

Alkali elemental and potassium isotopic compositions of Semarkona chondrules

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Abstract–We report measurements of K isotope ratios in 28 Semarkona chondrules with a wide range of petrologic types and bulk compositions as well as the compositions of CPX-mesostasis pairs in 17 type I Semarkona chondrules, including two chondrules with radial alkali zonation and 19 type II chondrules. Despite the wide range in K/Al ratios, no systematic variations in K isotopic compositions were found. Semarkona chondrules do not record a simple history of Rayleigh-type loss of K. Experimentally determined evaporation rates suggest that considerable alkali evaporation would have occurred during chondrule formation. Nevertheless, based on Na CPX-mesostasis distribution coefficients, the alkali contents of the cores of most chondrules in Semarkona were probably established at the time of final crystallization. However, Na CPX-mesostasis distribution coefficients also show that alkali zonation in type I Semarkona chondrules was produced by entry of alkalis after solidification, probably during parent body alteration. This alkali metasomatism may have gone to completion in some chondrules. Our preferred explanation for the lack of systematic isotopic enrichments, even in alkali depleted type I chondrule cores, is that they exchanged with the ambient gas as they cooled.

INTRODUCTION

Volatile elements can, in principal, provide some of the best constraints on the nature of the chondrule formation process and of chondrule precursors. For instance, volatilepoor chondrules may have formed either from volatile-poor material or by partial evaporation of volatile-rich material during melting. Given their abundance and volatility, the alkalis are potentially the most useful in this regard.

At the liquidus temperatures of most porphyritic chondrules (1700–2100 K) (Hewins and Radomsky 1990), experimental and thermodynamic data indicate that Na and K should be lost very rapidly in a nebular environment (Ebel and Grossman 2000; Yu et al. 2003). However, many chondrules contain significant concentrations of these elements. Alkali abundances in ordinary chondrite (OC) porphyritic chondrules vary by almost three orders of magnitude, but tend to be lower in the most refractory (i.e., high Al/Si or Ca/Si) type I chondrules (Jones and Scott 1989; Jones 1990; Jones and Lofgren 1993; Alexander 1994; Jones 1994, 1996).

If the range of alkali abundances in chondrules were produced by variable degrees of evaporation under Rayleigh conditions, K should exhibit large heavy-isotope enrichments in chondrules with low K abundances. Experiments show that Rayleigh-type evaporative loss of K from synthetic chondrules produces rapid increases in δ^{41} K, even at modest levels of evaporation (Yu et al. 2003). This has been confirmed through measurements of cosmic spherules, which show that large isotopic fractionations, consistent with Rayleigh-type behavior, are associated with evaporative K loss during atmospheric entry heating (Taylor et al. 2005). The degree of isotopic fractionation as a function of the fraction of K lost in both the experiments and the cosmic spherules are consistent with a Rayleigh fractionation factor α that is equal to the inverse square-root of the ratio of the masses of the K isotopes. This value of α for K is assumed throughout the remainder of this paper.

To date, no systematic K isotopic fractionations have been found in chondrules (Humayun and Clayton 1995a; Alexander and Grossman 2000; Alexander et al. 2000). Two possible explanations for this lack of isotopic fractionation are: 1) volatile loss was suppressed by high fO_2 in the nebula, and 2) evaporation of K, enhanced by H_2 , occurred under non-Rayleigh conditions. However, experiments have shown that neither explanation is able to sufficiently suppress K evaporation and isotopic fractionation under realistic nebular conditions (Yu et al. 2003). A third explanation for the lack of measurable K isotopic fractionation in chondrules is that the alkalis have been affected by secondary processes, such as parent body metamorphism or aqueous alteration. The alkalis are very mobile even at modest temperatures and it is possible that exchange with fine-grained rims and interchondrule matrix (henceforth referred to collectively as "matrix") during parent body processing has erased the isotopic signature of evaporation.

