*Canadian Mineralogist*
Vol. 30, pp. 639-651 (1992)

# THE CRYSTAL CHEMISTRY OF SPODUMENE IN SOME GRANITIC APLITE–PEGMATITE OF NORTHERN PORTUGAL*

BERNARD CHAROY AND FRANÇOIS LHOTE
*École Nationale Supérieure de Géologie et Centre de recherches pétrographiques et géochimiques,*
*Boîte postale 20, 54501 Vandoeuvre-Nancy Cedex, France*

YVES DUSAUSOY
*Laboratoire de Minéralogie et Cristallographie, UA CNRS 809, Université de Nancy I,*
*Boîte postale 239, 54506 Vandoeuvre-Nancy Cedex, France*

*Centro de Geologia, Faculdade de Ciências da Universidade do Porto,*
*Instituto Nacional de Investigação Cientifico, 4000 Porto, Portugal*

## ABSTRACT

Lithium-rich aplite–pegmatite bodies intruding the metamorphic basement of northeastern Portugal are described for the first time. They constitute only a small percentage of an important granitic aplite–pegmatite population associated with Hercynian synorogenic two-mica granites. Aplites and pegmatites are deformed by the last event of deformation, which postdates the peak of metamorphism. This paper focuses on the mineralogy and crystal chemistry of spodumene that is present mainly in the pegmatites but also in some associated aplites and, locally, in late ductile shear zones. Comparison with pegmatitic spodumene from Galicia (northwestern Spain) and with spodumene of gem quality ("kunzite") from pocket pegmatites from elsewhere in the world confirms the nearly constant composition of the pyroxene. Compositions of all spodumene examples are close to the theoretical formula, regardless of the location and paragenesis (early to late) in the aplite–pegmatite sequence of crystallization. Cell parameters determined by single-crystal or powder techniques present only slight variations, whatever the origin of the spodumene samples.

*Keywords*: granitic aplite–pegmatites, Hercynian, spodumene, crystal chemistry, Portugal.

## SOMMAIRE

Des corps aplitiques–pegmatitiques riches en Li recoupant le socle métamorphique de la province nord orientale du Portugal sont décrits pour la première fois. Ils constituent une faible fraction d'une importante population de corps aplitiques–pegmatitiques associés à un ensemble de granites syntectoniques à deux micas. Aplites et pegmatites sont déformées et sont à relier génétiquement à la dernière phase de déformation, postérieure au pic du métamorphisme régional. La minéralogie et la cristallochimie du spodumène, essentiellement présent dans les pegmatites, mais également dans certaines des aplites associées et dans des zones de fracturation ductile tardive, sont particulièrement étudiées. La comparaison avec le spodumène de pegmatites de Galice (nord ouest de l'Espagne) et la "kunzite" hydrothermale de cavités miarolitiques de diverses pegmatites dans le monde confirme la quasi-constance de la composition du pyroxène. Celle-ci est très proche de la composition théorique, quelque soit la localisation et l'association paragénétique (précoce ou tardive) du spodumène dans la séquence de cristallisation des corps aplitiques–pegmatitiques. Les paramètres de la maille déterminés sur monocristaux ou sur poudres sont également très constants.

*Mots-clés*: aplites, pegmatites granitiques, cristallochimie, spodumène, Hercynien, Portugal.

## INTRODUCTION

In the context of a program of regional mapping and a study of granite petrology, two of the authors studied an apparently representative collection of aplite–pegmatite granitic bodies very numerous in the Covas de Barroso district, northern Portugal (Figs. 1, 2). They discovered a previously unknown example of lithium mineralization expressed in a few of the pegmatites as spodumene, phosphates of the amblygonite series and, locally, lepidolite. The aim of this paper is to present paragenetic

---

*CRPG contribution number 930.

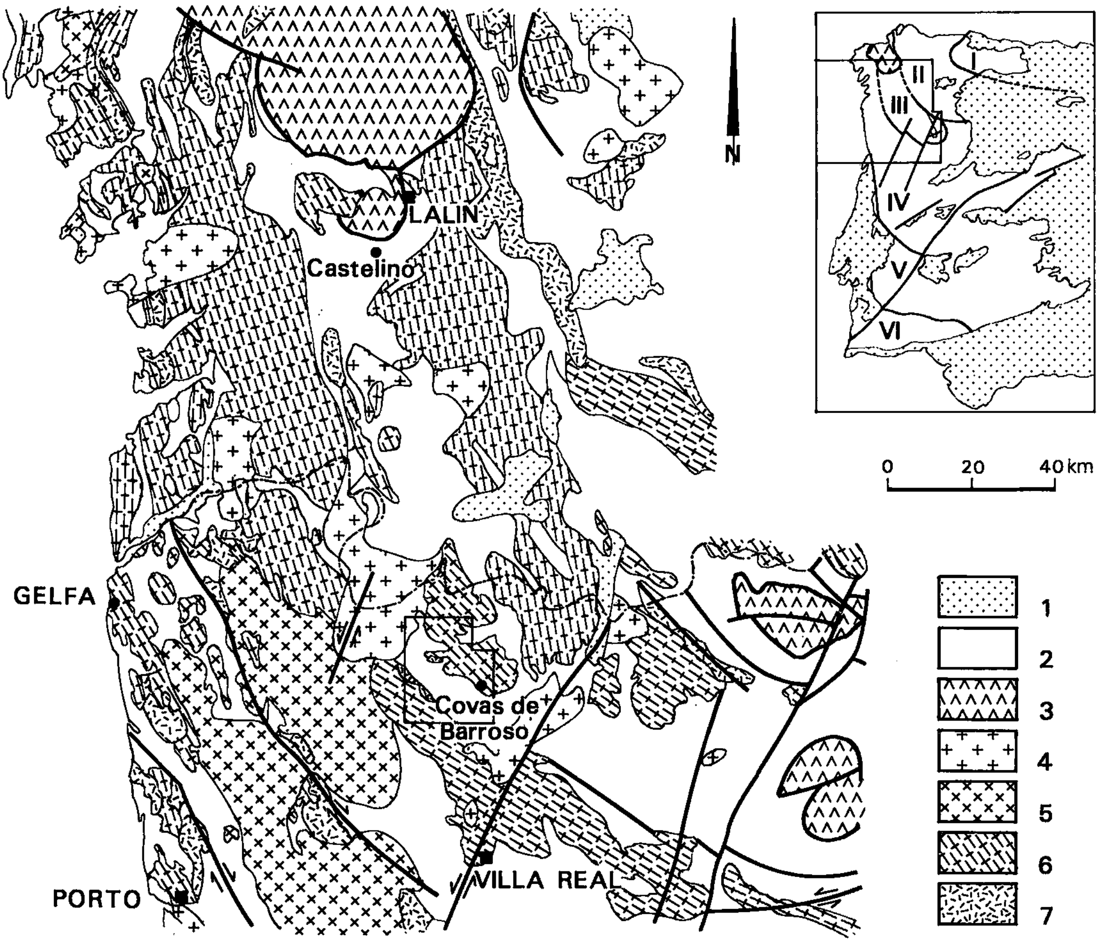


FIG. 1. Geological sketch-map of the northwest part of the Iberian Peninsula. 1) Mesozoic and Tertiary, 2) undifferentiated Paleozoic and Precambrian metamorphic rocks, 3) catazonal complexes from Galicia and Portugal, 4 to 7) Hercynian granites: 4) post-tectonic biotite granites, 5) late tectonic biotite granites, 6) syn- to late tectonic two-mica granites, 7) syntectonic biotite granites. Inset: major geotectonic units of the Iberian Peninsula: I) Cantabrian Zone, II) Asturian-Leonese Zone, III) Middle Galicia - Tras-os-Montes Zone, IV) Centro-Iberian Zone, V) Ossa-Morena Zone, VI) South Portuguese Zone.

details and data concerning the spodumene occurrences in these Li-rich aplite-pegmatite bodies. The lepidolite-rich occurrences will only be briefly discussed.

