DNPM

Departamento Nacional de Produção Mineral

Núcleo de Geoprocessamento - SUP/DNPM/CE

Ores for the production of a Brazilian lithium ion battery

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Lithium world-wide offers

- 10,6 millions tons
- Bolivia – 51%; Chile – 28%; China – 10%
- Brazil – 0,57%
- There was never a Brazilian effort to increase the lithium reserves in the country
- The existing reserves are in Minas Gerais (Araçuaí e Itinga), Ceará (Quixeramobim e Solonópole).

Lithium Ore-Minerals in Brazil

- Araçuaí e Itinga – Espodumene, Ambligonite, Lepidolite e Petalite
- Quixeramobim – Lepidolite
- Solonópole – Ambligonite
- These minerals are associated wih a rock called pegmatites
- The single Brazilian Company that has a lithium mine is Brazilian Company of Lithium, wich works in Araçuaí, Minas Gerais

Minerals that contains lithium oxide and their some phisical characteristics

Minerals	Composition	D1	D2	%Li2O	
				Teory	Typical
Ambligonite	$LiAl(P0_4)(F,OH)$	3	5,5-6	11,9	5,0
Eucryptite	$LiAl(SiO_4)$	2.65	6,5	11,9	5,0
Lepidolite	$K(Li,Al_3)\ (Si,Al)_4O_{10}(F,OH)_2$	2,8-3,3	2,5-3	3,3-7,8	3,0-4,0
Montebrasite	$LiAlP0_4F$	3,0	5,2-6	7,0	
Petalite	$LiAl(Si_4O_{10})$	2,3-2,5	6-6,5	4,9	3,0-4,5
Espodumene	$LiAl(Si_2O_6)$	3-3,2	6,5-7,5	8,0	1,5-7,0
Zinnwaldite	$K(Li,Al,Fe)_3(Al,Si)_4O_{10}(F,OH)_2$	2,9-3,3	2,5-4	5,6	2,0-5,0

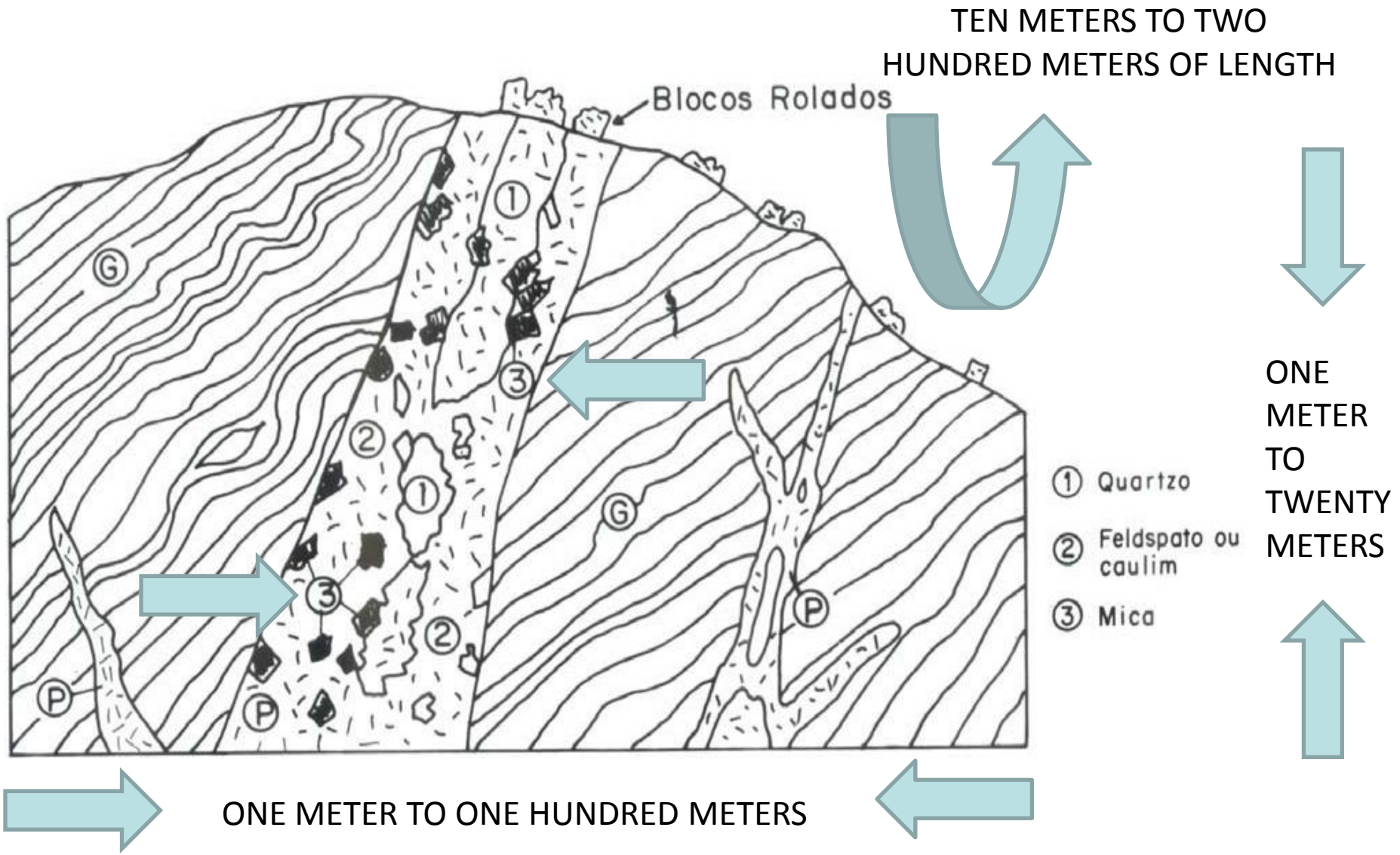
D1 – Density D2 – Hardnes Moh.

