LITHIUM POTENTIALITIES IN NORTHERN PORTUGAL

Conference Paper · March 2004

Jorge Manuel Ferreira Carvalho
Laboratório Nacional de Energia e Geologia

LITHIUM POTENTIALITIES IN NORTHERN PORTUGAL

by

Jorge M. F. Carvalho, Instituto Geológico e Mineiro, Portugal
João A. L. B. Farinha, Instituto Geológico e Mineiro

ABSTRACT

The Portuguese territory has many rich in Li-rich mineral occurrences that are mainly associated with aplite-pegmatite dykes and sills intruded in granitic and metasedimentary rocks of the Central Iberian and Galicia – Trás-os-Montes geotectonic zones. Some of those occurrences have a higher economic potencial value, as is the case of the Gonçalo region in the Guarda district and the Barroso - Alvão region near Boticas in the Vila Real district.

Geological studies carried out by the Geological and Mining Institute of Portugal (IGM) showed this areas as attractive targets for Li-rich raw material for the ceramic and glass industries of the Iberian market or even for Li-rich standard ore concentrates.

1. INTRODUCTION

Lithium is an alkali metal with an atomic number of 3 and a single valence electron which gives it special properties, namely it is the lightest metal element and has a strong electrochemical reactivity. Lithium was discovered in 1817 but its properties as a free metal or as the form of compounds only started to be fully investigated and exploited after the World War II. It is one of those elements about which no one hears about but used in very small quantities has an important role in our daily life. The lithium main applications are:

- the ceramic and glass industries;
- the process of primary aluminium production by increasing power efficiency;
- production of lithium-based all-purpose and high-temperature lubrificants and greases;
- batteries;
- light-weight alloys as those used in aircrafts and in the aerospace industry;
- synthetic rubbers and sophisticated textiles;
- air conditioning and drying and dehumidification systems;
- pharmaceuticals and
- nuclear applications.

The primary aluminium production and the ceramic and glass industries account for the main lithium compounds and minerals consumption. Although the use of lithium in the primary aluminium industry is decreasing, its consumption rates are being compensated and even have optimistic forecasts due to the expanding markets associated with ion lithium batteries, high-tech glasses and ceramics, industrial catalysts and other high-end uses.

2. OCCURRENCE AND WORLD PRODUCTION

Lithium occurs as trace quantities in most rocks, soils and natural waters. Because it is extremely reactive it does not occur as a free metal in nature. The more important minerals containing it are:

- Spodumene ($LiAlSi_2O_6$) which is the most important and abundant of lithium ores. Production deposits are located in Australia (the main producer), Brazil, Canada and Zimbabwe.
- Lepidolite ($K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$) also called the lithium-mica is produced in Zimbabwe and Portugal.
- Petalite ($LiAlSi_4O_{10}$) is the main lithium ore produced in Zimbabwe.
- Amblygonite ($((Li,Na)Al(PO_4)(F,OH))$) occurs in small quantities and minor deposits. Production is referred to Zimbabwe.

These minerals can be used as ore concentrates, like for the ceramic and glass industries, or to produce the most desired commercial compound that is lithium carbonate. Due to the high cost associated with the production of this compound from mineral ores, the actual most important raw material source for lithium carbonate are the subsurface brines in “salars” of remote and inhospitable regions in Chile and Argentina. These are large deposits with lithium concentrations around 200 and 2000 ppm that can be further concentrated using low cost efficient solar evaporation. Also China, USA and Russia are lithium carbonate producers but very poor information is provided.
According to data from USGS and presented in table 1 (J. OBER, 2002), two brine operations in Chile dominate actually the world market for lithium carbonate production (31 500 tons in 2002) but most of the lithium minerals mined in the world were consumed as ore concentrates. Here Australia dominates with a production of 100 000 tons of spodumene in 2002, followed by Canada (22 500 tons spodumene) and Zimbabwe (32 000 tons, mainly petalite).
Portuguese lithium production (IGM source) is referred to 16 000 tons in 2002 of lepidolite-rich quartz and K-feldspar pegmatite that is used as raw material for the ceramic industry.
The United States are the leading consumers of lithium minerals and compounds and at the same time are the leading producers of value-added lithium materials.

TABLE 1

LITHIUM MINERALS AND BRINE: ESTIMATED WORLD PRODUCTION, BY COUNTRY[1, 2]

(Metric tons)

Country[3]	1998	1999	2000	2001	2002
Argentina:[4]					
Lithium carbonate	6,000	1,592 [r, 5]	2,161 [r, 5]	-- [r, 5]	906 [5]
Lithium chloride	2,500	2,794 [5]	5,182 [5]	4,512 [5]	4,729 [5]
Spodumene and amblygonite	-- [r]	-- [r]	-- [r]	-- [r]	--
Australia, spodumene	63,190 [5]	75,824 [5]	81,891 [5]	63,443 [5]	100,000
Brazil, concentrates	9,485 [5]	11,122 [5]	10,875 [5]	11,000	11,200
Canada, spodumene[6]	22,500	22,500	22,500	22,500	22,500
Chile, carbonate from subsurface brine	28,377 [5]	30,231 [5]	35,869 [5]	31,320 [r, 5]	31,500
China, carbonate	13,000	12,500	13,000	13,000	13,000
Namibia, concentrates, chiefly petalite	500	--	--	--	--
Portugal, lepidolite	7,000	14,862 [5]	9,352 [5]	10,000	9,500
Russia (minerals not specified)[7, 8, 9]	2,000	2,000	2,000	2,000	2,000
United States, spodumene and subsurface brine	W	W	W	W	W
Zimbabwe, amblygonite, eucryptite, lepidolite, petalite, and spodumene	28,055 [5]	36,671 [5]	37,914 [r, 5]	36,103 [r, 5]	32,000

