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## Experimental study of evaporation and isotopic mass fractionation of potassium in silicate melts

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**Abstract**—The behavior of Na and K during evaporation from chondrule composition melts was studied using a vacuum furnace. Though Na is the less volatile of the two as an element, it is lost more rapidly than K from silicate melts. Mass fractionation of K isotopes was measured by ion microprobe and Rayleigh fractionation is observed for vacuum evaporation ( $10^{-5}$  atm). With higher pressures of air, the K loss rate decreases but with increasing hydrogen pressure, K is lost more rapidly.  $\delta^{41}\text{K}$  decreases with higher pressures, because of back reaction between melt and K in the gas. With long heating duration, the release of light K condensed within the furnace leads to interaction with the K-depleted melt and a further reduction of  $\delta^{41}\text{K}$ . Natural chondrules differ in some ways from our experimental residues. Some (especially type IIA) have superchondritic Na and K, despite their assumed formation in nebular hydrogen, which enhances volatile loss, and chondrules do not show K isotopic fractionation. Type I chondrules in Semarkona (LL3.0) either plot on our evaporation trend, or are depleted in K but slightly enriched in Na, relative to K. In Bishunpur (LL3.1), type I chondrules are mostly K-depleted but moderately to strongly enriched in Na. In petrologic type 3.2 to 3.4 chondrites they are enriched in both K and Na, like type II chondrules. The alkali contents suggest type I chondrules experienced evaporation and subsequent metasomatism. Their normal  $\delta^{41}\text{K}$  values suggest closed-system evaporation of a chondritic precursor in a gas with relatively high K pressures due to vaporization of dust accompanying chondrule precursor aggregates. Type II chondrules are volatile-rich, as well as unfractionated in K isotopes. They probably formed in a gas with higher pK than in the case of type I chondrules, due to heating of a more dust-rich parcel of gas. Copyright © 2003 Elsevier Science Ltd

### 1. INTRODUCTION

Understanding the origin and evolution of the solar system depends greatly on how well we understand the solar nebular environment. Meteorites, and particularly the chondrules in them, are a record of early solar system events and, when unmetamorphosed, potentially good candidates for clarifying the nebular environment in which they formed. Both planets and asteroids are depleted in moderately volatile elements (e.g., Humayun and Clayton, 1995; Allègre et al., 2001), due either to nebular or planetary processes. We examine here alkali loss from silicate melts to evaluate the role of evaporation in chondrules, which might possibly contribute to large scale fractionations.

Chondrules are small silicate-metal spherules, and are widely believed to have been formed by high temperature melting in the solar nebula (Grossman, 1988). The nature of the processes that actually formed them, however, is under intense debate. Alternatives to nebular melting include asteroidal events (Kitamura and Tsuchiyama, 1996; Chen et al., 1998) and formation by condensation of liquids or liquids plus crystals (Ebel and Grossman, 2000; Krot et al., 2001). One reason that neither of these possibilities has been widely accepted is that some chondrules are complex texturally and isotopically. They may contain CAI, amoeboid olivine inclusions, relict grains and other chondrules, they may be surrounded by one or more rims, and they may have isotopic heterogeneities, all difficult to explain

without a complex history. While the issue is not settled, it seems that the standard model is still that many chondrules formed by heating of dust aggregates in some nebular environment (Grossman, 1988; Jones et al., 2000; Alexander et al., 2001).

Grossman (1988) argued that most chondrules had experienced very little evaporative loss of alkalis, although chondrules formed by heating at nebular pressures should show evaporation (Sears et al., 1996). Absence of evidence for evaporation from chondrules would require non-canonical nebular environments, extraordinarily rapid heating or planetary and condensation models for chondrule formation. Finding evidence for chondrule evaporation would greatly improve our understanding of the heating process itself as well as of the surrounding nebular environment. This is because evaporation depends not just on the melted material, but to a greater extent on the properties of the environment in which melting takes place, such as the temperature, heating duration, gas partial pressures, and so on.

Sodium has been the main focus of prior evaporation studies. This is because it is a moderately volatile element that evaporates easily at chondrule-forming temperatures and is also easy to analyze. Many observations and experiments on Na in chondrules have generated results interpreted either in favor of or against evaporation as the dominating mechanism to form various types of chondrules (Shirley, 1983; Grossman, 1988; Alexander, 1996; Sears et al., 1996; Hewins et al., 1997). However, if one takes a careful look at the arguments from both sides and the recent Na loss experimental results under various conditions (Tsuchiyama et al., 1981; Yu and Hewins, 1998;

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Shirai et al., 2000), it should be clear that resolving the issue by looking at Na alone would be difficult, if not impossible. This is because Na contents of chondrules can be affected by many factors such as heating time, composition and pressure of ambient gas, or even alteration after chondrule formation. Constraints from other sources are needed.

Potassium could provide such constraints. It is also a moderately volatile element, and is believed to behave similarly to sodium, but it has three isotopes. Since in general isotopic mass fractionation can be easily induced by evaporation and is therefore a good indicator for such a process, it was hoped that K isotopes would solve the problem. Yet in a pioneering study on the K isotopes in meteoritic materials, Humayun and Clayton (1995) measured K isotopes in a single Allende chondrule, with surprising results for those who believe chondrule evaporation is unavoidable: they did not find any K isotopic mass fractionation in the meteoritic materials they analyzed. A similar result was obtained for Bishunpur and Semarkona chondrules by Alexander et al. (2000) and Alexander and Grossman (2000). Before ruling out evaporation, however, we need to know more about K. We need answers to the following questions: How do K isotopes behave during evaporation? Studies have shown that free evaporation of Mg, Si and O isotopes from silicate melt yields ideal Rayleigh fractionation (Wang et al., 2001), but evaporation of Zn apparently under similar conditions does not (Xue et al., 1996). What are the factors that could affect K isotopic fractionations? How does H<sub>2</sub>, the dominating gas species in the nebula, affect K evaporation and isotopic fractionation? How does the evaporative behavior of K compare to that of Na? Unfortunately so far we do not have answers to these questions.

There have been only limited studies on the volatility of K (e.g., Kreuzberger et al., 1986; Shimaoka et al., 1994) and, despite that work, there is a widespread belief that K and Na are similar in their evaporative behavior. Even for Na, most of the evaporation experiments were performed at 1 atm gas pressure (Tsuchiyama et al., 1981; Yu and Hewins, 1998; Shirai et al., 2000), which is inappropriate considering the much lower canonical nebular pressure. There have been no experiments on K isotopic mass fractionation in the chondrule-forming temperature range and we do not know how K isotopes will respond to different gas species and pressures. To address these questions, we have designed and conducted a systematic high temperature experimental study on K and Na evaporation and on K isotopic fractionation properties using various gas species and pressures. This is made possible by recently established high temperature vacuum furnace facilities and the progress made in ion probe technology to analyze K isotopes in "micron" size areas. This paper reports our experimental results and our interpretations of those results.

## 2. MATERIAL AND METHODS

Evaporation experiments were conducted at Rutgers University using a vacuum furnace (Fig. 1) and a Deltech 1 atm gas mixing furnace. The vacuum furnace is modified from a Deltech furnace using ceramic-metal welding techniques to create vacuum seals, and can be evacuated to  $\sim 10^{-7}$  torr at room temperature (or  $\sim 10^{-9}$  atm, we will use atm as the pressure unit here). We used an HPS TC61 turbopump and an HPS 941 cold cathode pressure gauge positioned close to the lower cooling head. A gas bleeding valve allows the introduction of desired gas species into the system and the adjustment of the system gas pressure

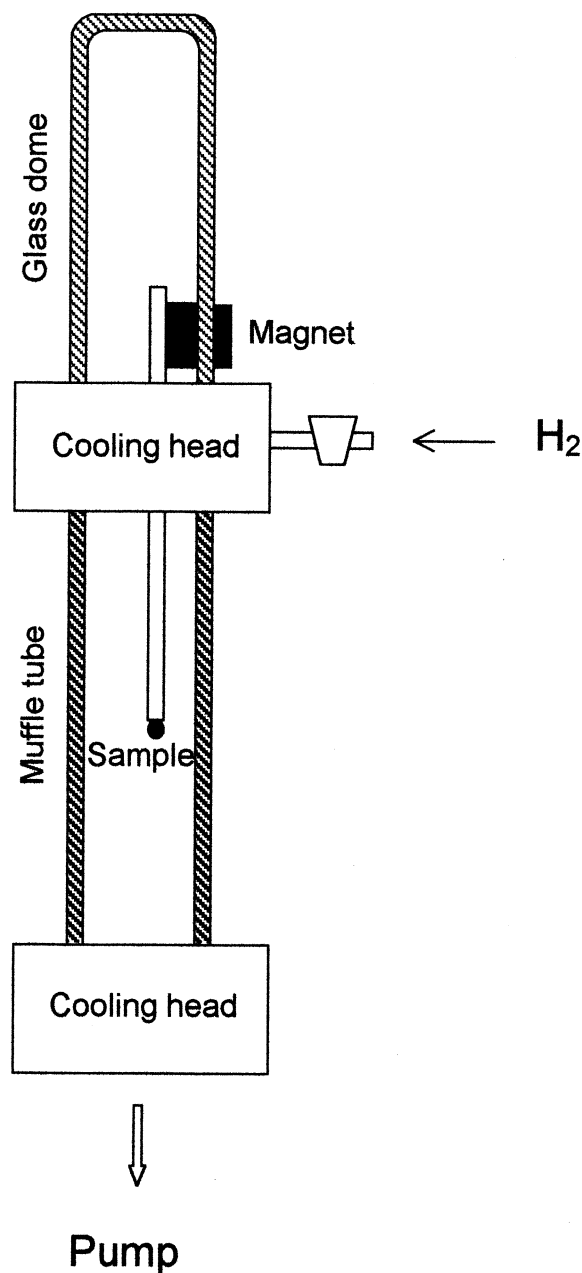


Fig. 1. Schematic of vacuum furnace. Sample has been slid into the hot spot after pump down and establishment of desired atmospheric conditions.

at will. The position of the sample in the furnace is controlled with a magnet slider. The sample can be easily positioned in either the cold zone or the hot zone at any time during the experiment, which allows flash heating experiments and quenching at pressures of interest for nebular environments (Fig. 1). A Pt-Pt90/Rh10 thermocouple was placed 2 mm above the sample. The thermocouple was frequently calibrated with the melting points of Au and Pd, and the uncertainty of the temperature measurement for the sample was estimated to be  $\pm 5^\circ\text{C}$ . The muffle tube is alumina, which might possibly evaporate when corrosive hydrogen is used, but we observed no changes in the Ca/Al ratios of our charges as a function of time. The 1 atm experiments followed the procedures described in Yu and Hewins (1998).

The experiments were performed under three different gas environments: 1 atm with gas mixing; low pressure air; and low pressure

Table 1. Starting Compositions and Chondrules.