Reference: Harben e Kuzvart (1996); (Roskill, 2002)

What is a Pegmatite?

- Intrusive igneous rock of coarse grain, composed mainly of quartz, feldspar and muscovite.
- Contains gems (aquamarine, tourmaline, topaz), fluorite, apatite, cassiterite (tin), schelite (tungstene),columbite (niobium), tantalite (tantalum) and lithium minerals.
- Can be granitic, boron-granitic, with lithium and boron-lithium.

GEOLOGICAL SCHEME OF A PEGMATITIC BODY



03 – SPODUMENES, AMBLIGONITES AND LEPIDOLITES (LITHIUM MINERALS)

Sample of pegmatite composed maily of altered feldspar, corundum and mafic minerals

Ocorrence Mode of pegmatite

- Dykes, veins, bands and sills in size from centimeters to tens of meters, cutting granitic rocks.
- Crystals dimension changes from 20mm to 10 meters inside the veins and dykes.
- One of the biggest pegmatitic provinces in the world occurs in Brazil (Jequitinhonha Valley and Mucuri Valley, Minas Gerias; Borborema Massiff, in Ceará) and Afghanistan.

This is a rock gnaissic-granite with bands and veins of pegmatites.

The dark parts are biotites, the clear parts are composed of quartz and feldspar.

The diverse others minerals occur into the bands and veins, a huge variety of minerals, also of lithium

Espodumene, ambligonite, lepidolite and petalite are common

The crystals are due to a crystallization called hidrotermal - hot water in the end of the formation of granitic intrusive rock,

Lithium Ores of Ceará State

Chemical Analyses: Ambligonites of Solonópole

	SAMPLES				
OXIDES (%)	**1**	**2**	**3**	**4**	**5**
Al2O3	36,40	42,10	32,80	31,36	36,20
P2O5	49,27	39,64	48,18	47,44	43,54
Li2O	**8,56**	**8,14**	**8,06**	**8,13**	**8,80**
Na2O	1,14	- 0,63	0,21	1,16	
K2O	0,00	0,00	0,00	0,00	0,00
CaO	0,55	0,53	1,09	0,44	0,66
MgO	0,16	0,24	0,24	0,71	0,94
SiO2	0,00	0,00	- 0,00	0,00	
Fe2O3	-	-	-	-	-

