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Lithium Minerals and their Applications in the "Glass Age"

Minerales de Litio y sus Aplicaciones en la "Edad del Vidrio"

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ABSTRACT

A brief review is provided of the applications of lithium mineral resources for the manufacture of vitreous materials: glass, enamels, and glass-ceramics. First, are reviewed the general situation regarding lithium applications in other fields of products and main sources of lithium-containing minerals and rocks are also reviewed. It is shown and described the pioneer research conducted in Spain in last decades for the crystallization of glasses in the Li_2O-SiO_2 binary system, without and with oxide nucleating agents, as well as the use of this basic system for the formulation of new glasses and glass-ceramics with applications as neutron absorbent materials. Otherwise, it is reviewed the results in the obtaining of those vitreous materials formulated from Spanish and Portuguese lithium minerals of amblygonite, lepidolite, vermiculite, and muscovite mining wastes. Main conclusion it was that is possible to obtain aventurine glass-ceramics where is formed a new lithium phosphate spodumene with surface segregation of iron oxides. Finally, the main future prospects in this field are discussed.

Keywords: Lithium Minerals; glasses; glass-ceramics; rock wastes; research Spanish evolution.

RESUMEN

Se presenta una breve revisión de las aplicaciones de los recursos minerales de litio para la fabricación de materiales vítreos: vidrio, esmaltes y vitrocerámicas. En primer lugar, se revisa la situación general de las aplicaciones del litio en otros campos de materiales y las principales fuentes de minerales y rocas que lo contienen. Se revisa la investigación realizada en España en las últimas décadas en la cristalización de vidrios en el sistema binario Li_2O-SiO_2 con y sin agentes nucleantes de óxido, así como el uso de este sistema básico para la formulación de nuevos vidrios y vitrocerámicas con aplicaciones como materiales absorbentes de neutrones. También se revisan los resultados obtenidos en la obtención de dichos materiales vítreos formulados a partir de residuos mineros españoles y portugueses de ambligonita, lepidolita, vermiculita y moscovita. La principal conclusión es que es posible obtener un nuevo tipo de vitrocerámicos formados por una nueva fase de espodumena de fosfato con segregación superficial de óxidos de hierro. Finalmente, se discuten las principales perspectivas de investigación en este campo.

Palabras clave: Minerales de litio; vidrios; vitrocerámicos; residuos de rocas; evolución investigación española.

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Introduction

Since the 70s (during the last five decades), broad and continuous research on glasses and glass-ceramics containing lithium (as Li_2O) has been carried out in Spain, initially at the ICV-CSIC (Instituto de Cerámica y Vidrio- Consejo Superior de Investigaciones Científicas) and after in other CSIC research centers. After this pioneering work, this research was followed by research conducted on glass-ceramics from lithium minerals from Spanish and Portuguese resources in the Glass-ceramics Lab at the IETcc-CSIC (Instituto Eduardo Torroja de Ciencias de la Construcción- Consejo Superior de Investigaciones Científicas). This research was continued at the Department of Geology of the MNCN-CSIC (Museo Nacional de Ciencias Natural Consejo Superior de Investigaciones Científicas), simultaneously with the UMH-Elche (Universidad Miguel Hernández- Elche, Department of Agro-chemistry and Environmental Sciences). After the glass-ceramics research at the beginning of 1970, other Spanish university departments, research centres and even some industries, conducted R+D+i (Research+ Development+ innovation) on a wide range of glass-ceramics, some of which containing lithium oxide. Although is pending an extended review about the research on lithium glass-ceramics in Spain, here is shortly reviewed a first revision on this specific scientific research carried out in the CSIC as an academic tribute to the Professor Garcia Guinea due to his contribution on application of mineral raw materials for ceramics and glasses.

Explaining the "Glass Age" and its relation to natural raw materials

Last 2022 year it was celebrated worldwide, after being named by the United Nations, and under the proposal of the International Commission of Glass, as the International Year of Glass (IYOG2022) (Durán & Parker, 2024; Sánchez-Soto, 2024). Cultural, industrial and research communities, among others, all celebrated the recognition and expansion of the glass and derived vitreous materials and products in the Circular Economy and the effect in the daily life of citizens. Prior to this IYOG2022, the international glass community had already named this century for some years the "Glass Era" (Pye, 2016). Even more, vitreous materials have aroused great interest among geological scientific community as was revised in 2016 in a complete review of natural glasses (Glass, 2016). Glassy products and materials production strongly depend of availability of raw materials (Fernández-Navarro, 2003; Rincón, 2005; Pellón-González, 2014).

General applications of lithium resources and for the production of glassy materials

Glasses, enamels and glass-ceramics

Lithium resources have received highly significant interest in recent decades due to the use of lithium batteries for the Energetic Transition to electrical transport, which is the most favourable for the environment. There are a wide range of applications for these natural or synthetic resources of Lithium (Fig. 1 and S1) (Ebensperger et al., 2005).

Since the first decades of last century, lithium minerals have garnered great interest, which can be seen in the significant literature, monographic books and reviews of papers (Aubert, 1963; Lithium Corporation of America, 1970; Russel, 1987; Regueiro & Lombardero, 1997; Gourcerol et al., 2019). Without going into a detailed analysis of these monographies, it is worth mentioning here as an example that the earliest monograph was edited in 1964 by Russian authors (Dubrovo & Grebenshchikov, 1964). However, nowadays the main interest in lithium ores stems from its application in the development of the electric vehicle industry (Grosjean et al., 2012).