In ordinary chondrites, equilibration between chondrules and matrix is almost complete by petrologic type 3.5-3.6 (Hewins 1991; McCoy et al. 1991; DeHart et al. 1992). Previous measurements of K isotopes were conducted on Bishunpur (L/LL3.1) and Allende (CV3) chondrules (Humayun and Clayton 1995a; Alexander et al. 2000). Allende chondrules have devitrified, chemically altered mesostasis that is enriched in halogens; they also show Fe/Mg zoning of olivine (Ikeda and Kimura 1995; Ash et al. 1999) consistent with modification during parent body processing (Krot et al. 1995, 1997; Bonal et al. 2004). Bishunpur is a relatively robust meteorite, suggesting that it experienced some sintering (metamorphism). Grossman and Brearley (2005) placed Bishunpur in the upper part of subtype 3.1 (type 3.15), partly because the alkali content of glass in type I chondrules was, on average, over four times higher than some type 3.0 chondrites as a consequence of parent body metamorphism.

Semarkona (LL3.0) is the least metamorphosed ordinary chondrite known (Grossman and Brearley 2005). Its matrix has alkali/Al and S/Si ratios that are the highest of any of the OCs (Alexander 1995; Grossman and Brearley 2005) and its type I chondrule mesostases are accordingly low in alkalis. Despite the fact that Semarkona has experienced extensive alteration of its matrix (Hutchison et al. 1987; Alexander et al. 1989) and some chondrules (Hutchison et al. 1987; Grossman et al. 2000, 2002), it has apparently experienced the least exchange between matrix and chondrules.

Nevertheless, some Semarkona chondrules may have experienced secondary modification of alkalis at either high or low temperature. Many type I Semarkona chondrules exhibit alkali zonation (Matsunami et al. 1993; Nagahara et al. 1999; Grossman et al. 2002), with mesostasis near their surfaces being richer in alkalis than that in their cores. Matsunami et al. (1993) and Nagahara et al. (1999) suggested that this zonation is due to re-entry of alkalis as chondrules cooled after formation. Given the mobility of Na, preservation of such zoning would imply very rapid cooling and/or recondensation at temperatures that were well below the solidus (Alexander 1995). However, Grossman et al. (2002) found that isotopically heavy H (presumably present as OH or H₂O) and halogen abundances in zoned chondrules correlate with the alkali abundances, leading them to conclude that some alkalis entered chondrules during aqueous alteration on the Semarkona parent body.

Type I chondrules also have alkali contents that are related to mineralogy: pyroxene-rich chondrules (type IB) have higher alkali and Si contents than olivine-rich chondrules (type IA) (Grossman et al. 2002; Libourel et al. 2003). The observation that Na in clinopyroxene (CPX) correlates with Na in surrounding glass, consistent with igneous partitioning (Jones 1994; Libourel et al. 2003), is evidence that alkalis were present in chondrules at high temperature. This has led Libourel et al. (2003) to the conclusion that the process responsible for chemical zoning must be identical to that which produced differences between type IA and IB chondrules, hypothesized to be recondensation of moderately volatile elements and Si into chondrules at supersolidus temperatures.

In an attempt to reconcile these conflicting observations and interpretations and search for K isotopic fractionation in the most pristine chondrules, we present measurements of elemental and K isotopic compositions of 28 Semarkona chondrules. In addition, we report the compositions of CPX and adjacent mesostasis in 17 type I and 19 type II chondrules. Here the boundary between type I and type II chondrules is taken to be Fa or Fs = 3 mol% (Grossman and Brearley 2005). In particular, we present detailed petrologic and chemical observations of CPX and mesostasis compositions in two alkali zoned type I chondrules.

EXPERIMENTAL METHODS

The Semarkona chondrules selected for K isotopic study exhibit a wide range of compositions and textures. They included approximately equal numbers of type I and II chondrules. One dark-zoned chondrule was measured, as were two matrix areas and a melt inclusion in a chondrule olivine. Using previously acquired elemental maps, care was taken to only analyze interior regions of chondrules; in zoned chondrules only alkali-depleted glass areas were measured. These areas are most likely to preserve the pre-accretionary compositions of the chondrule glasses.