	1	s.d.	2	3	4
SiO <sub>2</sub>	52.36	0.93	50.05	55.1	48.9
TiO <sub>2</sub>	0.20	0.16	0.21	0.19	0.12
Al <sub>2</sub> O <sub>3</sub>	3.56	0.03	1.03	4.8	3.23
Cr <sub>2</sub> O <sub>3</sub>	0.32	0.08	0.44	0.44	0.54
FeO	13.91	0.67	20.37	14.3	12.3
MnO	0.36	0.13	0.42	0.40	0.40
MgO	21.25	1.25	23.90	18.7	30.8
CaO	0.81	0.09	1.02	2.5	2.32
Na <sub>2</sub> O	2.75	0.50	1.31	2.4	2.17
K <sub>2</sub> O	3.21	0.16	1.72	0.29	0.23
Total	98.72		100.46	99.12	101.01

1. Type IIAB starting material, enriched in K, with standard deviations.
2. More olivine- and pyroxene-normative type IIAB starting material.
3. Selected type IIAB chondrule, Semarkona (Jones, 1996).
4. Selected type IIA chondrule, Semarkona (Jones, 1990).

hydrogen. For the 1 atm experiments, samples were run in a CO-CO<sub>2</sub> gas mixture, and the fO<sub>2</sub> was controlled at 0.5 log unit below the iron-wüstite buffer. For the air experiments, we initially pumped down to  $\sim 10^{-5}$ , and then bled air into the system as needed while pumping to maintain pressures of  $1.0 \times 10^{-5}$ ,  $1.8 \times 10^{-5}$ ,  $1.8 \times 10^{-4}$ ,  $1.4 \times 10^{-3}$  and  $1.3 \times 10^{-2}$  atm. The system was under continuous pumping during heating experiments. For each run, there was a sudden increase in gas pressure when the charge was inserted into the hot zone (approximately 1 to 2 orders of magnitude increase in total gas pressure), then the system pressure returned to the set value in  $\sim 2$  to 3 min. For the hydrogen experiments, the system was first evacuated to  $1.0 \times 10^{-5}$  atm, then hydrogen was introduced. Hydrogen flow rate was adjusted to maintain the chosen pressure. The samples were run in the hydrogen-dominated gas at pressures of  $7.2 \times 10^{-5}$ ,  $1.7 \times 10^{-4}$ , and  $1.4 \times 10^{-3}$  atm.

The majority of the experiments used isothermal heating, meaning that the furnace was preheated to a preset temperature and the desired atmospheric conditions were reached, while the sample waited in the antechamber at  $< 250^\circ\text{C}$ . Then the sample was inserted into the hot zone and kept at the set temperature for a certain length of time. The heating temperatures for all sets of isothermal experiments are  $1450^\circ\text{C}$  or  $1485^\circ\text{C}$ , depending on bulk composition, and the heating times range from 5 to 90 min. At the end of each experiment, the sample was quenched either in vacuum or in air (1 atm experiment). We have also performed some flash heating/cooling simulation experiments, in which the sample was at peak temperature ( $1450^\circ\text{C}$ ) for 50 s, then cooled at  $5000^\circ\text{C/h}$  or  $500^\circ\text{C/h}$  to  $1000^\circ\text{C}$ .

The experiments were done on two starting materials of powdered synthetic silicate glass. The first is similar to a type IIAB chondrule composition (Jones, 1996), but the K<sub>2</sub>O content was increased to 3.3 wt. % and Na<sub>2</sub>O to 2.8 wt. % by mixing KCl and Na<sub>2</sub>CO<sub>3</sub> with the original type IIAB glass and remelting the material (Table 1). The second is a more olivine- and pyroxene-normative IIAB, also with enhanced K, approaching type IIA in composition. Calculated liquidus temperatures are  $1410 \pm 30$  and  $1492 \pm 30^\circ\text{C}$ , respectively. Each sample was pressed into a 50 mg pellet 3 mm in diameter and hung on the platinum loop at the end of the sample holder. Run temperatures were chosen so as to give totally molten charges.

The mass loss of each charge was measured by weighing the sample before and after the heating, but the results show non-systematic variations probably related to cracking and loss of glass. Chemical analyses of the charges were performed using a JEOL 8600 electron microprobe at Rutgers University, measuring  $\sim 100$  points per charge. The accelerating voltage was 15 kV and the beam current was 15 to 20 nA. A rastered  $5 \mu\text{m}$  beam and short counting times from 2 to 5 s were used to minimize the K and Na loss during analyses.

K isotope analyses were performed using the Carnegie Cameca IMS 6f ion probe at a mass resolution of 5500 needed to resolve  $^{39}\text{K}$  from  $^{23}\text{Na}^{16}\text{O}$ , and  $^{41}\text{K}$  from  $^{25}\text{Mg}^{16}\text{O}$  and  $^{40}\text{CaH}$ . Operating conditions were

12.5 kV O<sup>-</sup> primary beam and 10 kV secondary accelerating voltage with a 50eV energy window. Repeated analyses give a standard deviation of  $\sim 1.5$  ‰ for  $\delta^{41}\text{K}$ , defined as

$$\delta^{41}\text{K} = \left( \frac{\left( \frac{^{41}\text{K}}{^{39}\text{K}} \right)_{\text{SAM}}}{\left( \frac{^{41}\text{K}}{^{39}\text{K}} \right)_{\text{STD}}} - 1 \right) / 1000$$

As in our study of Bishunpur chondrules (Alexander et al., 2000), the basaltic glass BHVO is our primary standard, although the NSB 610 glass has also been used. Both give very similar instrumental mass fractionations. Field aperture sizes and presputter times were chosen to minimize surface contamination.

### 3. EXPERIMENTAL RESULTS

Charges from isothermal runs contain mostly glass with some quench olivine needle crystals. Charges from flash heating/cooling experiments show microporphyrritic or sometimes barred olivine textures with glass matrix. Microprobe analysis shows that only alkalis vary significantly and there are no concentration gradients in the charges. Iron losses to the Pt support wire were minor in these rather short duration experiments. Potassium and Na contents for all the experimental charges and K isotopes, where available, are listed in Table 2. Standard deviations are shown in some of the figures.

#### 3.1. Evaporative Loss of K and Na

The evaporative losses of both K and Na are greater than those of other elements, and the Na loss results at 1 atm agree with previously reported data (Tsuchiyama et al., 1981; Yu and Hewins, 1998). Both compositions 1 and 2 are peralkaline, because K and Na were incorporated as salts rather than as feldspar as in many evaporation studies, e.g., Kreuzberger et al. (1986). When heated they rapidly become peraluminous. For composition 1, only the runs at 1 atm and one cooled at  $5000^\circ\text{C/h}$  remained peralkaline. Composition 2 has lower Al, and all the charges run for only 5 min, and one charge heated for 20 min at the highest pressure, remained peralkaline.

A significant difference in loss rate between K and Na is observed (Fig. 2), confirming the fractionation effects observed by Blander et al. (1970) and Shimaoka et al. (1994) for different temperatures. The curve in the K/K<sub>0</sub> vs. Na/Na<sub>0</sub> diagram (Fig. 2) is a best fit to the data for composition 1, for which the largest number of experiments was performed. This curve, which is close to a calculated loss line based on evaporation rates obtained below, shows that Na is lost faster than K. The K/Na ratios are not sensitive to whether the bulk composition is peralkaline (data points surrounded by circles in Fig. 2) or peraluminous, but they are higher for continuous cooling experiments than for isothermal experiments, and for composition 1 than for composition 2 (Fig. 2). The K/Na ratios are not sensitive to the gas, air or hydrogen, or the pressure used in these experiments.

In Figure 3 we show the fraction of K and Na remaining in the charges as a function of time and pressure, for all the charges run in hydrogen. Whereas evaporative losses are normally greater at lower pressures (Table 2), when hydrogen is used more alkalis are lost at higher pressure than at low pressure. Figure 3 indicates the efficiency of the reactive hy-

Table 2a. Analytical Results for Composition 1.\*

	P-air (atm)	P-H <sub>2</sub> (atm)	Time (min)	K/K <sub>0</sub> **	Na/Na <sub>0</sub> **	δ <sup>41</sup> K	err
V-54			0	1	1	0	0.9
V-5	1.0 × 10 <sup>-5</sup>		5	0.50	0.29		
V-6	1.0 × 10 <sup>-5</sup>		10	0.35	0.15		
V-7	1.0 × 10 <sup>-5</sup>		15	0.29	0.08		
V-8	1.0 × 10 <sup>-5</sup>		5	0.53	0.32		
V-9	1.0 × 10 <sup>-5</sup>		10	0.37	0.16		
V-10	1.0 × 10 <sup>-5</sup>		15	0.28	0.08		
V-11	1.0 × 10 <sup>-5</sup>		20	0.20	0.04		
V-12	1.0 × 10 <sup>-5</sup>		30	0.08	0.01		
V-13	1.0 × 10 <sup>-5</sup>		40	0.05	0.003		
V-43	1.0 × 10 <sup>-5</sup>		5	0.500	0.290	20.4	0.9
V-44	1.0 × 10 <sup>-5</sup>		15	0.287	0.084	44.0	0.8
V-45	1.0 × 10 <sup>-5</sup>		30	0.082	0.010	68.4	0.9
V-46	1.0 × 10 <sup>-5</sup>		48	0.047	0.006	87.6	0.9
NV-61	1.0		30	0.900	0.797	1.6	0.7
NV-62	1.0		60	0.770	0.589	2.3	0.4
NV-63	1.0		90	0.590	0.438	5	0.5
V20		9 × 10 <sup>-5</sup>	5	0.52	0.33	18.4	1.4
V21		9 × 10 <sup>-5</sup>	15	0.22	0.06	27.3	1.6
V22		9 × 10 <sup>-5</sup>	30	0.03	0.01	57.4	1.0
V-59*	1.00 × 10 <sup>-5</sup>		5000°C/hr	0.760	0.441	7.5	1.3
V-60*	1.00 × 10 <sup>-5</sup>		500°C/hr	0.530	0.188	22.6	1.8

\* Note: All experiments isothermal at 1450°C, except V-59 and V-60 are flash heating runs.

\*\* Concentrations in residues divided by initial composition.

drogen at stripping oxygen and alkalis from silicate melts. At low pressure (<10<sup>-4</sup> atm), concentrations of K and Na are not much influenced by the presence of air or H<sub>2</sub> (Table 2). The absolute loss rates of K and Na in hydrogen are not well constrained, because of the very low concentrations retained for all except the 5 min runs.

Curves of C/C<sub>0</sub> plotted against time for the low pressure experiments with no hydrogen show that the loss of alkalis is approximately logarithmic. To compare the average loss rates of Na with those determined previously by Tsuchiyama et al.

(1981) and Shimaoka and Nakamura (1989), we made diagrams showing ln(C/Co) vs. time (Fig. 4 and 5). These diagrams document the significant effect of gas pressure on the vaporization rates of both K (Fig. 4a,b) and Na (Fig. 5a,b). The experiments plotted here were run in low pressure air, except for those at 1 atm, which used CO-CO<sub>2</sub>. Note that K is lost faster from composition 2 than from composition 1 (Fig. 4a,b) and the same seems true of runs in low pressure hydrogen (Fig. 3) though we do not have experiments run at identical pressures in air and hydrogen. Errors in Figure 4 are the standard devi-

Table 2b. Analytical Results for Composition 2 at 1485°C.