[r]Revised. W Withheld to avoid disclosing company proprietary data. -- Zero.
[1]Table includes data available through March 28, 2003.
[2]Estimated data are rounded to no more than three significant digits.
[3]In addition to the countries listed, other nations may produce small quantities of lithium minerals. Output is not reported; no valid basis is available for estimating production levels.
[4]New information was available from Argentine sources, prompting major revisions in how lithium production was reported.
[5]Reported figure.
[6]Based on all Canada's spodumene concentrates (Tantalum Mining Corp. of Canada Ltd.'s Tanco property).
[7]These estimates denote only an approximate order of magnitude; no basis for more exact estimates is available.
[8]Lithium contained in concentrates and brine.
[9]Other countries from the former Soviet Union, including Uzbekistan, could have produced or could be producing lithium, but information is not available for estimating production levels.

3. LITHIUM IN PORTUGAL

Portugal is a small country but with a considerably diverse and complex geology. The Portuguese territory can be divided into 2 large units: the Hesperian Massif of mainly Palaeozoic age and hercynian deformed, and the Epi-Hercynian covering which includes the western and southern Meso-Cenozoic borders.
The Hesperian Massif in which predominantly metallic mineral resources occur, can be divided into 4 geotectonic units (A. RIBEIRO et al., 1979; C. QUESADA, 1991):

- Galicia – Trás-os-Montes Zone. This zone is characterized mainly by the existence of 2 mafic and ultramafic polymetamorphic massifs surrounded by Silurian formations of acid and basic volcanic rocks. Several types of granites do also occur.
- Central Iberian Zone. It is characterized by the predominance of the so-called Schist-Greywacke Complex which is a flysch-type series dating form the Cambrian period. Large areas are occupied by alkali and calco-alkali granitic intrusions.

- Ossa Morena Zone. This unit is extremely complex and lithologically diverse with formations aged since the Precambrian till a flysch sequence of Late Devonian. Diverse granitic rocks occur as well an ophiolitic sequence with gabbros, diorites, serpentinites and anorthosites.
- South Portuguese Zone. It is a unit typified by the occurrence of a volcanic sedimentary complex of late Devonian – early Carboniferous period that is underlain by a phyllite-quartzit group and overlain by a flysch sequence. The acid volcanic rocks in that volcano-sedimentary sequence are the metallotect of the massive polymetallic sulphides of the Iberian Pyrite Belt.