Electron microprobe data for mesostasis in these chondrules were acquired on the JEOL 8900 electron microprobe at the U.S. Geological Survey, Reston, Virginia. Most analyses were done using a $5 \times 5 \mu m$ rastered beam with 15 kV accelerating voltage and 20 nA beam current. Conventional silicate mineral standards were used and the data were reduced using the CITZAF method of (Armstrong 1995). Sodium loss due to the interaction of the electron beam with the sample is minimal under the experimental conditions used: Na was determined in the first 10 sec after the beam was unblanked and a low current density is produced by rastering the beam over 25 μm^2 .

Seventeen type I and nineteen type II chondrules in Semarkona were selected for analysis of coexisting CPX and mesostasis. The type I chondrules were selected on the basis of their low average atomic number in BSE images and classic type I textures (Scott and Taylor 1983). Their olivine and low-Ca pyroxene compositions were not determined. Because the CPX occurs as small crystals and thin overgrowths, it was analyzed by electron microprobe with a focused spot located at least 3 μ m from any grain boundary, a distance at which we determined that Na is not being fluoresced in surrounding glass. Two of the type I chondrules showed strong alkali zoning as described by Grossman et al. (2002). A series of mesostasis-CPX pairs were analyzed in each zoned chondrule, with the mesostasis area being as close to the CPX as practical, separated by no more than ~10 μ m.

The isotope analyses were performed using the Carnegie Cameca IMS 6f ion probe at a mass resolution of ~5000 needed to resolve ³⁹K from ²³Na¹⁶O and ⁴¹K from ²⁵Mg¹⁶O and ⁴⁰CaH. Operating conditions were 12.5 kV O⁻ primary beam and +10 kV secondary accelerating voltage with a 50 eV energy window and a 400 μ m field aperture. Both shaped (flat bottom) and focused primary beam modes were used, depending on the sizes of the areas that were analyzed. Primary beam currents ranged between 2 nA and 6 nA. Spot sizes for the two primary beam modes vary from ~20 μ m to <10 μ m, respectively. In a typical analysis, 50 to 100 cycles were acquired depending on the count rates, with counting times of one second on ³⁹K and five seconds on ⁴¹K. Other masses included in the analyses, Na, Al, and ³⁰Si, were counted for 1 sec.

The standard used to establish the K instrumental mass fractionation and the elemental sensitivity factors was a glass made from the USGS BHVO Hawaiian basaltic standard (K = 16,886 ppm). The absolute isotopic composition of the BHVO standard is not known, but within the accuracy of the analyses reported here, it is assumed that the K isotopic composition of the BHVO glass is that of bulk Earth and bulk chondrites. This is consistent with the results of Humayun and Clayton (1995a, 1995b), who found no significant variations between the K isotopic compositions of terrestrial rocks (including a Hawaiian basalt) and bulk chondrites. Consequently, all K isotopic compositions are referenced to the BHVO glass. Comparison of the BHVO glass with the synthetic NBS-610, -612, and -614 glasses show that they have similar isotopic compositions and that there is not a strong compositional dependence on the K instrumental mass fractionation (Alexander et al. 2000). This is consistent with the fact that, while chondrule mesostases compositions vary considerably (SiO₂ 44-77 wt%, Al₂O₃ 10-31 wt%), there are discernible systematic variations of K isotopic no compositions with the elemental compositions of mesostases.

Repeated analyses of the BHVO glass gave a standard deviation of ~0.6‰ for δ^{41} K. This is smaller than the standard deviation of 1.6‰ found in a more extensive previous study that included NBS-610, NBS-612, and NBS-614 glasses (Alexander et al. 2000). The δ^{41} K errors given in Table 1 reflect the uncertainty in the instrumental mass fractionation determined on the BHVO glass standard in this study and the

internal precision of each analysis. However, because the standard deviation of the BHVO analyses is less than in the previous study, it is possible the errors in Table 1 have been underestimated somewhat.