## GEOLOGICAL SETTING

The Covas de Barroso district (Figs. 1, 2) is located close to the boundary between two large tectonic units of the Iberian Hercynian belt (Ribeiro *et al.* 1979): the Middle Galicia - Tras-os-Montes Zone to the north and the Centro-Iberian Zone to the south (Fig. 1). Numerous granitic aplite-pegmatite dykes and veins, locally in dense swarms of more than 10 bodies, sharply cross-cut the metasediments (Fig. 2), which form the larger part of the Middle Galicia - Tras-os-Montes structural zone. Metasediments of Silurian age are mostly composed of quartziferous schists and micaceous schists with minor interbedded black schists. A few calc-silicate horizons contain some tungsten (scheelite) mineralization. At least three episodes of deformation affected the area, but only two schistosities are recognizable in the field (Noronha & Ribeiro 1981). The peak of metamorphism preceded the main Wesphalian episode of compression ($F_3$). Maximum conditions of metamorphism correspond to the andalusite zone: the temperature

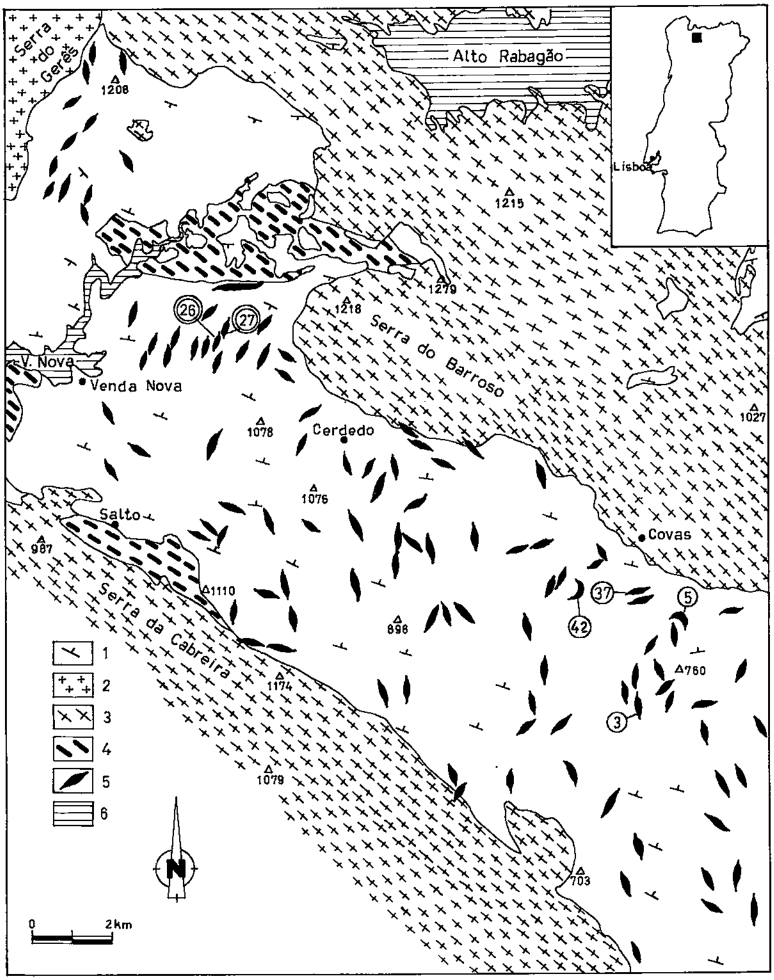


FIG. 2. The Covas de Barroso pegmatite field (outlined in Fig. 1): 1) Silurian metasediments, 2) post-tectonic biotite granites, 3) syn-to late-tectonic two-mica granites, 4) syntectonic biotite granites, 5) granitic aplite–pegmatite dykes, 6) dam reservoir. Single circle: spodumene occurrences; double circle: lepidolite occurrences.

attained 500°C, and the confining pressure was from 300 to 350 MPa (Holdaway 1971). Different types of granites, all of Hercynian age, are distributed in the area. Three types have been identified, according to their structural and temporal relations with the main $F_3$ phase of deformation (Ferreira *et al.* 1987): i) synorogenic biotite granites (syn-$F_3$), ii) synorogenic two-mica granites (syn-to late-$F_3$), and iii) post-tectonic biotite granites (post-$F_3$). The synorogenic two-mica granites are dominant in the Covas de Barroso district, where they define two large northwest-trending structures that broadly correspond to the core of $F_3$ antiforms (Fig. 2). Aplite–pegmatite bodies also are commonly distributed throughout the two-mica granites, but are very sparse in the biotite granites.

## GEOLOGY OF THE APLITE–PEGMATITE BODIES

The relations of the aplite–pegmatite bodies, with regard to the main metamorphic fabric, are variable even in a single swarm of dykes. They range from concordant to highly discordant, but all are more or less deformed. Dykes are vertical, flat or have a variable dip; they are elongate (more than 100 m along strike) or lenticular in shape. Largely because of the poor quality of outcrop (weathering and superficial Mn staining), the internal structure of the dykes commonly is difficult to determine. Some common characteristics of these pegmatite dykes include a heterogeneous texture, ranging from fine-grained aplitic to coarse-grained pegmatitic. Textural layering is locally a prominent morphological feature. Layers range from a few cm to one m thick. Aplite–pegmatite couplets alternate rhythmically or are randomly and intimately mixed, with aplite mainly in the footwall as a substrate for the pegmatite unit, which consists of more or less radial clusters of large alkali feldspar crystals. Slivers of the enclosing schists can be present close to the walls of the dykes. However, pegmatitic units are dominant in the larger dykes and bodies, whereas aplitic units (with only a few scattered coarse crystals of feldspar) make up most of the thinner veins (less than 1 m wide). By far, the majority of the aplite–pegmatite dykes exhibit a fracture control (linear or *en échelon*). Deformation, manifested by brittle deformation, "boudinage", lineation and even folding, is statistically correlatable with that of the enclosing metasediments, and is considered to have been generated during the $F_3$ phase of compression (Borges *et al.* 1979). Many of the aplite veins host low-grade tin mineralization (0.1 to 0.3 vol.% cassiterite: Maijer 1965, Noronha 1983) and were mined on a small scale after the Second World War, wherever argillic alteration made digging by hand possible.

As stated previously, large bodies (up to 4 m across) of pegmatite with a minor aplitic fraction are commonly encountered throughout the synorogenic two-mica granites; they also are deformed. In these bodies, muscovite is the dominant mica; biotite, together with tourmaline (schorl) and spessartine-rich garnet, occur as minor phases and may outline a crude layering; beryl is a rare accessory mineral. Lithium mineralization is apparently absent, suggesting a less extreme degree of chemical fractionation; however, a more systematic investigation would be necessary to confirm this hypothesis. These intragranitic aplite–pegmatite bodies have not yet been studied in detail and will not be discussed further.

## PETROGRAPHIC AND COMPOSITIONAL FEATURES OF THE LITHIUM-RICH APLITE–PEGMATITE UNITS

The spodumene- or lepidolite-bearing aplite–pegmatite population of the Covas de Barroso district represents a very small fraction (a few percent) of all the aplite–pegmatite occurrences encountered in the belt. However, the survey is still in progress, and other Li-rich occurrences will certainly be recognized in the future.

Bulk compositions of minerals, phase relationships and the primary *versus* metasomatic nature of mineral assemblages in the crystallization sequence of Li-rich pegmatites are generally complex (Jahns 1953, 1982, Stewart 1978, London & Burt 1982, Norton 1983). Relative to some of the most complex pegmatite deposits discussed by these authors, the occurrences studied in the Covas de Barroso district appear to have a relatively simple paragenesis. Albite is commonly the only feldspathic phase in the aplite units. Alkali feldspar may be present as late-stage, interstitial, weakly perthitic crystals. Phengite (characterized using electron-microprobe data) is largely dominant over biotite, minor tourmaline (schorl) and spessartine-rich garnet. In contrast, the pegmatite units are dominated by strongly perthitic megacrysts of alkali feldspar, which locally display a branching or brush-like habit. They are present either on aplite floors or on fine-grained tourmaline–garnet-rich layers. Phengite (identified from results of wet-chemical analyses on mineral concentrates) is ubiquitous, locally in radiating aggregates, and obviously of several generations. A fluorine-poor phosphate of the amblygonite series (characterized using electron-microprobe data) occurs in both aplites and pegmatites, but is generally rare and highly altered. Spodumene occurs mainly in the pegmatitic part of some dykes (CHN 3, CHN 37, CHN 42). Only one dyke (CHN 5), at this stage of the survey, shows spodumene in both aplitic and pegmatitic units.

