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## LITHIUM CONTENT IN SEDIMENTARY ROCKS IN GALE CRATER, AEOLIS MONS, AS A TRACER FOR AQUEOUS ALTERATION AND SOURCE ROCKS.

K. W. Nikolajsen<sup>1</sup>, J. Frydenvang<sup>1</sup>, E. Dehouck<sup>2</sup>, P. J. Gasda<sup>3</sup>, C.C. Bedford<sup>4</sup>, L. Le Deit<sup>5</sup>, A. Ollila<sup>3</sup>, A. Cousin<sup>6</sup>, R. C. Wiens<sup>4</sup>, S. Maurice<sup>6</sup>, O. Gasnault<sup>6</sup>, N. L. Lanza<sup>3</sup>  
<sup>1</sup>University of Copenhagen ([katrine.nikolajsen@sund.ku.dk](mailto:katrine.nikolajsen@sund.ku.dk)), <sup>2</sup>LGL-TPE, Université Lyon 1, France, <sup>3</sup>Los Alamos National Laboratory, <sup>4</sup>Purdue University, <sup>5</sup>Nantes Université LPG - Laboratoire de Planétologie et Géosciences, <sup>6</sup>Institut de Recherche en Astrophysique et Planétologie

**Introduction:** Lithium is an excellent tracer element owing to its unique geochemical behavior in magmatic and alteration systems. Its moderately incompatible nature and high solubility results in it being widely spread in the geochemical cycle, leaving only trace amounts in igneous rocks and their derived sediments [1]. However, due to its small ionic radius, Li can be incorporated into major rock-forming minerals such as feldspar, amphibole, mica, and pyroxene, typically by substituting for Mg, as the melt reaches sufficient Li concentrations. Li partitions strongly into some minerals, such as lepidolite, spodumene, amblygonite, and petalite which crystallize in highly evolved granites and pegmatites [2] and secondary phyllosilicates (e.g., [3,4]). These, along with rare Li-rich salts and late-stage evaporitic brines (e.g., [1,5,6]) constitute the few geological reservoirs able to accumulate Li. Furthermore, the high solubility of Li means that rocks preserve signatures of the latest fluid alterations with respect to Li contents.

NASA's MSL Curiosity rover landed at the Bradbury Rise landing site on Mars in August 2012. The objective of the mission is to investigate the ~155 km diameter impact crater, Gale, in search of habitable environments. Since landing, Curiosity has traversed 31 km across fluvio-deltaic sandstone and conglomerates, deep lacustrine mudstone, lake-margin sandstone, and aeolian sand dunes (figure 1) (e.g., [7]).

The ChemCam instrument onboard Curiosity is the only science instrument capable of detecting Li *in-situ* [8],[9] using laser-induced breakdown spectroscopy (LIBS), and the Li chemostratigraphy throughout the Gale crater bedrock sampled by ChemCam thus represents a powerful tracer for aqueous alteration and potentially igneous source rocks.

**Results:** The chemostratigraphic groups fall into three main groups based on their Li contents: Murray and Glen Torridon have the highest Li abundance, with median values of ~14 ppm, rocks in the clay-sulfate transition (CST) zone, and Stimson formation, a younger eolian sandstone unit unconformably overlying the Mt. Sharp group units, have intermediate Li contents with median values of ~12-13 ppm. The Bradbury group rocks and the Sulfate unit have the lowest Li, plotting near Gale soils at median values of ~10 ppm (figure 2).

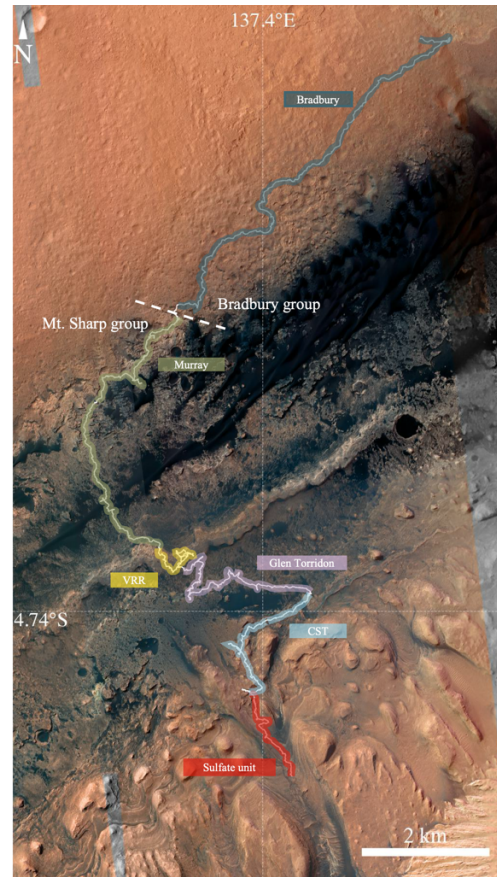


Figure 1: Curiosity rover's traverse with major chemostratigraphic regions annotated. CST: Clay-sulphate transition zone, VRR: Vera Rubin ridge.