	P-air (atm)	P-H <sub>2</sub> (atm)	Time (min)	K/K <sub>0</sub>	Na/Na <sub>0</sub>	δ <sup>41</sup> K	err
V-85	1.8 × 10 <sup>-5</sup>		5	0.396	0.236	17.4	0.7
V-86	1.8 × 10 <sup>-5</sup>		20	0.046	0.017	62.6	0.8
V-87	1.8 × 10 <sup>-5</sup>		40	0.007	0.010	34.0	2.1
V-88	1.8 × 10 <sup>-4</sup>		5	0.406	0.233	15.6	0.7
V-89	1.8 × 10 <sup>-4</sup>		20	0.057	0.024	48.8	1.0
V-90	1.8 × 10 <sup>-4</sup>		40	0.020	0.013	38.7	1.2
V-91	1.4 × 10 <sup>-3</sup>		5	0.630	0.508	6.6	0.6
V-92	1.4 × 10 <sup>-3</sup>		20	0.372	0.219	13.6	0.7
V-93	1.4 × 10 <sup>-3</sup>		40	0.206	0.091	13.3	0.9
V-94		7.2 × 10 <sup>-5</sup>	5	0.424	0.239	21.4	0.6
V-95		7.2 × 10 <sup>-5</sup>	20	0.021	0.020	57.3	1.1
V-96		7.2 × 10 <sup>-5</sup>	40	0.006	0.012	14.8	2.7
V-97		1.8 × 10 <sup>-4</sup>	5	0.418	0.215	20.1	0.6
V-98		1.8 × 10 <sup>-4</sup>	20	0.010	0.012	59.8	1.6
V-99		1.8 × 10 <sup>-4</sup>	40	0.007	0.011	7.4	3.0
V-100		1.4 × 10 <sup>-3</sup>	5	0.228	0.081	21.7	0.9
V-101		1.4 × 10 <sup>-3</sup>	20	0.013	0.008	15.4	1.8
V-102		1.4 × 10 <sup>-3</sup>	40	0.007	0.007	4.9	2.2
V-103		1.3 × 10 <sup>-2</sup>	5	0.185	0.056	5.0	0.7

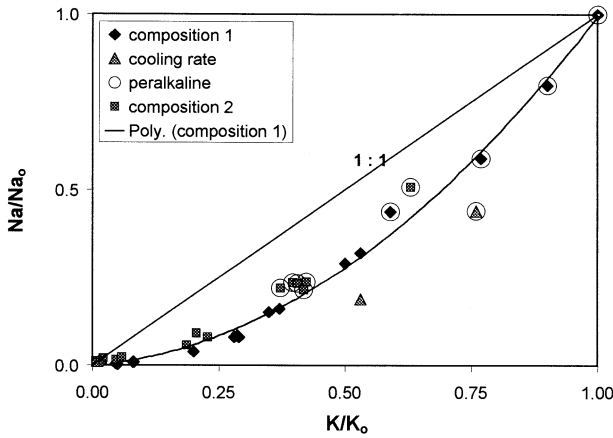


Fig. 2. Summary of all evaporation experiments, showing fraction of K and Na remaining in residue, after isothermal heating or (triangles) continuous cooling of chondrule composition. Symbols for charges with peralkaline compositions are surrounded by circles. The curve is a polynomial fit to the data for composition 1.

ations of the microprobe analyses, and they are omitted for the higher concentrations where the error bar is not much bigger than the size of the symbol.

The linear fits to the data for the 1 atm charges (all peralka-

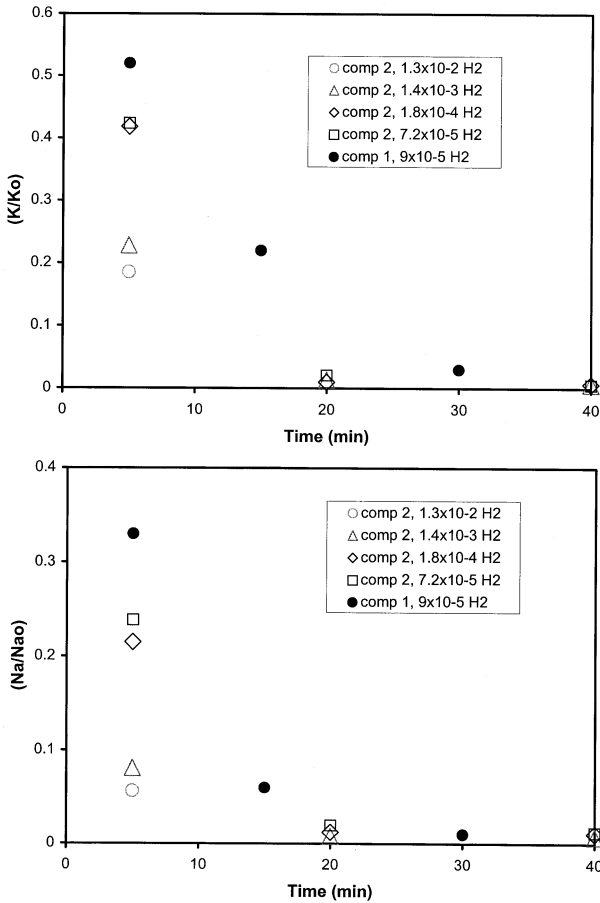


Fig. 3. Fraction of evaporated species remaining as a function of heating time and pressure of H<sub>2</sub>. (a) K (b) Na.

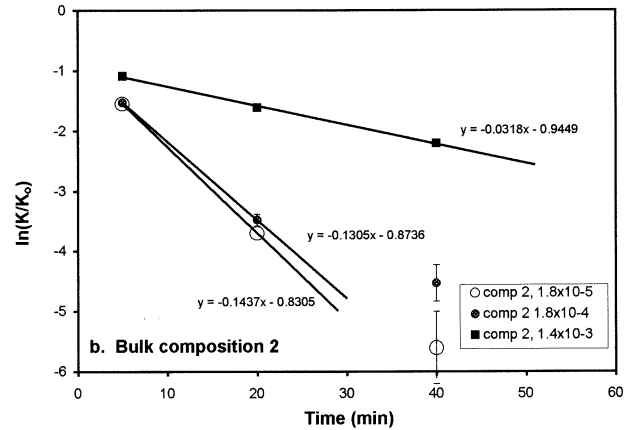
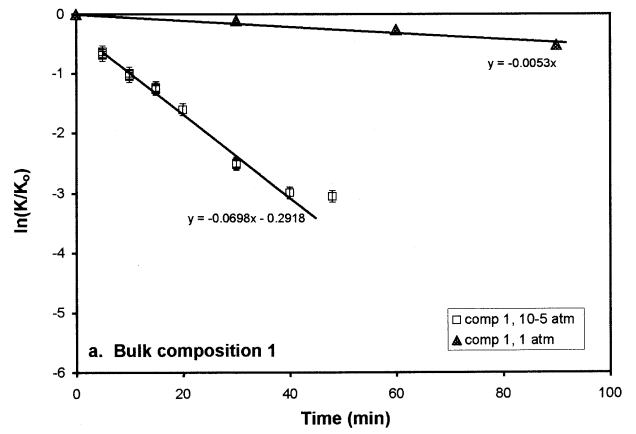


Fig. 4. Fraction of K remaining as a function of heating time and pressure (of air or, for 1 atm, CO<sub>2</sub>). (a) composition 1 (b) composition 2. Standard deviations are shown where they are bigger than the symbol for the data point.

line) pass through the origin, within error, but the lines for lower pressure charges project back to a composition more alkali-poor than the original bulk composition (Fig. 4). In the first few minutes of the experiments loss rates are higher than afterwards, possibly because the initial compositions are highly peralkaline (Alexander, 2001). The final compositions of the low pressure charges for composition 1 are all peraluminous and the loss data are colinear, except for the one run for the longest time. For Al-poor composition 2, the shortest runs are still peralkaline, though for 1.4x10<sup>-3</sup> the combination of peralkaline and peraluminous charges yields colinear loss data. In some of the runs for the longest times, the K and Na concentrations are anomalously high. Then the overall pattern of the data is concave rather than linear, and a similar tendency has been observed in other evaporation studies, e.g., in Figure 4 of Tsuchiyama et al. (1981). In general such a tendency may be attributed to changing activity-concentration relationships. Most of our runs with anomalously high concentrations have concentrations that are close to background values of the electron microprobe, with large errors, and may simply be unreliable. However, we cannot rule out some kind of alkali contamination or back reaction affecting some of the longest duration

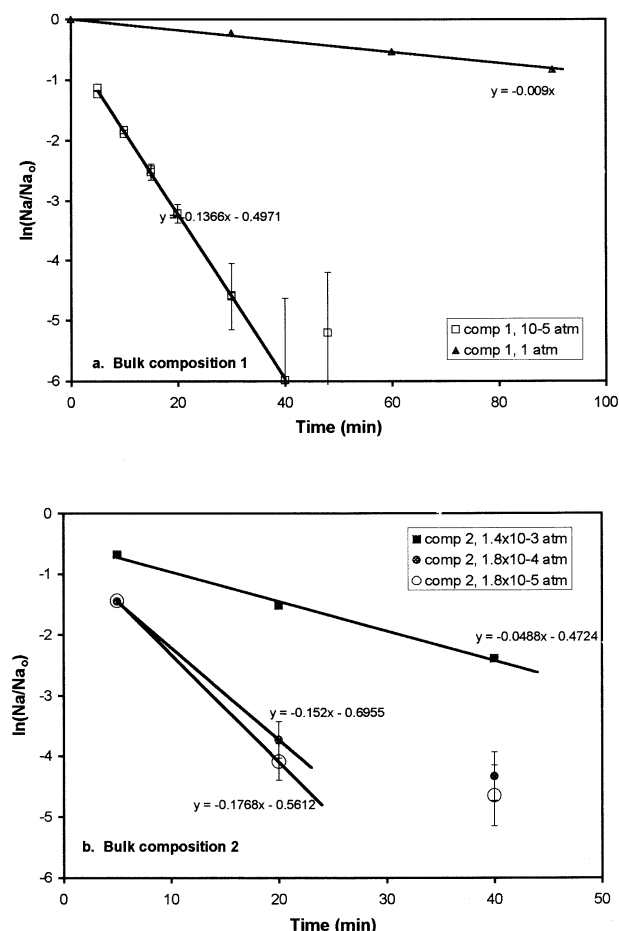


Fig. 5. Fraction of Na remaining as a function of heating time and pressure (of air or, for 1 atm, CO-CO<sub>2</sub>). (a) composition 1 (b) composition 2.

runs. This possibility is treated below in the discussion of the K isotope data.

To make specific comparisons, we have calculated the vaporization rate constant  $k$  of Na and K for each composition at different pressures, using the relationship

$$\ln(C/C_0) = -3kt/r$$

from Tsuchiyama et al. (1981), as a first order approximation, taking the slopes of the linear fits in Figures 4 and 5 as  $3k/r$  and assuming a radius of 0.15 cm for each charge. In fitting lines to the loss data in Figures 4 and 5, we have ignored long duration runs which have anomalously high values. The calculated vaporization rate constant of K from composition 1 at 1450°C, for example, is an order of magnitude higher at  $10^{-5}$  atm than that at 1 atm pressure, e.g.,  $3.49 \times 10^{-3}$  cm/min vs.  $2.65 \times 10^{-4}$  cm/min. The rate constant for Na calculated in this way is, on average, 1.5 times the K rate constant.