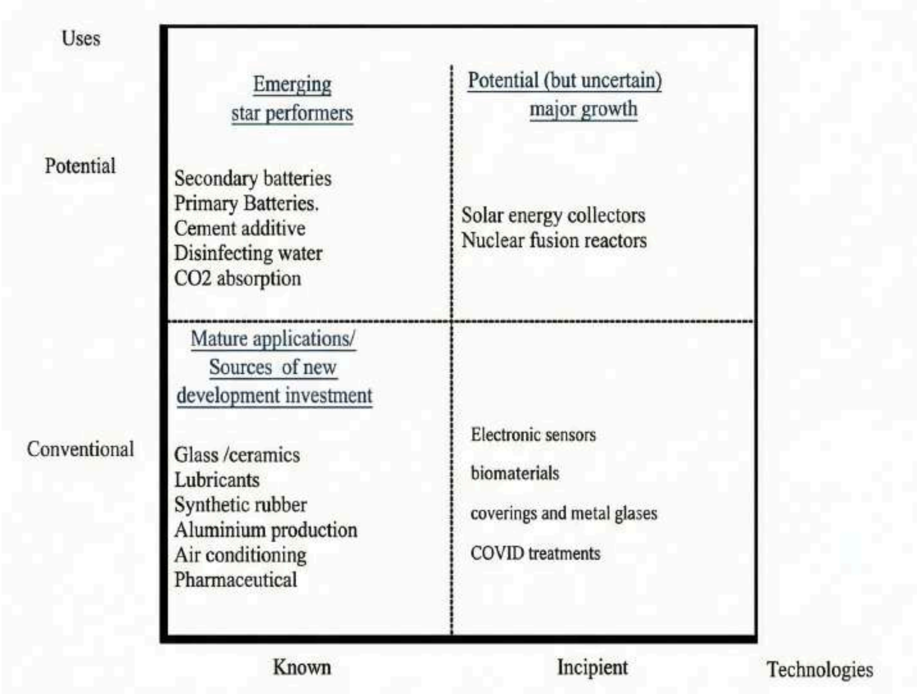

Figure 1.— Applications for mineral and lithium compounds and their future considering the uses and the evolution of technologies (modified from Ebensperger, 2005). In the Supplementary File, it is showed the economical ratios depending of each raw material in a Table improved-modified from the same author.

Glass-ceramics as materials for glass production and the use of lithium resources for their production

Glass-ceramics are materials composed, as any other ceramic material, of one or several crystalline phases embedded into a vitreous (glassy or "amorphous") matrix. This "liquid or vitreous" matrix is usually called "residual glassy phase" and it determines also the final properties and performance of glass-ceramics (Nuernberger et al., 2019). However, unlike other traditional ceramics that are usually obtained by thermal treatments (sintering), the manufacture of glass-ceramics involves obtaining an original or glass (also named "mother glass"), which is subjected to a controlled thermal treatment in two or more steps for the promotion of nucleation and the growth of crystalline phases.

There are several ways of processing glass-ceramics, which entail the successive operations of:

a) melting→ moulding→ thermal treatment (*conventional glass-ceramics*),
b) melting followed by a slow cooling (*petrurgical glass-ceramics*) or
c) melting→ fritting or sudden cooling of the melted substance to obtain a glassy powder→ sintering + simultaneous crystal growth (*sintered glass-ceramics.*).

Each type of process (Zanotto, 2010) is usually designed according to the target objectives for specific properties and performances, functions and applications required from the final materials. From the onset of glass-ceramics research, science and technology in 1957 by Stookey, from the Corning Glass Works (USA), which patented the first glass-ceramics containing Li_2O (Stookey, 1959) (Barrachina et al., 2018), their definition as products has evolved in line with the fast and major developments in the field of these materials in recent decades. Although many glass-ceramics can be designed without Li_2O in their composition, a majority of these materials with the best properties require this oxide in their composition. Since 1957, different names (vitro-cristallines, ceramic-crystals, etc.) were given to these materials, until a new definition of "glass-ceramics" was finally provided by the ICG (International Commission of Glass) (Deubener et al., 2018).

Lately, glass-ceramics technology has been considered an efficient “vitrification process” has reached great relevance because has been proven to be very useful for the recovery of wastes as “secondary raw materials” and for the inertize or immobilize of all type of industrial wastes, included the radioactive wastes (Vicente-Mingarro et al., 1993; Colombo et al., 2003; Ojovan, 2007).

The applications of lithium in the field of ceramics and glasses have allowed new glass-ceramic materials, whose production started in the 1960s, to have a wide range of uses in recent decades for all types of commercial and industrial sectors. These uses range from the more common household uses (kitchen table tops) to mirrors of large telescopes, sophisticated industrial applications, and even new functions in electronic components and biomaterials (Rincón, 2016). They have been widely described in many papers and numerous reviews (Zanotto, 2010; Barrachina et al., 2018). As mentioned above, the importance of lithium for the design and manufacture of marketed products can be seen in more than eighteen commercial glass-ceramic materials (Rincón, 2005). Thus, the reliance on lithium to manufacture glass-ceramics has been decisive and is always included in any type of study or investigation of raw materials in the case of ceramics, glasses and related products (Dondi et al., 2018).

Glass-ceramics from the Li_2O-SiO_2, Li_2O-CdO-SiO_2 and Li_2O-MgO-Al_2O_3-SiO_2 basic composition systems

The origin of glass-ceramic reseach in Spain: the 70s and 80s.

Publications about these glass-ceramics in Spain date back to 1968 (Fernández-Navarro, 1968), with the first Spanish scientific paper mentioning these innovative materials. This paper reviewed the knowledge on the fundamentals of nucleation and crystal growth in glasses, which is the basic thermal process for a controlled devitrification of glasses or vitreous materials. However, the first news about these “new materials” (at that time) reached Spain thanks to Professor Antonio García-Verduch in 1958, after his time as a visiting professor at Alfred University, USA. He notified the ICV-CSIC of the existence of prior Stookey patents (Stookey, 1959) and brought several samples of the first commercial glass-ceramics from the USA (García Guinea, *personal communication*) (Fig. 2). Then, in 1972, a review article of the Spanish Royal National Academy of Pharmacy gave mentioned extensively of the functional applications of these glassy materials (Aleixandre, 1972). It is worth mention that the usual Spanish term at that time was “vitrocristalinos”, which evolved to “vitrocerámicos” due to the continuous increased worldwide research with the English term “glass-ceramics”, which was finally adopted by the entire scientific community.

Figure 2.— First glass-ceramics taken to Spain in1958 from Alfred University, USA (García- Guinea, *personal communication*).

On the other hand, the lithium oxide compounds and minerals were well known for the compositional design and improvement of properties of enamel, glazes and glasses, and even as conventional additives in industrial glass production. It is a well- known fact that these additions improve the melting, moulding and final properties of glazes, enamels and glasses. In fact, using lithium compounds as additives improves the melting fluidity, as lithium volatilisation is lower than that of fluoride compounds and they are less corrosive for refractories. Even more, the use of lithium in the composition of glass batches is beneficial from an environmental point of view.