Bulk compositions of some aplite–pegmatite couplets of the Covas de Barroso district are listed in Table 1, together with data on spodumene-bearing pegmatites from the literature. Pegmatite samples were obtained by channel-sampling by DGGM (SFM, Portugal), and are considered to be representative. Concentrations of elements were determined by inductively coupled plasma (ICP) spectrometry (K. Govindaraju, CRPG); concentrations of F, Li Sn and W were obtained by classical wet-chemical techniques (M. Vernet, CRPG). Associated aplite and pegmatite units are roughly identical in composition except for alkalis, with a higher Na content in the aplites reflecting the presence of albite as the only feldspar present. Within the aplites, K is mainly contained in the mica. This is in accordance with the model of Jahns & Burnham (1969) of alkali partitioning in aplite–pegmatite pairs. Lithium content is low in the aplites, except for sample CHN 5, where spodumene is present. Fluorine content invariably is low. Comparatively, the lepidolite-bearing aplite–pegmatite body (CHN 26) is strongly enriched in Rb and F. Both aplite and pegmatite units are strongly peraluminous: the aluminum saturation index [A/CNK = mole $Al_2O_3/(CaO + Na_2O + K_2O)$] is significantly greater than 1.1.

TABLE 1. BULK COMPOSITION OF APLITE-PEGMATITE PAIRS FROM NORTHERN IBERIAN PENINSULA AND THE LITERATURE

| | CHN3 | CHN5 | | CHN37 | | CHN42 | | GELFA | CAST 1 | CAST 2 | CHN26 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Wt % | sh. zone | apl. | pegm. | apl. | pegm. | apl. | pegm. | apl. | apl. | apl. | | 1 | 2 | 3 | 4 |
| | Sp | Sp | Sp | | Sp | | Sp | | | | Lep | Sp | Sp | Sp | Sp |
| $SiO_2$ | 74.71 | 73.47 | 73.15 | 74.39 | 76.06 | 72.68 | 78.34 | 74.98 | 72.71 | 73.90 | 70.13 | 72.16 | 72.1 | 74.6 | 73.5 |
| $TiO_2$ | tr. | tr. | tr. | tr. | tr. | tr. | tr. | 0.05 | tr. | tr. | tr. | - | 0.02 | | |
| $Al_2O_3$ | 16.88 | 16.26 | 16.14 | 15.25 | 16.56 | 15.78 | 16.60 | 14.10 | 16.43 | 16.13 | 17.38 | 17.68 | 18.2 | 16.4 | 16.7 |
| $Fe_2O_3t$ | 0.13 | 0.54 | 0.81 | 0.24 | tr. | 0.72 | tr. | 0.70 | 0.25 | 0.30 | 0.26 | 0.53 | 1.83 | | |
| MnO | tr. | 0.03 | 0.04 | tr. | 0.02 | 0.03 | 0.04 | 0.20 | 0.03 | 0.07 | 0.08 | 0.04 | 0.10 | | |
| MgO | tr. | tr. | 0.15 | tr. | tr. | 0.02 | tr. | tr. | tr. | tr. | tr. | - | 0.02 | | |
| CaO | 0.05 | 0.07 | 0.19 | 0.26 | tr. | 0.48 | tr. | 0.18 | 0.51 | 0.22 | 0.17 | 0.09 | 0.02 | | |
| $Na_2O$ | 3.37 | 5.13 | 2.45 | 5.30 | 2.31 | 5.83 | 0.56 | 5.28 | 7.53 | 6.63 | 4.89 | 6.56 | 3.20 | 3.3 | 3.4 |
| $K_2O$ | 2.59 | 2.24 | 3.54 | 2.52 | 2.07 | 1.79 | 1.08 | 2.36 | 1.11 | 1.41 | 2.85 | 0.92 | 2.02 | 2.4 | 2.6 |
| $P_2O_5$ | 0.97 | 0.21 | 0.40 | 0.40 | 0.39 | 0.59 | 0.16 | 0.24 | 0.51 | 0.22 | 0.70 | - | 0.07 | | |
| F | 0.11 | 0.03 | 0.03 | 0.06 | 0.04 | 0.05 | 0.02 | 0.08 | 0.07 | 0.05 | 0.99 | nd | nd | | |
| LOI | 0.87 | 1.19 | 2.12 | 1.16 | 1.53 | 1.53 | 1.89 | 0.78 | 0.80 | 0.92 | 2.15 | 0.86 | 0.68 | | |
| $O \equiv F$ | 0.05 | 0.01 | 0.01 | 0.03 | 0.02 | 0.02 | 0.01 | 0.03 | 0.03 | 0.02 | 0.42 | | | | |
| Total | 99.63 | 99.26 | 99.01 | 99.55 | 98.96 | 99.48 | 98.68 | 98.92 | 99.92 | 99.83 | 99.18 | 100.02 | 97.58 | | |
| Rb | 989 | 603 | 770 | 521 | 370 | 305 | 191 | 220 | 269 | 436 | 2393 | | 363 | | |
| Li | 9050 | 2890 | 6270 | 180 | 8900 | 505 | 12800 | 203 | 111 | 124 | 3565 | 5600 | 10967 | 7000 | 6533 |
| W | 1.9 | 2.1 | 0.8 | 1.4 | 1.9 | 2.0 | 1.2 | 0.7 | 3.4 | 1.5 | 19.9 | | | | |
| Sn | 210 | 41 | 45 | 78 | 36 | 29 | 111 | 20 | 243 | 104 | 728 | | | | |
| Be | 236 | 137 | nd | 104 | nd | nd | nd | nd | 145 | 140 | 175 | | | | |
| % spod (modal) (point counting) | | 15 | | | | | | | | | | 21.6 | 33 | | |
| A/CNK | 2.02 | 1.47 | 1.95 | 1.33 | 2.74 | 1.28 | 8.15 | 1.25 | 1.21 | 1.25 | 1.56 | 1.50 | 2.44 | 2.04 | 1.98 |

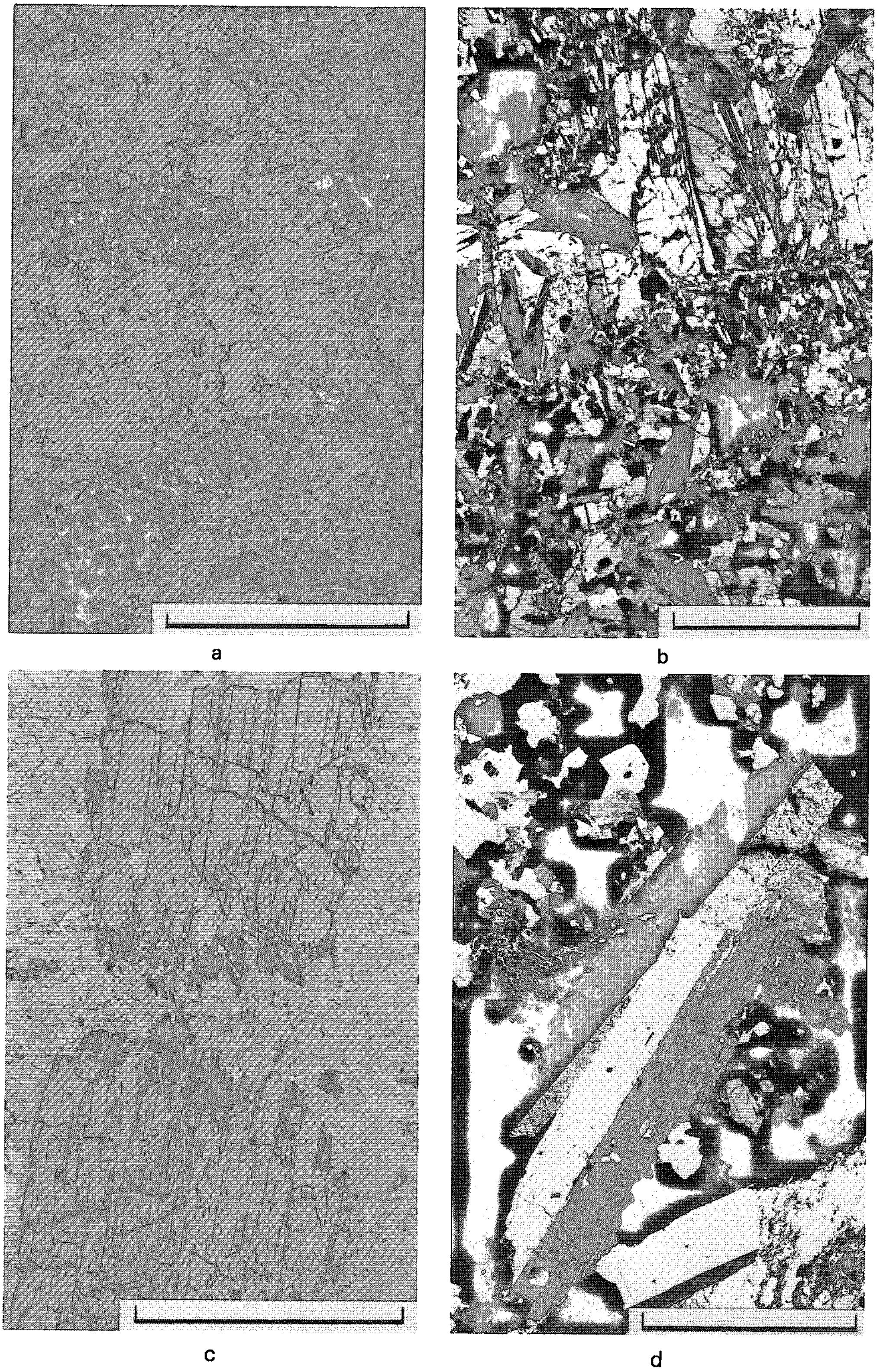
1. Spodumene–bearing pegmatite, Lalin, Galicia (von Knorring & Vidal Romani 1981). 2. Coarse–grained spodumene–bearing pegmatite, Ireland (Luecke 1981). 3–4. Spodumene–bearing pegmatites: results of partial analyses (Stewart 1978); 3: Kings Mountain, North Carolina, 4: Pegmatite Claims, Maine. Sp: spodumene is present. Lep: lepidolite is present. nd: not determined.