Lithium Ores of Ceará State

Chemical Analyses of Spodumene of Solonópole

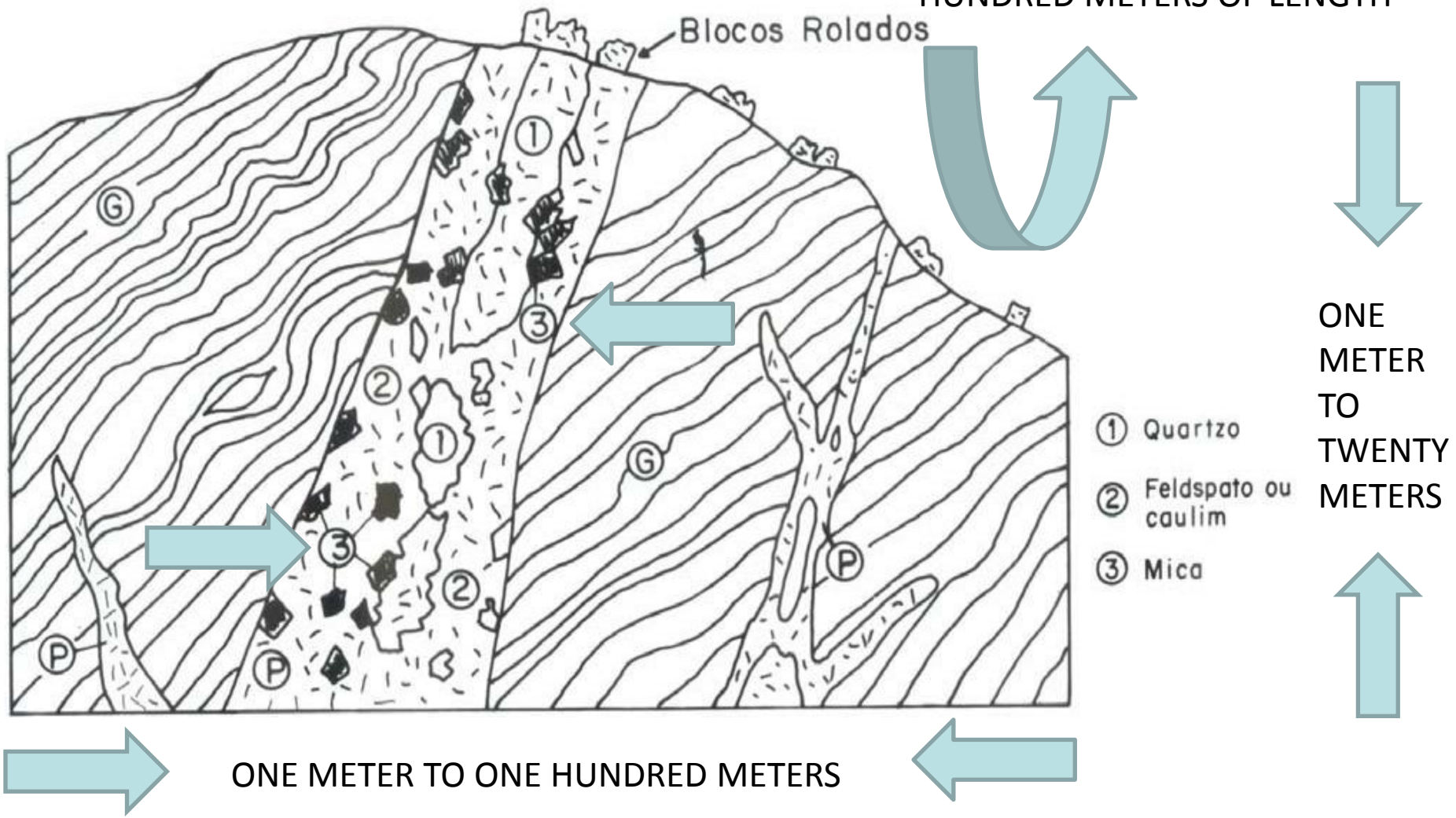
	SAMPLES			
OXIDES (%)	**1**	**2**	**3**	**4**
SiO2	56,90	50,70	52,20	64,90
Al2O3	26,54	28,70	26,37	22,58
Li2O	**6,90**	**7,33**	**6,70**	**6,59**
Na2O	0,54	0,45	0,97	0,79
K2O	-	-	-	-
P2O5	0,04	0,08	0,14	0,13
Fe2O3	0,20	1,65	0,06	0,09

