EXPERIMENTAL STUDY OF LITHIUM EVAPORATION UNDER CIRCUMSTELLAR CONDITIONS.

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Introduction: Chondrules are generally described as the products of the direct condensation of liquids or liquid+crystal assemblages (nebular materials), or as the result of the reheating of precursor materials. These two models imply complex interactions between solid, liquid and gas phases and a complex chemical path leading to the formation of these objects. Among all chemical elements present in chondrules, lithium is one of the most mobile and tends to volatilize easily. Beside, it is an interesting element because the solar photosphere is depleted in Li, compared to CI chondrites [1]. In this respect, understanding Li behaviour would help to better understand the distribution of chemical elements between solar system bodies. Furthermore,evaporation is an important process affecting materials present around young stars. Once carefully calibrated, Li concentrations could be used as a proxy to determine the extent of evaporation experienced by chondrules, which in turn would improve our description of the thermal history of chondrules.

Here we investigate experimentally the evaporation of Li from a molten silicate of 'pristine' chemical composition. The effect of temperature, heating duration, gas fugacity and composition are described, with emphasis on the effect of H_2 because dihydrogen is the most abundant gas around stars.

Experimental: A $CaO-MgO-Al_2O_3-SiO_2$ (CMAS) chondrule-like composition [2] was doped in Li_2O (10 wt%). We used the wire-loop technique to maximize the free surface between the silicate bead and its environment. Glass samples were loaded in a Deltech vertical furnace. The fO_2 was imposed by the gas mixture (pure CO_2, $CO-CO_2$, CO_2-N_2/H_2 (1% H_2)). For all experiments, the total pressure in the furnace was one bar. The temperature range investigated was from 1450°C to 1650°C. Run durations were from 30 minutes to 24 hours. Experiments were conducted at the Geophysical Laboratory, Washington. Analysis were performed on electron microprobe (Geophysical Laboratory) and MC-ICP-MS (University of Maryland).

A total pressure of one atm is fairly high compared to the pressure in the circumstellar medium. Nevertheless, we consider that it is an upper limit condition. Moreover, our setup helps to avoid significant recondensation processes at the surface of the samples (e.g. [3]), because gas flowes continuously inside the furnace during the experiment. We can thus reasonably consider that the main process operating during experiments was free evaporation of Li, that we initially assumed to be:

$$Li_2O_{(l)} = 2\ Li_{(g)} + \tfrac{1}{2}\ O_{2\ (g)}. \qquad (1)$$
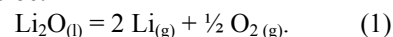
Results: First of all, electron microprobe analyses show that Mg/Si and Ca/Si ratios do not vary between and during experimental runs. This clearly indicates that only lithium evaporates from the silicate liquid. On the other hand the lithium content varies significantly as a function of experimental conditions.

It decreases with run duration. It is found that Li_2O content in the sample is directly proportional to its surface and to the Li_2O content of the liquid, for a given duration and gas mixture. The rate of lithium evaporation becomes greater with increasing temperature and with decreasing fO_2. Clearly, a $CO-CO_2$ gas mixture is more efficient than pure CO_2 to evaporate lithium. The effect of hydrogen is even more dramatic and the CO_2-N_2/H_2 mixture outclasses the others in terms of evaporation efficiency.
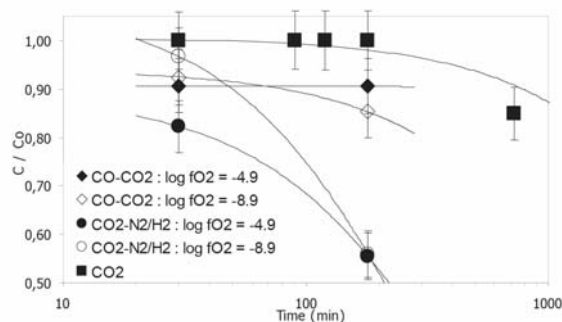

Fig. 1 : C/Co ($Li_2O/Li_2O|_0$) values at 1500°C for different gas compositions and fO_2.