## SPODUMENE

### *General features*

The presence of spodumene has been reported only once in Portugal, as an accessory phase in a dense dyke swarm of aplite–pegmatite bodies (several generations) that cross-cut the strongly foliated two-mica granite of Gelfa (Torre de Assuncao 1954; Fig. 1). This locality was sampled for comparison. Spodumene is present as isolated crystals up to 10 cm long and as clusters scattered throughout the tourmaline- and garnet-bearing aplites of the composite bodies. It is associated with rare megacrysts of alkali feldspar. Spodumene is absent in the spatially associated pegmatite units.

In contrast, several occurrences of spodumene in southern Galicia, Spain, have already been described (Parga-Pondal & Cardoso 1948, Hensen 1967, von Knorring & Vidal Romani 1981); two spodumene-bearing aplite–pegmatite dykes at one locality (Castelino, Fig. 1) were sampled for comparison. The dykes are vertical and approximately 10 m thick; they are composite, with a thin aplitic margin along the contact with the enclosing schists. Abundant elongate laths of spodumene (locally forming inward-radiating clusters) occur together with large crystals of alkali feldspar; both are distributed with a well-expressed alignment normal to the fine-grained margins, which is indicative of conditions of rapid growth from a metastably supersaturated melt (D. London, pers. comm.). A quartz-rich core devoid of spodumene and alkali felspar contains only muscovite coating fractures. The composition of aplites from Gelfa and Castelino also is reported in Table 1. In all the Iberian pegmatite occurrences sampled during this study, spodumene forms coarse (1 to 10 cm long) euhedral lath-shaped crystals flattened on (100). They are milky white to pale yellowish, are bent, and in many cases, broken (Fig. 3c), with healed fractures normal to their elongation. These fractures are filled by quartz or, in cases, by the enclosing aplitic matrix (Gelfa). In some cases (CHN 5 and CHN 37, Fig. 3d), the large laths are coated by an aggregate of fine-grained white or pale greenish mica. In comparison, the spodumene in aplite CHN 5 is anhedral (Fig. 3a). The position of spodumene in the sequence of crystallization of the aplite–pegmatite bodies remains ambiguous; several generations of spodumene are obvious: i) it is an early phase, preceding the first appearance of albite, in the aplite occurrence (CHN 5; Fig. 3a); ii) in the pegmatite occurrences, it has a euhedral habit (in contrast to that in the aplite), and occurs as isolated laths or radiating aggregates (Figs. 3b,


a
b
c
d

d). However, its relationship to coarse alkali feldspar is difficult to constrain. In several cases, coarse-grained spodumene appears to be partly coated, and even partly replaced by a thin rim of cloudy K-feldspar. Both ends of most spodumene crystals in pegmatite assemblages exhibit a symplectitic intergrowth with quartz (Figs. 3c, 4a). A similar texture was described by Hensen (1967), who interpreted it as a product of growth at the expense of the contiguous alkali feldspar. Such a quartz–spodumene intergrowth also was described by Černý & Ferguson (1972) as the breakdown product of petalite. In the present examples, this association corresponds to a late generation of spodumene. iii) In one occurrence (CHN 3), several late $F_3$ ductile shear-zones (3 to 5 cm across) cross-cut a large, crudely layered, vertical, spodumene-bearing aplite–pegmatite body. These shear-zones contain preferentially oriented, symplectitic quartz–spodumene aggregates (Fig. 4b) enclosing mechanically transported fragments of the host aplite–pegmatite (alkali feldspar, a few coarse fragments of spodumene, amblygonite). This late generation of spodumene appears very similar to the sheaf-like aggregates reported by Hensen (1967) or even to the dykes of aphanitic

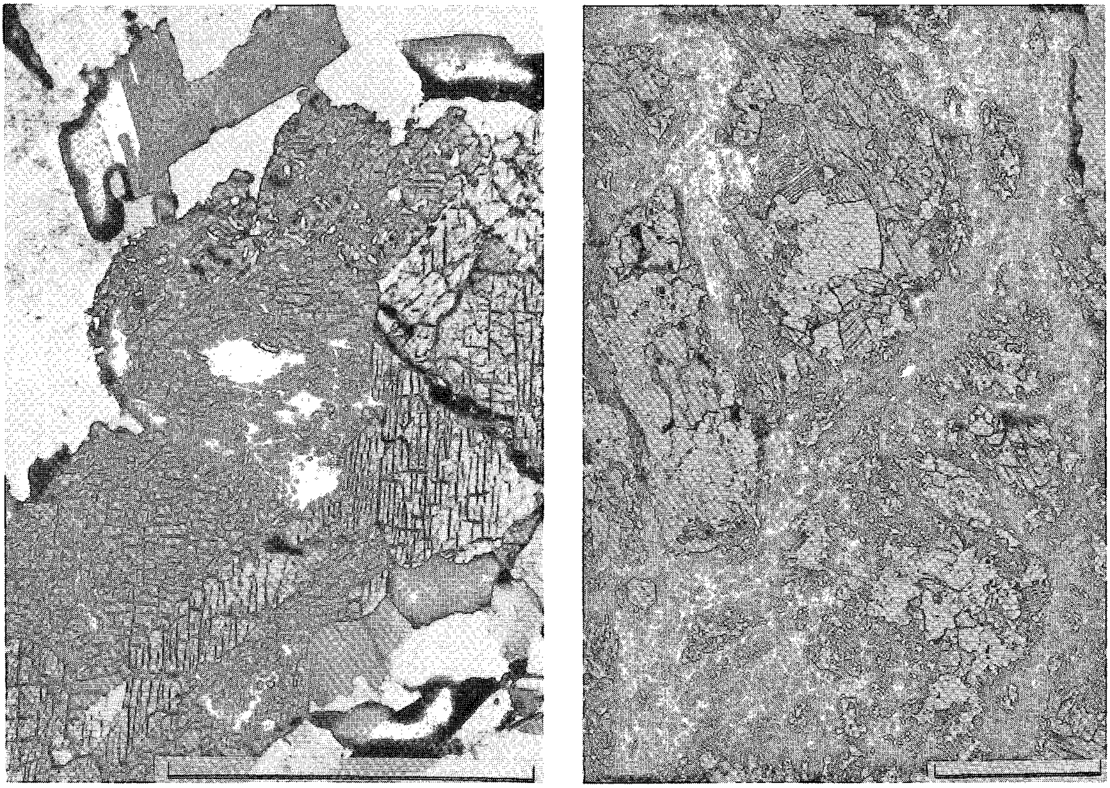


FIG. 4. a. Symplectitic rim of spodumene (with quartz). CAST. 2. Crossed polars; scale bar: 2 mm. b. Matted aggregates of very fine-grained needles of spodumene surrounding early coarser-grained spodumene. Shear zone cross-cutting the CHN 3 aplite–pegmatite body. Plane-polarized light; scale bar: 2 mm.