20 YEARS AGO: PEGMATITIC LITHIUM ORES
MINERAL RESEARCH IN THE SOLONÓPOLE REGION, CEARÁ STATE

ABANDONED MINES IN THE REGION OF SOLONÓPOLE - CEARÁ

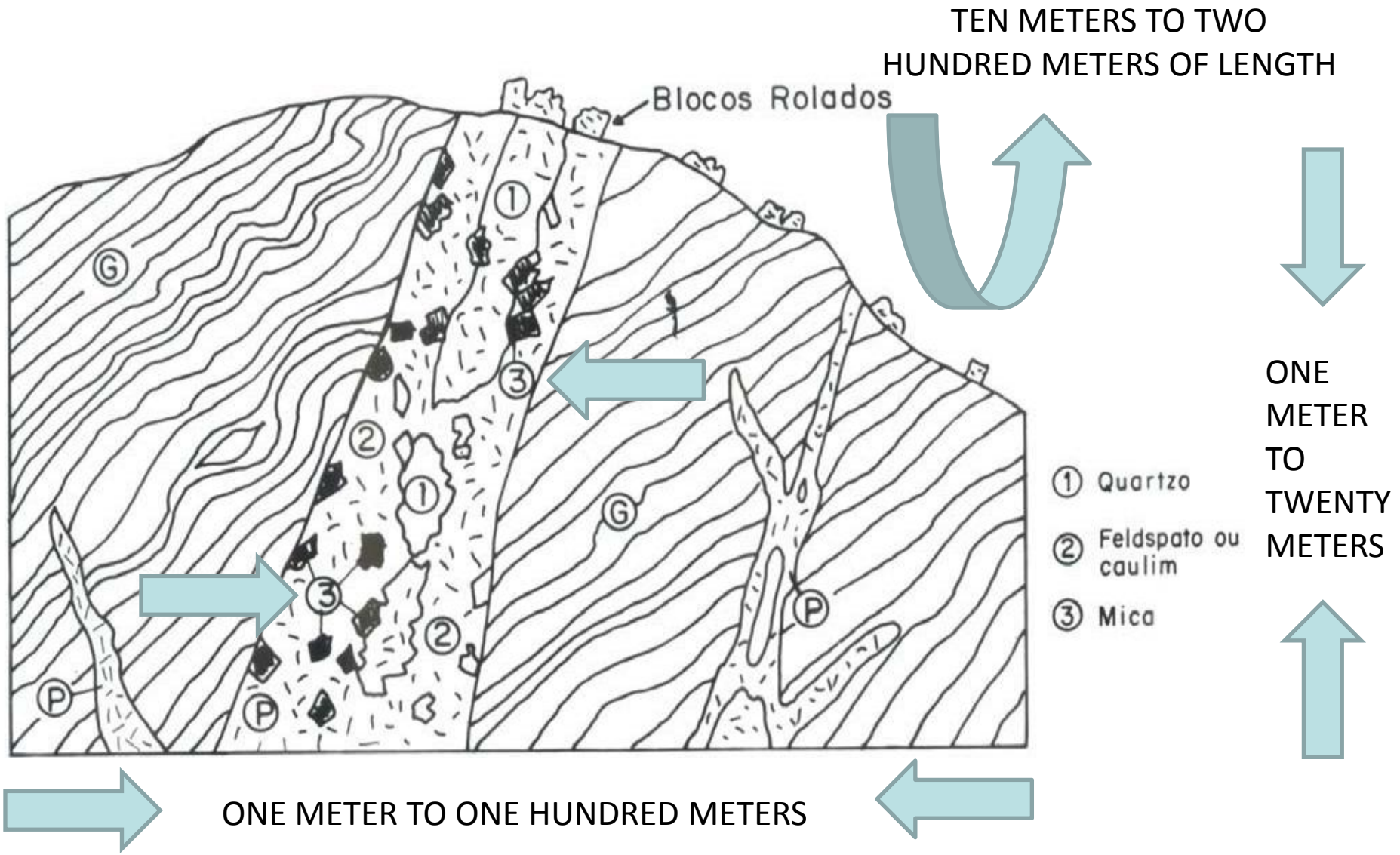
GEOLOGICAL SCHEME OF A PEGMATITIC BODY

There are 41 bodies in Solonópole Region - Ceará



03 – SPODUMENES, AMBLIGONITES AND LEPIDOLITES (LITHIUM MINERALS)