Thus, in a comprehensive review cited by Sánchez (Sánchez et al., 2006) it was mentioned that the common additives in industries include Li_2CO_3, petalite and spodumene, mainly as fluxing modifiers. Even, additions of Li_2CO_3 were explored for the synthesis of the eucryptite ($Li_2O.\ Al_2O_3.2SiO_2$) (García-Verduch & Moya-Corral, 1970). Thus, time ago Spanish scientists were interested not only in glasses with Li_2O, but also in other applications in ceramics. A paper from 1964 addressed the importance of adding Li_2O to the composition of these materials, as well as the use of main natural raw materials containing this lithium oxide for the formulation of glazes and enamels as substitutes of PbO for the production of ceramic glazes (Aleixandre & Fernández-Navarro, 1964; Fernández-Navarro,1968). In subsequent years, several investigations focused on obtaining and characterising phosphate glasses containing Li_2O (Fernández Arroyo & Prod´Homme, 1972).

The first Spanish lithium containing glass-ceramic was obtained by Aleixandre, González-Peña and Rincón in the 1970s (Aleixandre et al., 1971). In the Supplementary file it is showed an old picture about the melting and cooling of the first original glass for obtaining of this first Spanish glass-ceramic.

This first glass-ceramic was designed in the cordierite ($2MgO.2Al_2O_3.5SiO_2$)- spodumene ($Li_2O.\ Al_2O_3.4SiO_2$) binary composition system. Therefore, the oxide composition was designed in the 50/50 (in wt. %) eutectic point cordierite- spodumene subsection of the four-oxides equilibrium diagram Li_2O-MgO-Al_2O_3-SiO_2 (Karkhanavala & Hummel, 1953) (Figure 3a).

This research investigated the role of TiO_2 additions (at 4 and 12 wt. %) as the nucleating erant for promoting the nucleation of crystals inside the glassy matrix. Figure 3a shows the binary section of cordierite-spodumene, where the lower limit of liquid at approximately 1,350ºC can be seen. On the right, Figure 3b depicts a representative micrograph obtained by a Balzer’s Photoemission Electron Microscope of the glass-ceramic crystallised with 12 wt. % of TiO_2. As described by Alexander et al. (1971), well dispersed and very dark crystallites of rutile, size close to 1µm, can be seen decorating the β-spodumene solid solution with µ-cordierite crystals.

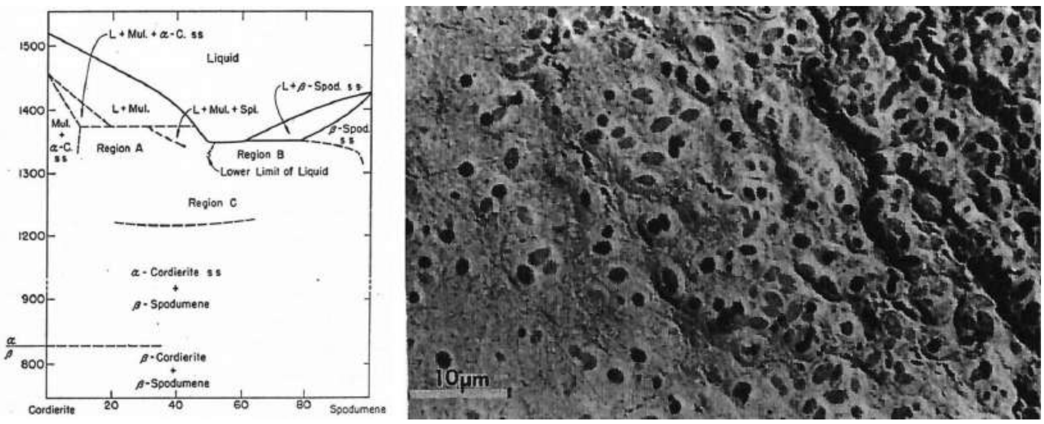

Figure 3.— a) The cordierite-spodumene equilibrium binary phase diagram showing the eutectic point at 50 wt. % of phases (Karkhanavala & Hummel, 1953); b) Photoemission electron microscopy of a final glass-ceramic containing 12 wt. % of TiO_2 (Aleixandre et al, 1971). (As Supplementary File is showed a Figure of the evolution of crystalline phases with thermal treatment and corresponding micrographs of microstructure)

These types of glass-ceramics precipitate β-spodumene solid solutions with quartz and µ-cordierite microcrystals. The corresponding glass- ceramics were also fully characterised by the TEM-replicas method and the extraction-replicas method by Electron Diffraction (SAED) (Aleixandre et al, 1971). In some areas of this glass-ceramics also was detected a solid solution of Silica K and Silica O high temperature quartz phases, which coexist with β-spodumene and µ-cordierite (Roy et al., 1950).

As a starting point for understanding the glass-ceramic process, this research was followed up by exploring the Li_2O-SiO_2 simple binary phase equilibrium system. Several decades later, new research demonstrated the utility of these phases in synthetic dental prostheses as biomaterials (Hölland & Beall, 2002). In the initial research in the binary Li_2O-SiO_2 system it was determined the growth for $Li_2O.2SiO_2$, $Li_2O.SiO_2$, lithium disilicate and lithium metasilicate crystalline phases. The subsequent research on this binary system was focused on the study of the nucleation and crystallisation of four compositions near the eutectic point of the Li_2O-SiO_2 binary system with additions of V_2O_5, Cr_2O_3 and MnO_2 (added as 1 mole%) as nucleating agents (also known as " nucleation catalysers") (Rincón, 1992).

Due to the addition of Cr_2O_3 at high temperatures as colorant and nucleating agent it is difficult to introduce in conventional glasses, because of its very stable spinel cubic structure (Fernández-Navarro, 2003), it was also investigated the addition of 0.05 to 1.00 mole% of Cr_2O_3 to a $24Li_2O.76SiO_2$ (wt%) composition. As this way, it was experimentally demonstrated that a minimum percentage of 0.05 mole% is the most effective for obtaining the maximum volume fraction of the disilicate phase (Rincón-Mora et al., 2019). Several crystalline phases of lithium silicates can be precipitated inside the Li_2O-Cr_2O_3-SiO_2 ternary system that shows also an extended area of immiscibility along the Cr_2O_3-SiO_2 (Izquierdo and West, 1980). The $Li_2O.2SiO_2$ crystallization volume fraction was estimated from the XRD (X-Ray Diffraction) relative intensities. Thus, intensity (110), Bragg distance 0.540 nm, was followed in the glass-ceramics obtained from these glasses with Cr_2O_3 additions and treated at 650ºC for 2 hours (Fig. 4).