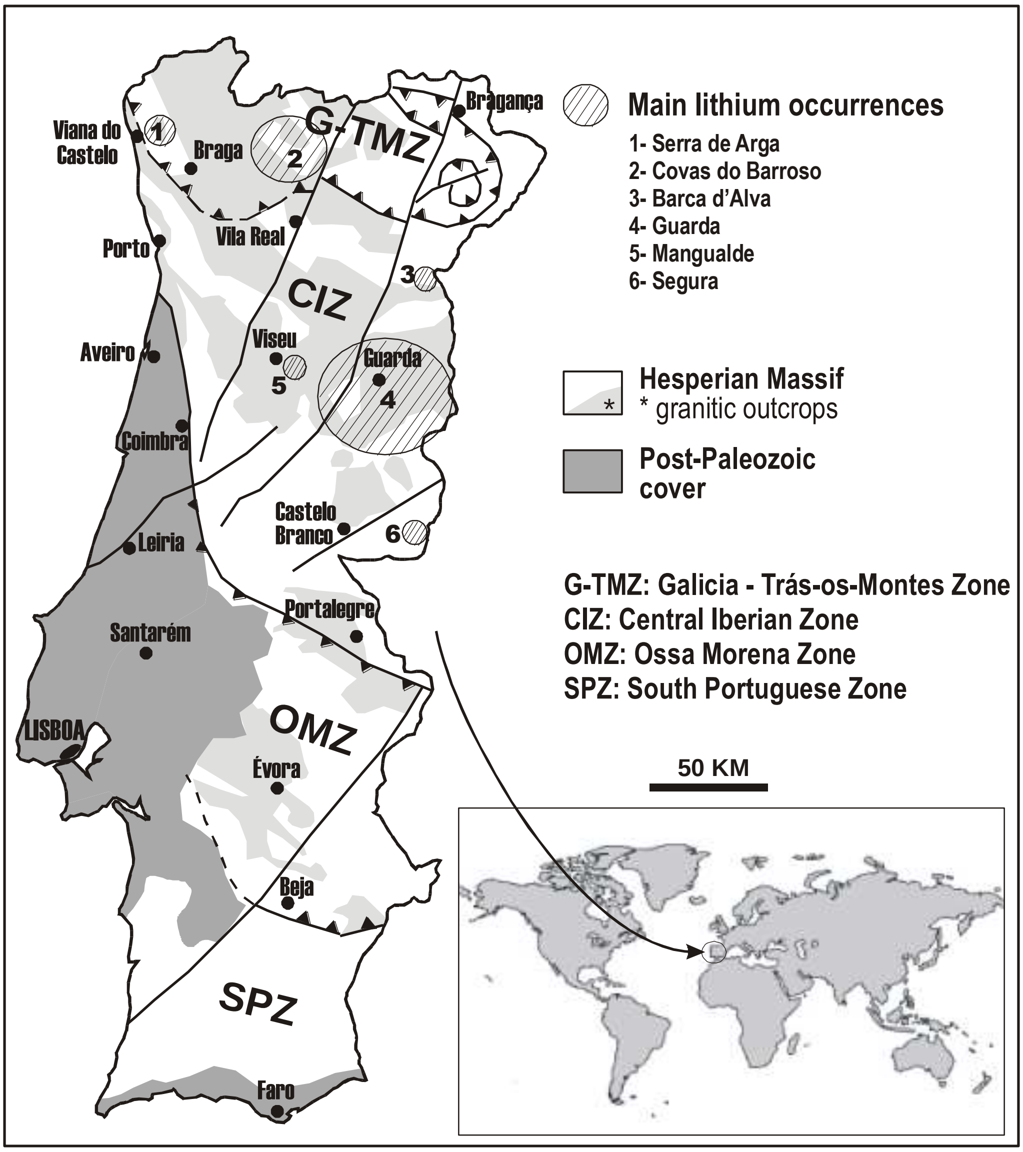

Figure 1- Main Portuguese Li-rich mineral occurrences.

The element lithium tends to be concentrated in the most differentiated granitic magmas and also in the aplitic, pegmatite and hydrothermal residues frequently formed after the consolidation of those magmas. This kind of granitic rocks widespread in the north and centre of Portugal, namely the Galicia – Trás-os-Montes and Central Iberian Zones. Therefore and according to J. F. RAMOS (2000[a]), the most important Portuguese lithium occurrences (figure 1) are localized in those zones as intra-granitic dikes and sills or even intruded in the meta-sedimentary sequences:

1. **Serra de Arga**: several types of aplite-pegmatite dykes and sills with petalite, spodumene, amblygonite, elbaite and lepidolite. Resources are not evaluated but some data refers to 4690 – 12400 ppm Li.
2. **Covas do Barroso**: spodumene-rich aplite-pegmatite dykes intruding the meta-sedimentary Silurian aged sequence. Resources evaluated.

3. **Barca d'Alva**: aplite-pegmatite dikes intruded in the Schist-Greywacke Complex with amblygonite, lepidolite and spodumene. Some data refers to 140 – 1574 ppm of lithium. Resources not evaluated.
4. **Guarda**: this large region comprises 3 main occurrences that are Massueime, Gouveia and Gonçalo. The resources of the first 2 are not evaluated and they are related with dikes and sills that were partially exploited for the ceramic industry (Gouveia) or for tin (Massueime). The Gonçalo area is a large field of aplite-pegmatite dykes and sills mainly intruded in the Guarda granite. The lepidolite-rich structures contain also amblygonite and petalite and are partially under exploitation as lithium-rich raw material for the ceramic and glass industries. Resources are evaluated.
5. **Mangualde**: pegmatitic bodies with lithiophilite in a granitic intrusion. These structures were exploited for quartz, feldspar and beryl. No resources evaluated.
6. **Segura**: some dykes with cassiterite, lepidolite and phosphates (amblygonite – montebrasite) intruding the Schist-Greywacke Complex. No resources evaluated.

Several other minor occurrences could be referred but the mentioned ones are certainly the economically relevant specially those of Gonçalo and Covas do Barroso that will be discussed with more detail in the next section.

3.1. The Gonçalo aplite-pegamtite field

The aplite-pegmatite field of Gonçalo, also called Gonçalo – Seixo Amarelo, is located 15 km southwest of the district capital Guarda and was studied in detail by IGM as a subject of a PhD thesis, being the most relevant results published (J. F. RAMOS, 2000[b]). This important field is part of a very large region (~100 km^2, *vd.* figure 1) where several occurrences of rare element-rich aplite-pegmatite veins are referred intruding several types of granitic rocks and also the Schist-Greywacke Complex of the Central Iberian Zone of the Hesperian Massif. The detailed study of the Gonçalo area (figure 2) was carried out because it has dozens of acid and basic dykes, sills, veins, etc. and at the same time is the richest in structures with lithium. These are intruding mainly a porphyritic biotite granite – the Guarda granite.

Table 2- Chemical composition (medium values) of the different types of sills in the Gonçalo area (adapted from J. F. RAMOS, 2000[b]).

