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CONTRIBUTION TO THE PROBLEMATICS OF GEOGENIC LITHIUM TO HUMAN HEALTH

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Abstract: Since Paracelsus in the 15th century, the effect of medicine and poison is a numerical relationship between concentration, beneficial effect, or mortality, which can be measured by dose/response findings. Lithium contents, whether coming from medicinal products of geogenic origin or bioaccumulative, are no exception to the rule. Lithium is a chemical element that occurs widely in nature and is economically associated with granitic bodies and pegmatites, concentrations in brines and salts, and in clayey sedimentary rocks.

The positive effect of medicated lithium is widely seen as a treatment for mood, manic-depressive psychoses, and suicide. The negative effects of prolonged use are associated with kidney disease. Geogenic lithium, which, due to its natural presence in waters consumed by populations, where there are important concentrations, economic or not, of lithium resulting from the weathering of minerals and carrier rocks, is still a point that needs research, especially with the aim of determining the content in mg/L, ideal for beneficial effects for populations.

Nowadays, the growth in the use of lithium for the electronics industry is exponential according to the World Mine Products and Reserves, from the year 2018 to the year 2022, there was a growth of around 40% in the use of lithium, especially in the electronics and automotive industries. The proportionality of the growth of e-waste has a directly proportional factor, given the difficulty of recycling this element in ion batteries. Due to its great geochemical mobility, which is related to its chemical potential, lithium is easily assimilated by plants. This biofortification through contamination will develop problems in the consumption of vegetables, especially leafy vegetables, becoming a serious problem for societies, especially given the strong appeal of vegetarian foods.

Keywords: Medical Geology; Geogenic Lithium; Biofortification

INTRODUCTION

Medical Geology is the science that deals with the impacts of geological materials and processes on animals and human health (Burnnell et al. 2007). Consequently, Medical Geology began to require geoscientists and biomedical scientists and public health managers to become concerned with health problems caused or exacerbated by geological materials such as trace elements, rocks, minerals, water, oil and geological processes.

The Brazilian Geological Service (CPRM) characterizes Medical Geology as an interdisciplinary science that studies regional variations in the distribution of chemical elements, mainly metallic elements and metalloids, their geological-geochemical behaviors, natural and anthropogenic contaminations and possible damage to human health, animal and/or vegetable due to excesses or deficiencies of such elements. This specialty emerges on the international scientific scene as a link between professionals in medical sciences and those in geosciences, in search of quality of life for populations.

Lithium (Li) is a monovalent, light, very reactive alkaline metal that does not occur freely in nature. Although its content is relatively low, it is widely distributed. In geochemical classifications, lithium is considered a lithophile element and despite being the third element in the periodic table, its average abundance is lower than expected, and it is estimated that in the Earth's crust it occurs in concentrations between 17 and 20 ppm and in the order of 6000 ppm in hypersaline brines (Warren, 2017).

In metallogenetic terms, the lithium element occurs in three types of primary deposits i) associated with pegmatite bodies and igneous granites, hydrothermalized, greisenified, associated with clay materials, ii) lithium concentrations associated with continental evaporitic brines and iii) concentrations associated with deposits lacustrine clayey sedimentary sediments and geothermal brines.

It is used as an industrial raw material for the production of greases, glass, ceramics, etc. Its physical and chemical properties, such as low density, high hardness, high melting point and high reactivity make it the main element in contemporary industry, such as lithium batteries used in communication technologies and, more currently in electric vehicles and in the field of strategic industries, especially in countries like China (Zhiyong Zhou et al, 2022)

In river water the Li concentration is around 3 µg/L (Aral and Vecchio-Sadus, 2008), surface waters have concentrations between 1 and 10 µg/L, in sea water this concentration is 0.18 µg/L , in groundwater it can reach 500 µg/L (Schrauzer, 2002) and in mineral waters it varies approximately between 0.05 and 1 mg/L (LaMoreaux and Tanner, 2001; Hassoun and Schnug, 2011).

