Evaporation experiments of alkali elements from silicate melts: clues for early solar system processes. M. Gellissen[1], A. Holzheid[1], Ph. Kegler[1] and H. Palme[2], [1]Institut für Geowissenschaften, Christian-Albrechts-Universität zu Kiel, 24118 Kiel, Germany (marko.gellissen@rub.de), [2] Forschungsinstitut und Naturmuseum Senckenberg, 60325 Frankfurt a.M., Germany.

Introduction: The prevailing chondrule type in ordinary chondrites is ferroan (type II chondrules with about 15 wt. % FeO) and comparatively high Na and K contents. Chondrule melts in the low pressure nebular environment are unlikely to behave as closed systems, at which different chondrule bulk compositions would just reflect the random spectrum of precursors [1]. The open system behavior of chondrule melts implies interaction with the ambient gas during melting, i.e. evaporation and condensation processes [2]. The lack of alkali element depletion in type II chondrules cannot be explained by rapid cooling as the volatile content is too high even for the fastest cooling rates and highest assumed total pressure [3]. In fact petrologic evidence of Semarkona type II chondrules records Na evaporation followed by recondensation. To reach the required high partial pressures (P_{Na}: 10^{-3} to 10^{-5} atm [4]) by evaporation of the precursors, chondrule generation in dense clumps [5], nebular shock wave models [6] and melting in bow shocks around protoplanets [7] are discussed in the literature. To test the hypothesis of evaporation and recondensation processes in the protoplanetary disk, vaporization experiments with synthetic silicate melts were performed at controlled temperature, total pressure and oxygen fugacity.

Experimental: All experiments were performed with melts of synthetic silicate powders.

In set 1 experiments (*"multi sample arrangement", MSA*) the silicate samples had a molar Si/(Al+Na+K) ratio of 3/1 (i.e., the albitic ratio), but various Al/alkali and Na/K ratios (9 different sample compositions with NBO/T ratios from 0 to 0.67). All experiments were performed in CO/CO_2 gas mixing furnaces with heating times from 60 to 240 min at 1450 and 1550 °C, oxygen fugacities (fO_2) ranging from air to IW -2 and gas flows of 350 and 1000 ml/min. Samples with different composition were together in the furnace.

In set 2 experiments (*"individual sample arrangement", ISA*) 3 peralkaline silicates with a molar Al/alkali ratio of 0.42/0.58 and various Na/K ratios were used. Only one sample was in the gas mixing furnace. Samples' weights were 41 ± 2 mg (except samples of the weight series). Time series experiments (1-1140 min) were done at different temperatures (T: 1150-1550 °C) and oxygen fugacities (fO_2: air to IW -2). Experiments at various gas flow rates (0-2500 ml/min) and samples' weight (10-60 mg) were performed as well.

A third experimental set (*"vacuum sample arrangement", VSA),* was conducted in a vacuum furnace under controlled pressure ($P_{tot(air)}$: 0.1-100 mbar, T: 1150-1450 °C), and with sample composition is identical to ISA.

Sample mounting was by Pt wire loop technique [8], using pressed pellets of the silicate powder in the ISA and VSA setup to exclude any influences of used organic glue on the evaporation behavior and to better control the samples' weights.

The chemical compositions of all post-run silicates were analyzed by electron microprobe with defocussed electron beam. Line scans were done from the entire samples and in detail of the samples' surface regions as well as statistically distributed spots were analyzed to estimate the bulk composition. To obtain very precise mass balances, the mass loss of the samples during the experiments was determined using a microbalance.

Results: (1) Individual runs with several samples of different composition simultaneously in the furnace (set 1 experiments - MSA setup) show, that Na and K are lost from high Na, K samples and gained by low Na, K samples, with all samples reaching an approximately constant level after several hours (Fig 1). This observation is valid for all MSA experiments. The process of gain and loss is faster with increasing temperature and decreasing oxygen fugacity. The Na concentration at the converging point decreases with increasing gas flux, but is independent of Al concentration in the starting composition.
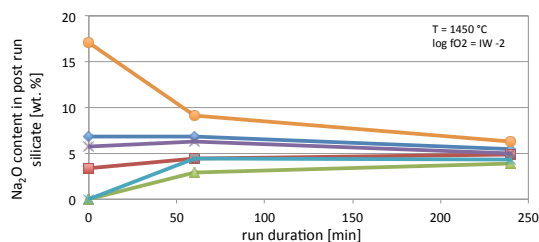

Fig. 1: Even original Na free samples approximate their Na content to a T and fO_2 dependent level, which is common for all samples being at once in the furnace.

(2) Peralkaline samples (set 2 experiments - ISA setup) release Na and K depending on duration, T and fO_2 of the experiments. Under all conditions losses of Na are more pronounced than of K. The losses do not increase proportional with run duration, but proportional with temperature and fO_2. At reducing conditions Na losses are strongly enhanced. This effect is

less pronounced for K. Samples containing both Na and K show reduced Na losses and increased K losses compared with samples bearing only one of the alkali elements, i.e. the presence of K inhibits Na-eva-poration and the presence of Na enforces K-evaporation. Surprisingly the Na vaporization lessens with increasing CO/CO_2 flow and also with synthetic air flow.

