

EVAPORATIONAL LOSS OF LITHIUM DURING HIGH TEMPERATURE EXPERIMENTS: IMPLICATIONS FOR CHONDRULE FORMATION. M. O. Schoelmerich¹, H.-M. Seitz¹ and K. Klimm¹,

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Introduction: The high temperature chondrule forming process led to distinct geochemical and isotopic characteristics. Lithium concentrations in chondrules, for example, are predominately depleted relative to bulk abundances [1,2], whereas Li-isotope compositions of carbonaceous and ordinary chondrites depict a narrow range, those of their chondrules being highly variable ($\delta^7\text{Li}$ of -8.5 to $+15\%$) [1]. It was suggested that these features either result from the presence of discrete solar nebular reservoirs [1,3] or are the consequence of primary and secondary processes, such as hydrous alteration or thermal metamorphism on the chondrite parent body [2,4]. However, the nature of the process or processes leading to the observed chemical and isotopic differences still remains a point of debate. In order to achieve a better understanding of elemental and isotope fractionation during high temperature chondrule formation, we conducted a series of evaporation experiments, at chondrule forming conditions, with a special emphasis on Fe, Mg and Li.

Evaporation experiments: A large ($1 \times 2 \times 2$ cm), homogeneous San Carlos olivine crystal, of known major element (Fo_{91}), trace element and Li-isotope composition was chosen for high temperature evaporation experiments. Six equally sized cubes ($2 \times 0.5 \times 0.5$ mm) were cut from the large crystal, and used for different runs in a high temperature GERO gas-mixing furnace. Each cube was placed on a Pt-wire basket and inserted into the hot furnace at run conditions of 1550°C at $\log(f\text{O}_2)$ of IW-2. The $f\text{O}_2$ was adjusted by a CO-CO_2 gas mixture at 1 atm total pressure. Experiments were conducted with different run durations (10 min, 40 min, 2h, 6h, 12h and 24h). At the end of each experiment, samples were quenched to room temperature in the reducing (IW-2) CO-CO_2 gas mixture, by dropping the Pt-basket in the cold end of the GERO furnace.

Analytical techniques: Major elements were measured by electron probe microbeam analysis (EPMA, Goethe University, Frankfurt, GUF) using a spot size of $1\ \mu\text{m}$, an acceleration voltage of 15 kV and a beam current of 20 nA. Before and after the experiments, profiles were measured from core to rim in three different crystallographic directions (a,b,c).

Trace elements were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS at GUF). Measurements were conducted with a 193 nm excimer laser using a laser energy of 130 mJ,

a pulse rate of 15 Hz and a spot size of 37 by $37\ \mu\text{m}$. Analytical profiles from core to rim were done according to the EPMA transect. In order to obtain a better spatial resolution, two parallel profiles were placed adjacent to one another, offsetting each spot by $18.5\ \mu\text{m}$.

Lithium isotopes and Li concentrations were determined using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS, at GUF) and rock digestion and column chemistry for Li separation followed the procedure of Seitz et al. (2004) [5]. Isotope compositions are expressed as per mil deviations [$\delta^7\text{Li}$] from the NIST L-SVEC standard.

Results: After the experimental runs, all originally homogeneous olivine cubes reveal distinct chemical zoning within the first 10 to $250\ \mu\text{m}$. Beside the major and minor elements (e.g. Mg, Fe and Mn), Li concentrations follow an evaporation trend, revealing a distinct loss with increasing run duration (Fig. 1).

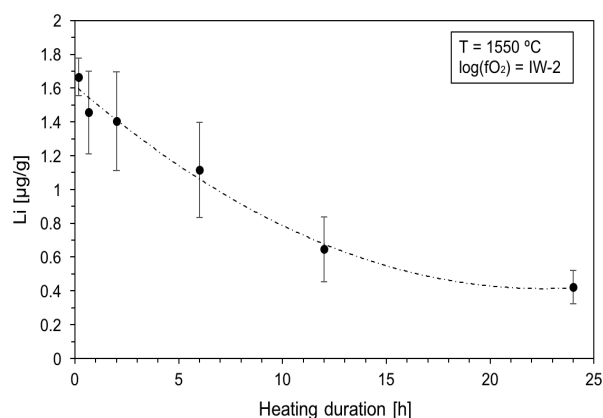


Fig. 1. Li concentrations [$\mu\text{g/g}$] plotted as a function to heating durations [h].

In the 24h experiment, for example, Li zonation is prominent within the first $250\ \mu\text{m}$, exhibiting a correlation with Mg#, the progressive loss of Li corresponding to increasing Fo content (Fig. 2). Also, Li isotopes fractionate drastically with increasing run duration and the preferential loss of ^6Li over ^7Li leads to increasingly heavier compositions - from initially $+0.3\%$ to $+4.6\%$ (10 min) up to $+69.4\%$ in the 24h experiment (Fig. 3).