The Na/Al and K/Al ratios in the Semarkona chondrules determined by ion microprobe (IP) and by electron microprobe (EP) are on average in excellent agreement: (Na/Al)_{EP}/(Na/Al)_{IP} = 1.1 ± 0.2 and (K/Al)_{EP}/(K/Al)_{IP} = 0.96 ± 0.2 . The errors are the standard deviations in the ratios. There are no systematic variations between ion microprobe and electron microprobe results with the compositions of the mesostases. One factor contributing to the 20% standard deviations simply reflects that the areas analyzed by electron and ion microprobe are never identical and that chondrule mesostases, including crystallites, can be heterogeneous.

RESULTS

Bulk Mesostasis Compositions

The L chondrite-normalized alkali/Al ratios, (Na,K/Al)_L, vary by more than two orders of magnitude in the chondrules analyzed for their K isotopes (Tables 1 and 2), and the alkali abundances are highly correlated (Fig. 1). The L chondrite Na/Al and K/Al weight ratios are 0.574 and 0.0676, respectively (Wasson and Kallemeyn 1988). In general, type I chondrules have lower alkali abundances than type II chondrules, but there is considerable overlap. The range of alkali abundances and the highly correlated behavior between alkalis is similar to that seen in Bishunpur and other UOC chondrules (Grossman and Wasson 1982, 1983; Alexander 1994; Alexander et al. 2000). However, of the 11 Bishunpur chondrules analyzed by Alexander et al. (2000), only one had super-chondritic (Na,K/Al)_L ratios, and proportionally more of them had low $(Na,K/Al)_{I}$ ratios $((Na,K/Al)_{I} < 0.1)$. These differences reflect sampling biases. In the Bishunpur study, no attempt was made to analyze a representative suite of chondrules and samples are biased in favor of type I chondrules. The chondrules in the Semarkona study include examples of types I and II, and barred, porphyritic, and radial textures. There are correlations in the Semarkona mesostasis compositions between the $(Na,K/Al)_L$ ratios and the SiO₂ and Al₂O₃ contents (Fig. 2), and the Ca/Al ratios (Fig. 3).

Potassium Isotopes

Most of the Semarkona chondrules analyzed have K isotopic compositions within the range -3% to +3% (Fig. 4 and Table 1). The range of $\pm 3\%$ was also the 2 σ reproducibility of a number of standard glasses in a previous study (Alexander et al. 2000). Analyses from seven chondrules fall significantly outside of this $\pm 3\%$ range, but there is no systematic variation with (K/Al)_L ratio. Multiple analyses from two of these chondrules, Sem-6 and Sem-9,

