

VAPOR EVOLUTION DURING DEGASSING OF ALKALIS IN CL-FREE AND CL-BEARING MELTS: EXPERIMENTAL INSIGHTS INTO CHONDRULE FORMATION G. Ustunisik¹, D. S. Ebel¹, and H. Nekvasil², ¹Department of Earth and Planetary Sciences, American Museum of Natural History, New York, NY, 10024 (gustunisik@amnh.org) ²Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100.

Introduction: The chemical variability of chondrule volatile element contents may provide a wealth of information on the processes that shaped the early solar system and its compositional heterogeneity. An essential observation is that chondrule melts contain very low alkalis and other volatile elements such as Cl. The primary reason for this depletion is understood and accepted to be the combined effects of likely cooling rates (10 to 1000K/hr), the small size of chondrules, and their high melting temperatures (~1700 to 2100 K) [e.g., 1,2] resulting in extensive loss of volatiles [e.g., 3] at canonical pressures (e.g., 10^{-4} bar). However, we observe some chondrules with significant amounts of volatiles such as Na [e.g.,4] as well as Cl, as evidenced by minerals such as sodalite, scapolite, nepheline, and abundances found in mesostasis and feldspar (e.g., Chainpur LL3.5 and Parnallee LL3.6 chondrules [5]), and in mesostasis (e.g., Qingzhen EH3 with ~4 wt% Cl [6]). These chondrules differ markedly from most chondrule compositions that are depleted in alkalis and Cl but enriched in refractory elements. How can such very different chondrule compositions form from the same part of the solar nebula? Why are chondrules so chemically diverse? Could such heterogeneity arise from loss of alkalis and Cl to a gas phase that itself later condenses, thereby yielding variations in volatile enrichments in chondrules? What is the role of Cl in such a process in terms of enhancing the volatility of the alkalis Na and K to varying extents?

Here we report heating/degassing experiments on the alkali and Cl-rich chondrule composition AI3509 [4], conducted to determine the effect of Cl on absolute and relative abundances of Na_2O and K_2O in the melt. Experiments on Cl-bearing and Cl-free melts of equivalent composition reveal systematic effects of Cl on alkali volatility.

Results: In the Cl-bearing system the highest percentage loss occurred within the first 10 minutes of degassing (48% Na_2O , 66% of K_2O , 96% of initial Cl). After 10 mins, the rate of alkali loss decreased due to the absence of Cl in the melt (Fig. 1a)

In the Cl-free system the percentage loss for the alkalis was lower compared to the Cl-bearing system. At the end of 10 minutes degassing, the melt lost 15% of its Na_2O and 33% of its K_2O to the vapor phase (Fig. 1a). At the end of 4 and 6 hours of bulk degassing, the melt lost a third of its initial Na_2O (34-42% Na_2O) and half of its initial K_2O (52-59% K_2O) to the vapor phase.

Higher Cl in the melt resulted in more rapid alkali loss, even in short duration (10 minutes) degassing experiments. In both the Cl-free and Cl-bearing systems, Na_2O was always more compatible in the melt relative to K_2O . Therefore, the vapor phase has a K/Na ratio higher than the melt through time in spite of the much higher initial Na abundance in the melt. This is consistent with previous Cl-free experiments on planetary analogs, and the lower vaporization temperature of K_2O (877°C) compared to Na_2O (1057°C) at 10^{-3} atm [7]. The enhanced vaporization of alkalis from Cl-bearing melt suggests that if the alkalis evaporate as chlorides, NaCl is less volatile than KCl, and both are more volatile than the monatomic species in the absence of Cl.

Fig. 1: a: Volatile loss (%) as a function of time for Cl-free and Cl-bearing melts. **b:** Changes in the normative mineralogy of Cl-free and Cl-bearing chondrule compositions after 6 hour degassing.



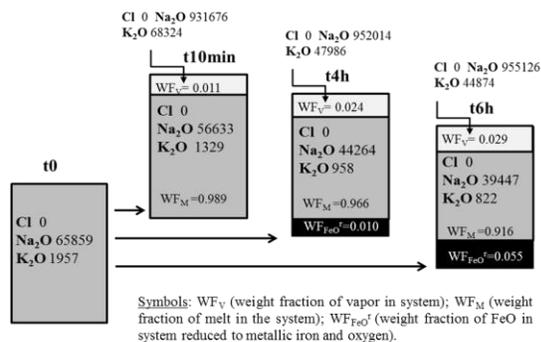
The loss of alkalis and volatiles also distinctly influences the normative mineralogy of initial and degassed melts (Fig. 1b). Normative plagioclase and olivine change dramatically between Cl-free and Cl-bearing melt compositions after 6 hour degassing. Cl-free initial melts with normative plagioclase ($\text{An}_{50}\text{Ab}_{44}\text{Or}_6$) evolved to slightly normal zoned plagioclase ($\text{An}_{49}\text{Ab}_{50}\text{Or}_1$). On the other hand, Cl-bearing initial melts normative to albitic plagioclase ($\text{An}_{46}\text{Ab}_{50}\text{Or}_4$) evolved to anorthitic and reverse zoned plagioclase ($\text{An}_{52}\text{Ab}_{45}\text{Or}_1$) due to extensive Na and K loss.