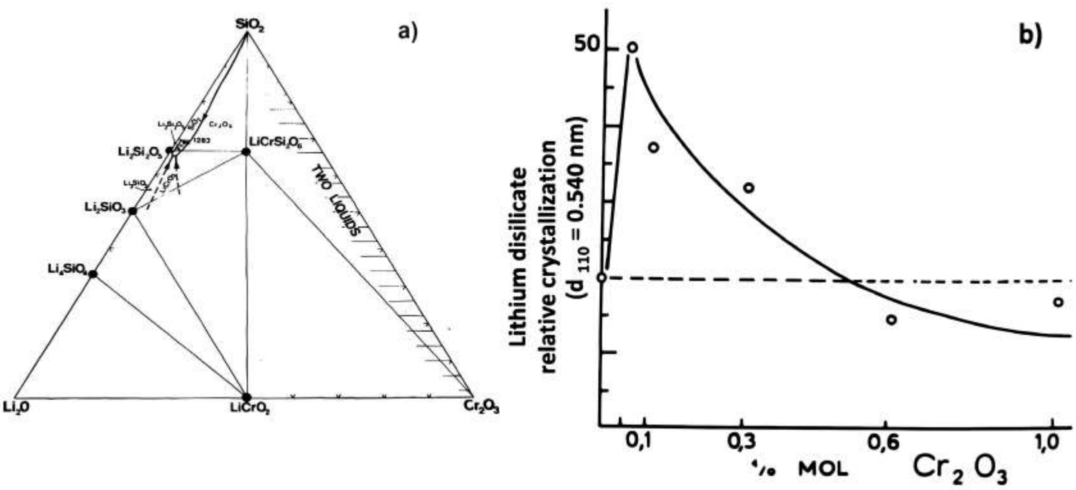

Figure 4.- a) Li_2O-SiO_2 ternary system with Cr_2O_3 showing an extended area of immiscibility along the Cr_2O_3-SiO_2 binary system (Izquierdo and West, 1980). b) Lithium disilicate content in the lithium silicate glass-ceramics versus the %mol of Cr_2O_3 added and the limit for dissolution of chromium oxide in these glasses heat treated at 650ºC (Rincón-Mora et al., 2019).

This research work on the Li_2O-SiO_2 binary system was complememted with the investigation of the Li_2O-CdO-SiO_2 glass and glass-ceramic ternary system with the aim of obtaining new glasses with a high refractive index, and others, which could be interesting for the nuclear industry as neutron-absorbing materials due to the high-neutron effective section of cadmium. Additionally, it was investigated the addition of V_2O_5, Cr_2O_3 and MnO_2 as nucleating agents in these ternary glasses. This way, in these new and not previously investigated glasses and glass-ceramics, researchers demonstrated their high capability of absorbing thermal neutrons with irradiation experiments carried out in the former Junta de Energia Nuclear, nowadays named as CIEMAT (Centro de Investigaciones Energéticas y Medio Ambientales) in the Madrid nuclear reactor JEN1 (2 Mw). Figure 5 shows the respective ratio of neutron transmission flux versus the thickness of glass and glass-ceramic prismatic samples of 20x50 mm. The thicknesses explored were 5, 10 and 15 mm on samples with specular polished surfaces. Materials, both transparent and opaque, were able to absorb 95 % of the thermal neutrons produced in the JEN1 reactor (Rincón et al., 1987).

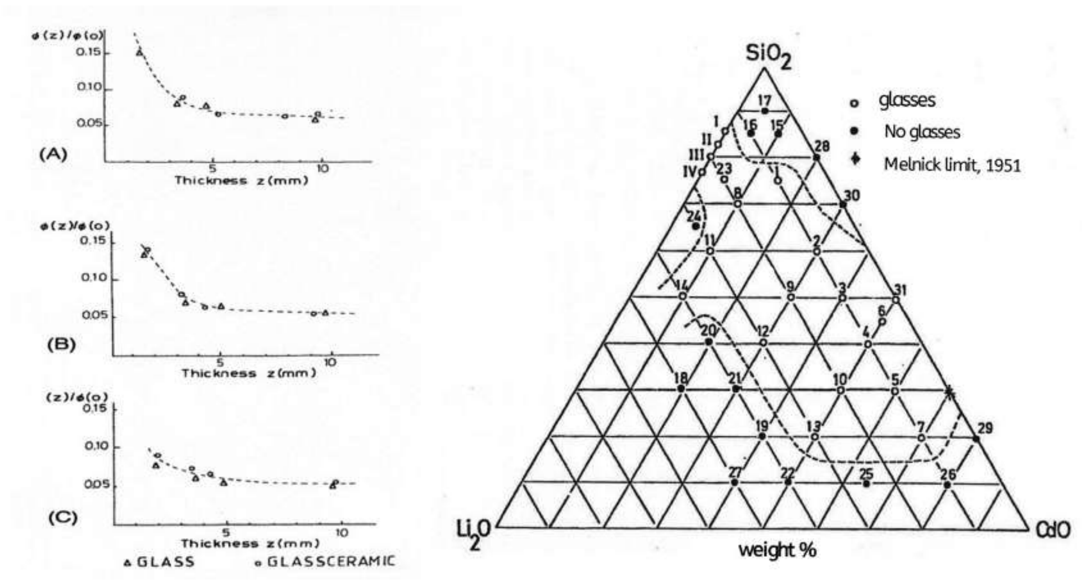

Figure 5.— a) From the top to the lower curves: transmission flux of thermal neutrons for Li_2O-CdO-SiO_2 glasses and glass-ceramics containing 10wt% Li_2O and 30, 40 and 60wt% CdO respectively. The experiment was carried out in the JEN1 reactor in 1977, results were published in the American Ceramic Society Bulletin (Rincón et al., 1987). b) Glass formation area first explored in the Li_2O-CdO-SiO_2 system showing wide area for transparent glasses. This glassy system was included in Handbook of Glassy Phase Diagrams (Mazurin et al., 1983).

This research also showed for the first time that a wide range of transparent glasses can be obtained in this ternary system, even with higher CdO content of up to 60 wt. % of this oxide (Fig. 5a), glass forming area was reported by Mazurin in his edited book of Handbook of Glass Data in the 1983 (Mazurin et al.,1983). The final glass-ceramics contain several proportions of the following crystalline phases: CdO.SiO_2, Li_2O.SiO_2 and Li_2O.2SiO_2, as well as some residual quartz. Because, the resulting glass-ceramics showed good absorption to the thermal neutrons (Rincón et al.,1987), these results were registered as CSIC patents in 1977 (Gonzalez-Peña & Rincón, 1977a,b). Due to the radiation could affect the properties of these glasses and glass-ceramics, some experiments with gamma radiation were additionally investigated in that time by using the Co^{80} Nayade Source, JEN, Madrid (further information available online as supplementary file).