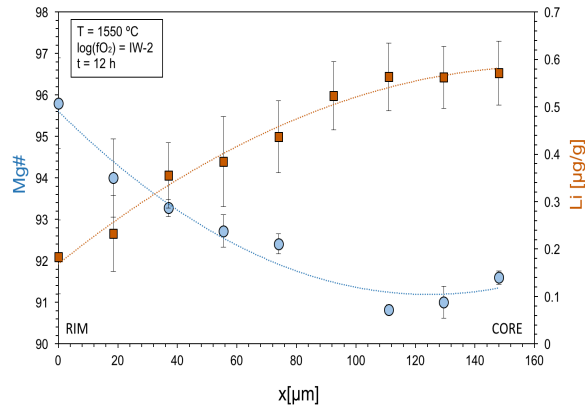


Fig. 2. [Li] and Mg# profiles from the surface ($x = 0 \mu\text{m}$) of the c-axis of a SC olivine crystal after 12 h heating duration at 1550 °C.

Discussion and conclusions: Our evaporation experiments provide valuable new information about element and isotope fractionation during chondrule formation.

Based on the experimental conditions and initial Li concentrations, approximately 10-20 $\mu\text{g/g}$ Li was lost per hour (Fig. 1). Preferential loss of Li and Fe over Mg is exemplified by the decrease of Li and increasing Fo content towards the rim. (Fig. 2).

Our experimental results are consistent with those from previous studies on chondrites, which have shown that lithium abundances in chondrules are generally depleted relative to the bulk [1,2,6] (Fig. 3). Additionally, in an situ study [6], a similar Li/Fo-relationship for Allende chondrule olivines was observed and an evaporational loss during chondrule formation was suggested.

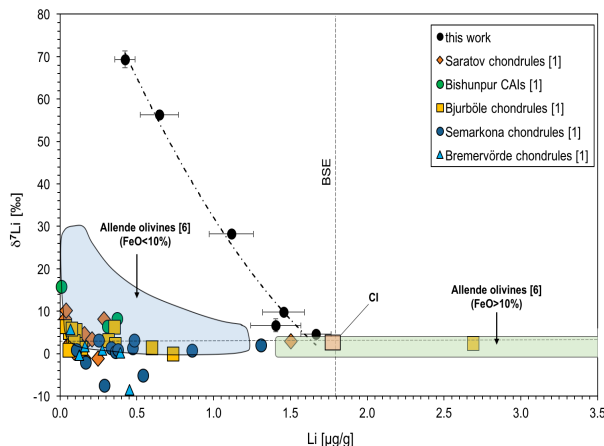


Fig. 3. Li concentrations [$\mu\text{g/g}$] with regard to $\delta^7\text{Li}$ [‰]. Black circles indicate our data, with Bulk Silicate Earth (BSE, dashed lines) and CI values. Other data are from [1] and [6]. Note that measurements from [6] for Allende olivines can be divided into FeO-rich and FeO-poor groups.

Our high temperature experiments clearly prove elemental loss through evaporation and also show a very explicit fractionation of Li isotopes - up to about 70 ‰ in the 24h run. Whilst a 24h heating event may be unrealistically long for chondrule formation, the compositional and isotopic trend of these experiments is manifested in almost all chondritic meteorites. Lithium isotope compositions of chondrules from Allende, Semarkona, Bishunpur, Bremervörde, Saratov, and Bjurböle reveal a considerable compositional spread, whereby the isotopic variability increases with decreasing Li concentration [1,6] (Fig. 3). At low Li concentrations ($<0.5 \mu\text{g/g}$), an increasing isotope fractionation (up to 40‰) becomes apparent, with a predominant shift to heavier isotope compositions (up to +30‰).

These observations not only support our experimental data, but also suggest that the differences of Li isotopes as well as Li concentrations between chondrules and matrix are, indeed a result of evaporation and not the consequence of parent body processes as previously proposed [2,4]. If Li concentrations in chondrule forming reservoirs were already depleted with regard to CI and there had been partial Li re-condensation in the chondrule forming reservoir, then Li concentrations as well as $\delta^7\text{Li}$ values of measured chondrules can be easily achieved within heating durations of less than one hour. Moreover, a consequence of the Li loss from chondrules is the re-condensation and subsequent enrichment in the immediate cooler chondrule vicinity, which in turn is recorded by the higher Li concentration not only in matrix phases, such as olivine or low Ca-pyroxene, but also in higher bulk compositions, relative to average abundances in the chondrules [1].

We therefore, conclude that the observed Li patterns in our experiments support the theory of matrix-chondrule complementarity, proposed by [3]. Plausible formation mechanisms could be local heating events, such as a gas dynamic shock wave or a nebular lightning strike. As the latter process, for example, is perhaps spatially more confined it may more readily explain the characteristics commonly found in chondrites.

References: [1] Seitz, H.M. et al. (2012) *EPSL* **239-330**, 51-59; [2] Maruyama, S. et al. (2009) *GCA* **73**, 778-793; [3] Palme, H. et al. (2015) *EPSL* **411**, 11-19; [4] Sephton, M.A. et al. (2013) *Meteoritics & Plan. Sci.* **48**, 872-878; [5] Seitz, H.M. et al. (2004) *Chemical Geology* **212**, 163-177; [6] Bell D.R. et al. (2008) *LPS XXXIX*, Abstract #2276