Concentrations between 10 and 40 mg/kg are accepted as geochemical background concentrations in soils, with the general average value being 20 mg/kg and 30 mg/kg in the case of granitic soils (Kavanagh et al., 2018). On average, lower values are found in sandy soils and higher values in calcareous soils (Kabata-Pendias et al., 2010). However, the highest concentrations of the element are thought to be associated with areas with plutonic igneous rock (such as granite) and aluminosilicate sediments (Kabata-Pendias et al., 1984).

In the human body, the amount of Li is approximately 7 mg (Lenntech, 2015). and although it is not yet recognized as an essential element, it can influence human metabolism; Schrauzer (2002) recommended a provisional daily dose of 1 mg Lili/day for a 70kg adult (14.3 µg/kg weight).

In the human diet, the largest sources of lithium are cereals and vegetables (0.5-3.4 µg/kg), dairy products (0.50 mg/kg), meat (0.012 µg/kg) and in some areas public drinking water (0.1-2.0 µg/L) (Peixer, 2013). Several studies have indicated that some bottled mineral waters are naturally enriched; the highest value (9860 µg/L) was recorded in bottled water from Slovakia (Reimannn et al. 2010). In Portugal, Neves et al. (2020), recorded that natural mineral water with a Li content greater than >1500 µg/L) was highly mineralized and of the hydrogen carbonated-sodium type and naturally carbonated ((>250 mg/L free CO2).

The relationship between Li and health has been demonstrated over time, from its recommendation for the treatment of gout (which proved to be ineffective) to its successful use in the treatment of mental illnesses, administered essentially in the form of carbonate and in therapeutic doses of 600 to 1200 µg/day. Although the effect of these doses is well defined, their adverse effects are relevant. The narrow therapeutic window and its toxicity recommend regular monitoring of its blood concentration. On the other hand, in recent years several studies have emerged that suggest that ingesting Li in low doses, such as those found in drinking water, may also promote benefits for people's mental health.

LITHIUM METALLOGENY

Type 1 lithium deposits, associated with genetically igneous pegmatites and granites, come from residual melts derived from the crystallization of granitic plutons, where incompatible components are transported together with volatiles and rare metals, which are concentrated in these residual melts. The presence of fluxing and volatile elements lowers the crystallization temperature, decreases the rates of nucleation, polymerization and melt viscosity, and increases the diffusion rates and solubility, which is considered essential for the development of giant crystals and pegmatite textures. (Warren, 2017). The enrichment of the fluid in incompatible elements, volatile substances and rare metals (Be, Nb, Ta, Li, Rb, Ce and Ga) reflects the unique mineralogy of pegmatites, such as the presence of gems, rare minerals and industrial minerals, which allows the economic exploitation of this type of rock. These types of primary lithium deposits are present in Brazil, in the Araçuaí area and in the state of Paraíba-Brazil, in Portugal, Australia, Africa among others and have a strong geotectonic component, associated with geological zones of orogenic domains. The main minerals in these types of deposits are spodumene and lepdolite.

Type 2 lithium deposits, associated with salt flats, an example that occur in the Andes, are concentrated in ancient halokinetic evaporites, where, initially, the salts dissolved in the waters came from the weathering of volcanic rocks enriched with K, Li, Mg, B and, to a lesser extent Na and Ca were deposited by water evaporation. These layers of salts are then enriched by additional amounts of Li, coming from the exudation of volcanic formations basal to hypersaline basins (Warren, 2017). The mineralogy of this type of deposit is lithium salts, chlorides and carbonates.

Type 3 lithium deposits, associated with concentrations associated with lacustrine clayey sedimentary deposits and geothermal brines, consist of the presence of these elements in lithic levels found close to the surface, consisting of a mixture of clays (smectite, illite, chlorite, kaolin) and salts (halite and gypsum) and widespread pedogenic calcite. Lithium is derived from weathering and leaching of volcaniclastics in ashfall tuffs.