FIG. 3. a. Spodumene crystals (high relief) scattered in a fine-grained matrix of quartz, albite and muscovite. CHN 5 aplite. Plane-polarized light; scale bar: 2 mm. b. Large laths of spodumene of variable size in aggregates of quartz, albite and muscovite. CHN 5 pegmatite. Crossed polars; scale bar: 4.5 mm. c. Fine-grained intergrowth of spodumene and quartz on both sides of a fracture in a large lath of spodumene, Gelfa. Plane-polarized light; scale bar: 2.5 mm. d. Large subhedral lath of spodumene coated by perthitic alkali feldspar. CHN 37. Crossed polars; scale bar: 5 mm.

spodumene that cross-cut spodumene-bearing pegmatites described by Rossovskiy *et al.* (1976). We postulate that this late spodumene is contemporaneous with the symplectitic overgrowth described above.

### *Chemistry*

After crushing, spodumene was concentrated using heavy liquids and then further purified by hand-picking. The purity of the final separates was checked by X-ray diffractometry. Wet-chemical methods were used for analysis (M. Vernet, CRPG). Large single crystals of gem-quality spodumene ("kunzite" variety) from different pocket-pegmatites from a broad range of geographic locations and geological environments also were analyzed for comparison with the Iberian samples. The chemical composition and structural formula of the spodumene specimens (on the basis of 24 atoms of oxygen in the unit cell) are listed in Table 2. The abnormally high $P_2O_5$ content of sample CHN 3 is due to an unavoidable contamination by amblygonite. This excess of phosphorus was artificially removed assuming P–Li stoichiometry in amblygonite. Spodumene compositions do not show any significant deviation from the ideal formula $LiAlSi_2O_6$, as already pointed out by Deer *et al.* (1978) and London & Burt (1982). However, the Fe content is significantly higher in the Iberian material than in the "kunzite" specimens. Water content, reported as $H_2O_t$ (only a few $H_2O^+$ determinations), is low in the Iberian samples, but significant relative to the nearly water-free "kunzite" crystals. This anomaly might be related to small amounts of micaceous products of alteration; however, there is apparently no correlation between $H_2O_t$ and $K_2O$ contents (see, for example, sample CHN 37, with a relatively high $K_2O$ content but no clear X-ray-diffraction maximum observed at 10 Å). In thin fragments, the Iberian samples of spodumene are heavily clouded by fluid inclusions distributed parallel to the crystals' elongation. In contrast, the "kunzite" fragments are perfectly clear. It does not seem necessary to invoke structurally bonded OH to account for the presence of water, which may be totally confined to the fluid inclusions. Conse-

TABLE 2. COMPOSITION OF SPODUMENE

| Wt % | CHN3 shear zone | CHN5 (apl) | CHN5 (pegm) | CHN37 (pegm) | GELFA (pegm) | CAST 1 (pegm) | CAST 2 (pegm) | PALA | ANJANA | SAHATANY | MINAS GERAIS | Theoretical Composition |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 64.05 | 64.11 | 64.25 | 64.99 | 64.27 | 63.83 | 64.27 | 64.43 | 64.45 | 64.46 | 64.52 | 64.57 |
| $TiO_2$ | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.02 | 0.02 | <0.01 | <0.01 | 0.02 | <0.01 | |
| $Al_2O_3$ | 26.86 | 27.13 | 26.29 | 25.75 | 26.35 | 26.98 | 26.63 | 27.46 | 27.58 | 27.46 | 27.19 | 27.40 |
| $Fe_2O_3$T | 0.23 | 0.40 | 0.41 | 0.34 | 0.49 | 0.42 | 0.47 | 0.10 | 0.04 | 0.07 | 0.22 | |
| MnO | 0.03 | 0.03 | 0.03 | 0.02 | 0.11 | 0.08 | 0.09 | 0.05 | 0.07 | 0.07 | 0.10 | |
| MgO | 0.02 | 0.02 | 0.01 | 0.02 | 0.06 | 0.01 | 0.02 | <0.01 | <0.01 | <0.01 | <0.01 | |
| CaO | 0.15 | 0.03 | <0.01 | <0.01 | <0.01 | 0.03 | 0.01 | <0.01 | <0.01 | <0.01 | <0.01 | |
| $Na_2O$ | 0.09 | 0.09 | 0.16 | 0.16 | 0.23 | 0.16 | 0.16 | 0.26 | 0.21 | 0.22 | 0.16 | |
| $K_2O$ | 0.04 | 0.04 | 0.16 | 0.60 | 0.25 | 0.22 | 0.07 | 0.07 | 0.05 | 0.07 | 0.01 | |
| $P_2O_5$ | 0.22 | 0.06 | 0.04 | 0.05 | 0.01 | 0.07 | 0.04 | 0.01 | 0.02 | 0.01 | <0.01 | |
| $CO_2$t | 0.12 | 0.11 | 0.25 | 0.13 | 0.10 | 0.11 | 0.10 | 0.07 | 0.04 | 0.07 | nd | |
| $H_2O$t | 0.43 | 0.44 | 0.55 | 0.65 | 0.51 | 0.35 | 0.30 | 0.19 | 0.14 | 0.18 | 0.06 | |
| $Li_2O$ | 7.60 | 7.63 | 7.69 | 7.28 | 7.58 | 7.64 | 7.69 | 7.70 | 7.73 | 7.75 | 7.75 | 8.03 |
| Total | 99.86 | 100.09 | 99.84 | 99.99 | 99.96 | 99.92 | 99.87 | 100.34 | 100.27 | 100.38 | 100.01 | 100.00 |
| Rb (ppm) | <5 | <5 | nd | nd | nd | <5 | <5 | 5 | <1 | <1 | <1 | |
| Cs (ppm) | <0.5 | <0.5 | nd | nd | nd | <20 | <20 | 0.2 | 0.2 | 0.1 | 0.3 | |
| F% | 0.009 | 0.004 | <0.002 | 0.004 | 0.009 | 0.023 | 0.009 | 0.003 | 0.004 | <0.002 | <0.002 | |
| $H_2O^+$ | | 0.31 | | | | | 0.19 | | | | | |
| STRUCTURAL FORMULA (ON THE BASIS OF 24 O) | | | | | | | | | | | | |
| Si | 8.012 | 7.999 | 8.059 | 8.156 | 8.055 | 7.987 | 8.030 | 7.997 | 7.993 | 7.971 | 8.016 | 8.000 |
| Al | - | 0.001 | - | - | - | 0.013 | - | 0.003 | 0.007 | 0.029 | - | |
| Al | 3.959 | 3.987 | 3.890 | 3.811 | 3.891 | 3.968 | 3.925 | 4.015 | 4.027 | 3.974 | 3.982 | 4.000 |
| $Fe^{3+}$ | 0.020 | 0.037 | 0.039 | 0.030 | 0.045 | 0.040 | 0.045 | 0.010 | 0.005 | 0.005 | 0.020 | |
| Li | 3.818 | 3.829 | 3.881 | 3.680 | 3.826 | 3.846 | 3.865 | 3.845 | 3.856 | 3.856 | 3.868 | 4.000 |
| Mg | 0.004 | 0.004 | 0.002 | 0.004 | 0.011 | 0.001 | 0.004 | - | - | - | - | |
| Mn | 0.003 | 0.003 | 0.003 | 0.002 | 0.011 | 0.007 | 0.007 | 0.007 | 0.007 | 0.007 | 0.010 | |
| Ca | 0.020 | 0.004 | - | - | - | 0.004 | 0.001 | - | - | - | - | |
| Na | 0.021 | 0.039 | 0.039 | 0.039 | 0.056 | 0.039 | 0.039 | 0.060 | 0.049 | 0.052 | 0.039 | |
| K | 0.006 | 0.006 | 0.026 | 0.096 | 0.039 | 0.035 | 0.011 | 0.010 | 0.008 | 0.010 | - | |
| P | 0.006 | 0,006 | 0.004 | 0.005 | 0.001 | 0.007 | 0.004 | 0.001 | 0.005 | 0.001 | - | |
| Ti | - | - | - | - | - | 0.002 | 0.002 | - | - | 0.002 | - | |
| CRITICAL CHEMICAL RATIOS | | | | | | | | | | | | |
| Si/Al | 2.024 | 2.006 | 2.072 | 2.140 | 2.070 | 2.006 | 2.046 | 1.990 | 1.981 | 1.991 | 2.013 | 2 |
| Si/Li | 2.098 | 2.089 | 2.077 | 2.216 | 2.105 | 2.077 | 2.078 | 2.080 | 2.073 | 2.067 | 2.072 | 2 |
| Mn/Fe | 0.15 | 0.08 | 0.08 | 0.07 | 0.24 | 0.17 | 0.15 | 0.70 | 1.4 | 1.4 | 0.50 | - |

Samples of the variety "kunzite": Pala, California; Anyanaboina and Sahatany, Madagascar; Araçuai, Minas Gerais, Brazil. nd: not determined. $H_2O^+$ was determined for two samples only.