Chondrule	Туре	Fa	Fs	(Na/Al) _L	(K/Al) _L	δ ⁴¹ K (‰)
Sem-1	POP/IIAB	17.0	15.3	1.5	2.0	3.5 ± 0.8
Sem-1	POP/IIAB	17.0	15.3	1.4	1.3	1.7 ± 0.6
Sem-2	POP/IIAB	7.7		1.4	2.2	3.7 ± 0.7
Sem-3	PO/IIA	13.0		1.2	1.4	3.9 ± 0.8
Sem-3	PO/IIA	13.0		1.2	1.4	3.6 ± 1.1
Sem-4	PO/IIA	13.7		1.2	1.6	2.2 ± 0.7
Sem-5	RP-PP/IIB		4.5	0.90	1.1	4.8 ± 0.8
Sem-5	RP-PP/IIB		4.5	0.92	1.1	2.4 ± 0.8
Sem-6 ^a	POP/IAB	1.0	1.5	0.11	0.062	5.4 ± 2.9
Sem-6 ^a	POP/IAB	1.0	1.5	0.13	0.097	17.8 ± 2.8
Sem-6 ^a	POP/IAB	1.0	1.5	0.14	0.067	0.0 ± 2.2
Sem-7	POP/IIAB	14.3	18.7	0.89	0.49	2.9 ± 0.9
Sem-8	PP/IB	3.2 ^b	2.9	0.20	0.059	1.6 ± 1.6
Sem-8	PP/IB	3.2 ^b	2.9	0.19	0.053	1.3 ± 1.9
Sem-8	PP/IB	3.2 ^b	2.9	0.22	0.15	-3.8 ± 2.0
Sem-9 ^a	PO/IIA	11.5	13.9	0.96	0.41	6.3 ± 1.2
Sem-9 ^a	PO/IIA	11.5	13.9	1.0	0.48	0.9 ± 0.9
Sem-9 ^a	PO/IIA	11.5	13.9	1.0	0.43	9.6 ± 0.8
Sem-9 ^a	PO/IIA	11.5	13.9	0.95	0.48	7.1 ± 1.0
Sem-10	BO/IA	0.9		0.20	0.15	2.0 ± 1.2
Sem-10	BO/IA	0.9		0.24	0.15	-2.1 ± 1.5
Sem-11 ^a	PP/IB	2.5	2.3	0.37	0.39	0.5 ± 1.2
Sem-12	PP/IB	3.0 ^b	2.4	0.19	0.062	8.2 ± 4.1
Sem-13	BO/IIA	18.7		1.3	1.8	0.9 ± 1.0
Sem-13	BO/IIA	18.7		1.7	2.4	2.9 ± 1.1
Sem-14	RP-PP/IIB		13.2	1.3	2.0	8.6 ± 1.8
Sem-15 ^a	PP/IB	2.7 ^b	2.4	0.59	0.39	-1.4 ± 1.1
Sem-16	POP/IIAB	13.4		0.064	0.035	2.4 ± 3.4
Sem-17	Dark zoned ^c	24.5		1.2	1.6	0.0 ± 1.3
Sem-18	PP/IB	1.5 ^d	2.3	0.13	0.061	10.0 ± 1.6
Sem-18	PP/IB	1.5 ^d	2.3	0.12	0.061	15.0 ± 2.0
Sem-19	PO/IA	1.3		0.15	0.12	2.4 ± 1.5
Sem-20	POP/IIAB	13.2	11.4	0.71	1.3	0.8 ± 0.7
Sem-21	RP/IIB		21.7	1.2	1.6	2.2 ± 0.8
Sem-22	?O/IIA	16.3		0.075	0.086	-1.2 ± 2.2
Sem-23	POP/IIAB	10.2		1.7	1.6	0.0 ± 0.6
Sem-24	PO/IA	1.4		0.0026	0.0049	-9.5 ± 3.8
Sem-25	POP/IIAB	5.3		0.84	0.98	0.2 ± 0.6
Sem-26	PP/IIB		3.2	0.84	0.41	5.6 ± 0.9
Sem-26	PP/IIB		3.2	0.74	0.36	5.2 ± 1.2
Sem-27	POP/IIAB	21.7	41.8	1.3	1.8	2.7 ± 0.7
Sem-28	PO/IIA	10.8		1.2	1.6	0.8 ± 0.9
Sem-28 (incl.)	PO/IIA	10.8		1.1	1.7	11.5 ± 1.2
Matrix				3.5	3.4	0.1 ± 0.8
Matrix				2.0	2.5	-0.3 ± 0.9

Table 1. Summary of the properties of the 28 Semarkona chondrules analyzed for their K isotopic compositions. The L chondrite-normalized (Na,K)/Al ratios are those measured by ion microprobe during the isotopic analyses.

^aZoned in alkalis, only core analyzed.

^bPoikilitic olivine.

^cHas a fine-grained PO core.

^dContains altered/partially resorbed olivine bars.

have ranges of 0–18‰ and 1–10‰, respectively. These chondrules are zoned in alkalis, but only the cores were analyzed and the K isotopes do not correlate with the small measured variations in K/Al ratios. Two chondrules, Sem-14 and Sem-24 with δ^{41} K = 9‰ and –10‰, respectively, have

only one analysis each, so their compositions must remain questionable. Two chondrules have two analyses each that are consistently heavy (Sem-18, $(K/Al)_L = 0.06$ and $\delta^{41}K = 10$, 15‰; Sem-26 $(K/Al)_L = 0.37$ and $\delta^{41}K = 5$, 6‰). Therefore, it seems possible that these two chondrules have indeed

Table 2. Analyses by electron microprobe of chondrule glasses analyzed for K isotopes (Table 1).