GEOLOGICAL SCHEME OF A PEGMATITIC BODY

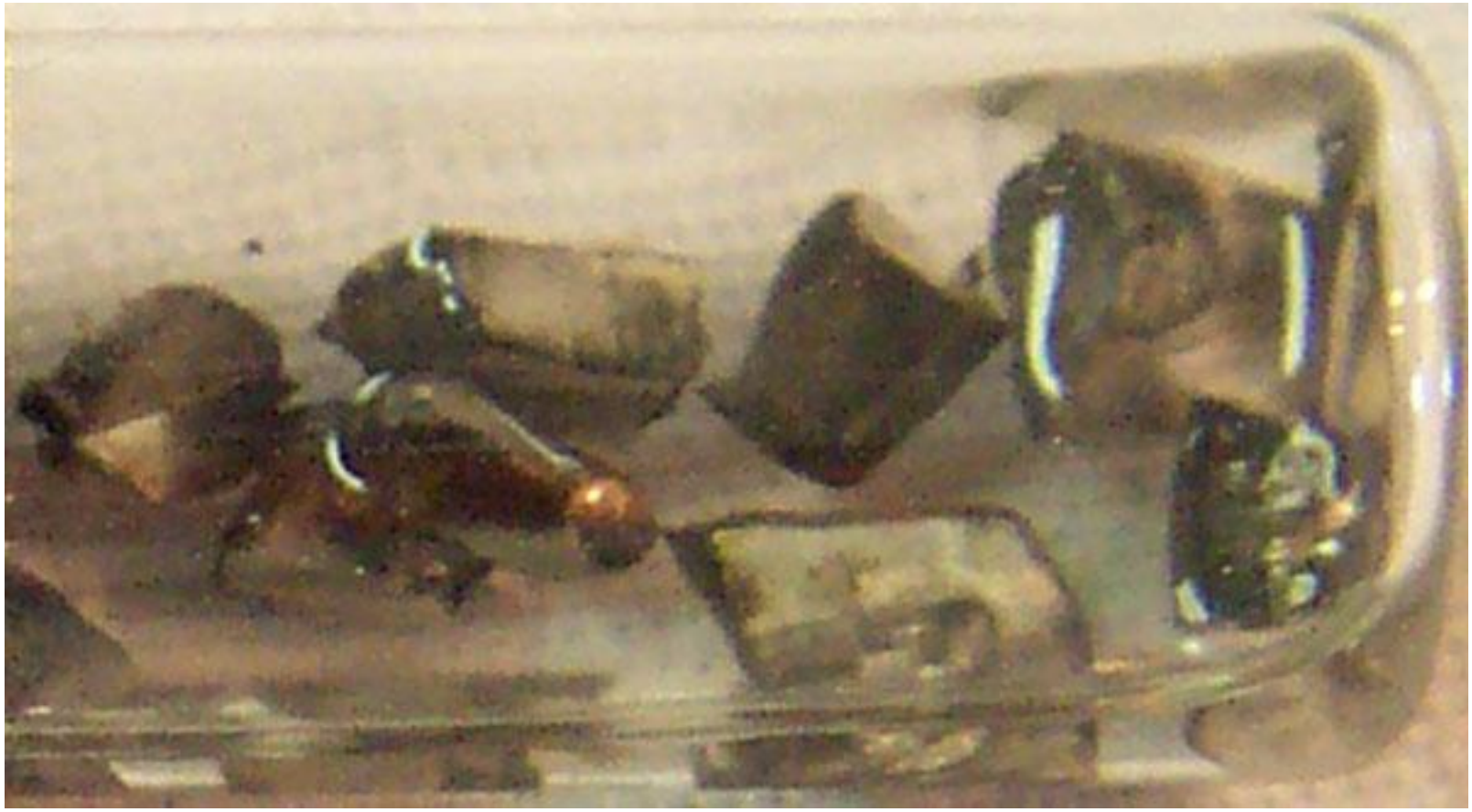


03 – SPODUMENES, AMBLIGONITES AND LEPIDOLITES (LITHIUM MINERALS)

What it is lithium?

- Lithium (Greek lithos, rock) is a chemical element of symbol Li, atomic number 3, and atomic mass 7u, contening in its structure three protons and three electrons. In the periodic table of the chemical elements, belonging to the group (or family) 1 (previously called 1A), between the alkaline elements.

- In its pure form, it is a soft metal, of white-silver-plated coloration, wich is becomes quickly oxidated in air or water. It is a solid element however lightweight, being used especially in the production of heat conducting metal alloys, in electric batteries and in the treatment of bipolar disorder.



It is the lightest metal, its density is only, about, the half of water. As the others alkaline metals, it is monovalent and very reactive, however less than the sodium and other metals of the group. For this reason it is not found free in the nature. In the flame test it becomes red, however if the combustion occurs violently, the flame acquires a shining white coloration.

Precautions and security when using lithium in its applications

- As other alkaline metals, the pure lithium is highly inflammable and explosive when slightly displayed to air and, especially, to water.
- Moreover he is corrosive, requiring the employment specific way of manipulation to avoid the contact with the skin.
- Must be stored in a liquid hydrocarbon, for example, the gasoline.
- The lithium is considered slightly toxic.

Lithium Applications (1)

- Due to its high heat capacity, the biggest of all the solids, it is used in applications of heat transference and, because of its electrochemical potential raised one he is used as an anode adjusted for the electric batteries. Beyond these it has other uses:

- Lithium salts, particularly the lithium carbonate (Li2CO3) and the lithium citrate are used in the treatment of the bipolar desorder, despite, lately, its use has been extended to the treatment of the single-pole depression.

  •Lithium choride (LiCl) and lithium bromide (LiBr) have a high hygroscopicity, therefore they are excellent siccatives. LiBr it is used in bombs of absorption heat, amongst other composites as lithium nitrate (LiNO3).

  •The hydride of aluminum and lithium is a employed reducing agent in the organic composite synthesis.

  The lithium stearate is a lubricant generally applied in high temperature conditions .

Applications of lithium (2)

•The base lithium hydroxide (LiOH) is used in spaceships and submarine to purify air, extracting the carbon dioxide produced by its occupants.

•The lithium is a usual component in metal alloys of aluminum, cadmium, copper and manganese, used in aeronautical construction, and is being employed with success in manufacture of ceramics and lenses, as of the Reflecting Telescope Hale of 5,0 meters in diameter “Palomar Mount”.

•It Also has nuclear applications.

•it is used as powerful analgesic in operations of risk.

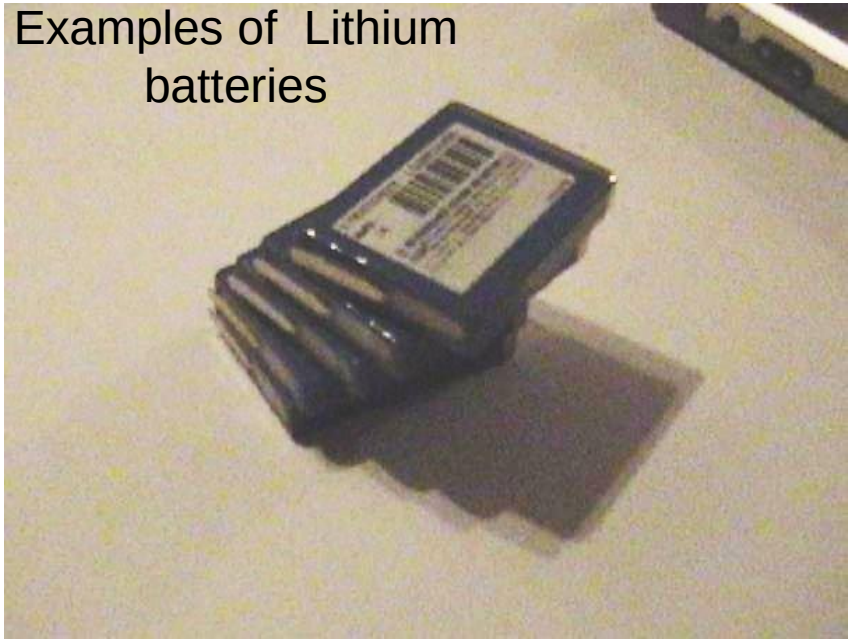
Ion Lithium Battery

- The ion lithium batteries are a type of rechargeable batteries commnly used in portable electronic equipment.