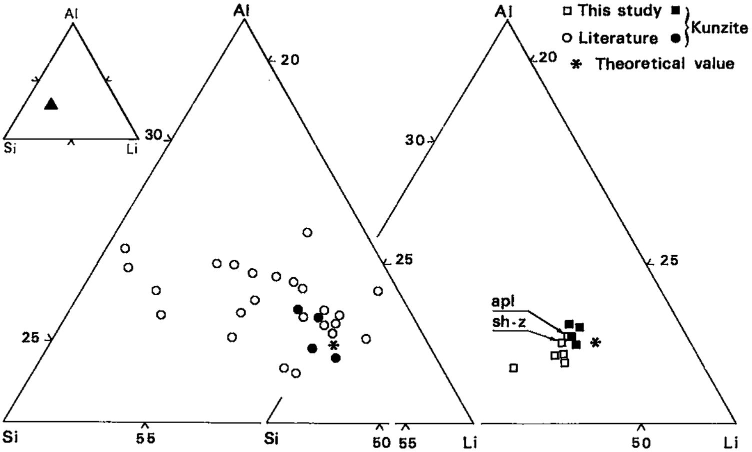


FIG. 5. Plot of spodumene compositions in terms of Si–Al–Li (atomic proportions). The data are taken from this study and from the literature. Sp: ideal structural formula; sh-z: shear zone (CHN 3); apl.: aplite (CHN 5).

quently, structural formulae are expressed as being OH-free.

The spodumene samples from the Iberian localities commonly have a small excess of Si relative to the ideal stoichiometry, whereas most of the gem-quality specimens have higher Al (even in tetrahedral coordination). This may represent either a real excess of Si in the structure, or the presence of quartz-spodumene symplectitic overgrowths described above, or some silica residual from the replacement of spodumene by muscovite (below detection limit for diffractometry) according to the reaction:

$3LiAlSi_2O_6 + K^+ + 2H^+ \rightarrow KAl_2AlSi_3O_{10}(OH)_2 + 3SiO_2 + 3Li^+$.

There is no significant substitution of Li by Na; however, Li is always deficient relative to the theoretical value; this is also true for the large majority of spodumene compositions in the literature. Černý & Ferguson (1972) found a significantly higher concentration of Na in secondary spodumene after petalite, which is not the case here. Compared to ordinary spodumene, manganese content does not seem significantly higher in the "kunzite" variety. Claffy (1953) and Hassan & Labib (1978) suggested, from an analysis by emission spectrography, that a high Mn content or a high Mn/Fe ratio is responsible for the lavender color in "kunzite". Rossman (1982) confirmed the importance of $Mn^{3+}$ as a chromofore element. Mn/Fe atomic ratios (Table 2) are, in fact, significantly lower in the Iberian samples; iron, as a minor component in fluid inclusions, could explain this variation. Concentrations of trace elements such as Rb, Cs and F are very low, close to or even below the limit of detection.

All the available spodumene compositions (including data from the literature) are plotted in terms of Si–Al–Li in atomic % in Figure 5. The scatter of the data reflects variable intensity of alteration, with leaching of Li being accompanied by an increase in Si and a decrease in Al. The composition of pristine, unaltered spodumene from this study is virtually constant and close to the theoretical formula, regardless of its paragenetic placement in the aplite-pegmatite sequence, the P–T conditions of crystallization or the geological environment.

### *X-ray and physical characteristics*

Unit-cell dimensions, calculated from data obtained by X-ray powder or single-crystal diffraction, are reported in Table 3, together with some optical and physical properties. Determination of cell dimensions (in the *C2/c* space group) was undertaken on single crystals (approximately 1 mm) on an ENRAF NONIUS CAD4 automatic diffractometer (graphite monochromator; Cu*K*$\alpha$ X radiation) using the least-square program INDEX for angular data on 25 well-defined reflections between 15 and 25° $\theta$ (Y. Dusausoy, analyst). A powder-diffraction pattern was recorded on four samples (* in Table 3), using a Guinier–Hägg focusing camera, synthetic spinel standard, Cu*K*$\alpha_1$ radiation; between 39 and 44 indexed peaks were treated in a least-square refinement using the program of Appleman & Evans (1973) (R.F. Martin, analyst).

TABLE 3. UNIT-CELL DIMENSIONS AND PHYSICAL PROPERTIES OF SPODUMENE VARIETIES

| | CHN 3* shear zone | CHN 5* (apl) | CHN 5 (pegm) | CHN 37 (pegm) | GELFA (pegm) | CAST 1 (pegm) | CAST 2 (pegm) | PALA | ANJANA | SAHATANY* | ARAÇUAI* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Unit cell dimensions** | | | | | | | | | | | |
| a (Å) | 9.468(1) | 9.467(1) | 9.466(1) | 9.469(1) | 9.476(3) | 9.467(1) | 9.475(2) | 9.463(2) | 9.474(1) | 9.469(1) | 9.469(1) |
| b (Å) | 8.392(1) | 8.392(1) | 8.390(1) | 8.393(1) | 8.397(2) | 8.398(1) | 8.397(1) | 8.390(2) | 8.391(1) | 8.392(1) | 8.398(1) |
| c (Å) | 5.220(0.4) | 5.221(0.6) | 5.227(0.8) | 5.221(1.4) | 5.226(2.6) | 5.221(0.7) | 5.223(1.3) | 5.218(0.6) | 5.222(1.2) | 5.219(0.5) | 5.222(0.5) |
| β (°) | 110°21(1) | 110°21(1) | 110°15(1) | 110°17(2) | 110°16(4) | 110°18(1) | 110°22(2) | 110°16(2) | 110°26(1) | 110°19(1) | 110°16(1) |
| V (Å³) | 389.25 | 389.27 | 389.72 | 389.48 | 390.27 | 368.61 | 389.94 | 388.90 | 389.45 | 389.26 | 389.83 |
| **Physical properties** | | | | | | | | | | | |
| Dm measured | nd. | nd. | nd. | nd. | 3.170 | 3.183 | 3.172 | 3.190 | 3.178 | 3.176 | 3.181 |
| Dx calculated | 3.210 | 3.181 | 3.181 | 3.189 | 3.182 | 3.186 | 3.179 | 3.187 | 3.182 | 3.186 | 3.187 |
| **Optical properties** | | | | | | | | | | | |
| γ | nd | nd | 1.661 | nd | 1.658 | 1.660 | 1.661 | 1.661 | 1.660 | nd | nd |
| β | nd | nd | 1.666 | nd | 1.663 | 1.664 | 1.665 | 1.667 | 1.665 | nd | nd |
| α | nd | nd | 1.677 | nd | 1.677 | 1.674 | 1.675 | 1.678 | 1.675 | nd | nd |
| mean refractive index (calc) | nd | nd | 1.671 | nd | 1.674 | 1.674 | 1.674 | 1.679 | 1.678 | 1.679 | 1.678 |
| $2V_Z$ meas.(°) | nd. | 63 | 65 | 58 | 63 | 63 | 62 | nd | nd | nd | nd |
| $2V_Z$ calc (°) | nd | nd | 66.4 | nd | 64.6 | 65.0 | 63.6 | 65.5 | 70.4 | nd | nd |
| γ : z (°) | ≅ 24 | 25 | 25 | 26 | 24 | 25 | 24 | 26 | 24 | 23 | 24 |

Unit cell dimensions determined on powder using a Guinier-Hägg chamber (*); otherwise, determined on single crystal using a CAD 4 Nonius automatic diffractometer.
Dm (g/cm$^3$) measured with a picnometer and Dx calculated using the formula = formula weight x Z x 1.6603 x $10^{-24}$ / unit cell volume (Å$^3$) x $10^{-24}$.
Refractive indices measured by the immersion method (at 20°C ambient temperature) on small flattened elongated fragments.
Mean refractive indice calculated with the law of Gladstone and Dale (1864) : $(n-1)/\rho = K$, with $K = \Sigma\, k.p.$ K = specific refractive energy of the mineral, k = specific refractivity of constituent oxide, p = weight percent of the constituent oxide (data in Jaffe, 1988) : computation systematically gives higher values.
Optical axial angle measured on a universal stage and calculated from the relations between the refractive indices in the triaxial ellipsoid.
γ : z (°) statistically measured on thin elongated fragments.