	Na ₂ O	MgO	Al_2O_3	SiO ₂	P_2O_5	Cl	K ₂ O	CaO	TiO ₂	Cr ₂ O ₃	MnO	FeO	Total
Name	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Sem-1	8.47	0.45	15.42	68.32	0.21	n.d	0.86	0.99	0.54	0.02	0.25	7.81	103.33
Sem-2	6.51	1.90	9.46	76.57	0.04	0.02	0.91	0.66	0.40	0.05	0.51	6.65	103.67
Sem-3	5.10	3.46	9.76	63.81	0.94	n.d	0.65	7.39	0.42	0.37	0.44	10.43	102.76
Sem-4	5.76	3.11	10.99	63.58	0.79	0.01	0.71	7.34	0.44	0.22	0.28	9.10	102.32
Sem-5	5.88	1.54	14.73	69.10	n.d	0.01	0.60	5.57	0.46	0.09	0.73	3.07	101.79
Sem-6	1.12	5.42	18.70	59.07	n.d	n.d	0.06	14.31	0.60	0.58	0.25	0.49	100.60
Sem-7	9.31	0.48	21.87	62.83	0.28	0.03	0.34	4.39	0.28	0.03	0.06	1.62	101.51
Sem-8	1.58	7.20	19.43	50.64	0.02	0.01	0.04	15.04	0.62	0.73	0.85	2.44	98.60
Sem-9	8.66	1.41	17.10	63.30	0.15	n.d	0.32	4.01	0.62	0.05	0.21	5.10	100.93
Sem-10	1.57	3.70	20.62	58.20	0.03	n.d	0.09	14.44	0.65	0.38	0.04	0.54	100.25
Sem-11	3.22	4.75	18.88	59.93	n.d	0.01	0.25	11.39	0.55	0.33	1.00	2.24	102.54
Sem-12	1.90	6.20	20.35	52.15	0.05	0.02	0.09	14.21	0.65	0.64	0.68	3.64	100.58
Sem-13	7.91	1.74	10.36	74.91	0.30	0.01	1.00	0.50	0.40	0.05	0.23	6.45	103.85
Sem-14	6.42	1.03	10.35	79.06	0.05	n.d	0.96	0.71	0.35	0.04	0.16	4.58	103.74
Sem-15	4.96	4.71	20.12	56.88	0.02	n.d	0.31	9.74	0.48	0.22	0.97	1.67	100.09
Sem-16	1.11	2.42	28.47	49.92	0.20	0.01	0.04	16.46	0.12	0.04	0.04	1.93	100.77
Sem-17	4.75	4.17	11.58	60.54	1.15	0.03	0.64	8.72	0.56	0.27	0.18	8.04	100.62
Sem-18	2.70	4.85	23.85	55.02	0.03	0.02	0.09	13.33	0.29	0.23	0.16	0.89	101.45
Sem-19	1.29	2.41	24.86	55.45	n.d	0.01	0.06	16.24	0.44	0.25	0.18	0.58	101.78
Sem-20	8.11	1.12	15.08	70.52	0.14	0.01	0.95	1.03	0.56	0.03	0.29	5.88	103.71
Sem-21	7.96	0.33	14.33	72.87	0.05	0.02	1.08	1.77	0.44	0.03	0.19	5.37	104.44
Sem-22	0.13	4.87	31.16	44.04	0.06	0.03	0.01	17.68	0.04	0.03	0.01	2.47	100.53
Sem-23	7.35	1.30	10.77	70.91	0.48	0.02	0.82	0.61	0.41	0.03	0.40	10.16	103.24
Sem-24	0.13	10.25	21.61	48.26	0.02	n.d.	n.d.	18.70	1.02	0.36	0.11	0.95	101.41
Sem-25	8.71	1.62	19.47	64.29	n.d	n.d	0.70	4.05	0.45	0.03	0.42	3.37	103.12
Sem-26	7.59	2.49	20.70	58.67	0.03	0.04	0.27	5.48	0.28	0.05	0.84	2.61	99.04
Sem-27	5.65	0.16	10.52	76.08	0.22	n.d	0.97	1.32	0.38	0.05	0.22	7.52	103.09
Sem-28	5.54	2.81	12.61	67.08	0.98	n.d	0.95	4.30	0.52	0.12	0.16	5.36	100.42