Due to the wide range of colour variation and high refraction index obtained from these lithium silicate materials, after these initial investigations in collaboration with García Guinea (1988) were investigated for their utility as synthetic polished gems, being characterised by the Bannister- Webster diagram (Fig. 6). It was proven their capabilities for the production of synthetic "pseudo-gems". Thus, the polished aspect and the optical properties and densities were fully characterised (García Guinea & Rincón, 1988).

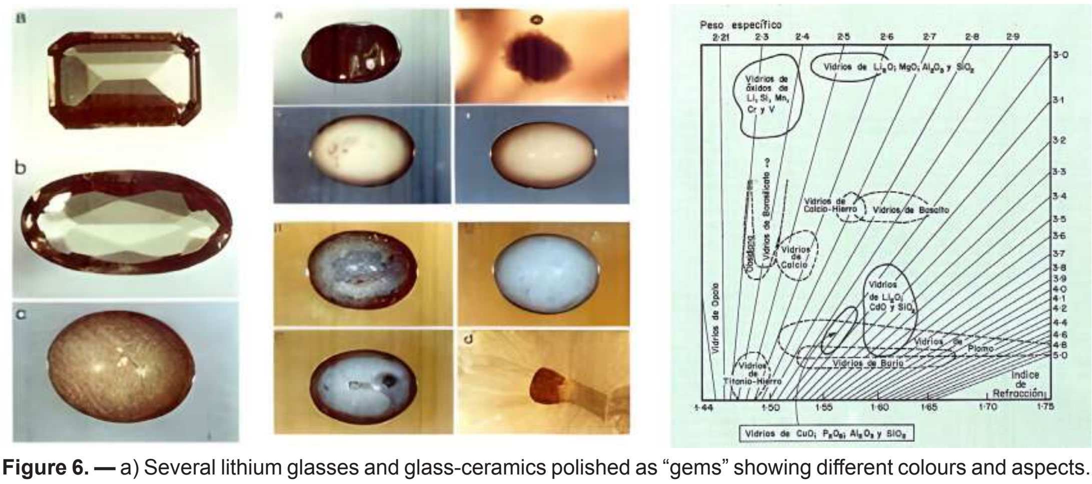

Figure 6. — a) Several lithium glasses and glass-ceramics polished as "gems" showing different colours and aspects. b) Their location in the Bannister-Webster diagram is also shown, which reflects the density versus the refraction index in the case of materials that could be compared with "gems" (García Guinea & Rincón,1988).

Lithium minerals in the Iberian Peninsula: Glass-ceramics from lithium minerals: muscovite, vermiculite and lepidolite all formulated with amblygonite

Research in glass-ceramics in the 90s and subsequent decades

In the mid 1980 decade an investigation was started to study the capabilities of some mining resources and wastes from the Iberian Peninsula containing lithium for obtaining of new glass-ceramics (Spain and Portugal), all enclosed in pegmatite rocks (Rincón, 2016). This research was carried out and funded in the frame of the 1985 Spanish governmental scientific research project "Aplicación de minerales de litio y micáceas a la obtención de nuevos materiales vitrocerámicos".

It is well known that lithium minerals are produced from brines in South America, where there are large lithium salt deposits (Foote Mineral Corp, 1970), and other locations worldwide. The most abundant ores are pegmatites (75-80 %). Li_2CO_3 used to have a wide variety of applications, but, since the start of the 21st century, lithium production was expected to increase significantly due to the manufacturing of batteries and then for the development of nuclear fusion reactors (Rincón and Jordan, 2024). Until 1950, it was used mainly for the production of special glasses and for the reflector mirror of telescopes, like the one in the Monte Palomar, as well as for some metallic alloys and ceramic materials. However, after that year, lithium production grew very suddenly. In fact, USA Atomic Commission consumed 75 % of the worldwide production (1957 data from Industrial Minerals). Since 1970, lithium production increased sharply for vehicle batteries and glass-ceramics with technological applications. As it is showed in the Table 1, lithium is included in composition and structure of a wide range of minerals.

Table 1. Lithium minerals and their respective properties (extracted from Rincón, 2005. Quartz is given as a comparison).

Mineral	Formula	Li_2O wt. %	Original rock	Density (g/cm^3)	Melting T (ºC)	α x 10^7 (º C^{-1})
Petalite	$Li_2O.Al_2O_3.8SiO_2$	4.50	Lithium pegmatites	2.4-2.5	1350	3 (20-1000 º C)
Lepidolite	$Li_2O.KF.Al_2O_3.3SiO_2$	6.43	Mica rose, pegmatites	2.85	< 1200	5.05- 6.08 (658-735 º C)
Spodumene	$Li_2O.Al_2O_3.4SiO_2$	8.10	Pegmatites	2.60	1420	9 (20-1000 º C) 0 (20-1000 º C)
Zinwaldite***	$K(Li,Fe,Al)_3(Al,Si)_4O_{10}(F,OH)_2$	5.6	Lithium phyllosilicate	2.90-3.10	1145-1400	
Amblygonite	$2LiF.Al_2O_3.P_2O_5$	10.10	Sn,W pegmatite ores	3.04-3.11	800*	(no data found)
Eucryptite	$Li_2O.Al_2O_3.2SiO_2$	11.90	Altered spodumene	2.67	1410	- 86 (20-700 ºC) - 64 (20-1000 ºC)
Lithium carbonate	Li_2CO_3	40.40	Brines	2.11	720**	-
Quartz	SiO_2	-	Widely spreaded	2.62	1700	237 (20 -600 ºC) 132 (20- 300 ºC) 112 (20-1000 ºC)

* Value from Jimenez- Calvo et al. (1976) and Rincón (2005). ** According to Aleixandre & Fernández-Navarro (1964) is 618ºC. ***This mineral used in the past "is not yet considered as industrial mineral due to low lithium content" (Sánchez-Muñoz and Carda-Castelló, 2003).

Previous to this research, it was collected information about lithium ores in Spain and Portugal. Time ago, a well complete review was edited by the Instituto Geológico y Minero de España (IGME, 1975). It is well- known by geologists that content of lithium into pegmatites, that was investigated time ago by Professor Arribas (page 224 of the recently edited History of the "Lucas Mallada" Institute, Perejon- Rincón, 2023). Very recently, García-Guinea (2024) has given a short revision of the lithium quarries in Spain.