Loss rate data derived from the slopes of the lines in Figures 4 and 5 are plotted against pressure in Figure 6. Sodium vaporization rate constants are in every case greater than those for K. For Na, the calculated rate constant at 1 atm for our composition 1 is  $4.5 \times 10^{-4}$ , which is higher than the value of  $2.6 \times 10^{-4}$  found by Tsuchiyama et al. (1981) for their

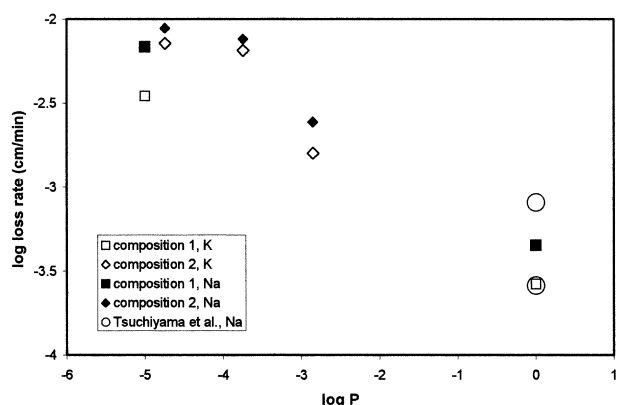


Fig. 6. Evaporation rate constants derived from slopes of lines in Figure 4 and 5 of K (open symbols) and Na (filled symbols) as a function of pressure of air or, for 1 atm, CO-CO<sub>2</sub>. Open symbols are Na evaporation rates from Tsuchiyama et al. (1981) for their compositions 1 and 2 under similar conditions to those of the present experiments.

composition 1 at the most similar conditions, 1456°C and an oxygen fugacity of  $10^{-9.2}$ . However, it is lower than the value for their composition 2 extrapolated down temperature. Our calculated rate for Na at  $10^{-5}$  atm,  $6.8 \times 10^{-3}$ , is close to the value given by Shimaoka and Nakamura (1990) for vacuum.

The evaporation rate of any component from a multi-component system is not constant, but decreases with decreasing concentration. For example, Hashimoto (1981) reports an order of magnitude drop in the evaporation rate of FeO from CMFAS melts at a given temperature, as the concentration of FeO falls. We calculated evaporation rates from the differences between successive charges heated for longer times at the same pressure, in moles/cm<sup>2</sup>sec. In Figure 7 we show the evaporative fluxes of K and Na, as a function of pressure. The initial (maximum) evaporation rates increase with decreasing pressure. They decrease at any pressure by over two orders of magnitude from the high-concentration low-duration runs to the long runs that had little remaining alkalis. The final evaporation rates decrease with decreasing pressure, since they depend on concentration, which becomes lowest at the lowest pressures. Fluxes for experiments in hydrogen, not shown, show a similar pattern, except that the range of values is higher for higher pressures.

Calculation of the changing fluxes with time at a given pressure (Fig. 7) throws additional light on the relative evaporation rates of Na and K. Figure 8 shows the ratio of the flux of K to the flux of Na as a function of Na concentration. The ratio decreases with decreasing Na, which is roughly equivalent to increasing time. Sodium evaporation rates are greater than those of K until the concentration of Na<sub>2</sub>O has been reduced to less than ~0.1 wt. % (Fig. 8).

### 3.2. Mass Fractionation of K Isotopes

Evaporation-induced mass fractionation of K isotopes occurred in samples from all sets of experiments. However, the detailed behavior of K isotopes differs among charges and depends on the environment in which the sample was run. For the purpose of comparison, we calculated theoretical Rayleigh fractionation values assuming monatomic K is the evaporating

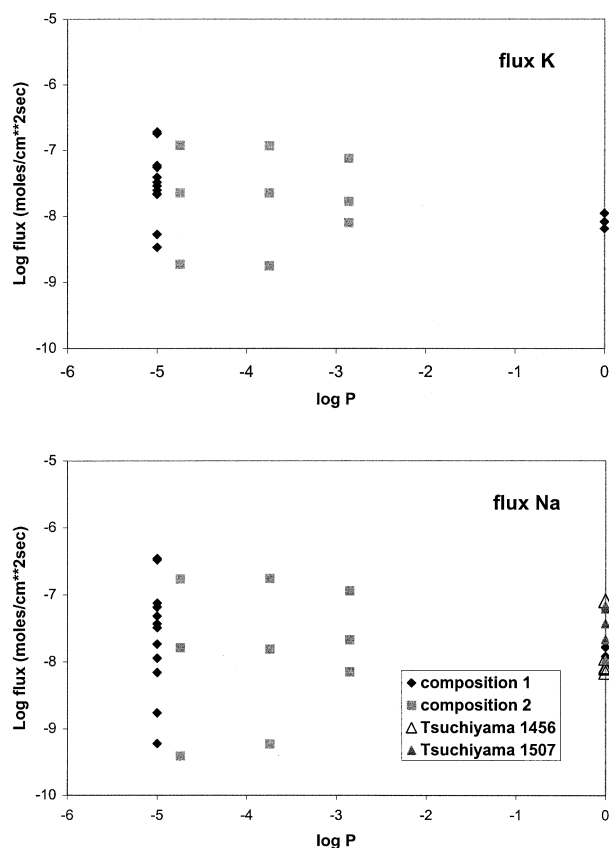


Fig. 7. Evaporation rates derived from differences in charge compositions of successive runs at the same pressure, for (a) K (b) Na. The highest rates are for high concentrations, i.e., for short run durations. Triangles are for runs from Tsuchiyama et al. (1981) for their compositions 1 at two different temperatures.

species. The highest degree of K isotopic fractionation as a function of K loss was observed in samples run in air at the lowest pressure of this study,  $1.0 \times 10^{-5}$  atm. The data, including cooling rate as well as isothermal runs, virtually overlap with the Rayleigh fractionation line but are slightly higher, almost certainly because of analytical error (Fig. 9a).

Increasing the gas pressure of the system from  $1.0 \times 10^{-5}$  atm towards 1 atm causes the K isotopic fractionation trend to gradually deviate from the Rayleigh line (Fig. 9a,b, Table 2). Composition 1 samples run under 1 atm gas environment show the smallest fractionation of K isotopes, though their  $\delta^{41}\text{K}$  values are still significantly different from the unfractionated baseline.

The extent of K isotopic fractionation is also time dependent in the lower pressure hydrogen-free runs (Fig. 9a). The K isotopic fractionation increases linearly with increased K loss in the early stages of evaporation, but decreases between 20 and 40 min for most pressures. A similar effect is observed in the runs with hydrogen, except that the maximum mass fractionation is achieved sooner, in the 5 to 20 min time range (Fig. 9b), and  $\delta^{41}\text{K}$  values for long run times are very low.

The presence of  $\text{H}_2$  in the system modifies the K isotopic fractionation systematics. For the same heating time, the K loss is much greater in  $\text{H}_2$ , and the data are further to the right in

Figure 9. As the extent of mass fractionation decreases with fraction of K retained after  $\sim 20$  min (Fig. 9 and Table 2), the deviation from the Rayleigh line in Figure 9b is usually much greater than for equivalent residues heated without hydrogen. Samples run in  $\text{H}_2$  always exhibit a greater deviation from Rayleigh behavior than those run for the same times at the same pressures without  $\text{H}_2$ .

The charges run with flash heating followed by continuous cooling contain numerous olivine phenocrysts grown during cooling because olivine nuclei survived dissolution during the brief melting episode. These charges lost less K and Na compared to charges run isothermally at peak temperature for the same length of furnace time. However, on the  $\text{K}/\text{K}_0$  vs.  $\text{Na}/\text{Na}_0$  diagram (Fig. 2a), they show faster loss of Na relative to K than the isothermally heated charges. The flash heating/cooling charges show a degree of K isotopic fractionation that is consistent with isothermally heated charges under the same gas pressure and species. Specifically, Figure 6a shows that the two flash heating/cooling charges with numerous olivine phenocrysts plot on the Rayleigh fractionation line along with their isothermally heated and quenched glassy counterparts (the other  $10^{-5}$  charges). These observations indicate that the presence of large non-K-bearing crystals in the melt (olivine in this case) has little effect on the degree of K isotope fractionation.

## 4. DISCUSSION

### 4.1. Evaporation and Mass Fractionation in Experiments

The probable importance of evaporation as a process in the solar nebula has led to numerous evaporation experiments, at 1 atm and at lower pressures, for elements such as alkalis from silicate melts (Tsuchiyama et al., 1981; Mura, 1989; Shimaoka and Nakamura, 1990; Yu and Hewins, 1998; Yu et al., 1998; Tissandier et al., 1998; Wang et al., 1999; Nagahara and Ozawa, 2000b). An important result of these experiments has been the development of a theoretical framework for understanding evaporation and its consequences on isotopic mass fractionation (e.g., Young et al., 1998; Humayun and Cassen, 2000; Nagahara and Ozawa, 2000a; Alexander, 2001) and numerous alkali condensation experiments (Ikeda and Kimura, 1985; Biggar, 1986; Lewis et al., 1993; Georges et al., 2000).

The evaporation rate depends on the difference between the equilibrium partial pressure of a species in the melt and its ambient partial pressure. With heating in vacuum, sometimes assumed as an analog of nebular conditions, free evaporation occurs accompanied by Rayleigh fractionation. However, the evaporation rate is higher with higher hydrogen pressure because of the reactive nature of the hydrogen. Chemical reactions with the gas involving  $\text{H}_2$  could play an important role in chondrule formation, depending on  $P_{\text{H}_2}$  and  $P_{\text{total}}$  in the chondrule-forming environment. In a closed system, possibly corresponding to some restricted nebular domain, the amount of isotopic mass fractionation will be less than Rayleigh, because of back reaction with the evaporated gas. The extent of mass fractionation will increase and then decrease as evaporation goes towards completion (Tsuchiyama et al., 1999; Nagahara and Ozawa, 2000b).