n.d. = not detected. Detection limits were $K_2O = 0.008$ wt%, $P_2O_5 = 0.015$ wt%, and Cl = 0.009 wt%.

retained evidence of some K evaporation. Finally, the analysis of the melt inclusion in Sem-28 produced an isotopically heavy composition (δ^{41} K = 11.5 ± 1.2‰) compared to the chondrule glass (δ^{41} K = 0.8 ± 0.9‰), although they both have very similar, enriched (Na,K/Al)_L ratios.

Zoned Chondrules and CPX Compositions

Backscattered electron images of the two zoned type I chondrules analyzed are shown in Fig. 5. Data for coexisting mesostasis and CPX in zoned chondrules are listed in Tables 3 and 4 and are shown in Fig. 6. Zoned chondrule A has a barred-olivine texture and contains abundant glass and grains of Ni-poor Fe metal; it is a type IA. CPX occurs as isolated crystallites, mainly in the outer portions of the chondrule as is typical of many type I chondrules, including a barred one studied by Grossman et al. (2002). Zoned chondrule B has a porphyritic-pyroxene (type IB) texture, again with Fe metal grains, but with much less mesostasis than chondrule A. CPX occurs as overgrowths on low-Ca pyroxene crystals and as isolated crystallites in the mesostasis. Chondrule A has low Na contents in its core (~0.5 wt% Na₂O) and chondrule B has relatively high Na contents (~4 wt% Na₂O) in its core (Figs. 5 and 6a).

A plot of the Na₂O content of CPX versus that in mesostasis (Fig. 6a) for the 17 unzoned type I chondrules (Tables 5 and 6) is very similar to that shown by Libourel et al. (2003). There is a significant correlation with a slope similar to that expected by igneous partitioning of Na between glass and CPX (Blundy et al. 1995). However, data on CPX-mesostasis pairs in the zoned chondrules lie along nearly horizontal lines (Fig. 6a) where Na₂O in CPX is constant while Na₂O in coexisting mesostasis varies significantly. The lowest-Na₂O points in each zoned chondrule, representing material from near the cores of the chondrules, are near the igneous partitioning line.

Figure 6b compares the Na₂O contents of CPX and mesostasis in type I chondrules with the 19 type II chondrules measured here (Table 7 and 8) and those reported by Jones (1990, 1996). The mesostasis compositions reported by Jones have systematically lower Na₂O contents, possibly due to Na loss during the analyses. We found that Na can be extremely labile in these glasses. Some of our type II chondrules fall on the extension of the type I trend, but most fall significantly above it, implying that either Na distribution coefficients were higher during formation of CPX in most type II chondrules or that the alkali distributions in these chondrules have been disturbed.



Fig. 1. The L chondrite-normalized Na/Al versus K/Al ratios of mesostasis analyses in 28 Semarkona chondrules determined by ion microprobe (Table 1). The alkalis are highly correlated and show a similar range to previous studies of Semarkona and other UOC chondrules.



Fig. 2. The L chondrite-normalized Na/Al ratios versus SiO₂ (top) and Al₂O₃ (bottom) contents (wt%) of the Semarkona chondrule mesostases listed in Tables 1, 2, and 5. When measured, the $(Na/Al)_L$ ratios determined by ion microprobe (Table 1) are used rather than those determined by electron microprobe. The $(Na/Al)_L$ ratio exhibits a rough positive correlation with SiO₂ content and inverse correlation with Al₂O₃ content.