The lithium content is retained in the clay fraction of the sediments and is part of the clay structure. The mineralogy of this type of deposit is predominantly associated with hectorite clay [$Na0_{.33}(Mg, Li)_3Si4O_{10}(F, OH)_2$] is a clay mineral from the smectite group, where the replacement of aluminum by lithium and magnesium is essentially complete (Warren, 2017).

LITHIUM INDICATIONS IN THE STATE OF BAHIA

In Bahia there are signs of mineralization associated with the three types of lithium metallogenic occurrences described above.

Type 1 evidence is related to the Araçuaí Orogen, this geological belt is located between the São Francisco Craton and the continental margin. Atlantic on the eastern Brazilian margin developed at the end of the Neoproterozoic, marked by the end of the Brazilian cycle and the amalgamation of Western Gondwana (Silva et al. 2096; Pedrosa-Soares et al. 2011). Included in these geological domains are the important lithium mineralization, in spodumene, from the homonymous region of the orogen.

Composing this geological context is the Brazilian Eastern Pegmatitic Province, which extends from the south of Bahia to Rio de Janeiro,

In the State of Bahia is the pegmatite district of Itambé, located in the region of Vitória da Conquista in the south of Bahia, positioned on the limits of the São Francisco craton with the Araçuaí Orogen (Silva et al. 1996; Pedrosa-Soares et al. 2011). Ferreira et al, (2020) citing several authors described this province as a group of homogeneous and heterogeneous pegmatite bodies according to the degree of differentiation of the internal structure. In the bodies of heterogeneous structures, embedded in biotite gneisses, in addition to the classic graphic textures and cores of quartz bed, minerals associated with beryl and lithium minerals such as spodumene and lepdolite are described.

These igneous, pneumatolytic bodies, carrying lithium minerals, affected by weathering phenomena, show the presence of lithium, an element of great geochemical mobility, passes through the soils and groundwater of the region's fissure aquifer and, secondarily, evidence of secondary levels is found in sediments. Quaternaries in the region, according to surveys by the National Geological Service (Paes et al.2016).

According to Pena (2021), he raised the possibility that the faint geochemical anomalies of lithium detected in chemical analyzes of soils and sediments in the region of Guanambi, state of Bahia, could be associated with the pneumatolytic manifestations described in the region's alkaline Zionistic igneous complex, described by Rosa (1999).

Evidence of the second type of anomalous lithium occurrences was also suggested by Pena (2021) and Cruz et al. (2022) in the domains of carbonate sites in the central south region of Bahia, close to the town of Iuiú. In this region, lithium geochemical anomalies were detected in autochthonous soils that overlie the carbonate rocks associated with the Bambuí deposits. In this region Gonçalves (2014) referred to the evaporite levels present as strata interspersed with Neoproterozoic carbonate deposits, thus indicating the possibility of this type of lithium deposit in the great Brazilian carbonate basin, thus expanding a real prospective perspective of this important element.

Evidence of the third type of lithium occurrences is being researched by Santos (in preparation), in the Alagoinhas region, Recôncavo sedimentary basin. In the 1980s, important lithium anomalies were found and described in clayey rocks, the analyzes and surveys of which were carried out, at the time, by the extinct company Paulipetro (Sergio Nascimento, verbal communication).

In recent chemical analyzes of mineral waters from the Alagoinhas region (Rodrigo Santos, in preparation) he detected the presence of lithium and, carried out research looking for the characterization of hectorite (?) in this region, thus defining the third of signs of lithium and also opening, a region of prospective appeal.

It is important to point out that, although the values have been shown to be very low Linch (2001), the objective of geochemical prospecting is always to detect the presence of primary mineralized bodies on the surface and/or hidden in the subsurface, through the presence of strong geochemical anomalies (1st order) which in this case is lithium and its sniffing/indicating elements, which are always associated with Sérgio (Nascimento de Moraes, verbal communication).

GEOGENIC LITHIUM

Undoubtedly the positive action of the element, lithium through drugs, as proven by Blúml et al, (2013). Lithium doses are effective in treating suicide risk, mood disorders and stabilizers (Cipriani et al., 2013). There is a recommendation for lithium dosage in maintenance therapies for bipolar disorders between 0.6 and 1.0 mmol/L, even so, the ideal blood level at which lithium exerts its possible preventive effect on suicide has not been identified (Kabacs et al., 2011).