The results from the present experimental study have demonstrated that the evaporative loss of Na and K in chondrule-

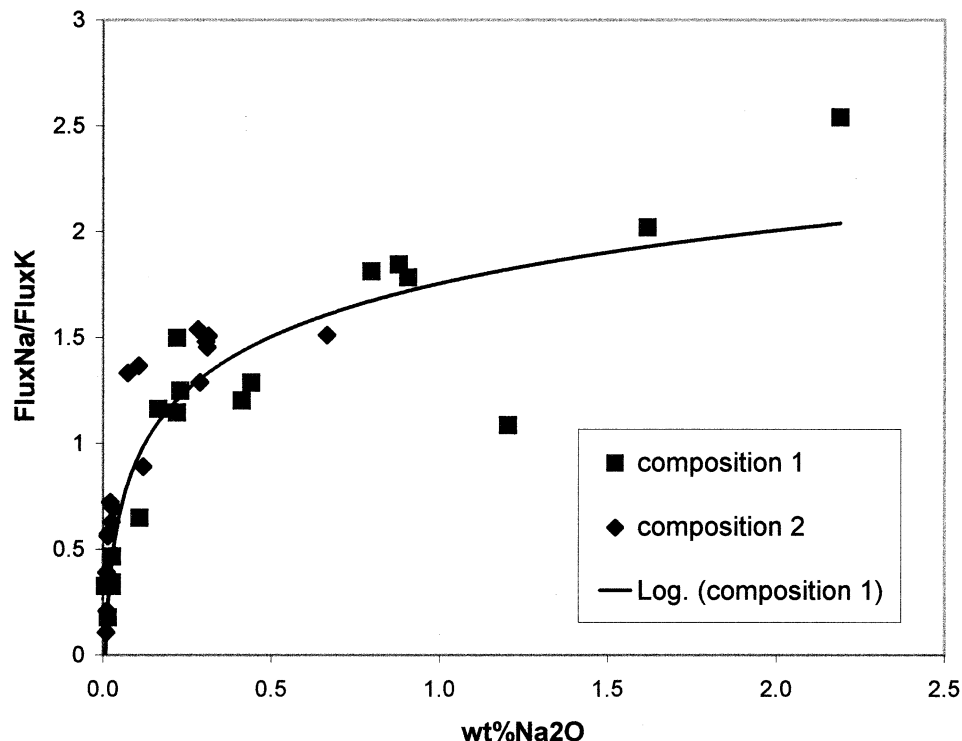


Fig. 8. Change in evaporation rate of K relative to Na, as a function of decreasing Na (increasing time).

like melts depends greatly on the gas composition and pressure. Evaporation rates decrease with increasing pressure in the air runs (Fig. 4, 5) but they increase with pressure if hydrogen is used (Fig. 3, Table 2). They decrease with time (Fig. 7), as the concentration of alkali falls.

For hydrogen-free experiments, and excluding for the moment the longest duration runs, we see that K isotopic mass fractionation behaves systematically (Fig. 9a). Only the lowest pressure air runs match the calculated Rayleigh distillation. Since absolute evaporation rates decrease with increasing pressure in the air experiments (Fig. 9a), we can rule out diffusion-limited evaporation as the explanation for the non-Rayleigh behavior in the higher pressure runs. The gradual deviation from the Rayleigh line as gas pressure increases can be attributed to the back-recoil of evaporated components from the gas and is consistent with the requirement that the Rayleigh fractionation law only applies to free evaporation.

Un-like our air runs, our low pressure runs with hydrogen only show Rayleigh-like relationships between  $\delta^{41}\text{K}$  and  $\text{K}/\text{K}_0$  for the shortest run times (Fig. 9b). Hydrogen has the effect initially of increasing  $\delta^{41}\text{K}$ , relative to the air runs. Both 20 and 40 min runs show less mass fractionation than expected from the respective 5 min runs, whereas for air only the 40 min runs fall off in this way. This decrease in isotopic fractionation with run time is discussed below.

The bulk composition of the melt has been found to influence Na loss rates, as well as temperature and oxygen fugacity, with greater loss from less polymerized melts (Tsuchiyama et al., 1981; Yu and Hewins, 1998). The lower K loss from composition 1 than for the composition 2 (Fig. 4a,b) could be because the latter is more olivine- and pyroxene-normative. It might

also be influenced by the slightly lower temperature (35°C lower) used for composition 1, but note that the effect on Na is much smaller.

The relative volatilities of Na and K are of some importance. Considering the pure elements or simple oxides, K is known to be the more volatile (e.g., Kreutzberger et al., 1986). We find, however, that Na is more easily lost from chondrule-like silicate melts, consistent with findings for partially melted chondrite (Gooding and Muening, 1977; Shimaoka et al., 1994). The evaporation rate of Na is also higher than for K from molten basalt at very high temperatures (Blander et al., 1970; Masuda and Tanaka, 1979). However, Kreutzberger et al. (1986) found the evaporation rate of K from basalt at 1400°C to be greater than for Na. Gibson and Hubbard (1972) found K evaporated from basalt faster than Na at low temperatures, but not at 1400°C. These differences must depend on the different activity coefficients of the alkalis in melts of different compositions. For chondritic melts and chondrules it is clear that Na evaporates faster than K, until very low Na concentrations are achieved (Fig. 8).

The K isotopic fractionation in our charges increases linearly with time for the early stages of evaporation but decreases again for longer times at most pressures. The deviation from Rayleigh fractionation at 40 min is generally greater than expected from shorter runs under the same conditions (Fig. 9a,b). We consider three possible explanations for the lower than expected  $\delta^{41}\text{K}$  values: (1) contamination of the charges; (2) back reaction between sample and evaporated gas; and (3) reaction between sample, evaporated gas and K from another source.

Since the longest runs tend to result in low K concentrations,



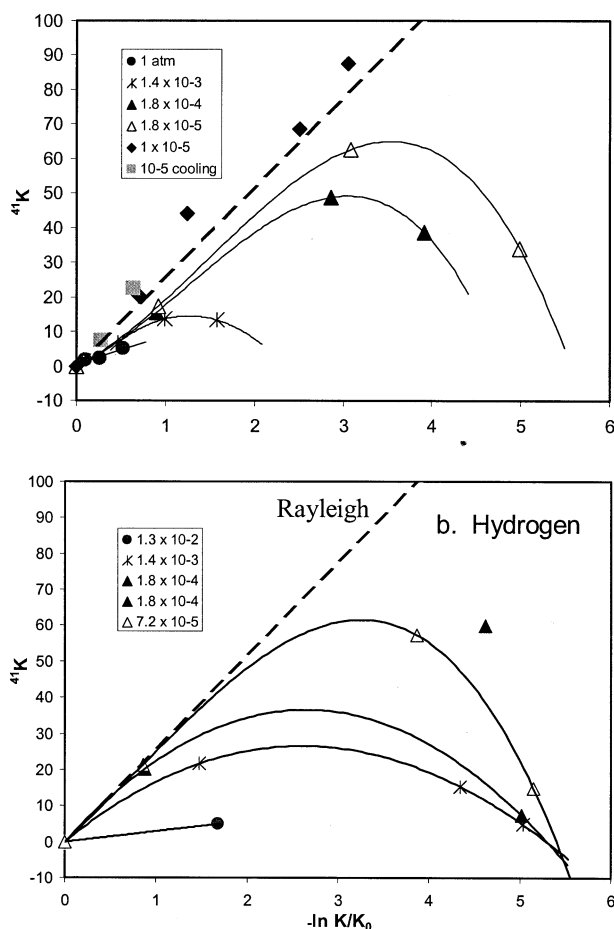


Fig. 9. Isotopic mass fractionation of K in compositions 1 and 2, shown as a function of fraction of K lost, increases with decreasing pressure. K initially becomes heavier, as expected, but later becomes lighter, as if the system were closed instead of open. Rayleigh fractionation is observed only for the lowest pressure in air, including for two flash-heated runs. (a) air or, for 1 atm, CO-CO<sub>2</sub>. (b) hydrogen.

surface contamination with isotopically normal K during sample preparation for ion probe analysis could be significant. If high deviation from the Rayleigh line were due to contamination, we would expect to see low  $\delta^{41}\text{K}$  for all the low K concentrations. For the  $10^{-5}$  atm air experiments we have linear  $\delta^{41}\text{K}$  vs.  $\log(\text{K}/\text{K}_0)$  all the way down to  $\text{K}/\text{K}_0$  of 0.0472 (Fig. 9a). For  $1.4 \times 10^{-3}$ , we see lower  $\delta^{41}\text{K}$ , attributed to recoil, but instead of a linear relationship there is a drop-off in  $\delta^{41}\text{K}$  between 20 and 40 min; i.e.,  $\text{K}/\text{K}_0$  between 0.37 and 0.21. The reduction in mass fractionation is not restricted to the lowest K concentrations, and we have as yet observed no increase in  $\delta^{41}\text{K}$  with depth during sputtering in the ion probe to lead us to believe we are dealing with surface contamination.

At the beginning of any evaporation experiment, there is a strong flux coming off the charge. In solar furnace work, this is observed as a thin vertical plume going straight up to the top of the glass dome (Ferrière et al., 1994, their Fig. 1). Conceivably in our experiments, some of the light K that initially rises in the muffle tube is pumped back down and exchanges isotopically with the small quantity of K remaining in the charge. However, there must be a net loss of light K from the furnace. During

evaporation, the isotopic composition of the charge is constantly getting heavier, and so is the vapor coming off it. This means that to get back to more normal compositions, the exchange cannot be with the vapor that the sample had just lost. Therefore we can eliminate the second possible explanation, simple back reaction with the gas.

The third possibility, reaction between the sample and K from a second source, can be viewed in two ways. Any furnace system in which evaporation occurs could conceivably become contaminated with isotopically light K. Deposits rich in alkalis were formed on cool upper surfaces during continuous pumping in several sets of evaporation experiments (Blander et al., 1970; Masuda and Tanaka, 1979; Fredricksson, 1985). Brown (1967) found that ceramic furnace parts could become sufficiently contaminated with K at 1 atm that when albite was subsequently heated in the furnace, it was converted to K-rich feldspar by transfer of K through the furnace atmosphere. At low pressures, evaporation of K from the charges still occurs, but exchange with furnace K could lead to isotopic modification with long run times. Alternatively, viewing the events in more detail, the decrease in  $\delta^{41}\text{K}$  for longer evaporation experiments could be explained as follows. Isotopically light K lost early from the sample later back-reacts with the charge. This could happen only if the light K lost in the early stage of the experiment is stored in the system where it does not exchange and later re-emerges. When back-reaction occurs, the K in the charge has almost been exhausted and the partial pressure of K has dropped below the vapor pressure of the recondensed material. During the early stages of evaporation, when our system is filled with light K, some of this K may plate out on the muffle tube between the hot spot and the cooling heads. The K vapor pressure in the system is likely to be related to the concentration in the sample and muffle tube, i.e., a steady state between evaporation, condensation and pumping rates is approached. Tissandier et al. (1998) observed that the Na evaporation rate was influenced by the pumping rate of the furnace gas. As the K vapor pressure gradually decreases during our runs, some K is baked off the muffle tube, and some light K can re-enter the charge, giving us the curved  $\delta^{41}\text{K}$  vs.  $\text{K}/\text{K}_0$ .

## 4.2. Application to Chondrules

If we compare the evaporative properties of K and Na from silicate melts revealed in this study with natural chondrule data, as well as with popular hypotheses for chondrule formation and the nebular environment, we can see that some contradictions exist between them. The major contradictions are summarized here and discussed in more detail below.

- All experiments at low pressure showed alkali depletion, but many chondrules (especially type IIA) have superchondritic Na and K.
- $\text{H}_2$  enhances volatile loss but, though  $\text{H}_2$  is the dominant species in the solar nebula, chondrule K and Na are not universally low.
- Evaporation residues show K isotopic fractionation but chondrules do not.

These contradictions are puzzling and need explanations. Below we consider some of the many possible factors that

could have affected the volatile loss and K isotopic fractionation.