The initial idea for obtaining of new glass-ceramics from Spanish and Portuguese ores was the investigation of several combinations of the original batch glass formulas: amblygonite, muscovite, lepidolite and vermiculite. The starting data were:

- Amblygonite mines from Cáceres (Valdeflorez) and Salamanca (La Barquilla) (both abandoned for over 50 years and are now interesting for restarting their exploitation) (Sos-Baynat, V., 1962 ; Santos-García, J.A. & Medina-Fernández, 1975).
- Lithium pegmatites from La Fregeneda (Salamanca) and from Guarda (Portugal), containing lepidolite. (Rincón & Jordán, 2024).

The more surprising effect of all this family of innovative glass-ceramics was that they showed iridescent and reflective surfaces, that look as metallic appearance (Callejas, 1988). Obtaining of these iridescent reflective surfaces with glass-ceramics lately garnered interest from some Spanish tile’s producers (Gozalbo et al., 2006).

The vermiculite mineral wastes were taken from Santa Olalla de Cala (Huelva). This mineral is inside a contact metamorphic zone of plutonic plying near Sevilla province in the Andalucia Region. This quarry contains granites with diorites and gabbros with a cordierite-quartz-monzonite formed at 1,050ºC. This vermiculite ore was investigated time ago in great detail by González-García et al. (1960). Also, it has been considered for the formulation of original glasses some “micaceous” mine wastes for the formulation of original glasses:

- Muscovite powders from a washing kaolin factory (Santa Comba, A Coruña).
- Vermiculite wastes from an abandoned mine in Huelva (Santa Olalla) (González- Garcia et al., 1960).

The use of spodumene was not considered in this investigation because its scarce resources only detected Lalin, Pontevedra. However, a muscovite waste coming from a galician washing kaolin factory was used as an additional raw material for the formulation of original glasses. In this way, and calculating the mineral ratios after inspecting the basic phase diagrams: amblygonite + muscovite, amblygonite + lepidolite and amblygonite+ vermiculte (Callejas, 1988). In fact, part of the original idea for these formulations came from the previous papers of Das & Thakur (1970) and Dalal & Davis (1977), which investigated the mixing of micas with spodumene for obtaining glass-ceramics.

Amblygonite always was used in original glasses, glazes and enamels (Jiménez-Calvo et al., 1976). This is because the existence of the Cáceres amblygonite (El Trasquilón) and in Salamanca (La Barquilla). Both were discovered time ago (1917) into veins of amblygonite and cassiterite intersecting Silurian and Devonian slates. This amblygonite is in the range of 9-20 wt% with average 14.25 wt% from several drill-hole samples (Dorpinghaus, 1918, 1917 and 1914). Due to recent interest of lithium resources for future electrical batteries the amblygonite deposits have been more recently widely revisited by recent investigations (Roda-Robles et al, 2016; Roda- Robles & Gil-Crespo, 2019; Pesquera et al., 2020). For the investigation in applications of amblygonite for obtaining glass-ceramics, years ago some original amblygonite samples were obtained after several requests to the mine owners and to Professor Arribas (Salamanca) (further information available online as supplementary file).

As it was showed by Fang (2002) it is possible obtaining glass-ceramics with lepidolite. Thus, the lepidolite was also investigated in the formulation of new compositions with amblygonite. Lepidolite wastes were obtained from the pegmatites of La Fregeneda, Salamanca (purchased by Locutura-Rupérez, geologist of the Instituto Geológico y Minero de España and first experiments for obtention of these types of glasses were published in the Boletin de la Sociedad Portuguesa de Cerámica (1984). Several samples of lepidolite from Guarda (Portugal) was included in this research after receiving some samples after a visit during 1984 to the Coimbra Glass and Ceramics Institute.

By mixing the glasses with the original composition containing muscovite wastes with amblygonite and the addition of several oxides introduced as nucleating agents, such as TiO_2, ZrO_2 and MgO, it was possible to obtain for the first time the respective crystallisation curves of a new synthetic spodumene (Rincón, 1992). The high volume fraction was quantitatively determined by XRD (X-Ray Diffraction) at 750ºC with zircon ($ZrSiO_4$) as additive. The MgO addition implies maximum crystallisation approximately at 760ºC and the addition of TiO_2 at lower temperature (730ºC). The range of crystallisation temperature generally coincide with the DTA results, as is shown in Figure 7, which also depicts the compositional sequence of the glasses La2, La3 and La4 (mixture compositions: 80/20, 70/30 and 60/40 wt%). In a parallel investigation by adding B_2O_3 from borax additions to the lepidolite, as was expected from this which is located in a granitic batholith, it is a mineral widely investigated also in recent decades and for applications in advanced ceramics (Avilés et al., 1993). In the contact area there are magnesium skarns and phlogopite transformed into vermiculite at 650-700ºC. The original glasses formulated from vermiculite/ amblygonite mixtures showed clear DTA exothermic peaks between 720°C and 1140°C (Fig. 7).

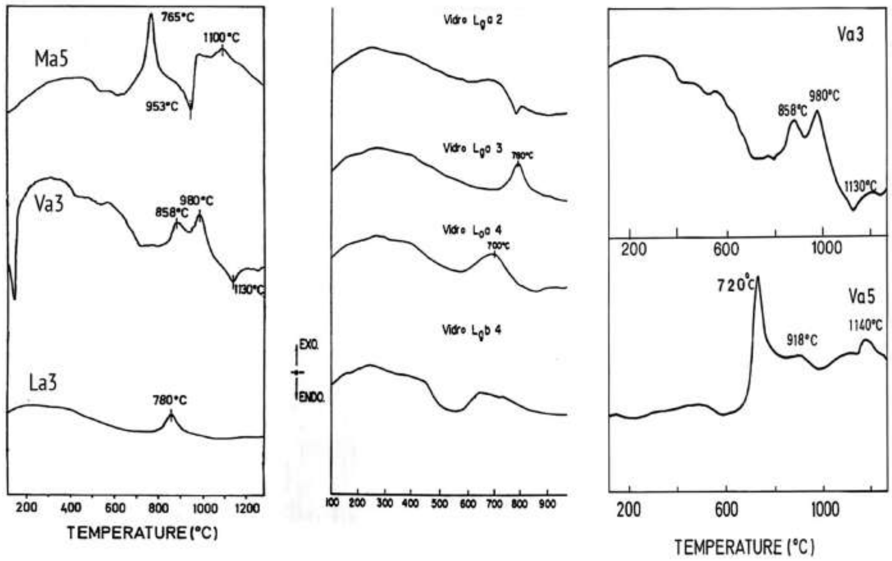

Figure 7.— DTA traces (rate 10ºC/min) in muscovite+amblygonite (Ma), lepidolite+ amblygonite (La) and vermiculite+ amblygonite (Va) glasses with increasing relative proportion of amblygonite from 40 to 60 wt. %, (Rincón et al., 1984). Exothermic bands correspond to crystalline phases formation and the first inflection band to the glass transformation, T_g).