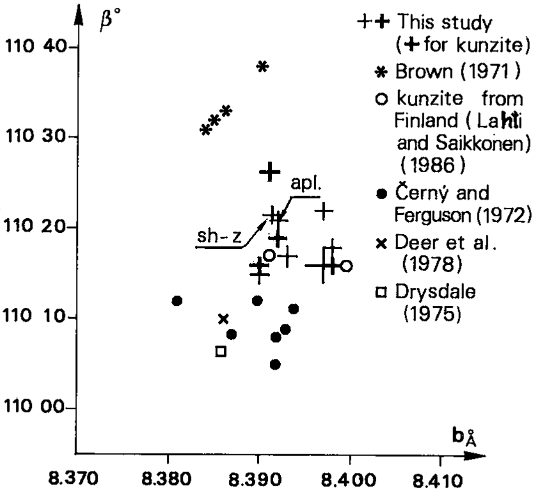


FIG. 6. Plot of *b* against *β* for spodumene. Data from this study and from the literature (error bars indicated).

Agreement between results obtained by the two techniques is reasonably good.

Physical constants are also in good agreement between the Iberian samples of spodumene and the "kunzite" varieties. However, the extinction angle (γ:Z) is slightly variable and seems to be a little lower for the "kunzite" samples. The calculated density $D_x$ is commonly slightly greater than that physically determined ($D_m$).

Data from this study and from the literature are compared in Figure 6, a plot of *b* against *β*. Brown (1971) demonstrated that cell parameters, particularly *b*, increase as does the radius of the trivalent cations populating the *M*1 sites; the increase is most important in the cell volume, and the parameters increase in the order *b*, *a*, *c* (see also Drysdale 1975). For natural examples of spodumene, in which Al is largely dominant, a positive correlation of *b* versus *β* was suggested by Brown (1971). However, this is not confirmed by the scatter of data from this study or from the literature (Fig. 6); *β* seems more variable than *b*, whereas the volume of the unit cell remains nearly constant.

## DISCUSSION

For the first time, spodumene-rich pegmatites from the northern part of Portugal are described in some detail. The present mineralogical work demonstrates the variability in the expression of spodumene mineralization; it commonly occurs in the pegmatite units, but also appears in a few of the associated aplites. Spodumene crystallization ranges from early to late with regard to the main stage of feldspar crystallization (albite in aplite and alkali feldspar in pegmatite, respectively). Crystallization during postconsolidation events also is evident: fine-grained spodumene in healed fractures (as in CHN 3 ductile shear-zones) is obviously late and implies that Li–Al-saturated fluids percolated through largely consolidated spodumene-bearing bodies of granitic pegmatite.

In most of the aplite–pegmatite bodies studied, fluorine activity (estimated from the F content in the whole-rock compositions in Table 1) was low throughout their consolidation and stabilized Li-aluminosilicate phases instead of lepidolite (Burt & London 1982). This is not true for the more evolved aplite–pegmatite bodies (CHN 26–27 in Fig. 2 and Table 1), where fluorine had a more significant role and stabilized the association of lepidolite, topaz and F-rich amblygonite, together with aggregates of albite (cleavelandite habit). However, these phases were developed at a subsolidus stage by replacement of an earlier assemblage (alkali feldspar but absence of a relict primary spodumene); cassiterite was preferentially precipitated or remobilized at this stage.

A fluid-inclusion study (Doria *et al.* 1989) has been performed on some of these Portuguese spodumene-bearing pegmatites. Results on spodumene and presumably coexisting quartz help to constrain possible interpretations about the genesis of these bodies. Fluids contemporaneous with spodumene precipitation (data from primary and pseudosecondary inclusions) were heterogeneous brines of variable density, in which Li was found to be roughly equivalent to Na, in order to stabilize the spodumene + albite + quartz assemblage (Lagache & Sebastian 1991). The volatile component of these fluids in spodumene and quartz was found to be dominated by low-density $H_2O$ and $CO_2$, with minor but detectable amounts of $CH_4$ and $N_2$ (Raman determination). Homogenization to the liquid or vapor phase occurs over the range 320–365°C. Virtually all primary inclusions are crystal-rich, although with a variable crystal/liquid ratio. A preliminary SEM–EDS investigation indicates that aluminosilicates and phosphates occur as daughter minerals. Most of them dissolve completely at a temperature of 475°C. A plot of these data in the P–T petrogenetic grid for Li-aluminosilicates proposed by London (1984) constrains the maximum conditions for precipitation of spodumene: 475–530°C at a confining pressure of 250 to 300 MPa, which is slightly lower than conditions estimated for the peak of regional metamorphism. These results are broadly concordant, in terms of P and T, with those determined by London (1985, 1986) for the Tanco pegmatite even if $CO_2$ is apparently lacking as a volatile component in spodumene. $CO_2$ also was absent during the evolution of Li-bearing pegmatites from southeastern Ireland (Whitworth & Rankin 1989). Chakoumakos & Lumpkin (1990) determined conditions of 550°C and 330–350 MPa for spodumene precipitation in the Harding pegmatite (with $CO_2$ present).

From geological evidence, the aplite–pegmatite population of the Covas de Barroso district is spatially (and presumably genetically) related to the adjacent synorogenic two-mica granites (Fig. 2), but the numerous, poorly fractionated aplite–pegmatite bodies hosted by these two-mica granites are apparently barren of Li. However, spodumene-bearing and other rare-element pegmatites are generally absent within the parental plutons; they are mostly located in distal parts of the regional pegmatite haloes surrounding fertile plutons, far beyond their contacts with their metamorphic cover (Černý 1990; pers. comm.). The reduced viscosity, the increased solubility of $H_2O$ and the enrichment in solidus-depressing constituents in these more fractionated, rare-element-enriched melts would explain this centrifugal segregation (Černý 1982). It is also true that lithium-rich pegmatites usually constitute a restricted percentage of the pegmatite (and aplite) population characteristically related to the final stages of evolution of two-mica granitic magmas (London & Burt 1982). This seems confirmed by the relatively rare occurrence of Li-rich bodies amongst the aplite–pegmatites in the Covas de Barroso district (Fig. 2), where there is no apparent spatial zonation within the pegmatite population. These mineralized pegmatites, even if poorly evolved in terms of mineralogy, chemistry and fractionation, seem to belong to the high-pressure, low-temperature spodumene subtype of the rare-element class in the classification of Černý (1990), whereas the mineralized aplites would be more representative of the albite–spodumene subtype. The two lepidolite-rich bodies (CHN 26–27) that are apparently isolated in the pegmatite belt (Fig. 2) probably belong to the lepidolite subtype, but as stated before, the key assemblage of minerals was only stabilized at a subsolidus stage. Physical conditions for precipitation of spodumene are variable, although pressure must always be high enough to preclude petalite stability (London 1984). The present study confirms the nearly constant chemical composition, close to the ideal composition, of all the spodumene samples, with only minor substitution of Al and Li. The gem varieties studied here for comparison occur in "pocket" pegmatites hosted by amphibolite metamorphic terranes and were precipitated from hydrothermal fluids. Small variations in Fe and $H_2O$ between the gem variety and the Iberian spodumene are most likely explained by the presence of fluid inclusions, which are prominent in the Iberian samples. Structural and physical characteristics of all the samples of spodumene are similar, and the unit cells are nearly constant.

The present study is part of a more general program of research concerning relationships between different types of Hercynian granite and the widespread Sn–W mineralization exhibited in this northern part of Portugal. A larger and more detailed investigation throughout the huge aplite-pegmatite belt, aimed at recognizing new mineral occurrences with possible economic potential, has already been started by DGGM (Servico Fomento Mineiro Portugal), and preliminary results are promising.

## ACKNOWLEDGEMENTS

The authors acknowledge the help of H.J. Schubnel, from the Museum d'Histoire Naturelle de Paris, for kindly supplying most of the "kunzite" samples. J.P. Lorand (of the same Institute) is thanked for his help with the determination of the indices of refraction. The help of R.F. Martin for the determination of the cell parameters of four samples is greatly acknowledged. The thorough criticisms and fruitful comments by Dr. P. Černý, R.F. Martin and two anonymous reviewers considerably improved the manuscript; all of them are gratefully acknowledged. Tables were carefully typed by J. Gerbaut.

