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

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ABSTRACT

In the region of Serra de Arga (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: $(Fe^{2+}_{0.90}Mg_{0.05\text{-}0.07}Mn_{0.02}Zn_{0.0\text{-}0.01})_{=0.95\text{-}1.01}Al_{2.0\text{-}2.1}(PO_4)_2(OH)_2$.

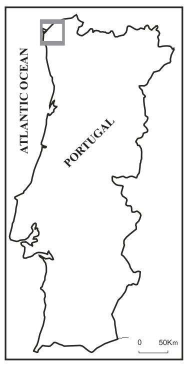
Wyllieite forms light blue corona-like overgrowths around primary scorzalite and also penetrate along fracture fillings of the scorzalite crystals, as revealed by transmitted light microscopy and EMP study. Electron-microprobe analysis provided P_2O_5 = 45.5-47.2; Al_2O_3 = 8-8.6, MnO = 15.2-16.3, FeO = 23.5-24.6, MgO = 0.44-0.54; Na_2O = 4.2-5.3 wt. %. The resulting formula, calculated on the basis of 12 O, is $(Na_{0.64\text{-}0.79}Ca_{0.02\text{-}0.03}Mn_{0.30\text{-}0.39})_{=1.01\text{-}1.22}(Mn_{0.60\text{-}0.71}Fe^{2+}_{0.29\text{-}0.40})_{=1}(Fe^{2+}_{0.27\text{-}0.61}Fe^{3+}_{0.34\text{-}0.67}Mg_{0.05\text{-}0.06})_{=1}(Al_{0.72\text{-}0.77}Fe^{3+}_{0.23\text{-}0.28})_{=1}(PO_4)_3$. Some of these compositions correspond to wyllieite, while oxidized grains correspond to rosemaryite (Hatert *et al.*, 2006).

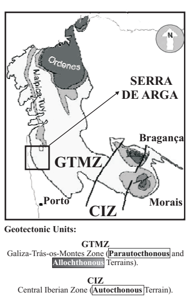
Such unusual previously undescribed scorzalite breakdown was caused by post-magmatic, Na bearing fluids interacting with the pegmatite. Na could have become available by feldspar breakdown. Both albite and K-feldspar occur in the matrix and reflect distinct high phosphorous contents. K-feldspar contains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

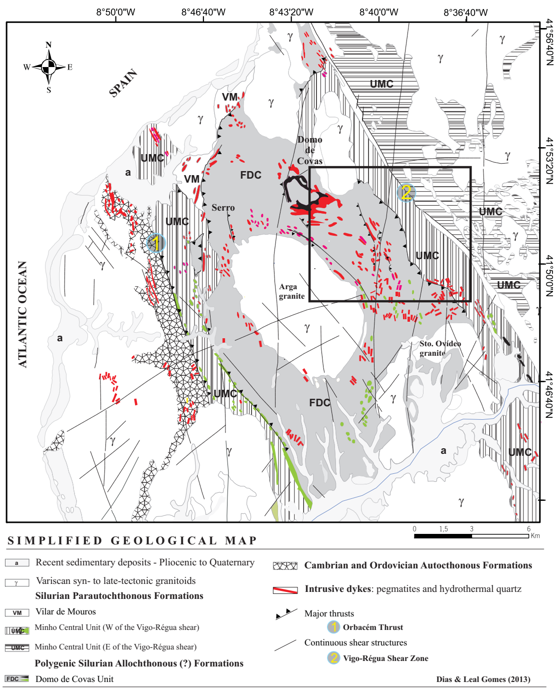
According to (Hatert *et al.*, 2006), wyllieite could have formed at temperatures lower than 400ºC, considering a pressure of 0.1Kbar. These estimates are within the considered field for scorzalite collapse (475-560ºC, 1-3Kbar) (Schmid-Beurmann *et al.*, 2000).