#### 4.2.1. Application to type I chondrules

Natural chondrules are diverse in their chemical compositions but, generally speaking, they vary between two end members. One is Mg-rich, Fe-poor (Fe mostly as Fe metal), with very low volatile contents (type I chondrules, Mccween, 1977; Jones and Scott, 1989), and the other relatively rich in Fe and volatile elements, with chondritic or even superchondritic proportions (type II chondrules, Jones 1990, 1996). Based on our data for K and Na, in a canonical nebula, with gas pressure close to  $\sim 10^{-5}$  atm, gas dominated by  $H_2$  and a very low  $fO_2$  of  $\sim 10^{-16}$  atm, the “ideal” chondrules formed by high temperature melting should have very low Na and K contents, essentially zero, assuming no recondensation. Experiments show that at a gas pressure of  $\sim 10^{-5}$  atm, high temperature melting of chondrule materials leads to mass fractionation of K isotopes very close to the theoretical Rayleigh values. Natural chondrules would also be expected to have fractionated K isotopes that should be easily observable. Such “ideal” chondrules, however, do not exist in nature. The “ideal” chondrules resemble natural type I chondrules in many respects, which have low though non-zero volatile contents, but do not show K isotopic fractionations (Humayun and Clayton, 1995; Alexander et al., 2000; Alexander and Grossman, 2000). Alexander et al. (2000) have suggested that chondrules did not form in the “ideal” nebula, and that this could be explained by isotopic exchange of K between chondrules and their environment, and/or reentry of K into chondrules, after evaporative losses.

Natural chondrules have various K and Na contents and the two elements are positively correlated (Grossman, 1996). A key question is why most type I chondrules are alkali-poor. Hewins et al. (1997) showed that the finest grained, i.e., least heated, type I chondrules in Semarkona are slightly superchondritic in Na and K. The fact that they also contain abundant troilite-kamacite droplets shows that the volatiles were present before melting. Their alkali abundances, which are just slightly higher than bulk Semarkona, may therefore represent those of the Semarkona parent reservoir. A few coarse-grained type IA chondrules in Semarkona also have very high Na and K (Jones and Taylor, 1989 and Fig. 10a) and these also contain Na-rich augite, suggesting that the alkalis were in the melt at the time of augite crystallization. Thus type I chondrules may well have experienced evaporation from chondritic precursors.

We compare Semarkona chondrules (Jones and Scott, 1989; Jones 1990, 1994, 1996) with our experimental residues, normalizing the chondrules to Semarkona bulk composition (Jarosewich, 1990) and the charges to the composition of the starting material. We plot  $K/K_o$  vs.  $(Na/K)/(Na/K)_o$  (Fig. 10a), and see both similarities and differences between the chondrules and evaporative residues. Most of the type II chondrules in Semarkona have two to three times chondritic abundances of alkalis and show no evidence of evaporation. However, some chondrules in Figure 10a, including more than half the type Is, fall close to the trend line of the experimental residues, consistent with evaporation. Most of the remaining type I chondrules, though depleted in K, have higher Na/K ratios than the experimental residues. One possible explanation of this is sec-

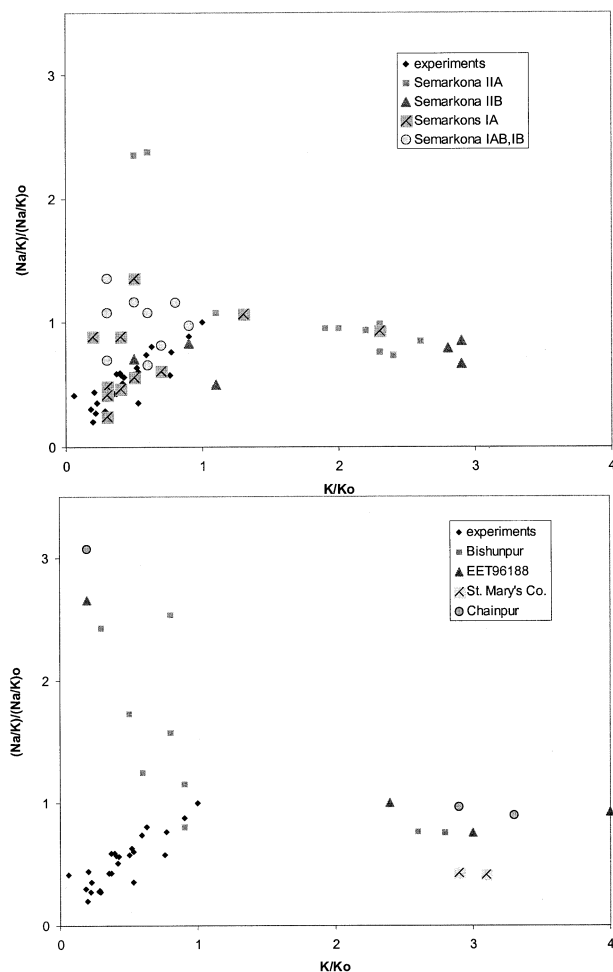


Fig. 10. K vs. Na for chondrules and experimental residues. (a) Semarkona type I and II chondrules (Jones, 1996, etc.) are normalized to the bulk Semarkona value (Jarosewich, 1990). Some type I chondrule data follow the evaporative loss trend of the experiments, though some are more Na-rich. Type II chondrules are superchondritic in K and Na. (b) Type I chondrules only, in slightly metamorphosed (3.1 to 3.4) chondrites, Bishunpur, EET 96188, Chainpur and St. Mary's County (Alexander et al., 2000). Some (Bishunpur) are K-poor but enriched in Na. Most of these type I chondrules have alkali contents similar to those of type II chondrules. This suggests secondary modification, possibly in the nebula for Bishunpur, and in the parent body for the higher grade chondrites.

ondary addition of Na after evaporative loss. Alexander (1994) and Grossman et al. (2002) observed rather similar distributions of Na and K (their Fig. 4 and 9, respectively). Alexander (1994) argued that Na redistribution could occur at very low metamorphic temperatures.

In Figure 10b we plot analyses by Zanda and Bourot-Denise of type I chondrules in LL3.1 Bishunpur (Alexander et al., 2000), as well as EET 96188 (L/LL3.2), St. Mary's County (LL3.3) and Chainpur (LL 3.4) chondrite, to look for effects of parent body modification. Unlike the Semarkona chondrules, these data do not plot near the evaporation trend, except for a couple from the lowest grade chondrite, Bishunpur. One group, mainly from Bishunpur, is depleted in K but has very high Na/K ratios (Fig. 10b). The other group of type I chondrules is

highly enriched in K and moderately to highly enriched in Na, with alkali concentrations resembling those of type II chondrules in Semarkona. In more metamorphosed chondrites (LL4,5), type I and II chondrules do not differ significantly in alkali concentrations (McCoy et al., 1991), and would lie between chondritic (1,1) and the field for Semarkona type II chondrules in Figure 10b. This confirms that alkali redistribution occurred during parent body metamorphism. Possibly the more Na-rich Semarkona type I chondrules and the similar Bishunpur chondrules show the beginnings of the parent body metasomatic effect superimposed on a volatile loss trend (Alexander, 1994; Grossman et al., 2000; Grossman et al., 2002).

Grossman (1996) and Grossman et al. (2000, 2002) studied the distribution of Na in Semarkona chondrules and found enrichment of Na in mesostasis near the chondrule surface in many chondrules. They also found Na depletion regions at the surfaces of all fine-grained, non-porphyrific chondrules. Grossman et al. (2002) found that many Semarkons type I chondrules (at least 15%) are zoned from core to rim, consistent with loss of elements like Ca, and gain of alkalis and water. The composition trend for mesostasis in these chondrules goes from very alkali-poor with chondritic ratios to high Na/K and in some cases to alkali-rich chondritic. Thus K may have been re-introduced even in K-depleted chondrules. Bishunpur is much less hydrothermally altered than Semarkona, but also shows alkali enrichment gradients near chondrule margins (Alexander et al., 2000). Furthermore glass inclusions inside chondrule olivine phenocrysts, which should have been protected from contact with parent-body fluids also lack K isotopic fractionation (Alexander et al., 2000; Grossman and Alexander, 2000). Though parent body metasomatism/metamorphism may have modified some volatile-depleted chondrules in Semarkona and Bishunpur, back reaction with alkali-rich nebular gas was probably the dominant influence on their alkali distributions and their K isotopic compositions.

If chondrules exchanged their K isotopes with ambient gas and lost the mass fractionation signatures of evaporation during melting, a source for the high concentration of K in the gas is needed. The calculated K content in the canonical nebula gas based on solar abundances is far too low for any significant exchange to happen. Provided that dust can be concentrated with respect to gas in the protoplanetary disk, transient high temperature events can evaporate fine grains while aggregates are melted (Wood, 1985; Hewins, 1989; etc.). In the limit, with very high amounts of dust evaporated, high alkali pressure in the gas means alkali loss from the chondrule melts would be prevented, and recondensation of the lost volatiles into the melt droplets would be possible, perhaps as in type II chondrules. We discuss the relation of chondrule formation models to dust enrichment in more detail below.

#### 4.2.2. Application to type II chondrules

In carbonaceous chondrites, there is a complementarity of composition between (type I) chondrules and matrix (Palme and Klerner, 2000), but in UOC like Semarkona, there is a certain complementarity between volatile-poor and volatile-rich type I and type II chondrules. Type II chondrules with volatile elements in superchondritic proportions (Jones 1990, 1996 Fig. 10a) have little in common with our ideal nebular

chondrules. The apparent absence of volatile loss from type II chondrules is not easily explicable in models for their origin in the canonical nebula. Nagahara et al. (1994) suggested higher ambient pressure than for type I chondrules, but it is difficult to boost nebular pressures much above typical values (Connolly and Love, 1998) and the 1 atm. required in the Yu and Hewins (1998) experiments would require an extremely massive disk and/or very high accretion rates. Sears et al. (1996) suggested less intense heating (lower temperature and/or shorter time) than for type I chondrules, whose compositions arose because of extensive evaporation. Flash heating has been a popular hypothesis to explain high volatile content in type II chondrules (e.g., Wasson, 1993). The basic assumption is that very fast heating could have prevented volatile elements from escaping chondrule materials through evaporation. We have shown that Na loss can be suppressed with rapid heating and cooling, which might be taken as supportive of the flash heating scenario, but 1 atm total pressure and high  $fO_2$  are needed if this is to work (Yu and Hewins, 1998). The flash heating scenario is incompatible with the current most popular chondrule-forming mechanism, shock wave heating where heating times are long (Desch and Connolly, 2002), and the high pressures could perhaps be explained only by planetary origins for chondrules (e.g., Kitamura and Tsuchiyama, 1996; Chen et al., 1998).

