

EXPLORING THE ROLE OF CHLORINE ON THE DEGASSING OF ALKALIS (NA AND K): IMPLICATIONS FOR CHONDRULE FORMATION G. Ustunisik¹ (gustunisik@amnh.org), D. S. Ebel¹, and H. Nekvasil², ¹Department of Earth and Planetary Sciences, American Museum of Natural History, New York, NY, 10024, ²Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100.

Introduction: Chondrules represent the smaller end of the solar system spectrum of objects that underwent melting. These roughly millimeter-sized quenched droplets are essentially silicate rocks with igneous textures, rich in olivine and pyroxene, and may represent melt derived from high temperature flash melting of dust aggregates in the solar nebula [e.g., 1, 2]. Their compositional variety, particularly in volatile elements, may provide a wealth of information on the processes that shaped the early solar system and its compositional heterogeneity.

As of today we still do not know to what extent the observed compositional variety of chondrules is influenced by loss of volatiles during chondrule-forming processes. When combined with likely cooling rates (10 to 1000K/hr), the small size of these particles and the high temperatures of melting (~ 1700 to 2100 K) [e.g., 3,4] should have resulted in extensive loss of volatiles [e.g., 5] at canonical pressures. Yet we observe some chondrules with significant amounts of volatile elements such as Na [e.g.,6] as well as Cl, as evidenced by minerals such as sodalite, scapolite, nepheline, and abundances found in mesostasis/feldspar phases [for example in Chainpur and Parnallee chondrules, 7], and in glasses (e.g., from Qingzhen (EH3) chondrules containing close to 4 wt% Cl [8]). 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 diversity/heterogeneity rise from loss of alkalis and Cl to a gas phase that itself later condenses, thereby yielding variations in volatile enrichments in chondrules? How important is Cl to such a process? Does Cl enhance the volatility of the alkalis Na and K to the same extent?

In order to explore answers to these questions, we have conducted heating/degassing experiments on the alkali and Cl-rich chondrule composition Al3509 [6] to determine the nature of the vapor phase lost during heating and to compare this with similar experiments on a Cl-free equivalent composition.

Experimental Design and Details: The experiments were designed to determine both the extent of alkali loss and the compositional nature of evaporative complexes during low pressure degassing of a Cl-free and Cl-bearing chondrule melt. As was the case for our previous experiments on planetary analogs [9, 10, 11] 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 [5].

Al3509 [6] was specifically selected as a target composition since its natural high sodium and chlorine contents (Na₂O:7.9 wt%, Cl: 2.5 wt% Cl in its core) and a 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 is 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 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 (Table 1) were then placed in Fe⁰-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 for 10 minutes, 4 hours, and 6 hours before quenching. The starting glasses, and the degassed glasses at the end of each degassing interval, were analyzed optically as well as by electron microprobe (EPMA) at the AMNH.

Table 1. Initial experimental compositions. Target reported by [6] and EPMA after synthesis of glass starting compositions at high pressure.

	Target Al3509	Cl-bearing glass	Cl-free glass
SiO ₂	46.05	48.73	49.56
TiO ₂	0.06	0.07	0.10
Al ₂ O ₃	13.89	14.08	14.72
FeO _T	5.72	5.72	6.05
MnO	0.08	0.08	0.12
MgO	9.19	8.73	9.04
CaO	14.50	12.89	13.62
Na ₂ O	7.86	7.24	6.59
K ₂ O	0.19	0.19	0.20
Cl	2.45	2.26	0
Total	100	100	100

Results and Discussion: Both the Cl-free and Cl-bearing synthesis and the degassing experiments yield-

ed glass with no crystals. The silica tube showed some vapor-induced reaction around the Fe⁰-capsule especially in Cl-bearing experiments, and deposition of light-colored precipitate at the cool end of the silica tube. For longer duration experiments, the precipitate was located further away from the Fe⁰-capsule. All degassed samples showed some extent of vesicularity.

A significant decrease in FeO_T abundance in the degassed glasses relative to the initial compositions was noted in the EPMA analyses of the silicate glasses after 4 and 6 hours of degassing. This appeared to be largely the result of reduction of ferrous iron to metallic iron, as evidenced by the presence of metallic Fe droplets along the interior walls of the capsule material, due to the shift in $f(\text{O}_2)$ between the high pressure synthesis and degassing experiments. Therefore, all glasses were normalized to the initial CaO values (as a refractory oxide) and Fe was added back in for mass balance purposes. Volatile loss in terms of Cl, Na₂O, and K₂O was then calculated by subtracting this corrected composition from the initial starting composition for each experiment as shown in Table 2.

Table 2. Percent volatile loss as a function of time.

	Cl	Na ₂ O	K ₂ O	Na ₂ O	K ₂ O
	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
	Cl-bearing system			Cl-free system	
t10min	96	44	63	14	32
t4hr	99	44	62	32	51
t6hr	100	46	68	37	56

Based on the initial and final values for Na₂O (wt%) and K₂O (wt%) in the Cl-bearing system, the highest percentage loss occurred within the first 10 minutes of degassing (43% Na₂O, 63% of K₂O, 95% of initial Cl). After this time, the rate of loss of alkalis was diminished due to the absence of Cl in the melt.

For the Cl-free system, the percentage loss for the alkalis was lower compared to the Cl-bearing system. At the end of 10 minute degassing; the melt with initial 6.6 wt% Na₂O and 0.2 wt% K₂O lost 14% of its Na₂O and 32% of its K₂O to the vapor phase. At the end of 4 and 6 hours of degassing, the melt lost 1/3 of its initial Na₂O (32-37% Na₂O) and 1/2 of its initial K₂O (50-56% K₂O) to the vapor phase. Thus higher Cl in the melt resulted in greater alkali loss, even in shorter duration (10 minutes) degassing experiments.

For both the Cl-free and Cl-bearing systems, Na₂O was always more compatible in the melt relative to the K₂O. Therefore, the volatiles given off have K/Na ratio higher than the melt through time in spite of the much higher initial Na abundance in the melt (Fig. 1). This is consistent with previous Cl-free experiments of [12] on planetary analogs, and the lower vaporization temperature of K₂O (877 °C) compared to Na₂O (1057

°C) at 10⁻³ atm. The enhanced vaporization of alkalis from Cl-bearing melt suggests that if the alkalis are given off as chlorides, NaCl is less volatile than KCl, and both are more volatile than the alkali volatile species in the absence of Cl.

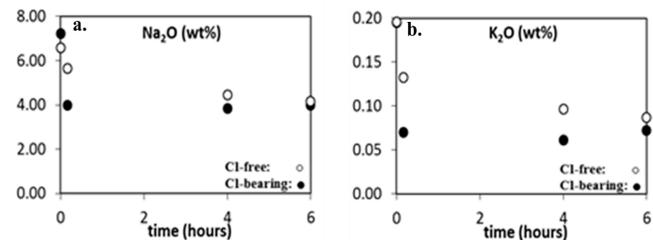


Figure 1. Initial and final alkalis wt% in melt with time.

These results suggest that in Cl-rich systems, the compositional nature of the vapor exsolved may have a bimodal character over time. Flash melting of a Cl-bearing chondrule might consist of a two stage volatilization process where the first vapors given off will contain NaCl and KCl while the successive vapors will be Cl-free, and degassing continues through the loss of alkalis as monatomic species. This bimodality in the vapor phase might also control the type of condensates formed during various time intervals of heating and degassing which might explain very different volatile contents of chondrules in the solar nebula that have been thermally processed repeatedly and contained recycled fragments of previous generations of chondrules.

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