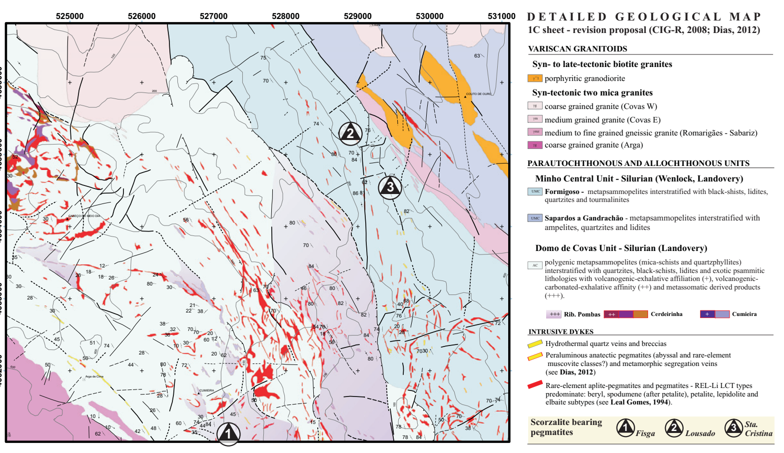
1. GEOLOGICAL SETTING OF SERRA DE ARGA PEGMATITES

The Serra de Arga pegmatite field consists of a swarm of granite-related aplite-pegmatite sills and dykes (Leal Gomes, 1994) and earlier highly peraluminous anatectic pegmatites (Dias, 2012), mostly emplaced in metassedimentary and metavolcanosedimentary-exhalative Silurian series (Minho Central and Domo de Covas Units). The first group, developed around the Arga granite plutonite (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 ºC). 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 abyssal or muscovite types is proposed, although a remarkable feature is the occurrence of tantalian rutile, ferrocolumbite and tapiolite in some of the vein deposits.



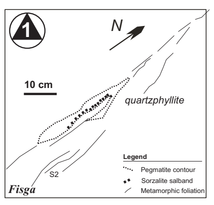




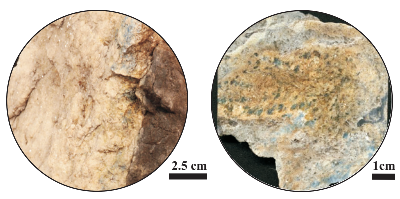


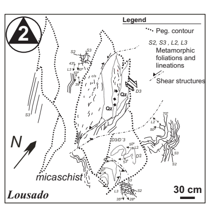
2. SCORZALITE-BEARING PEGMATITES

Three types of scorzalite bearing pegmatites were identified:

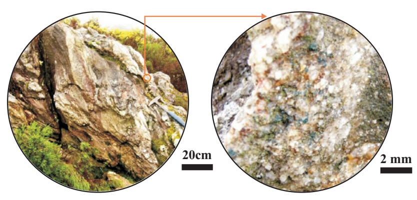


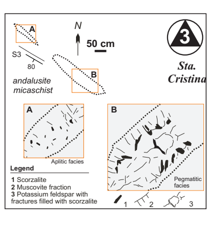
Fisga type *- Thin, highly deformed, fine-grained pegmatite veins hosted in metaquartzphyllite and lidite layers, possibly anatectic in origin. Although scorzalite is disseminated across the veins, is more persistent along a 3 cm thick border zone. Sillimanite is a widespread mineral mostly replacing scorzalite, and is related to a late-tectonic increase of regional P conditions.* ***(*1)***



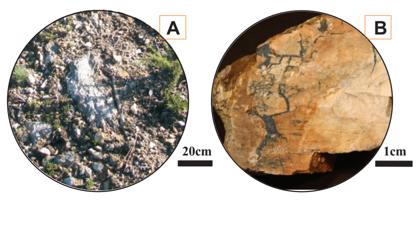


Lousado type *- Thicker (up to 1 m), deformed, fine-grained pegmatite lenses with simple structure hosted in a poly-deformed micaschist. The lenses are subconcordant and the contact with the host rock is not easily traced. Scorzalite occur as millimeter disseminated grains.* ***(*2)***