- They store two times the energy a battery of metallic nickel hidride and three times more than a nickel cadmium battery can store.

- Another difference of the lithium íons battery is the absence of the memory effect, wichmeans it is not necessary to fully charge the battery and to until the least, on the nickel cadmium batteries.

Examples of Lithium batteries



Never leave it exposed to it direct sunlight or short circuits; the opening of the package can also make with that the battery is inflamed

Basic principles of manufacture of a lithium battery

- The lithium batteries are primary cells that have metallic lithium anodes.

- The lithium cells produce a tension about to two times more than a common alkaline zinc-carbon battery or: 3 volts against 1,5 volts, respectively.

- Lithium batteries are used in many portable electronic equipment, and are also wide used in industrial electronics.

- The term “lithium battery”, in truth, mentions a chemical composite family to it, understanding many types of cathodes and electrolytes.

- A type of lithium cell with high-density energy is the “tionil-lithium chloride cell”.

- In this cell, one mixes chloride liquid of tionil with tetrachloroaluminate of lithium acts as cathode and electrolyte, respectively.

Basic principles of manufacture of a lithium battery

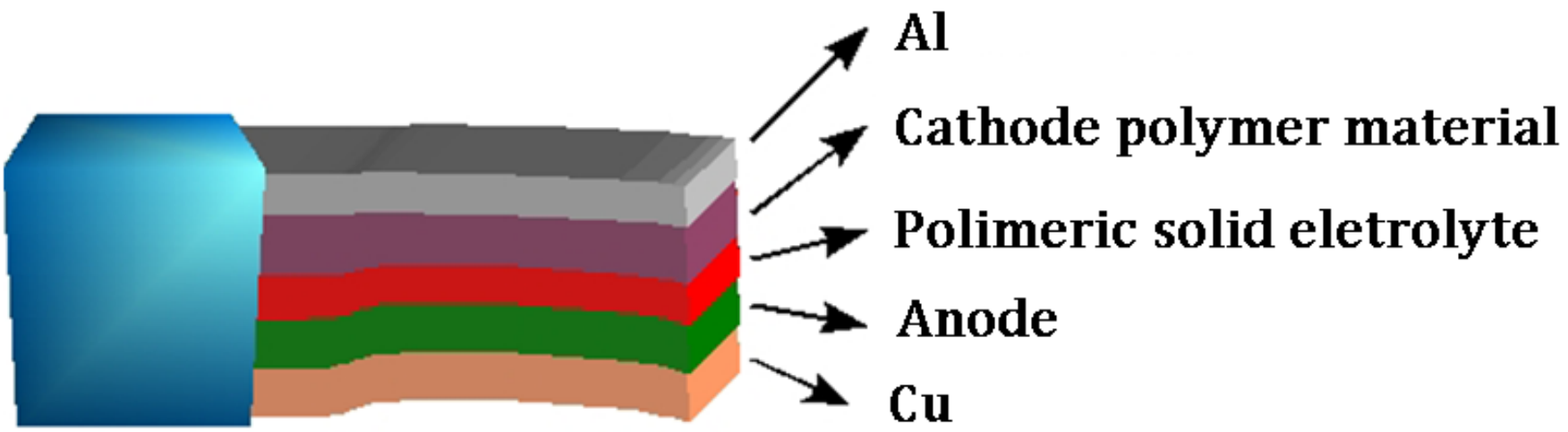
- The tionil-lithium chloride batteries are not, generally, sold for final consumers, finding more uses in commercial or industrial applications, or they are installed inside of devices where the exchange of batteries is not made by the consumer.

- The tionil-lithium chloride batteries are adapted for local current applications where a great durability is necessary, such as alarm systems wireless.

- The most common type of lithium cell used in electronics consumption uses an anode of metallic lithium and a cathode of manganese dioxide, with a composed inorganic lithium salt in a mixture of high permissiveness (for example propylene carbonate) dissolved in a low viscosity organic solvent (for example dimethoxyethane) as electrolyte
- The lithium batteries can supply extremely high chains and can unload very quickly when short-circuiteds.

- Although they are very useful in applications where high currents are required, a fast discharge of a lithium battery can result in superheating, rupture and even explosion..
- The commercial batteries generally incorporate protections against thermal overcurrent and protections to avoid explosions.
- Because of these risks, the sending and the transport of batteries are restricted in some situations, mainly when carried though airmail

Basic of manufacture of a lithium battery



Baterias	Catodo	Eletrólito	Anodo
Íon lítio	LiCoO2 ; LiMnO2 ; LiFePO4 ; Li2FePO4F	LiPF6, LiBF4, LiClO4 em um meio líquido (orgânico)	Li/grafite (LiC6)
Íon lítio polimérica	Politiofeno ; PEDOT; Nanocompósitos LiFePO4/C	LiPF6, LiBF4, LiClO4 em um meio polimérico orgânico	Nanocompósitos polímero/nanofibra de carbono

Technological challenges

•To use Brazilian ores and materials to construct cathodes, anodes and eletrolytic ways.