	LITHIUM SILLS	TIN SILLS	MIXED SILLS	BARREN SILLS
Oxides (%)				
SiO2	68.73	71.74	69.35	73.92
Al2O3	17.84	15.82	17.39	15.25
FeO	0.69	0.99	0.67	0.51
MnO	0.16	0.09	0.12	0.03
MgO	0.02	0.02	0.03	0.03
CaO	0.17	0.2	0.12	0.19
Na2O	4.11	4.81	3.74	3.16
K2O	3.13	3.41	4.25	5.25
TiO2	0.02	0.01	0.02	0.03
P2O5	1.07	0.61	0.43	0.19
LOI	2.33	1.6	3.06	1.08
Elements (ppm)				
F	14977 (2 samples)	4396 (1 sample)	not analized	not analized
Li	5705	1484	2512	55
Rb	2169	1088	1413	434
Ba	30	29	29	62
Ta	46	44	55	5
Sn	310	319	426	37
W	3	2	3	25

Three different mineralization types were mapped:

- The more geochemically evolved Lithium Sills. They are pinkish in color, enriched in Al, Mn, P, Li, Rb, Sr, Nb and Ta, and contain quartz, k-feldspar, albite, muscovite, lepidolite, petalite, montebrasite, topaz, etc., etc.. They occur at high structural and topographic levels but tectonically depressed.

- The less evolved Tin Sills. They present cream colors and are enriched with Si, K, Fe and Sn. Mineralogically they present quartz, k-feldspar, albite, muscovite, rare lepidolite, montebrasite, topaz, apatite, beryl, cassiterite, columbite-tantalite, etc. They occur at low structural and topographic levels in the region.
- The Mixed Sills have an intermediate composition and are located between the others, corresponding to a transition phase.

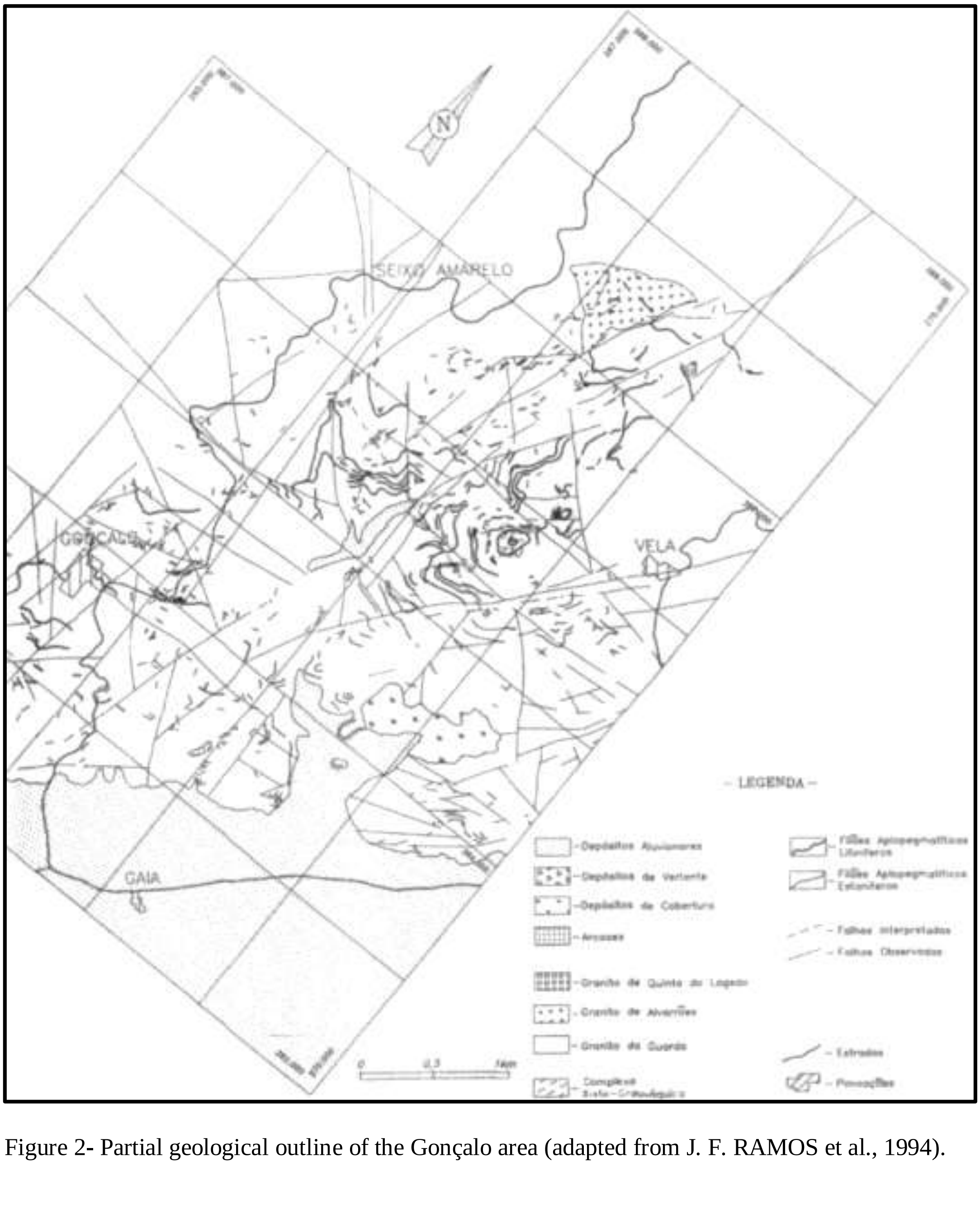

Figure 2- Partial geological outline of the Gonçalo area (adapted from J. F. RAMOS et al., 1994).