The possibility of type II chondrule formation in environments with high oxygen fugacities to minimize Na loss has long been considered, e.g., by Grossman (1988), following the work of Tsuchiyama et al. (1981) who showed a dependence of evaporation rate of Na on  $pO_2^{-1/4}$  in 1 atm experiments. At the lowest gas pressure employed in our study where no  $H_2$  was introduced, the  $fO_2$  is close to  $2 \times 10^{-6}$  atm. This value is roughly ten orders of magnitude higher than the canonical value (Rubin et al., 1988), five orders of magnitude higher than the Grossman (1988) estimation of  $\sim 10^{-10}$  atm to prevent Na loss, and two orders of magnitude higher than the  $fO_2$  at which Yu and Hewins (1998) achieved the highest Na retention in their 1 atm flash heating experiments. Yet, at this  $fO_2$  level, near Rayleigh fractionation of K isotopes is observed and Na and K loss is very fast. Consider that canonical nebula pressure is estimated to be only  $\sim 10^{-5}$  atm (Wood and Morfill, 1988), and that in the same pressure range the sample flash heated and cooled at  $5000^\circ C/h$  (most favorable condition to keep Na in 1 atm experiments) has lost approximately 40% of Na and 25% of K: it is clear that flash heating alone or in conjunction with high oxygen fugacity could not effectively prevent volatile loss.

The oxygen fugacity of the gas may control the amount of Na lost, if a chondrule melt evaporates in a high pressure environment, without removal of the evolved vapor, and equilibrium between the melt and the gas is approached. However, evaporation at low pressure is a highly dynamic process, and the composition of the melt itself and the vapor it evolves is likely to be more important to alkali loss than the initial ambient gas. This would be especially true in a highly dust-enriched nebular system. In a furnace there is an oxygen fugacity intrinsic to the evaporating charge, that cannot be experimentally controlled (Blander et al., 1970; Hashimoto, 1990). In our experiments, while evaporation rates are very different in higher pressures of air and hydrogen, they approach one another at low pressures, despite very different nominal oxygen fugacities. Thus, though the oxygen fugacity of ambi-

ent gas in chondrule-forming environments has been much discussed, partial pressures of the evaporating species and total pressure are certainly more important to the evaporation process.

High gas pressure might be invoked to reduce the volatile loss from chondrules and produce type II chondrules. However, higher hydrogen pressure enhances loss and K isotopes would still remain a problem: our experimental results show that even though high gas pressures hamper K isotopic mass fractionations, they do not totally eliminate them, contrary to what we see in natural chondrules (Humayun and Clayton, 1995; Alexander et al., 2000; Alexander and Grossman, 2000). It is, therefore, highly unlikely that suppression of either evaporation or K isotopic fractionation in chondrules is caused solely by gas pressure when melting occurred. Alexander et al. concluded that even when K was lost (from type I chondrules) there was subsequent exchange of K isotopes between chondrules and the gas, which must have had high partial pressures of K and other volatiles.

A chondrule melt of chondritic composition may be modified by recondensation in a gas with high partial pressures of moderately volatile elements. Alkali gain rather than loss has been demonstrated with 1 atm experiments with vapor and silicate melts (Biggar, 1986; Lewis et al., 1993; Georges et al., 2000), silicate glasses (Ikeda and Kimura, 1985) and even silicate crystals (Brown, 1967). In the work of Georges et al.,  $P_K$  was close to  $10^{-3}$  atm and rapid modification of the potassium isotopic composition of the charges was demonstrated. Condensation of Si into silicate melt has also been demonstrated at low pressures (Tissandier et al., 2000). There is no reason to doubt that if the partial pressure of alkalis were significantly raised when chondrules were formed, chondrules could retain high alkali contents, or could have gained K by recondensation, and have isotopic mass fractionation suppressed.

We have considered two possible explanations for the superchondritic compositions of type II chondrules. One possible interpretation of this is that the Semarkona parent reservoir was superchondritic, having about twice the Semarkona or Orgueil K/Si ratio (Jarosewich, 1990), and its chondrules were slightly to very highly depleted in alkalis during melting. Another possible interpretation is that the type II chondrules were derived from chondritic precursor material and enriched in alkalis by condensation (or secondary alteration). The first suffers from a mass balance problem: it is necessary to enrich the K/Si ratio over the CI value for a nebular reservoir of considerable size. Enrichment of alkalis in type II chondrules by recondensation of vapor produced by evaporation of dust grains therefore deserves serious consideration.

#### 4.2.3. Origin of type I and II chondrules

What is the cause of the differences between type I and type II chondrules, mainly environmental differences or mainly thermal history differences? Sears et al. (1996) proposed that the chondrule sequence IIA - IB - IA was due to evaporation of different intensities and the plausibility of this argument, at least as far as bulk and mineral compositions are concerned, has been demonstrated experimentally (Cohen et al., 2000). Our current experiments show that chondrules heated for 40 min in

low pressure hydrogen would be almost free of alkalis, and long heating times are consistent with shock heating (Desch and Connolly, 2002). If chondrules formed in some nebular environment, high partial pressures of alkalis are necessary to varying extents, to preserve some alkalis even in type I chondrules, and to exchange K isotopes. Different intensity heating extents in a dusty region which developed moderately high partial pressures, would not explain superchondritic alkalis in type IIs, and we would expect a continuum of alkali concentrations, not a bimodal distribution. However, a range of partial pressures would yield a bimodal distribution with chondritic to superchondritic K where  $pK$  exceeded the equilibrium value, and lower values otherwise. The tendency for these other values to be very low, and the lack of a bimodal distribution of FeO in chondrules (Sears et al., 1996) is consistent with the very much (at least 18 times) faster evaporation of alkalis than FeO, etc. (Cohen, 2002). We therefore suggest that environmental factors are more important than thermal history.

Any mechanism which favors higher partial pressures of the lithophile elements in the ambient gas will favor production of type II chondrules at the expense of type I. A well known way of achieving this is the heating of a concentration of solids within a domain of the solar nebula (Wood, 1985; Wood et al., 1989; Hewins, 1989; Ebel and Grossman, 2000; etc.). The high partial pressures of K and other moderately volatile elements could have been achieved when aggregates were accompanied by abundant dust which vaporized as the aggregates melted to form chondrules. Such differences in dust fraction are necessary, unless under some circumstances, separation of the vapor cloud from a small concentration of chondrules becomes important, resulting in evaporation and Type I chondrules.

The scenario of control of chondrule volatiles by high partial pressures in ambient gas places chondrule formation in environments where the solid/gas ratio is much enhanced over canonical values. Models of chondrule formation which explain high solid concentrations include transient atmospheres and collision clouds (Wood et al., 1989; Podolak et al., 1993; Kitamura and Tsuchiyama, 1996), and the planetesimal bow-shock model (Hood, 1998; Weidenschilling et al., 1998). Evaporation of dust concentrated 500 times would be required to stabilize Na at the levels found in chondrules (Ebel and Grossman, 2000) and Georges et al. (2000) argue for a similar enhancement of  $P_K$ .

The conditions required for the suppression of evaporation from volatile-rich chondrule melts in nebular domains are similar to those in some planetary and condensation models for chondrules. We consider that the K data for chondrules are not incompatible with an origin by melting of concentrations of aggregates in the nebula, and that textural and isotopic complexities also favor the remelting of condensate aggregates over the other models, for most chondrules.

## 5. CONCLUSIONS

1. The evaporation rate of Na is higher than that of K from chondrule-like silicate melts. Evaporation rates of Na and K increase with higher hydrogen pressure.
2. Rayleigh fractionation of K isotopes is observed for vacuum evaporation. With higher pressure of air or hydrogen  $\delta^{41}K$  in the evaporative residue decreases, because of back reac-

tion with the gas. With long heating duration, release of a small amount of light K condensed within the furnace is sufficient to further reduce  $\delta^{41}\text{K}$ .

3. Type I chondrules could have formed from alkali-rich precursors and experienced evaporation during melting. Though alkali-depleted, they do not have the positive  $\delta^{41}\text{K}$  expected for free evaporation. They are interpreted to have formed in a gas with sufficiently high K pressures that isotopic equilibrium was achieved between the chondrule melts and the gas. Readdition of Na to some type I chondrules in Semarkona and Bishunpur is probable, while in higher grade chondrites they incorporated both K and Na.
4. Type II chondrules did not experience evaporation, as they have superchondritic abundances of alkalis. They could have formed in a gas with higher concentrations of condensable elements than in the case of type I chondrules, due to extensive evaporation of fine-grained dust.

