

The Importance of Detecting Lithium on the Surface of Mars

A. Heredia (1,2), M. Colín-García (1), J. Valdivia Silva (3), H. Beraldi (1), A. Negrón-Mendoza (1), H. Durand-Manterola (1) J.L. García-Martínez (1), S. Ramos and F. Ortega (1) . (1) SIOV, Universidad Nacional Autónoma de México-04510 México DF, (2) Centre for Mechanical Technology and Automation, TEMA, University of Aveiro, Portugal, (3) NASA, USA. (alejandro.heredia@comunidad.unam.mx/ Fax: (52) +55-56-16-22-33)

Abstract

Lithium (Li) is the third element of the periodic table and was created in the Big Bang together with hydrogen and helium. In water solution it exhibits low vapor pressure and freezing point, and other colligative properties enhancing the range of liquid water availability. With organic compounds, it forms organo-lithium reagents with direct covalent bond allowing for organic complexity. Lithium accreted with the Sun and planets in minor amounts and later it originated by nuclear fission processes due to high-energy cosmic rays. Here, we suggest that detecting Li in the surface of Mars by instruments bound to Curiosity rover may provide crucial evidence for the potential chemical evolution in the red planet in the presence of liquid water.

1. Introduction

The origin of life as we know it is based on the presence of liquid water, a simple chemical compound formed by hydrogen and oxygen, which are the first and third most abundant elements in the universe. Lithium (Li) is the third element of the periodic table and was created during the Big Bang together with hydrogen and helium. It follows the water because of its highly incompatible geochemical behavior and delayed crystallization in water-enriched magmas. Because of its extreme solubility, it enters the composition of some clays, and may form the last common salts to precipitate in evaporating water bodies. The small ionic size of Li, similar to that of magnesium, favors its incorporation in the structure of olivine and pyroxene, which are the main phases forming the mantles of the terrestrial planets. However, altogether Li is a scarce element in nature (about 2 ppm in the Earth's mantle), but it increases by an order of magnitude in altered basalts and Archean greenstones (spilites). It is argued in this paper that the detection of Li in igneous or sedimentary rocks in proportions of several tens of

ppm in the surface of Mars, would imply the action of sub-aqueous and sub-aerial hydrothermal systems, and hence past lakes or oceans in considerable volumes and duration, increasing the possibilities for the origination of autochthonous life in that planet.

2. Li general properties

Among solids, lithium has the highest specific heat and therefore has a high heat transfer capacity. As ion, it has a coordination number of 4 to 8 with high charge to size ratio making it a small highly charged ion (0.076 nm) resulting in properties considerably different from other similar ions, such as sodium and potassium. In water solution, Li exhibits unique properties: very low vapor pressure and freezing point, and other colligative properties that enhance the range of liquid water availability. Lithium shows properties that are consistent with the group of alkaline metals (Group IA in the periodic table), but has key singularities compared to the elements in this group, such as its reactivity similar to magnesium of the Group 2A. In one important reaction, Li combines with nitrogen (N₂), yielding lithium nitride Li₃N (see reaction), only similar to magnesium from other periodic group.



Common salts from lithium are: borate, carbonate, nitrate and borohydride (LiBH₄). With graphite it forms carbide (Li₂C₂), which is one of an extensive range of lithium-carbon compounds. With other organic compounds, lithium forms organo-lithium reagents having a direct covalent bond between the carbon and lithium atoms effectively, creating extremely reactive bases.

3. Li sources and isotopes

Two processes make planets to acquire lithium. The first one, is the original lithium contained in the

nebula and added to the planetary body during its formation, whereas the second one is by nuclear fission on impact by high-energy cosmic rays. Li isotopes are scarce in the universe, although enriched by cosmic rays in the interstellar medium, when protons hit nuclei of heavy atoms, as oxygen and carbon, fragmenting them into lighter ones like lithium [1]. The bombardment of cosmic rays on the surface of a planet for billions of years produces substantial amounts of cosmogenic Li, particularly in atmospheres enriched in CO₂ or in surfaces with water. After the disappearance of the CO₂ atmosphere in Mars, the main cosmic ray interaction occurs with the ground but in the CO₂-rich permafrost and polar ice caps, cosmic rays might have produced considerable quantities of lithium. Other important universal peculiarity is the relative abundance of the two isotopes ⁷Li/⁶Li. Firstly, it is believed that such abundance has changed during the last 4.6 Gyr and authors are inclined to say that ⁷Li has been between 14 and 12 times more abundant than the ⁶Li. However, the production of ⁶Li is a continuous process and this proportion will still be decreasing. Secondly, such a change implies a significant source of ⁶Li. This can be interpreted as if the production of ⁶Li is being regularly enhanced via cosmic rays.

4. Lithium and minerals

Many minerals contain lithium and can also be found in natural brines, brines associated with oil wells, geothermal fields, and in sea water. The rare mineral hectorite (Na_{0.3}(Mg,Li)₃Si₄O₁₀(OH)₂), a Li-rich smectite clay, easily forms organo-clay complexes, and might contribute to coordinate the assembly of some amino acids and other prebiotic molecules [Fig. 1]. Although lithium chemistry has been intensively studied, it is still little known about the details of the activity that might affect a variety of chemical and biological systems. In the astrobiological context, it could have played a role changing the physicochemical properties of water and perhaps participating in the assembly and coordination of organic molecules. For this, our current research is aimed to understand the potential properties of lithium-related mineral surfaces, in the assembly of organics as amino acids and other important biomolecules. For example, the adsorption of hydrogen cyanide (HCN) in hectorite (Fig. 1) suggests that some (16%) of the HCN molecule (compared to 100% in montmorillonite at pH=2) is adsorbed in the clay, showing a potential role in stabilization of water

layers in lithium-related solids in organic chemical evolution. Maintenance of liquid water by the Li-rich solid might be important to increase reactivity of organics and possible assembly of bigger molecules.

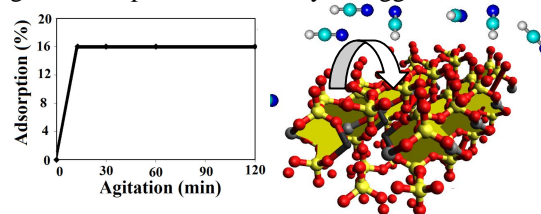


Figure 1: HCN adsorption on hectorite, the maximum percentage of adsorption is reached after 15 minutes of stirring (left). Water layers might prevent adsorption of HCN to the surface of the mineral (right).

5. Summary and Conclusions

The potential role of Li in hydrochemical evolution is of central importance as evidence of chemical complexation, thus making its detection in the surface of terrestrial planets extremely interesting. The formation of lithium and its further concentration and isotope fractionation by low and high temperature aqueous processes is or was quite possible in the surface of Mars, and therefore it is expected that if the probe Curiosity detects this element in Mars solids, it would have played a major role enhancing complexity in the chemical and even biological evolution of that planet.

Acknowledgements

This work was supported by PAPIIT grant IN110712-3 and CONACyT grant 168579. We are grateful to Prof. Dr. C. McKay (NASA) for providing us with helpful information about the possible role of Li in the evolution of Mars.

References

- [1] Clayton, D.: Isotopes in the cosmos. Hydrogen to Gallium. Cambridge University Press. 2003.
- [2] Müller, G., Maier, G.-M. and Lutz, M.: Lithium coordination to amino acids and peptides. Synthesis, spectroscopic characterization, and structure determination of lithium complexes of neutral and anionic glycine and diglycine, *Inorganica Chimica Acta*, 218: 121-131, 1994.