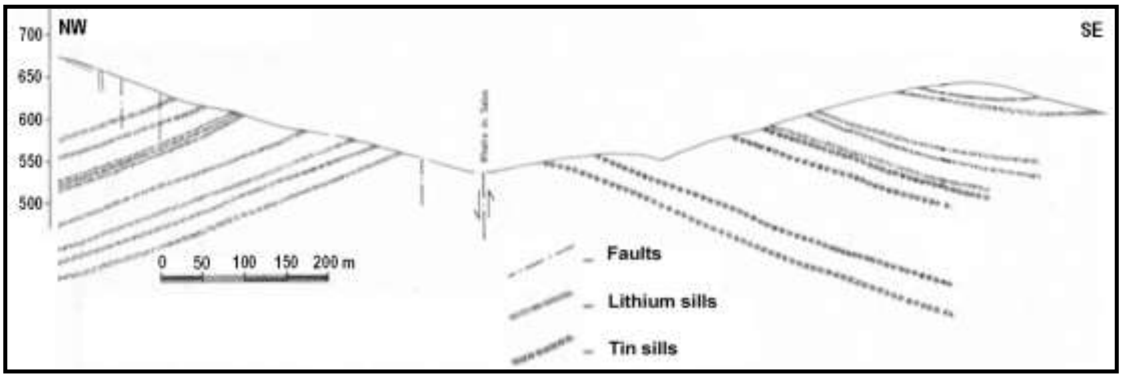

Figure 3- Geological cross section in Gonçalo area (adapted from J. F. RAMOS et al., 1994).

These mineralized structures as well the majority of the barren ones are sub-horizontal with a tabular form. Thickness ranges from a few centimeters to 10 m but generally is under 3,5 m. The relation between their sub-horizontal orientation and the marked topographic slope, as expressed in figure 3, has conditioned their exploitation. The resources evaluated for this area are 540 000 m^3. It is a minimum value because only were considered the lithium-rich sills and a maximum quarry front of 10 m high. Therefore it is an evaluation that considers only the superficial part of the ore deposit.

Since long time ago that large parcels of this area are mining concessions under open pit exploitation of raw material for ceramic industry. Although the total volume that was extracted is negligible and due to the global dimension of the aplite-pegmatite field it stills very attractive.

3.2. The Covas do Barroso aplite-pegmatite field

In northern Portugal the Barroso – Alvão region (figure 4) is characterized by the presence of a large field of several dozens of pegmatite and aplite-pegmatite dykes of granitic composition. Pegmatite dykes are mainly intruded in the granitic rocks of the region whilst aplite-pegmatite dikes are hosted by low- to medium-grade metasedimentary rocks of Silurian age that are strongly deformed (B. CHAROY et al., 1992). These host rocks are part of the Galicia – Trás-os-Montes geotectonic zone.

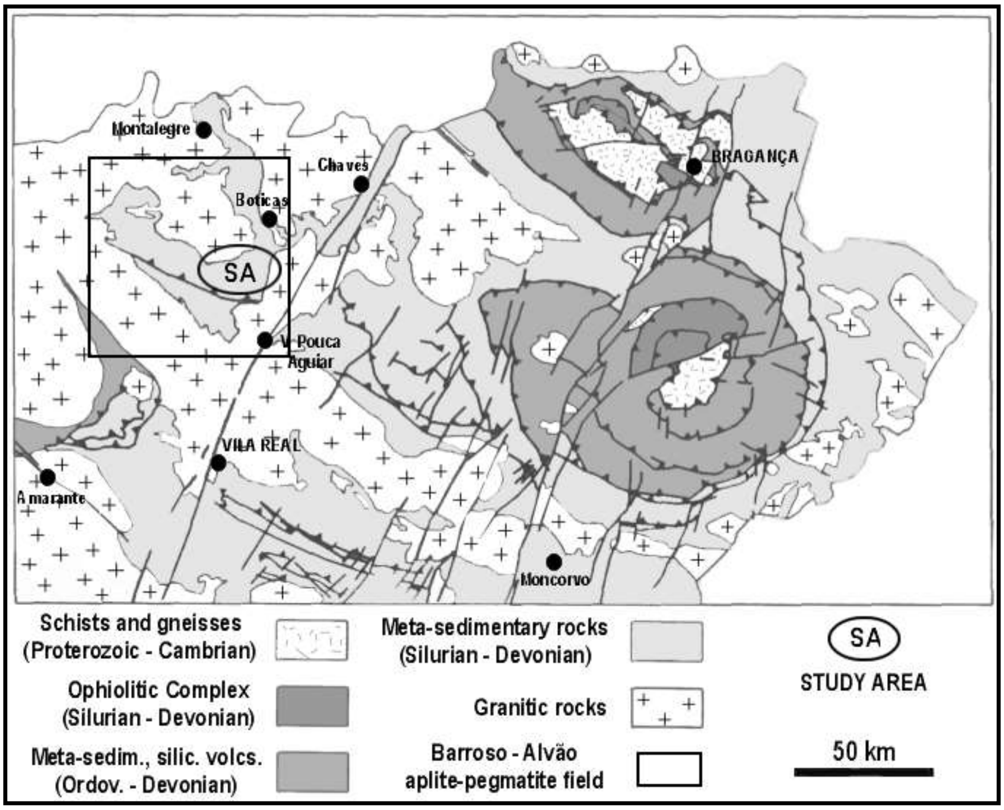

Figure 4- Geological setting of the Barroso – Alvão aplite-pegmatite field.