Most of these “aventurine or metallic reflecting surface” showed by this innovative glass-ceramics contain a spodumene (1:1:4) phase as the main crystalline phase by X-Ray Diffraction. For analysing the composition of iridiscent- metallic surface was carried out Reflected Mössbauer Spectroscopy and others spectroscopies: X-Photoelctrosn Spectroscopy, Electron Paramagnetic Resonance, TEM/EDS (Transmission Electron Microscopy with Energy Dispersive Spectroscopy) and Rutherford Surface Spectroscopy. The main result was the detection of a surface enrichment in iron oxides (Callejas, 1988). Figure 8a shows some of results of the Reflection Mössbauer Spectroscopy. Later experiments carried out in transversal sections (TEM/SAED, Selected Area Electron Diffraction) confirmed the presence of spodumene in this surface. Therefore, calculating the ratio of SiO_2/Al_2O_3 in these materials results show that these ratios are very close to the spodumene 1:1:4 ratio.

Thus, Figure 8b includes the wt% silica/alumina ratios versus the mole content of Li_2O, Al_2O_3 and SiO_2 for various lithium minerals: eucryptite (1:1:2), spodumene (1:1:4) and petalite (1:1:8). The lithium feldspar (1:1:6) with a silica/alumina = 3.53 has not been included in this graph due to its minor presence in lithium ores. Because this ratio is 2.25 in the case of spodumene, as can be seen in this graph, these ratios calculated from the original composition of the glasses are very close to spodumene. From the analytical results and considering different microanalyses results and the physical analytical methods, it was concluded this spodumene must be a “phosphate spodumene” with some octahedral Al_2O_3 being replaced with Fe_2O_3 and the simple substitution of Li_2O and K_2O (higher content). However, calculation of silica content requires the addition of $AlPO_4$ (berlinite, whose structure is similar to that of silica). Thus, the theoretic and hipothetic formula for this synthetic new “phosphate spodumene” from these glass-ceramics obtained from mixtures of spodumene with muscovite, lepidolite and vermiculite, would be: $[Li_2O.K_2O]$. $[Al_2O_3.Fe_2O_3]$.4 $[AlPO_4.SiO_2]$. As far as we know, this compound was not been previously described in the scientific literature (further information available online as supplementary file).

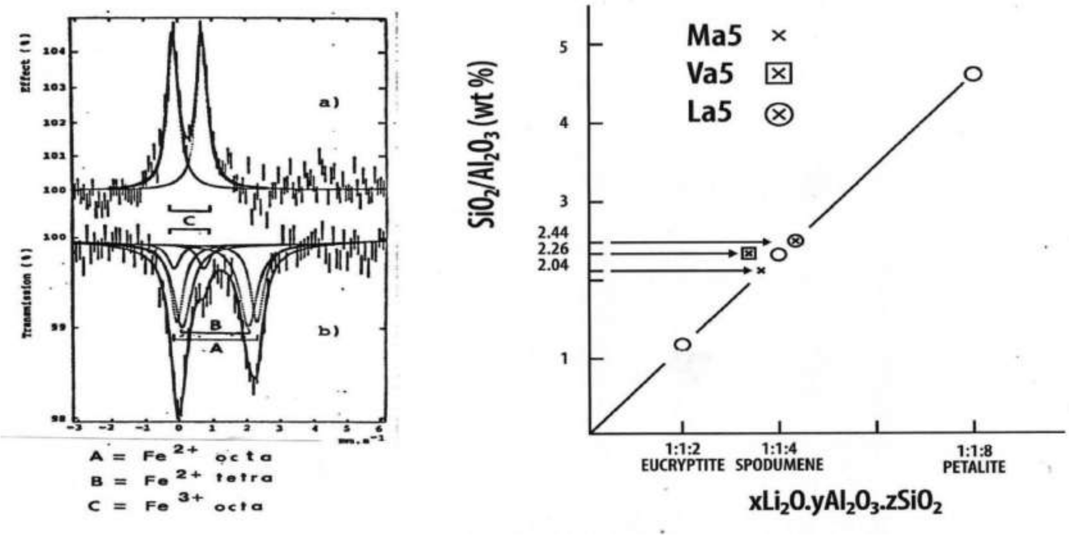

Figure 8.— a) Reflected Mössbauer Spectroscoy results. b) Ratios of SiO_2/Al_2O_3 in Ma5, Va5 and La5 glasses obtained from melting mixtures of amblygonite with muscovite from A Coruña (Santa Comba), vermiculite (Santa Olalla, Huelva) and lepidolites (Guarda, Portugal and La Fregeneda, Salamanca) (Callejas, 1988).

Role of lithium in liquid immiscibility in vitreous materials

At the beginning of the 80s decade last century, Cristalería Española (nowadays Saint-Gobain Group), showed interest in investigating the production of opal tableware from glasses including lithium for the production of household opal tableware. At that time it was well known that the metastable liquid immiscibility in glasses can be used for the production of opal and opaque glasses. Much of these glasses with liquid immiscibility were formulated including lithium and boron for producing opal and opaque glasses (Rincón & Durán, 1982) (Figure 9a). This monograph collected the respective metastable phase diagrams of the glassy immiscibility systems, such as: Li_2O-SiO_2, Li_2O-Na_2O-SiO_2, Li_2O-TiO_2-SiO_2, Li_2O-Al_2O_3-SiO_2, as well as those containing B_2O_3, Li_2O- B_2O_3 and the ternary system with SiO_2 which shows a wide immiscibility area along the SiO_2-B_2O_3 zone. The experimental results showed that is possible to obtain a "secondary phase separation", which was not previously reported in this Li_2O-SiO_2 binary. Usually, this type of "secondary phase separation" was observed in the past in glassy systems including large sized cations, such as BaO, PbO, etc. but never in this simple binary glasses (Vogel, 1985). In the same Figure (Figure 9b) even can be seen a coalescence between these "secondary phase separation" relicts, produced by cycled thermal treatments of original glasses (Rincón, 1992).