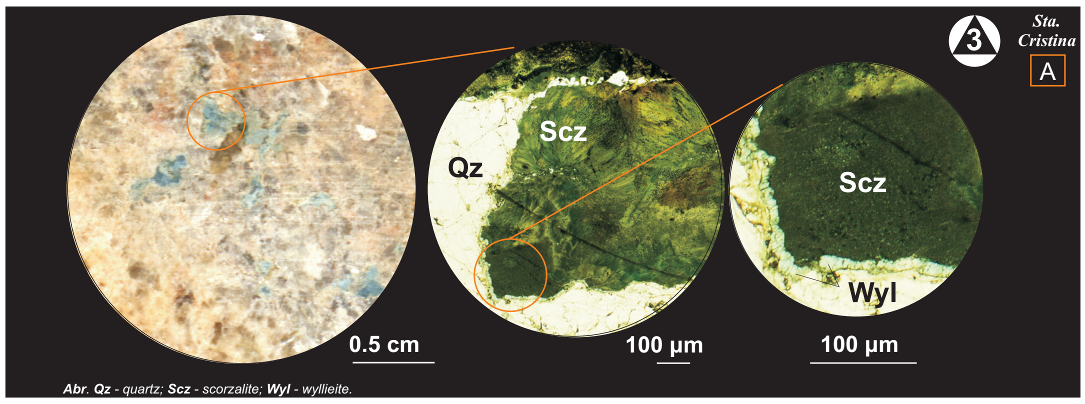


Sta. Cristina type *- Dikes up to 50 cm thick, ranging from aplite (A) to pegmatite (B), concordant to the metamorphic foliation of the andalusite micaschist host. The pegmatitic part display a muscovite enriched border zone followed inward by an intermediate zone composed of quartz, potassium feldspar, muscovite, albite and scorzalite. In the core zone potassium feldspar exhibits thin fractures filled with scorzalite.* ***(*3)***

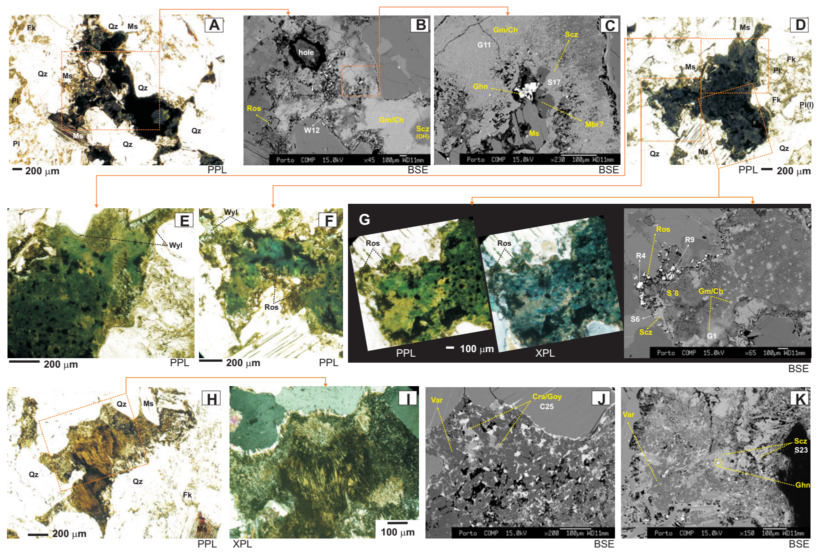


****1 and 2*** *- The composition of the veins is 45% quartz, 26% muscovite, 13% andalusite+sillimanite, 6% albite, accessory minerals (scorzalite, apatite, monazite, chrysoberyl, columbite-tantalite (?) and gahnite).*
****3*** *- The composition of the aplitic facies is: 41% quartz, 7.5% muscovite, 15.2% potassium feldspar, 29.6% albite, accessory minerals (scorzalite, wyllieite, rosemaryite, crandallite group phosphates, variscite, Mn-rich fluorapatite, montebrasite, brasilianite, andalusite, columbite-Fe, gahnite, uraninite).*

3. SCORZALITE-WYLLIEITE INTERGROWTHS



The polished specimen is of a fine-grained portion of a pegmatite dyke from Santa Crisitina 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.