Concerning the bodies intruded in the metasedimentary rocks two types of aplite-pegamtites are found (B: CHAROY et al., 1992; 2001). One is countless and is represented by thin (~1 m) aplitic dykes with low-grade cassiterite mineralization. Generally are strongly altered to kaolinite. The other type is the one of our interest and is represented by thicker aplite-pegmatite dykes and sills unevenly distributed. Although locally they show a tendency to form swarms of several dykes with a high special continuity (up to 1 km). The thickness of these dykes ranges from less than 1 meter up to 30 m and only a few are Li-rich.
The Li-rich aplite-pegmatite dykes show a spatial distribution of 3 sub-types (LIMA et al, 2003):

- spodumene-rich aplite-pegmatite dykes and sills are dominant at N and NE regions;
- petalite-rich are dominant at SW and
- lepidolite-rich occur at NW regions.

Due to the high economic importance of this kind of Li-rich orebodies as raw material for the ceramic industry or even as a source of lithium ore, the IGM carried out a detailed geological study of a restricted area of this wide aplite-pegmatite field that was chosen before the presence of large spodumene-rich dykes and sills. The geological works included (J. FARINHA, 2000):

- regional geological mapping of all the visible dykes at 1/25 000 scale (figure 5);
- detailed geological mapping at 1/500 scale of 3 large mineralized dykes (the Veral, the Adagói and the Alijó orebodies);
- drilling (10 drill holes with 475 m of total length) and sampling (340 samples);
- resources evaluation and
- ore processing beneficiation studies.

The petrographic studies of those 3 dykes points out that the lithium mineralization is represented mainly by spodumene, with subordinate petalite and late hydrothermal eucryptite. Pegmatite amd aplitic facies are intimately mixed within the aplite-pegmatite dykes and analytical results show that lithium is mainly concentrated in the pegmatite differentiates.
The exploration drill holes allowed to estimate for the Adagói structure 108 000 metric tons of ore with 1,05% Li_2O; 3,98% Na_2O; 3,2% K_2O and 0,6% Fe. For the Alijó bodie the results are 403 000 metric tons of ore with 1,40% Li_2O; 3,45% Na_2O; 2,21% K_2O and 0,7% Fe. These richest zones of the Adagói and Alijó dykes can be considered as an Indicated Mineral Resource (332) Economic to Potential Economic.

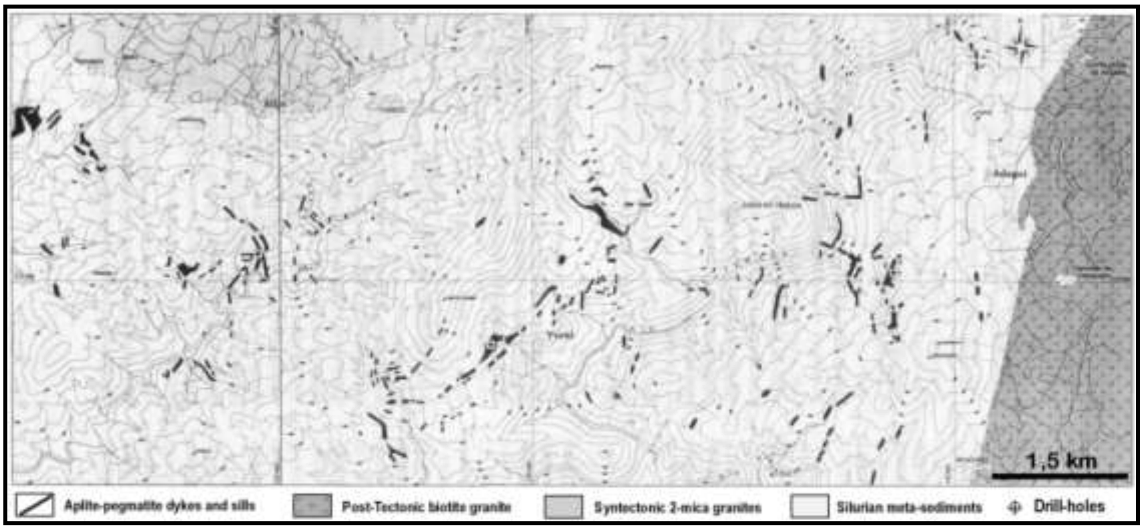

Figure 5- Aplite-pegmatite dykes mapped by IGM (Covas do Barroso region) and drill-hole localization (adapted from J. FARINHA, 2000).