**Discussion:** Li in sedimentary rocks is inherited from the source rocks, it is then affected by weathering leading to loss of Li though the formation of secondary phyllosilicates can retain a substantial fraction. After deposition, the Li abundance can be affected by later aqueous alteration. The Li abundances presented here are high relative to terrestrial basaltic compositions (~5 ppm in MORB, [10] and basaltic martian meteorites (~1-10 ppm in shergottites [11]). The only martian meteorite sampling the surface, the polymict regolith breccia, NWA 7034, has a bulk Li concentration of 7 ppm [11]. Still, the complex nature of the sample means that bulk value is not comparable to *in-situ* measurements on crustal rock on Mars. There is strong evidence that a complex catchment region with multi-

ple source rocks is needed to explain the chemistry and mineralogy observed in Gale crater sedimentary rocks (e.g., [12,13]), including an endmember protolith that is more felsic than basalt to dominate the Murray formation mudstones [14].

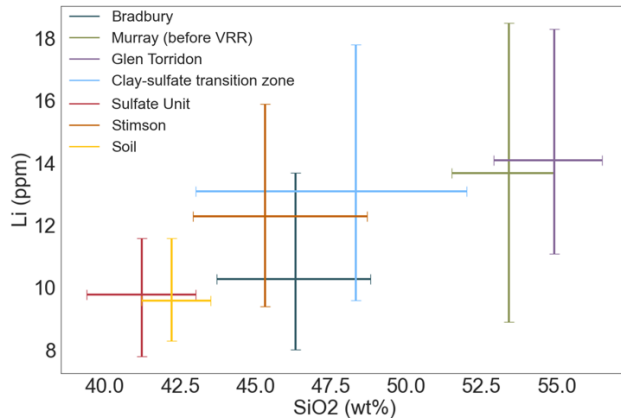


Figure 2: Median Li vs. SiO<sub>2</sub> abundance plotted for the major chemostratigraphic groups investigated in Gale crater. The error bars reflect the 25th to 75th percentile. For Stimson and Murray formation observations, points with SiO<sub>2</sub>>60 wt% are discarded to exclude observations related to high-silica diagenetic halos. VRR: Vera Rubin ridge.

The Li enrichment in the chemostratigraphic groups with the highest Li abundance (figure 2), the Murray formation and the Glen Torridon region, can partly be explained by the presence of phyllosilicates. Unless these phyllosilicates represent an accumulation of Li, the Li enrichment must be inherited from an enriched source rock. The latter is supported by the surprisingly high Li content in the CST zone sandstone where the abundance of phyllosilicates is low if they are not absent [15]. Three possible scenarios can explain the high Li abundance in the CST zone: (1) the presence of persistent Li-salts throughout the zone, (2) an overprint of aqueous alteration after sediment deposition, or (3) sourcing from a protolith endmember enriched in Li relative to terrestrial or martian basalts. No evidence indicates that the CST rocks contain primary evaporitic deposits [16], making the presence of Li-rich-salts highly unlikely. If the Li abundance in CST rocks results from an aqueous overprint it would imply that they experienced a substantial amount of fluid alteration, which is inconsistent with the mineralogy observed in the CST zone [16]. Thus, the Li enrichment in the CST rocks is best explained by continued substantial input from a more felsic endmember protolith.

The younger, eolian sandstones of the Stimson formation have lower Li abundances than the CST rocks but are still enriched (figure 2) relative to terrestrial and martian meteoritic basalts. The enrichment is

observed across both mafic and felsic components defined by [17], indicating that it likely does not originate from a Li-enriched protolith but rather from interactions with Li-bearing fluids. Moreover, there are small differences in Li content within Stimson sandstones at different exposure locations, including a slightly higher concentration of Li in the Greenheugh pediment relative to the Emerson and the Naukluft plateaus, which can be explained by the presence of poorly crystalline phyllosilicates in Greenheugh pediments leading to preferential retention of Li in these rocks relative to the other locations.

The fluvio-lacustrine rocks of the Bradbury group are among the rocks in Gale with the lowest Li concentrations, which are overall similar to basaltic compositions (figure 2). The Li abundance is thereby in agreement with previous studies of the chemical and mineralogical compositions of Bradbury rocks, which suggest input from a diverse catchment with at least a dominant subalkaline basaltic component and a K-rich alkaline component, the latter contributing to the K-rich rocks in the Kimberley formation (e.g., [12,18,19]). Kimberley rocks do show a distinctively low Li abundance (~8 ppm median) which might sample the shift in source contribution.

The low Li in the Sulfate unit (figure 2) follows a decrease in most elements quantified by ChemCam from the CST zone into the Sulfate unit [15] due to a dilution of the magmatic minerals which host Li in rocks at lower stratigraphy, as Mg-sulfates become more pervasive.

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