Turning now to the microscopic description of the evaporation process, it is of note that the Li_2O is homogeneously distributed within samples before and after the experimental run. Composition gradients were never observed, which indicates that Li_2O diffusion in the melt droplets is faster than its evaporation at the sample surface. Evaporation is thus the rate-limiting process.

Discussion: Rates of lithium evaporation show an Arrhenian behaviour between 1400-1650°C at log fO_2 varying from -5.9 to -6.9. The activation energy for lithium evaporation is approximately 150 kJ.mol^{-1}. Furthermore, the rate is also proportional to $fO_2^{-1/4}$ within the range of fO_2 from $10^{-6.9}$ to $10^{-5.9}$ at 1550-1600°C. This is consistent with an evaporation reaction of the form:

$$LiO_{1/2 (l)} = Li_{(g)} + 1/4 \, O_{2 (g)}. \qquad (2)$$
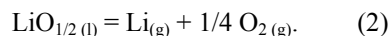
Turning to the kinetics of the process, Experimental data are used to define characteristic times for evaporation and diffusion, τ_{evap} and τ_{diff} which are only fonction of the sample radii (or any other characteristic distance for non spherical bodies), as defined by Crank (1975) [4] as $\tau_{evap} = r / 3k$ and $\tau_{diff} \approx r^2 / \pi^2 D$. Characteristic times are first calculated for each defined value of k and D, and represented in plain and dotted lines on fig. 2. This characteristic times are then used to estimate the effective volume diffusion coefficient of lithium, based on our experimentally determined k's. The τ_{evap} values suggest that diffusion coefficient D in the molten silicate should be at least $5 \, 10^{-7}$ cm^2.sec^{-1}, on a 1400°C-1600°C temperature range, because surface evaporation controls the reaction rather than volume diffusion. Some τ_{diff} values were proposed in previous studies (e.g. [5]), but only for magmatic materials (crosses on fig. 2). As diffusion coefficients are assumed to be larger in molten chondrules than in magmatic glasses, τ_{diff} in chondrules should be really smaller than τ_{evap} [6].

Based on experimental results and on the natural abundances of Li_2O, chondrules may have experienced an instant heating with a peak temperature of 1400-2000°C followed by a fast cooling in a low pressure hydrogenated environment. More detailed thermal history may be derived for each chondrule taken individually.

The effect of evaporation on hypothetical isotope fractionation are currently under the scope and will probably help to constrain more tightly timings and conditions of chondrule formation.

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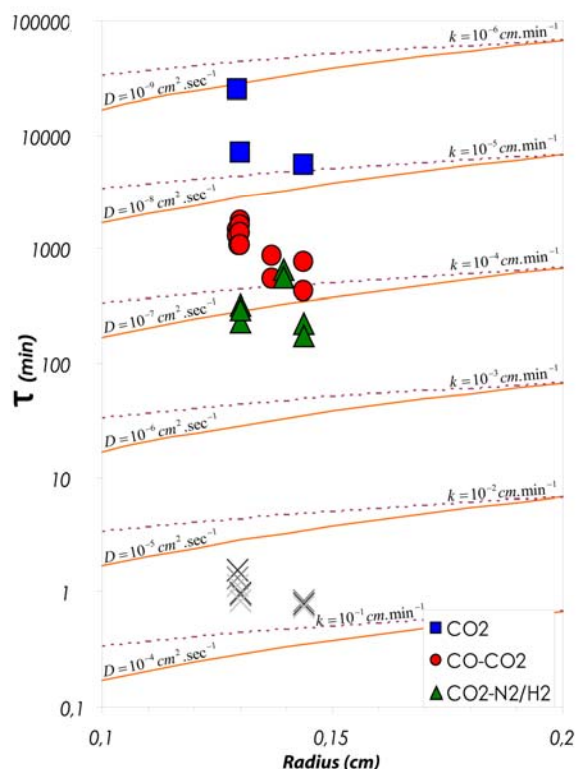

Fig. 2 : Characteristic times of evaporation and diffusion, τ_{evap} and τ_{diff}, versus molten silicate radii at different temperatures. k is the evaporation rate, and D is the diffusion coefficient. Adapted from [6].