- To make an ion battery or a polymeric ion lithium battery with Brazilian lithium polymers and mines.
- Brazilian Minerals: Espodumene, ambligonite, lepidolite, petalite and/or others that can be identified.
- To use the more appropriate technological routes with lesser cost and not long time for the battery manufacture.

What it is a espodumene

Chemical formula - $LiAlSi_2O_6$

Composition - 8,03 % Li_2O, 27,40 % Al_2O_3, 64,58 % SiO_2

Crystallography - Monophysician Class - Prismatic

Optic properties - Biaxial positive

Habit - It tabulate

Clivage - Reached in {110}

Hardness - 6,5 - 7

Relative density - 3,15 - 3,2

Brightness - Glass

Color - White, grey, pinkish (kunzite), yellow or green (hidolenite)

Where is espodumene found?

•Geologic association - It can be associated with other alkaline minerals in granitic igneous rocks and gnaissic and migmatític metamorfic rocks.

•Disgnostic properties - vertical prismatic Clivage and partition as frontal pinacoide. When warm it acquires the grayish color due to presence of Li.

•Occurrence - They occur in pegmatites, aplites and lithium-granites, being that in the pegmatites they occur in the form of huge crystals.

•Uses - It is a important raw material in the attainment of lithium salts employed in ceramics and manufacture of glass and the transparent varieties are of beautiful coloration and constitute precious stones of great value (kunzite).

Espodumene, when gem is kunzite

Ambligonite

•Ambligonite is a mineral, fluorophosphate, predominantly an aluminum phosphate and lithium or sodium, (Li, Lb) Al (PO4) (F, OH), with prominence in its composition for lithium

•The mineral occurs in pegmatite deposits and is easily confused with albite and other feldspars. Its density, clivage and test of flame for lithium identify it. Ambligonite forms a series with the montebrasite, lowest fluorinated in the terminations.

•Geologic occurrence is in pegmatites granites, bodies of high temperature tin, and greisens. Ambligonite occurs with espodumene, apatite, lepidolite, tourmaline, and other minerals carrying of lithium in pegmatite body. The main commercial sources have historically been the deposits of California and France

Ambligonite

Lepidolite

- Lepidolite (KLi2Al (Al, Si) 3O10 (F, OH) 2) is a mineral lilacs or pink-violet of the group of the filossilicatos. It is part of the group of micas, being a secondary lithium source. [1] It occurs associated with other you mine carrying lithium as espodumene in pegmatitic bodies. It is one of the main sources of rare alkaline metals rubidium and cesium.

•Color Properties : violet, lilacs, fron pink towhite, grey or from sometimes yellow. Brightness: from glass to pearly . Transparency: transparent the translucent one. System of crystallization: monophysician 2/m. Crystalline habit: tabular crystals the prismatic ones with prominent pinacoidal termination. Form “pseudo-hexagonal books”. Also micáceo or masses to granulate. Clivage: reached in the perpendicular direction to the axle-c. Fracture: different. Hardness: 2,5 specific Weight: >2.8 Trace: White.

- Mine associates: quartz, feldspar, espodumene, ambligonite, tourmaline.
- **Manly occurrences**: Brazil; Ural Mountains, Russia; California - USA
- In Portugal it can meet, for example, in the zones of Algodres and Fundão.

Lepidolite

Petalite

- Petalite is an important lithium mineral; it is a tectossilicate of lithium and aluminum, $LiAlSi_4O_{10}$; it crystallizes on monoclinic system.
- It is classified as a member of the feldspar group. However, its chemical composition is silica saturated, as such, it dosen't fit in the current felspatoids category.
- Colorless, grey, yellow or greysh yellow, occurr under the form of tubulars cristals or colunars masses in pegmatites, associeted to espodumene, lepidolite and turmaline.
- Discovered in 1800, at Utö island, Haninge, Stockholm.

Petalite

Brazilian lithium production

•Ores that have lithium contents: Feldspars with petalite and espodumene in form of lump or fine dust produced by Archean Ltda, CBL, in Araçuaí and Itinga for the ceramic industry of Minas Gerais and São Paulo.

•Lump is obtained for millings processes: the fine dust with proportion ranging of 1% to 4.6% of Li2O; 3,000 tons per year are sold;

Brazilian lithium production

•There is a destined production to chemical composites lithium hydroxide and carbonates.

• CBL produces 11.200 ton per year of concentrade ores wicth avarage content 5,38% Li20.

•The CBL takes this production of Araçuaí and Itinga for a chemical plant localized at Divisa Alegre, Minas Gerais, that produces close to 230 tons of dry lithium carbonate and 390 tons of mono lithium hydroxide – hydrated.