*Abr. **Scz** - scorzalite; **Wyl** - wyllieite; **Ros** - Rosemaryite, **Gm/Ch** - gormanite or childrenite-eosphorite; **Scz (OH)** - more hydrated and Mn-rich scorzalite; **Cra/Goy** - crandallite- goyazite; **Var** - variscite; **Qz** - quartz; **Ab** - albite; **Ms** - muscovite; **Fk** - potassium feldspar; **Mbr** - montebrasite; **Ghn** - gahnite.*

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 ($Zn_{0.85}Fe_{0.08}Mn_{0.002})_{=0.94}Al_{2.04}O_4$) and montebrasite (?). The brownish yellow color around the margin of scorzalite is a narrow mantle of rosemaryite 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 rosemaryite (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 rosemaryite 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 rosemaryite. Photopgraph 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 rosemaryite, 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-rosemaryite coronas are absent.*

4. SELECTED COMPOSITIONS - ELECTRON MICROPROBE ANALYSIS

	WYLLIEITE - ROSEMARYITE					SCORZALITE		OTHER PHOSPHATES		
	Wyl	Wyl	Wyl	Ros	Ros	Scz	Scz	Scz(OH)	Grm/Ch	Cra/Goy
wt.%	W7	W12	W13	R9	R4	S6	S23	S´8	G11	C25
TiO_2	0,02	-	-	-	0,02	-	0,008	-	0,0057	-
Al_2O_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_2O	4,98	5,20	5,31	4,69	4,24	0,008	-	0,04	0,21	0,01
K_2O	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	0,01
Cr_2O_3	0,07	-	0,02	0,06	-	-	0,01	0,04	0,08	0,01
P_2O_5	46,56	46,30	45,93	47,18	45,46	41,16	41,7	39,15	33,4	30,26
Y_2O_3	-	-	-	0,04		0,02	-	-	-	-
SrO	0,10	-	-	0,04	0,03	-	0,006	0,03	0,03	6,97
SO_3	-	0,04	0,05	-	-	-	0,05	0,06	0,002	-
As_2O_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.

ANALYTICAL PROCEDURES

Mineral chemical analyses were performed on representative sections using a five-channel wavelength dispersion JEOL JXA 8500F microprobe, routinely operated at an accelerating voltage of 15 kV and a beam current intensity of 10 nA.

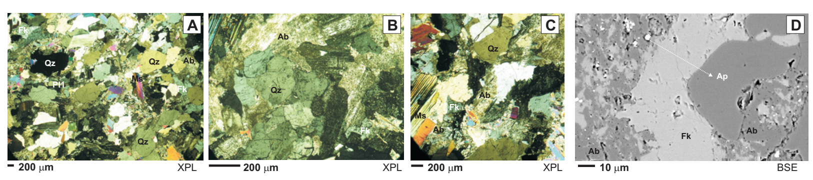
The standards used were (K lines): Orthoclase (Al, K), Albite (Na), MgO (Mg), Apatite (P, Ca), Volastonite (Ca, Si), Fe2O3 (Fe), MnTiO3 (Mn, Ti), Barite (Ba), Fluorite (F), Cr2O3 (Cr), SrTi O3 (Sr), Sphalerite (Zn), FeS2 (S), AsGa (As), Vanadinite (Cl), Yttrium Al Garnet (Y).

FORMULAS

Wyllieite-rosemaryite
$(Na_{0.64\text{-}0.79}Ca_{0.02\text{-}0.03}Mn_{0.30\text{-}0.39})_{=1.01\text{-}1.22}(Mn_{0.60\text{-}0.71}Fe^{2+}_{0.29\text{-}0.40})_{=1}(Fe^{2+}_{0.27\text{-}0.61}Fe^{3+}_{0.34\text{-}0.67}Mg_{0.05\text{-}0.06})_{=1}(Al_{0.72\text{-}0.77}Fe^{3+}_{0.23\text{-}0.28})_{=1}(PO_4)_3$; *N*=5.

Scorzalite
$(Fe^{2+}_{0.90}Mg_{0.05\text{-}0.07}Mn_{0.02}Zn_{0.0\text{-}0.01})_{=0.95\text{-}1.01}Al_{=2.0\text{-}2.1}(PO_4)_2(OH)_2$; *N*=5.

5. CO-EXISTENT FELDSPARS - TEXTURES AND COMPOSITIONS



	SiO_2	Na_2O	Al_2O_3	K_2O	P_2O_5	MnO	SrO	CaO	BaO	Total
Fk	61,36	0,58	21,29	12,48	3,60	0,02	0,23	-	0,07	99,64
Ab	67,07	8,43	21,68	0,08	1,98	0,01	0,30	0,13	0,09	99,77

Electron microprobe analysis; Rb_2O 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 (Pl1) 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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