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## REFERENCES

- Alexander C.M. O'D. (1994) Trace element distributions within ordinary chondrite chondrules: Implications for chondrule formation conditions and precursors. *Geochim. Cosmochim. Acta* **58**, 3451–3467.
- Alexander C. M. O'D. (1996) Recycling and volatile loss in chondrule formation. In *Chondrules and the Protoplanetary Disk* (eds. R. H. Hewins, R. H. Jones, and E. R. D. Scott), pp. 233–242. Cambridge Univ. Press, Cambridge.
- Alexander C.M. O'D. (2001) Exploration of quantitative kinetic models for the evaporation of silicate melts in vacuum and in hydrogen. *Meteor. Planet. Sci.* **36**, 255–284.
- Alexander C. M. O'D. and Grossman, J.N. (2000) The K isotopes in Semarkona chondrules. *Lunar Planet. Sci.* XXXI, **1850**, pdf.
- Alexander C.M. O'D., Grossman J.N., Wang J., Zanda B., Bourot-Denise M., and Hewins R.H. (2000) The lack of potassium isotopic fractionation in Bishunpur chondrules. *Meteor. Planet. Sci.* **35**, 859–868.
- Alexander C.M. O'D., Boss A.P., and Carlson R.W. (2001) The early evolution of the inner solar system: A meteoritic perspective. *Sci.* **293**, 64–68.
- Allègre C., Manhès G., and Lewin E. (2001) Chemical composition of the Earth and the volatility control on planetary genetics. *Earth Planet. Sci. Lett.* **185**, 49–69.
- Biggar G. (1986) Chemistry of protopyroxene, orthopyroxene, and pigeonite, crystallised from liquids close to chondrule compositions. *Bull. Min.* **109**, 529–541.
- Blander M., Keil K., Nelson L. S., and Skaggs S. R. (1970) Heating of basalts with a carbon dioxide laser. *Sci.* **170**, 435–438.
- Brown W. L. (1967) A reinterpretation of monalbite. *Min. Mag.* **36**, 80–82.
- Chen J. H., Papanastassiou D. A., and Wasserburg G. J. (1998) Re-Os systematics in chondrites and the fractionation of the platinum group elements in the early solar system. *Geochim. Cosmochim. Acta* **62**, 3379–3392.
- Cohen B. A. (2002) Chondrule formation by open system melting of nebular condensates. Ph.D. thesis, Rutgers University.
- Cohen B. A., Hewins R. H., and Yu Y. (2000) Evaporation in the solar nebula and chondrule texture-composition relations. *Nature* **406**, 600–602.
- Connolly H. C. and Love S. G. (1998) The formation of chondrules: Petrologic tests of the shock wave model. *Sci.* **280**, 62–67.
- Desch S. J. and Connolly H. C. Jr. (2002) A model of the thermal processing of particles in solar nebula shocks: Application to the cooling rates of chondrules. *Meteor. Planet. Sci.* **37**, 183–208.
- Ebel D. S. and Grossman L. (2000) Condensation in dust-enriched systems. *Geochim. Cosmochim. Acta* **64**, 339–366.
- Ferrière A., Lestrade L., and Rouanet A. (1994) In *Advances in Inorganic Films and Coatings; Proc. 8th CIMTEC* (ed. P. Vincenzi), pp. 319–326. Florence, Italy.
- Georges P., Libourel G., and Deloué E. (2000) Experimental constraints on alkali condensation in chondrule formation. *Meteor. Planet. Sci.* **35**, 1183–1188.
- Gibson E. K. Jr. and Hubbard N. J. (1972) Thermal volatilization studies on lunar samples. *Proc. Lunar Sci. Conf. Third* p. 2003:2014.
- Gooding J. L. and Muenow D. W. (1977) Experimental vaporization of the Holbrook chondrite. *Meteor.* **12**, 401–408.
- Grossman J. N. (1988) Formation of chondrules. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews), pp. 680–696. University of Arizona Press, Tucson.
- Grossman J. N. (1996) Chemical fractionations of chondrites: signatures of events before chondrule formation. In *Chondrules and the Protoplanetary Disk* (eds. R. H. Hewins, R. H. Jones, and E. R. D. Scott), pp. 243–253. Cambridge University Press.
- Grossman J. N., Alexander C.M. O'D., Wang J., and Brearley A. J. (2000) Bleached chondrules: evidence for widespread aqueous processes on the parent asteroids of ordinary chondrites. *Meteor. Planet. Sci.* **35**, 467–486.
- Grossman J.N., Alexander C.M. O'D., Wang J., and Brearley A. J. (2002) Zoned chondrules in Semarkona: Evidence for high- and low-temperature processing. *Meteor. Planet. Sci.* **37**, 49–73.
- Hewins R. H. (1989) The evolution of chondrules. *Proc. NIPR Symp. Antarct. Meteorites.* **2**, 202–222.
- Hewins R. H., Yu Y., Zanda B., and Bourot-Denise M. (1997) Do nebular fractionations, evaporative losses, or both, influence chondrule compositions? *Antarct. Meteor. Res.* **10**, 294–317.
- Hood L. L. (1998) Thermal processing of chondrule precursors in planetesimal bow shocks. *Meteor. Planet. Sci.* **33**, 97–107.
- Humayun M. and Clayton R. N. (1995) Potassium isotope cosmochemistry: Genetic implications of volatile element depletion. *Geochim. Cosmochim. Acta* **59**, 2131–2148.
- Humayun M. and Cassen P. (2000) Processes determining the volatile abundances of the meteorites and terrestrial planets. In *Origin of the Earth and Moon* (eds. R. M. Canup and K. Righter), pp. 3–23. U. Arizona Press, Tucson.
- Ikeda Y. and Kitamura M. (1985) Na-Ca zoning of chondrules in Allende and ALHA 77003 carbonaceous chondrites. *Meteor.* **20**, 670–671.
- Jarosewich E. (1990) Chemical analyses of meteorites: A compilation of stony and iron meteorite analyses. *Meteor.* **25**, 323–337.
- Jones R. H. (1990) Petrology and mineralogy of type II, FeO-rich chondrules in Semarkona (LL3.0): Origin by closed-system fractional crystallization, with evidence for supercooling. *Geochim. Cosmochim. Acta* **54**, 1785–1802.
- Jones R. H. (1994) Petrology of FeO-poor, porphyritic pyroxene chondrules in the Semarkona chondrite. *Geochim. Cosmochim. Acta* **58**, 5325–5340.
- Jones R. H. (1996) FeO-rich, porphyritic pyroxene chondrules in unequilibrated ordinary chondrites. *Geochim. Cosmochim. Acta* **60**, 3115–3138.
- Jones, R. H. and Scott, E. R. D. (1989) Petrology and thermal history of type IA chondrules in the Semarkona LL3.0 chondrite. In *Proc. 19th Lunar Planet. Sci. Conf.* 523–536, Lunar and Planetary Institute, Houston.
- Jones R. H., Lee T., Connolly H. C. Jr. Love S. G. and Shang H. (2000) Formation of chondrules and CAIs: Theory versus observation. In *Protostars and Planets IV*. (eds. V. G. Mannings, A. P. Boss and S. S. Russell) pp. 927–962. University of Arizona Press.
- Kitamura M. and Tsuchiyama A. (1996) Collision of icy and slightly differentiated bodies as an origin for unequilibrated ordinary chondrites. In *Chondrules and the Protoplanetary Disk* (eds. R. H. Hewins, R. H. Jones and E. R. D. Scott) pp. 319–326 Cambridge University Press.

- Kreutzberger M. E., Drake M. J. and Jones J. H. (1986) Origin of the earth's Moon: constraints from alkali volatile trace elements. *Geochim. Cosmochim. Acta* **50**, 91–98.
- Krot A. N., Meibom A., Russell S. S., Alexander C.M. O'D., Jeffries T. E., and Keil K. (2001) A new astrophysical setting for chondrule formation. *Science* **291**, 1776–1779.
- Lewis R. D., Lofgren G. E., Franzen H. F., and Windom K. E. (1993) The effect of Na vapor on the Na content of chondrules. *Meteor.* **28**, 622–628.
- Masuda A. and Tsuyoshi T. (1979) Experimental studies on behavior of major and minor lithophile elements in vaporization under evacuated condition. *Meteor.* **14**, 13–28.
- McCoy T. J., Scott E. R. D., Jones R. H., Keil K., and Taylor G. J. (1991) Composition of chondrule silicates in LL3–5 chondrites and implications for their nebular history and parent body metamorphism. *Geochim. Cosmochim. Acta* **55**, 601–619.
- McSween H. Y. Jr. (1977) Chemical and petrographic constraints on the origin of chondrules and inclusions in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **41**, 1843–1860.
- Nagahara H., Kushiro I., and Mysen B. O. (1994) Evaporation of olivine: Low pressure phase relations of the olivine system and its implication for the origin of chondritic components in the solar nebula. *Geochim. Cosmochim. Acta* **58**, 1951–1963.
- Nagahara H. and Ozawa K. (2000a) Isotopic fractionation as a probe of heating processes in the solar nebula. *Chem. Geol.* **169**, 45–68.
- Nagahara H. and Ozawa K. (2000b) The role of back reaction on chemical fractionation during evaporation of a condensed phase. *Lunar Planet. Sci.* **XXXI**, No. 1340.
- Palme H. and Klerner S. (2000) Formation of chondrules and matrix in carbonaceous chondrites. *Meteor. Planet. Sci.* **35**, A124.
- Podolak M., Prialnik D., Bunch T. E., Cassen P., and Reynolds R. (1993) Secondary processing of chondrules and refractory inclusions (CAIs) by gas dynamic heating. *Icarus*. **104**, 97–109.
- Rubin A. L., Fegley B., Brett R. (1988) Oxidation state in chondrules. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews), pp. 488–511. The University of Arizona Press.
- Sears D. W. G., Huang S., and Benoit P. H. (1996) Open-system behavior during chondrule formation. In *Chondrules and the Proto-planetary Disk* (eds. R. H. Hewins, R. H. Jones, and E. R. D. Scott), pp. 221–232. Cambridge Univ. Press, Cambridge.
- Shimaoka T. and Nakamura N. (1989) Vaporization of sodium from a partly molten chondritic material. *Proc. NIPR Symp. Antarct. Meteor.* **2**, 252–267.
- Shimaoka T. Nakamura N. (1990) Volatilization studies of alkali metals on a chondritic material. (V)—an effect of total pressure. *15<sup>th</sup> Symp. Antarc. Met.* 149–151.
- Shimaoka T. K., Miyano N., Baba T., Yamamoto K., and Nakamura N. (1994) Volatilization of alkali metals from the heated Murchison (CM2) meteorite. *Proc. NIPR Symp. Antarct. Meteor.* **7**, 164–177.
- Shirai T., Tachibana S., and Tsuchiyama A. (2000) Evaporation rates from Na<sub>2</sub>O-SiO<sub>2</sub> melt at 1 atm. *Lunar Planet. Sci.* **XXXI**, No. 1610.
- Shirley D. N. (1983) On the origin of oxygen isotopic variations in ordinary chondrite chondrules. *Meteor.* **18**, 396–398.
- Tissandier L., Libourel G., Toplis M. J., and Chaussidon M. (1998) Alkali volatilization at high temperature in silicate melts. *Meteor. Planet. Sci.* **33**, A154–A155.
- Tissandier L., Libourel G., Robert F., and Chaussidon M. (2000) SiO<sub>2</sub> condensation experiments and implications for presolar materials. *Lunar Planet. Sci.* **XXXI**, No. 1553.
- Tsuchiyama A., Nagahara H., and Kushiro I. (1981) Volatilization of sodium from silicate melt spheres and its application to the formation of chondrules. *Geochim. Cosmochim. Acta* **45**, 1357–1367.
- Tsuchiyama A., Tachibana S., and Takahashi T. (1999) Evaporation of forsterite in the primordial solar nebula; rates and accompanied isotopic fractionation. *Geochim. Cosmochim. Acta*. **63**, 2451–2466.
- Wang J., Yu Y., Alexander C. M. O'D., and Hewins R. H. (1999) The influence of oxygen and hydrogen on the evaporation of K. *Lunar Planet. Sci.* **XXX**, No. 1778.
- Wang J., Davis A. M., Clayton R. N., Mayeda T. K., and Hashimoto A. (2001) Chemical and isotopic fractionation during the evaporation of the FeO-MgO-SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> rare earth element melt system. *Geochim. Cosmochim. Acta* **65**, 479–494.
- Wasson J. T. (1993) Constraints on chondrule origin. *Meteor* **28**, 14–28.
- Weidenschilling S. J., Marzari F., and Hood L. L. (1998) The origin of chondrules at Jovian resonances. *Science* **279**, 681.
- Wood J. A. (1985) Meteoritic constraints on processes in the solar nebula. In *Protostars and Planets II* (eds. D. C. Black and M. S. Matthews), pp. 687–702. Univ. Arizona Press.
- Wood J. A. and Morfill G. E. (1988) A review of solar nebula models. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews), pp. 329–347. Univ. of Arizona Press.
- Wood J. A., Hashimoto A., and Holmberg B. B. (1989) Chondrules as near-equilibrium assemblages that formed in fractionated systems. *Lunar Planet. Sci.* **XX**, 1215–1216.
- Xue S., Yu Y., Hewins R. H., Hall G. S., and Herzog G. F. (1996) Zinc losses from and zinc isotopic abundances in residues formed by heating of Zn, ZnO, ZnS and Zn-doped silicate glass. *Lunar Planet. Sci.* **XXVII**, 1461–1462.
- Young E. D., Nagahara H., Mysen B. O., and Audet D. M. (1998) Non-Rayleigh oxygen isotope fractionation by mineral evaporation: Theory and experiments in the system SiO<sub>2</sub>. *Geochim. Cosmochim. Acta* **62**, 3109–3116.
- Yu Y. and Hewins R. H. (1998) Transient heating and chondrule formation: Evidence from sodium loss in flash heating simulation experiments. *Geochim. Cosmochim. Acta* **62**, 159–172.
- Yu Y., Wang J., Zanda B., Alexander C. M. O'D., Bourot-Denise M., and Hewins R. H. (1998) Mass fractionation of K isotopes in chondrule evaporation experiments. *Lunar Planet. Sci.* **XXIX**, No. 1642.