Studies linking geogenic lithium to mental health are quite scarce. In a recent attempt, Cruz et al. (2022) related the homicide rate in the region of Guanambi, Bahia, with geogenic lithium levels determined in the region (Pena, 2021), raising the hypothesis that the low level of suicide in these sites could be related to the beneficial effects of lithium geochemically. present in the region. However, this suggested possibility requires greater statistical data and targeted surveys taking into account, for example, different age groups, social stratigraphy, diet, targeted samples of blood and hair and other variables that allow a more effective conclusion of the positively beneficial effects of lithium.

Expanding the hypothesis of beneficial effects of geogenic lithium on the mental health of populations, Cruz et al. (2022) compared the findings in the region of Guanambi, Bahia, with surveys of suicides and lithium occurrences in the regions of Seridó, Paraíba and Minas Gerais, Araçuaí.

All surveys based on numbers published by health bodies publish national assessments of geologically present lithium levels, comparing with international research, for example Oliveira et al. (2019), Dawson et al. (1972) are not clear and require the development of more accurate biochemical studies of the action of this important element, to be consumed by populations in a geogenic way.

There is a need to define the numerical content of the element lithium present in water distributed to the population, such as fluoride and the beneficial effects on dental health. The question then arises what this ideal content will be (?).

CONTAMINANT FUTURE

The lithium present in the environment, naturally, results from the weathering of lithiniferous minerals present in rocks, mainly sedimentary rocks (Aral and Vecchio-Sadus, 2008). Lithium usually enters soil solution Topsoil generally contains less Li than underlying layers. The clay fraction of soil contains higher concentrations of Li than the organic fraction of soil (Schrauzer, 2002), with Li present in ditrigonal cavities in clay minerals.

Due to the characteristics of its chemical potential, geochemical mobility is significant, its diffusion into the exogenous environment and its reconcentration is processed by supergene processes, which develops detectable concentrations in soils, sediments and, occasionally, in surface water.

According to Franzaring et al. (2016) water and plants will provide the main routes of lithium exposure in the food chain. In areas where there is a natural presence of lithium (geogenic), it must be assumed that the local population is continually exposed to the action of this chemical element, through the daily intake of water and/or the consumption of plants that bioaccumulate this chemical element, such as potato and tomato.

Li's low toxicity has likely caused this element to be largely overlooked as an emerging environmental contaminant (Robson et al, 2018). However, currently, the spread of Li batteries will certainly result in contamination in soil and water, following from this Due to its strong geochemical mobility, it forms its rapid concentration in food crops.

While increases in Li consumption may be beneficial in some cases, the effect on society of prolonged exposure to high concentrations may lead to the strong development of renal disorders, including disturbance in urinary concentrating capacity and natriuresis, renal tubular acidosis, tubulointerstitial nephritis evolving for chronic kidney disease and hypercalcemia (Oliveira et al, 2010).

As lithium is relatively immobile in the phloem, leafy vegetables will provide a greater source of Li in food, thus becoming a potential future problem for societies where the vegetarian eating culture is strongly and daily implemented.

CONCLUSIONS

This article ratifies the pressing need to develop more in-depth research, in light of scientific rigor and development of specific methodologies, with the objectives: i) to seek to relate geogenic lithium levels, normally distributed in mineralized sites in nature, with health human nature of local populations; ii) seek to define the maximum levels, geogenically beneficial to the mental health of populations and the existence (or not) that these natural values would exert behavioral influences iii) develop methods, mainly with the use of statistics that allow comparisons of the universe of geological and geochemical data with state health numbers and surveys; iv) determine the effect of lithium biofortification in vegetables and the existence of a beneficial effect of this enrichment; iv finally, try to establish perspectives of possible contaminations that lithium, through its future residues arising from new technologies, will be confirmed.

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