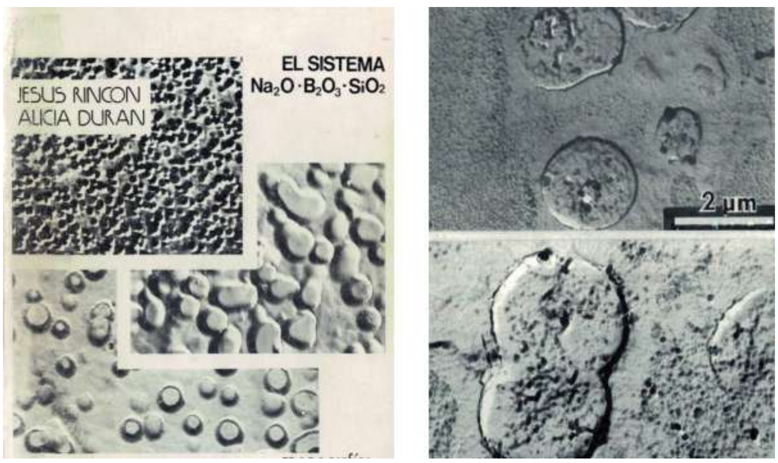

Figure 9.— a) Cover of monography from Rincón and Durán (1982) showing different droplets of liquid imnmiscibility in glasses and b) "secondary liquid phase separation" in the $26Li_2O$-$74SiO_2$ (mole %) glass (Rincón, 1992).

Lithium glass-ceramic glazes and lithium in bioglass-ceramics

More recent reseach in glasses and glass-ceramics from lithium (21st century)

In the recent decades of this 21st century, new glasses and glass-ceramics were developed with functional applications (Casasola et al., 2012). That was the case of glass-ceramic glazes researched to be used as glazes in the production of tiles and other innovative glass-ceramics for dental implants. Thus, lithium was explored in the Li_2O-CaO- Al_2O_3- B_2O_3-SiO_2 and the Li_2O-K_2O-Al_2O_3-B_2O_3-SiO_2 compositional systems for obtaining “frits” (glassy powders obtained by the sudden cooling of melts in water) designed with the specific compositions and have been applied for some ceramics industries of Castellon Ceramic Cluster. These are glazes covered with microcrystals and nano-crystals of several synthetic mineral structures: spodumene, cordierite, diopside, anorhite, nepheline, celsian and leucite, they are main components of glazes with high abrasion resistance and mechanical impact. An important aspect which must be considered for the production of this type of glass-ceramic glazes is the use of inorganic pigments as colorants for decorating this type of glazes. The proposed use of some wastes must be compatible with the glass-ceramic matrices (Monrós et al., 2019) (further information available online as supplementary file).

Following the recent uses of Li_2O-SiO_2 glass-ceramics in dental applications with strong commercial development (Hölland & Beall, 2002), more recently it has been investigated new glass-ceramics inside the complex composition Li_2O-K_2O-Al_2O_3-B_2O_3-SiO_2-P_2O_5 system as biomaterials (Callejas & Rincón, 2012) for dental implants (further information available online as supplementary file).

Dicussion and concluding remarks

Despite the vast research carried out for more than five decades much work is pending and in the case of Spain about the capabilities of lithium resources for obtaining glasses, glazes, enamels and glass-ceramics. There are some possibilities of research for next years, which are suggested, like the given in following paragraphs:

With respect to lithium resources:

- To explore the capability of recycling the commercial wastes of kitchen table-tops with include valuable lithium content and which now are rejected as RCDs (residues of construction and demolition).
- To investigate more sites of mining wastes containing lithium, especially nowadays due to the new quarry exploitations for obtaining lithium to manufacture batteries.
- If it were possible efficiently, to separate the lithium from used batteries. Although it cannot yet be recycled in new batteries, it would be interesting to study the possibility of using these “secondary residues” for obtaining of lithium glass-ceramics for uses as construction materials (pavements and coverings, enamels, glazes and in the body composition of tiles…).
- To explore the equilibrium phase formation in the $AlPO_4$-Fe_2O_3-spodumene system and in the Li_2O-B_2O_3-$AlPO_4$ systems which have not been yet investigated. Additionally, it is althought that this would give interesting or valuable information for geochemist scientists.

With respect to lithium and conventional glass-ceramics:

- A more systematic summary of theories and practical conclusions of the most relevant work carried out on the nucleation and crystal growth mechanisms.
- Enhanced research into sintered lithium glass-ceramics.
- Effects of water molecules (OH^-) in lithium glasses which affects the nucleation and crystal growth.
- Research for improving the mechanical properties of glass-ceramics.
- To investigate the abrasion and anti-slip properties of glass-ceramics glazes manufactured including lithium.

- To design new composite glass-ceramics with machinable properties and lithium bio-glass-ceramics including lithium synthetic mica.
- To investigate the effect of lithium minerals for obtaining of mate or opalescent glassy materials.
- To implement new functional applications available for specific market niches, even for overcoming the difficult tasks of marketing.

After this review it can be concluded that it was widely demonstrated last decades, that is possible to produce glasses, glazes, enamels and glass-ceramics from the Iberian sources of lithium. Furthermore, this technology could be a modern way of recycling of wastes generated in the new mine exploitations prevented for next years. The main advantage of this technology explored in the period 1994-2024 is not only the wide range of products and materials which could be obtained from lithium mine resources, such as: batteries, but also by the recycling of mineral wastes for their reduction and the additional production of construction materials. Despite the extensive research carried out in the last years, there are still many possibilities of research with the natural lithium resources in our country.

SUPPLEMENTARY FILES

Additional figures (Figs. S1 to S3) and tables (Tables S1 to S4) are available in the online version of this article.

DATA AVAILABILITY

The corresponding author can provide original data from private files for free under request.

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DECLARATION OF COMPETING INTEREST

The authors of this article declare that they have no financial, professional or personal conflicts of interest that could have inappropriately influenced this work.

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CRediT AUTHORSHIP

Jesús Ma. Rincón: Conceptualization, Data curation, Formal Analysis, Methodology, Resources, Supervision, Validation, Writing – original draft; **Pio Callejas**: Investigation, Formal Analysis, Methodology, Resources, Visualization, Writing – review & editing; **Manuel Miguel Jordan**: Supervision, Validation, Visualization, Writing – review & editing.

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