Prices of concentrated ores of lithium and chemical lithium composites

- The intent ore prices of espodumene vary of US$ 840 to US$ 1,700 for ton, depending on the negotiated amount and the propostion of Li2O.
- The chemical composite prices (carbonate of lithium, lithium hydroxide, lithium chloride) vary from US$ 8,180 to US$ 15,570 per ton.
- Petalita and the commercialized espodumene has the kilogram average price of US$ 0,85 for kg.
- The commercialized lithium chloride the kilogram has average price of US$ 7,42 to US$ 9,17 for kg.

Where lithium is applied in Brazil?

- Chemical industry: manufacture of polishes and lubricants.
- Metallurgy: primary aluminum manufacture.
- Ceramic industry.
- Nuclear industry as reactors sealer.
- Electrochemical industry: manufacture of batteries - Brazil does not use its lithium ores for this.

Brazilian lithium consumption
Sources: DNPM-DIPLAM; SECEX; CBL; ARCHEAN

Discrimination	2006	2007	2008	2009 (ESTIMADA)
Production	8,585 t of concentrated; 437 t of Li2O; 686 chemical composite t	7,991 t of concentrated; 430 t of Li2O; 809 chemical composite t	14,460 t of concentrated; 647 t of Li2O; 628 chemical composite t	15,000 t of concentrated; 700 t of Li2O; 700 chemical composite t
Import	15,000 t of concentrated; 700 t of Li2O; 700 chemical composite t	7 t de compostos químicos		
Export	13 t de compostos químicos			
Apparent consumption	8.585 t de concentrados; 700 t de compostos químicos	7.991 t de concentrados 816 t de compostos químicos	14.249 t de concentrados 628 t de compostos químicos	15.000 t de concentrados; 700 t de Li_2O; 700 t de compostos químicos

Lithium Salts and Salars

•Evaporites with economic viability is found in desert-like, next to cenozoic valcanos, geologically of more recent age (less than 50 million years).

•In the Atacama Salar, the lithium concentrations can vary of 0,02/0,03 ppm, close to the edges, 0,05/0,16 ppm, in the intermediate zones, and 0,15/0,64, in the center of salar.

•Some geothermal sources contain significant values of lithium, as the found ones in the Imperial Valley, California (Kusnasz, 2006).

•The relation magnesium/lithium is important, because, the more raised this relation, greater it will be the limestone consumption the necessary for removal of proper magnesium.

Main sources of lithium e its chemical compositions

Sources of Lithium	(%) Li	Mg	K	Na	Mg/Li	Mg/Li
Salar de Atacama, Chile	0,15	0,96	1,80	7,60	6,4	12
Salar de Uyuni, Bolivia	0,025	0,54	0,62	9,10	21,6	24,8
Salar del Hombre Muerto Argentina	0,06	0,07	0,60	9,50	1,2	10
Silver Peak, NV, U.S.A	0,02	0,03	1,00	7,50	1,5	50
Great Salt Lake, UT, U.S.A.	0,006	0,80	0,40	7,00	133	67
Sea Died, Israel/Jordan	0,002	4,0	0,60	3,00	2000	300
Water of the Sea	0,00002	0,13	0,04	1,80	6500	2000

Source : Roskill (2002).

Minining and concentration of lithium ores in brines

•The extraction and the processing of Li rich brines uses simpler methods and cheaper than mininig pegmatites, as the espodumene and the petalite.

•In the Atacama Salar, in Chile, the brines are pumped of a depth of 30 m, for the lagoons of evaporation in the surface.

•The crystallized NaCl (halite) is removed of the lagoons, and the remaining brine, is enriched with potassium, lithium and boron, is pumped for new lagoons of evaporation, where they are precipitated in the silvite form.

•After the removal of these, souses remaining brines contains 1% of Li e, after continuous evaporations, is precipitated in its point of saturation, with 6% of Li (equivalent to 38% of LiCl), more 1.8% of Mg and 0.8% of B% crystallized product is purifyed for withdrawal of Mg and B and later guided to the lithium carbonate plant.

In Brazil, the industrial lithium composite production is obtained directly of the espodumene

•Aluminossilicate ($LiAlSi_2O_6$) carryier of lithium, with concentration of 1 to 1.5% of Li_2O.

• Concentration of the espodumene for dense way or manual grooming, obtaining a concentrate with concentrations of 5,5 to 7.5% in Li_2O.

• Thermal treatment (decrepitation) in calciner rotating ovens 1.000-1.100°C, for conversion of a-espodumene in b-espodumene.

• Digestion of the concentrate of calcined espodumene can be accomplished with acid or alkali, and the obtained end item will be a lithium carbonate or hydroxide.

• In the process of acidic digestion, the sulfuric acid (98% p/p) in excess is used (30%) as lixiviant agent, to the temperature of 250º C, in ovens.

• The formed lithium sulfate is leached with water, purifyed and precipitated with barrilha, for attainment of lithium carbonate.

The big questions and challenges to construct the answers

- To buy foreign batteries or to manufacture batteries in Brazil?
- Courage and integration.
- Exploitation of accumulation of national technology.
- Faith in the chance and the trends of global economy of the sector of transport
- Competitive Strategy

Thanks a lot !

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