite, crandallite group phosphates, variscite, Mn-rich fluorapatite, montebrasite, brasilianite, andalusite, columbite-Fe, gahnite, uraninite).