(3) Losses in vacuum (set 3 experiments - VSA setup) are much more severe than under 1 atm (Fig. 2). Experiments with log fO_2 = - 4.68 (in ISA: reached by an appropriate mixture of CO/CO_2, in VSA: equivalent to normal air under P_{tot} of 0.1 mbar) at 60 min heating time and 1450 °C show a 'VSA/ISA ratio' of 4 in Na losses and of 14 in K losses. In accordance to observations of set 1 experiments, it was possible to transfer Na or K to former Na or K free samples via the gas phase under a P_{tot} of 0.1 mbar.
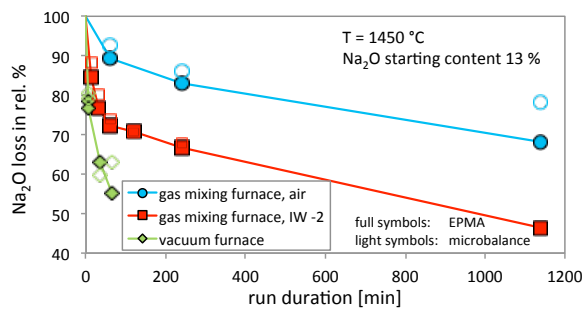

Fig. 2: Increasing vaporization of Na with reducing conditions (ISA setup). The strong effect of P_{tot} or low Na vapor pressure is illustrated by the vacuum experiment (VSA setup).

Besides the bulk losses of alkali elements, all samples show surface depletion, typical in a scale of 200 µm, progressive with heating time (Fig. 3). The surface de-
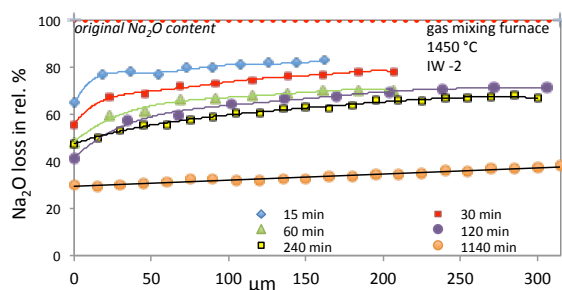

Fig. 3: Na_2O surface activity is a function of T and furnace atmos-phere. The depletion timescale is controlled by the gas flow and the melt surface area. Due to the finite extension of the sample, bulk Na_2O approximates the terminal surface concentration with pro-longed heating time.

pletion for Na is faster and more severe than for K. For a given set of the experimental parameters (T, fO_2 and heating time), a terminal surface activity seems to be reached, which then remains constant. With ongoing vaporization and declining bulk Na content, the surface

depletion gradient becomes flatter, and a constant alka-li element plateau develops from the center of the sample.

Discussion: We interpret the results of the MSA-experiments with the following model: High Na sam-ples loose Na and build up Na-partial pressure in the furnace surrounding samples. This happens despite considerable gas flow, as it is described by Richter et al. [3]. Na-poor samples will then acquire Na. This will ultimately lead to an uniform Na–content of all sam-ples. Increasing losses at reducing conditions argue for the release of elemental Na and K. Evaporation is in-congruent, as Si and Al remain constant. Alkali ele-ment concentration profiles give evidence for a diffu-sion controlled vaporization process. This is supported by the only proportional and not exponential depend-ence of alkali losses from temperature. Due to the giv-en high run temperatures, the kinetics of the melt-gas transition is fast and equilibrium between melt surface and the gas phase surrounding the melt exists. Assum-ing a terminal steady surface activity of alkali elements (cf. Fig. 3), if saturation, the vapor density must remain constant with time.
Stronger depletion in the VSA experiments compared to the ISA experiments argues for the dominant influence of the Na partial pressure for the evaporation.

Implication for evaporation and condensation pro-cesses: The rapid exchange (within minutes) of Na among 3 mm thick individual samples in a furnace (Fig. 1) supports the model of [9] for redistribution of Na through the vapor phase. The roughly albitic Al/Na ratio in many chondrules ([2], [3]) may reflect the sta-bility of such compositions established by Na-redistribution. To build up the necessary Na vapor pressure in the solar nebula, a high density of matter is required, providing a strong constraint for chondrule formation [9]. Our results strongly support an open system behavior of chondrules during their formation processes. Evaporation and recondensation from and between silicate melts could be experimentally repro-duced under air, in a CO/CO_2 atmosphere with fO_2 down to IW -2, and at a total pressure of 10^{-4} bar, simi-lar to the pressure assumed for the solar disk.

References [1] Sears D. W. G. et al. (1996) *Chon-drules and the Protoplanetary Disk*, University of Cam-bridge press, (eds. Hewins R. H., Jones R. H., Scott E. R. D.) 221–231. [2] Hewins R. H. et al. (2012) *Met. & Planet. Sci., 47,* 1120-1138. [3] Richter F. M. et al. (2011) *Met. & Planet. Sci., 46,* 1152-1178. [4] Mathieu R. (2009) *Ph.D. thesis*, INPL-CRPG, Nancy, France. [5] Desch S. J. et al. (2002) Met. *& Planet. Sci., 37,* 183–207. [6] Asphaug E. et al. (2011) *LPS XXXXII,* Abstract #1647. [7] Morris M. A. et al. (2012) *The Astrophysical Journal 752(1),* 27. [8] Donaldson et al. (1975) *Am. Min. 60,* 324-326. [9] Alexan-der C. M. O'D. et al. (2008) *Science 320,* 1617-1619.