## REFERENCES

APPLEMAN, D.E. & EVANS, H.T., JR. (1973): Job 9214: indexing and least-squares refinement of powder diffraction data. *U.S. Geol. Surv., Comput. Contrib.* **20**.

BORGES, F.S., NORONHA, F., PEREIRA, E. & RIBEIRO, A. (1979): Ocorrência de filoes apliticos deformados, com mineralizaçao estanifera (nota prévia). *Publ. Museu Lab. Min. Geol. Fac. Ciênc. Porto* **XCI**, 223-229.

BROWN, W.L. (1971): On lithium and sodium trivalent-metal pyroxenes and crystal-field effects. *Mineral. Mag.* **38**, 43-48.

BURT, D.M. & LONDON, D. (1982): Subsolidus equilibria. *In* Granitic Pegmatites in Science and Industry (P. Černý, ed.). *Mineral. Assoc. Can., Short-Course Handbook* **8**, 329-346.

ČERNÝ, P. (1982): Petrogenesis of granitic pegmatites. *In* Granitic Pegmatites in Science and Industry (P. Černý, ed.). *Mineral. Assoc. Can., Short-Course Handbook* **8**, 405-461.

______ (1990): Distribution, affiliation and derivation of rare-element granitic pegmatites in the Canadian Shield. *Geol. Rundschau* **79/2**, 183-226.

______ & FERGUSON, R.B. (1972): The Tanco pegmatite at Bernic Lake, Manitoba. 4. Petalite and spodumene relations. *Can. Mineral.* **11**, 660-678.

CHAKOUMAKOS, B.C. & LUMPKIN, G.R. (1990): Pressure-temperature constraints on the crystallization of the Harding pegmatite, Taos County, New Mexico. *Can. Mineral.* **28**, 287-298.

CLAFFY, E.W. (1953): Composition, tenebrescence and luminescence of spodumene minerals. *Am. Mineral.* **38**, 919-931.

DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1978): *Rock-Forming Minerals.* **2A**. *Single-Chain Silicates.* Longman, London.

DORIA, A., CHAROY, B. & NORONHA, F. (1989): Fluid inclusion studies in spodumene-bearing aplite-pegmatite dykes of Covas de Barroso, Northern Portugal. *ECROFI* **X** (London), 25 (abstr.).

DRYSDALE, D.J. (1975): Hydrothermal synthesis of various spodumenes *Am. Mineral.* **60**, 105-110.

FERREIRA, N., IGLESIAS, M., NORONHA, F., PEREIRA, E., RIBEIRO, A. & RIBEIRO, M.L. (1987): Granitoides da Zona Centro Iberica e seu enquadramento geodinamico. *In* Geologia de los Granitoides y Rocas Asociadas del Macizo Hespérico (F. Bea *et al.*, eds.). Editorial Rueda, Madrid (Libro Homenaje a L.C.Garcia de Figuerola), 37-51.

GLADSTONE, J.H. & DALE, T.P. (1864): Researches on the refraction, dispersion and sensitiveness of liquids. *R. Soc. London, Philos. Trans.* **153**, 337.

HASSAN, H. & LABIB, M. (1978): Induced color centers in spodumene called kunzite. *Neues Jahrb. Mineral. Abh.* **134**, 104-115.

HENSEN, B.J. (1967): Mineralogy and petrography of some tin, lithium and beryllium-albite pegmatites near Doade, Galicia, Spain. *Leidse Geol. Med.* **39**, 249-259.

HOLDAWAY, M.J. (1971): Stability of andalusite and the aluminum silicate phase diagram. *Am. J. Sci.* **271**, 97-131.

JAFFE, H.W. (1988): *Crystal Chemistry and Refractivity.* Cambridge University Press, Cambridge, England.

JAHNS, R.H. (1953): The genesis of pegmatites. 1. Occurrence and origin of giant crystals. 2. Quantitative analysis of lithium-bearing pegmatite, Mora

County, New Mexico. *Am. Mineral.* **38**, 563-598, 1078-1112.

______ (1982): Internal evolution of pegmatite bodies. *In* Granitic Pegmatites in Science and Industry (P. Černý, ed.). *Mineral. Assoc. Can., Short-Course Handbook* **8**, 293-327.

______ & BURNHAM, C.W. (1969): Experimental studies of pegmatite genesis. I. A model for the derivation and crystallization of granitic pegmatites. *Econ. Geol.* **64**, 843-864.

VON KNORRING, O. & VIDAL ROMANI, J.R. (1981): On the mineralogy of the O Castelino spodumene pegmatite near Lalin, Galicia, Spain. *Cuad. Lab. Xeol. Laxe* **2**, 259-262.

LAGACHE, M. & SEBASTIAN, A. (1991): Experimental study of Li-rich granitic pegmatites. II. Spodumene + albite + quartz equilibrium. *Am. Mineral.* **76**, 611-616.

LAHTI, S.I. & SAIKKONEN, R. (1986): Kunzite from the Haapaluoma pegmatite quarry, western Finland. *Comm. Bull. Géol. Finlande* **58**, 47-52.

LONDON, D. (1984): Experimental phase equilibria in the system $LiAlSiO_4$–$SiO_2$–$H_2O$: a petrogenetic grid for lithium-rich pegmatites. *Am. Mineral.* **69**, 995-1004.

______ (1985): Origin and significance of inclusions in quartz: a cautionary example from the Tanco pegmatite, Manitoba. *Econ. Geol.* **80**, 1988-1995.

______ (1986): Magmatic–hydrothermal transition in the Tanco rare-element pegmatite: evidence from fluid inclusions and phase-equilibrium experiments. *Am. Mineral.* **71**, 376-395.

______ & BURT, D.M. (1982): Lithium-aluminosilicate occurrences in pegmatites, and the lithium-aluminosilicate phase diagram. *Am. Mineral.* **67**, 483-493.

LUECKE, W. (1981): Lithium pegmatites in the Leinster granite (southeast Ireland). *Chem. Geol.* **34**, 195-233.

MAIJER, C. (1965): *Geological Investigations in the Amarante Region (Northern Portugal) with Special Reference to the Mineralogy of the Cassiterite-Bearing Albite-Pegmatites.* Ph.D. thesis, Univ. Amsterdam, Amsterdam, The Netherlands.

NORONHA, F. (1983): *Estudo Metalogénico da Area Tunstifera da Borralha.* Tese de doutoramento, Univ. Porto, Porto, Portugal.

______ & RIBEIRO, M.L. (1981): Carta geologica de Portugal na escala 1:50 000. Noticia explicativa da folha 6A, Montalegre. *Serv. Geol. Portugal.*

NORTON, J.J. (1983): Sequence of mineral assemblages in differentiated granitic pegmatites. *Econ. Geol.* **78**, 854-874.

PARGA-PONDAL, I. & CARDOSO, G.M. (1948): Die Lithiumpegmatite von Lalin in Galizien (Prov. Pontevedra, Spanien). *Schweiz. Mineral. Petrogr. Mitt.* **28**, 324-334.

RIBEIRO, A., ANTUNES, M.T., PORTUGAL FERREIRA, M., ROCHA, R.B., SOARES, A.F., ZBYSZEWSKI, G., MOITINHO DE ALMEIDA, F., CARVALHO, D. & MONTEIRO, J.H. (1979): Introduction à la géologie générale du Portugal. *Serv. Geol. Portugal.*

ROSSMAN, G.R. (1982): Origin of color in pegmatite minerals. *Am. Mineral.* **67**, 189.

ROSSOVSKIY, L.N., CHMYREV, V.M. & SALAKH, A.S. (1976): Genetic relationship of aphanitic spodumene dikes to lithium-pegmatite veins. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **226**, 170-172.

STEWART, D.B. (1978): Petrogenesis of lithium-rich pegmatites. *Am. Mineral.* **63**, 970-980.

TORRE DE ASSUNCAO, C. (1954): Notas de Mineralogia e Petrografia. III. Ocorrência de espodumena em Gelfa (Ancora). *Bolet. Museu Lab. Min. Geol. Fac. Ciênc. Lisboa, 7ª Serie*, **22**, 29-32.

WHITWORTH, M.P. & RANKIN, A.H. (1989): Evolution of fluid phases associated with lithium pegmatites from S–E Ireland. *Mineral. Mag.* **53**, 271-284.

*Received April 5, 1991, revised manuscript accepted January 17, 1992.*