A study conducted on the processing of spodumene ore from 2 big samples of the Adagói and Alijó dykes was carried out by the Laboratory Department of IGM in order to test the possibility of obtaining lithium and feldspar standard concentrates for the Portuguese ceramic industry (M. AMARANTE, 2000). This study was achieved by *heavy media separation* (HMS) and *flotation* tests. The samples with 150 kg each had an approximate mineral composition of 60-65% quartz, 30-35% spodumene, ~8% feldspar and ~2% muscovite.
By the HMS tests a *glass grade spodumene* concentrate with 5% Li_2O was obtained with a recovery of 50%. The flotation tests only gave commercial results when using feeding concentrations of more then

1,5% Li_2O: feeding concentrations bigger then 2% gave a *high grade spodumene* with 6% Li_2O and a recovery of 60% but when attempting to obtain >7% Li_2O concentrates the recovery fell to 30%. From the spodumene flotation tailings was obtained a feldspar concentrate with >17% alumina and > 6% alkalis (Na/K ~ 4/3) with a low iron content.
Based on these results two possible processing diagrams for the beneficiation of this ore were developed as illustrated by figure 6. The process is not so simple as the process I, although it has the advantage of reducing to less than 40% the amount of ore to be processed by flotation, and at the same time, the decrease in the production of high grade spodumene could be compensated by a greater quantity of glass grade spodumene, a higher overall recovery and a decrease in the losses to the slims.

As a final conclusion for the works carried out by IGM at Covas do Barroso region, it can be said that the studied dykes (as an application example) can be considered as raw material for standard spodumene concentrates with application in the ceramic and glass industries for the Iberian market. The divulgation of these results attracted some Portuguese enterprises that are now carrying out more specific exploration studies in these structures as well in other areas of the region.

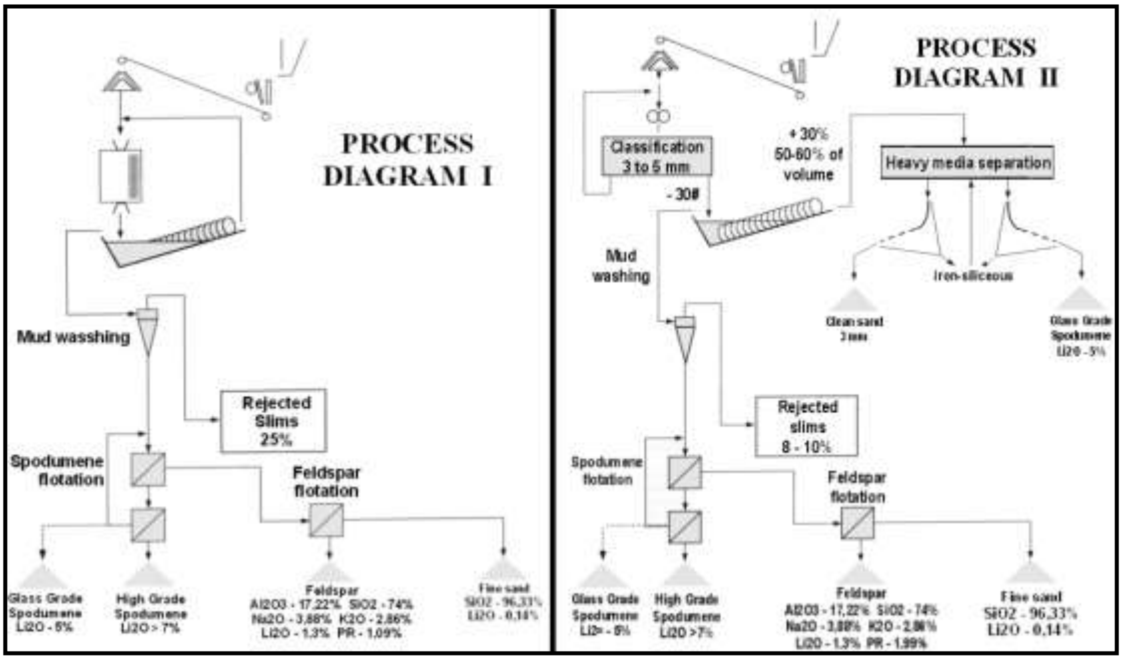

Figure 6 – Spodumene ore processing diagrams (adapted from M. AMARANTE, 2000).

4. PORTUGUESE LEGAL MINING FRAMEWORK

Portugal stills an attractive mining country in the European Union. The legal framework governing activity involving the prospecting, exploration and exploitation of geological resources involves a mineral licensing that will generally follow in the wake of an application submitted by the applicant for the granting of one of four different mineral licenses in accordance with the type of activity to be undertaken and the type of resource, depending on whether or not it is State owned:

- administrative prospecting and exploration contract;
- administrative mining contract;

in both cases covering certain resources within those which are State owned (ore deposits, and hydro-mineral or geothermal resources)

- quarry operating licence in respect of mineral masses; and
- spring-water operating licence.