A significant decrease in FeO_T in the degassed melts relative to initial melts was noted after 4 and 6 hours runs. This appeared to result from reduction of ferrous Fe to metallic Fe, as evidenced by the presence of metallic Fe droplets along the interior walls of the capsule, due to the shift in $f(\text{O}_2)$ between the 0.5 GPa synthesis and <1 bar degassing experiments. Therefore, all glasses were normalized to the initial CaO values and Fe was added back for mass balance purposes.

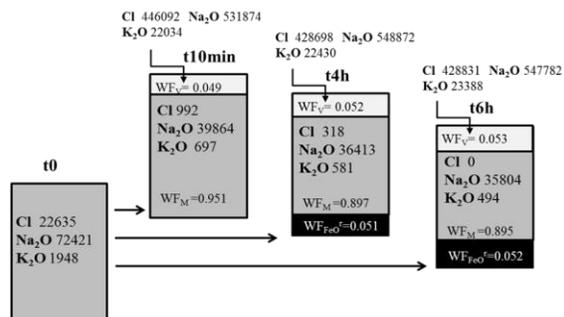
Mass balance computations made it possible to assess the changes in composition of the vapor phase produced over time for both Cl-free (Fig. 2a) and Cl-bearing (Fig. 2b) experiments. For the Cl-bearing systems, the vapor produced at the end of 10 min degassing was mostly Cl- and alkali-rich; the successive vapors were depleted in Cl and degassing was likely through the direct loss of monatomic alkali species (Fig. 2b).

Figure 2. Changes in the system due to degassing, t_0 =initial melt and $t_{10\text{min}}$, $t_{4\text{h}}$, $t_{6\text{h}}$ =computed proportions of phases and their compositions after degassing, for **a:** Cl-free and **b:** Cl-bearing systems (compositions in ppm).

a. Cl-free system



b. Cl-bearing system



Discussion: The vapor phase over Cl-bearing chondrule melts may have a bimodal character over time. Flash melting of a Cl-bearing chondrule might consist of a two stage process where the first vapors given off contain NaCl and KCl while successive vapors are Cl-free, and degassing is by the loss of monatomic Na and K. This bimodality might also control the types of condensate formed during various time intervals of heating and degassing. The heterogeneous volatile contents of chondrules may

result from quenching melt droplets at different stages of repeated heating, chondrule fragment recycling, and recondensation of exsolved volatiles.

Experimental Design and Details: The experiments are designed to determine both the extent of alkali loss and the composition of evaporative components during heating and degassing of a Cl-free and Cl-bearing chondrule melt. As was the case for our previous experiments on planetary analogs [8, 9] these experiments were designed to retain the exsolved gas, thereby permitting the development of vapor/melt equilibria and simulating a multi-component low-pressure atmosphere. This not only avoids Rayleigh distillation and loss of all volatiles, but is likely to be a more realistic reflection of the conditions of the solar nebula [3].

Al3509 [4] was specifically selected as a target composition since its natural high sodium and chlorine contents (7.9 wt% Na_2O , 0.2 wt% K_2O , 2.5 wt% Cl in its core) and low liquidus temperature makes it feasible to melt under laboratory conditions in a sealed silica tube. Al3509 is a large Na- and Cl-rich, radially-zoned chondrule from the oxidized CV carbonaceous chondrite Allende and consists of fine-grained ferroan olivine, ferroan Al-diopside, nepheline, sodalite, and andradite. It is crosscut by numerous veins of nepheline, sodalite, and ferroan Al-diopside.

Cl-free and Cl-bearing Al3509 glasses (~7 wt% Na_2O and ~0.2 wt% K_2O) were synthesized at 0.5 GPa and 1400°C (in order to avoid crystallization) in a graphite-lined cobalt capsule in a large volume piston-cylinder apparatus from a mixture of oxides and silicates which replicates the target composition. Cl-free and Cl-bearing glasses were then placed in Fe^0 -capsules and inserted into 42 cm long 6 mm i.d. silica tubes. After 20 minutes of vacuum evacuation, the tubes were sealed and suspended by a Pt-wire in a vertical furnace and heated above the liquidus at the quartz-iron-fayalite buffer for 10 minutes, 4 hours, and 6 hours before quenching. The starting and degassed glasses at the end of each interval were analyzed optically as well as by electron microprobe at the AMNH.

Acknowledgements: This research is supported by NASA Cosmochemistry grant NNX10AI42G (DSE) and the Kathryn Davis Postdoctoral Scholarship of the AMNH MAT program (GU).

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