Applications for prospecting and exploration contracts and mining contracts are addressed to and decided by the Minister for the Economy (ME) (or by his responsible Secretary of State), submitted to and processed by the Geological and Mining Institute (IGM) which will also monitor the exercise of the operations covered by the contracts. If so requested, the IGM may provide technical and administrative advice concerning the drawing up and submission of the applications, providing drafts and models, information concerning available areas or those licensed, and the IGM may allow consultation of

technical documentation and maps in the archives. The prospecting and exploration contracts and mining contracts usually follow the form of existing models.
As in any other industrial activity, natural persons or bodies corporate may undertake exploration and mining operations and, particularly, by companies, the latter being the form usually adopted by operators.
Applicants for prospecting and exploration licences and mining licences must, in accordance with legislation, submit together with their applications full identification and other information confirming their technical and financial capacities and their experience in the operations they intend to undertake.
Applications shall also include, as applicable, a prospecting and exploration work programme and the respective budget, or a mining plan. With regard to the candidature of non-residents a local agent should be appointed to simplify contacts with the IGM during the processing of the application and negotiation of the contract.
Other useful data is reported in Instituto Geológico e Mineiro (2000). *Portugal - Exploration and Mining.* Lisbon and can be accessed online by the web address:
http://www.igm.pt/edicoes_online/diversos/portugal_geology/default.htm.

USEFUL ADRESS:

Instituto Geológico e Mineiro
Administrative Headquarters
Rua Almirante Barroso, nº 38
1049-025 Lisboa
Portugal

Phone: +351. 21 311 87 00
Fax: +351. 21 353 77 09
Email: igmsede@igm.pt
Web Page: http://www.igm.pt

5. CONCLUSIONS

Portugal has many Li-rich mineral occurrences being the more economically interesting ones referred to the wide Gonçalo and Covas do Barroso areas, where IGM carried out regional geological exploration works.
If at Gonçalo the exploitation of these Li-rich orebodies is implemented since long time ago, at Covas do Barroso the mining works did not started yet. Although, since 2 years ago, mining Portuguese companies are doing specific exploration and evaluation works in this region. That activity was triggered by the divulgation of the results of the promotion geological works done by IGM in that region.
Because these two areas are very large and with a great number of aplite-pegmatite dykes and sills, there is still room for prospecting activities seeking Li-rich raw material for the ceramic and glass industries of the Iberian market.

6. REFERENCES

AMARANTE, M.; BOTELHO DE SOUSA, A.; MACHADO LEITE, M. R. (2000)- Ensaios de Beneficiação de espodumena em amostras do Alto Barroso. Estudos, Notas e Trabalhos, Instituto Geológico e Mineiro, tomo 42, pp. 51-65.

CHAROY B., LHOTE F., DUSAUSOY Y. NORONHA F. (1992): The crystal chemistry of spodumene in some granitic aplite-pegmatite of Northern Portugal: a comparative review. Canadian Mineralogist, 30, 639-651.

CHAROY B., NORONHA F., & LIMA A.M.C (2001) Spodumene-Petalite-Eucryptite: mutual relationships and alteration style in pegmatite-aplite dykes from Northern Portugal Canadian Mineralogist, 39; pp. 729-746.

FARINHA, J. A.; LIMA, A. M. C. (2000)- Estudos, Notas e Trabalhos, Instituto Geológico e Mineiro, tomo 42, pp. 3-49.

Instituto Geológico e Mineiro (2000). *Portugal - Exploration and Mining.* Lisbon

LIMA, A. M. C.; VIEIRA, R. C.; MARTINS, T. C.; NORONHA, F.; CHAROY, B. (2003)- A ocorrência de petalite como fase litinífera dominante em vários filões do campo aplitopegmatítico do Barroso-Alvão. Actas do VI Congresso Nacional de Geologia, Faculd. Ciências e Tecnol., Univ. Nova de Lisboa, Monte da Caparica, 4 – 6 Junho.

OBER, J. A. (2002)- Lithium. U S Geological Survey Minerals Yearbook – 2002. http://minerals.usgs.gov/minerals/pubs/commodity/lithium/lithmyb02.pdf

QUESADA, C. (1991)- Geological constraints on the Paleozoic tectonic evolution of tectonostratigraphic terranes in the Iberian Massif. Tectonophysics 185, pp.225–241

RAMOS, J. F. (2000[a])- Prefácio. Estudos, Notas e Trabalhos, Instituto Geológico e Mineiro, tomo 42, pp. I-IV.

RAMOS, J. F. (2000[b])- Mineralizações de metais raros de Seixo Amarelo – Gonçalo (Breve Nota). Estudos, Notas e Trabalhos, Instituto Geológico e Mineiro, tomo 42, pp. 67-160.

RAMOS, J. F.; RIBEIRO, A.; BARRIGA, F. J. A. S. (1994)- Mineralizações de metais raros de Seixo Amarelo – Gonçalo (Breve Nota Introdutória). Boletim de Minas, Instituto Geológico e Mineiro, vol. 31 (2), pp. 101-115.

RIBEIRO, A.; ANTUNES M. T.; FERREIRA, M. P.; ROCHA, R. B.; SOARES, A. F.; ZBYSZEWSKI, G.; ALMEIDA, F. M.; CARVALHO, D. & MONTEIRO, J. H. (1979)– Intruduction à la géologie générale du Portugal, Serviços Geológicos de Portugal, Lisboa, 114 p.