Fig. 3. The L chondrite-normalized Na/Al ratios versus CaO/Al₂O₃ (wt.) ratios of the Semarkona chondrule mesostases listed in Tables 1, 2, and 5. When measured, the (Na/Al)_L ratios determined by ion microprobe (Table 1) are used rather than those determined by electron microprobe. There is a rough correlation between these two ratios. The line connects Na/Al (at.) = 1 on the x-axis with Ca/Al (at.) = 0.5 on the y-axis. The mesostasis compositions would lie on this line if the Ca content was determined solely by the coupled substitution $Ca_{0.5}AlO_2 = SiO_2$, and re-entry of Na into chondrules was accomplished by the replacement of Ca in the mesostasis via the substitution $Ca_{0.5}AlO_2 = NaAlO_2$. With increasing Na (and K) content, the mesostasis compositions do seem to approach the line.



Fig. 4. The K isotopic compositions of 28 Semarkona chondrules versus their L chondrite-normalized K/Al ratios (Table 1). Also shown is the Rayleigh fractionation line (fractionation factor equal to the inverse square-root of the isotope masses) calculated for an initially L chondrite K/Al ratio. There is some isotopic variation, some of which may be artifacts. Even if the isotopic variations are real, it is clear that the chondrules do not record loss of K via a simple Rayleigh fractionation process.



Fig. 5. Backscattered electron micrographs of two CPX-bearing, alkali zoned chondrules. The chondrules are: a) a type IA and b) a type IB. The superimposed contours in Fig. 5a are for 1, 2, and 3 wt% Na₂O in the mesostasis. The contours were determined from elemental maps and spot measurements. Four of the five glass analyses without CPX (open circles) in Fig. 5a are in what appear in this 2D section to be inclusions. There is not enough data to draw contours in Fig. 5b. The glass and CPX analyses are given in Tables 3 and 4 and plotted in Fig. 6.

DISCUSSION

Potassium Isotopes

In a model in which all chondrules initially had roughly chondritic K/Al ratios, the (K/Al)_L ratio provides a measure of the fraction of K that was lost during chondrule formation. In this case, Rayleigh fractionation predicts a simple relationship between (K/Al)_L ratio and δ^{41} K (Fig. 4). Although we have tentatively identified at least two chondrules with modest enrichments in ⁴¹K, the enrichments are much smaller than would be expected for Rayleigh distillation from chondrules with initially chondritic K/Al ratios (Fig. 4).

The $\pm 3\%$ range of δ^{41} K in most chondrules is somewhat larger than would be expected from the typical measurement errors listed in Table 1, but it is the 2 σ reproducibility of a number of standard glasses in a previous study (Alexander et al. 2000). We have found that the reproducibility is always worse when analyzing polyphase materials like chondrule mesostasis. We suspect that the inclusion of multiple phases, associated surface roughness, fractures, and contamination all contribute to reducing the reproducibility. Another potential contribution is isotopic fractionation associated with alkali loss during electron microprobe analysis. We took care to minimize the loss of alkalis during electron microprobe analysis, but some loss is inevitable in the more sensitive glasses. Alkali-rich type II glasses are particularly sensitive to loss of Na, although loss of K is not generally seen (e.g., Grossman and Brearley 2005). However, only a 4% loss of K under Rayleigh conditions would produce a 1‰ increase in the δ^{41} K. This might explain the apparent slight systematic ⁴¹K enrichments of the glasses with superchondritic K/Al ratios (Fig. 4)—these glasses tend to be more susceptible to alkali loss during electron microprobe analysis—but it cannot be ruled out that glass composition weakly influences the instrumental fractionation.

In multiple analyses, two Semarkona chondrules showed much larger ranges in their K isotope compositions than $\pm 3\%$. Similar ranges were seen in some Bishunpur chondrules (Alexander et al. 2000). This may be due to indigenous isotopic variations in the chondrules. However, because there are no systematic correlations between K isotopes and (K/Al)_L ratios either within or between chondrules, the conservative interpretation that we prefer at present is that the measured isotopic variations are in most cases instrumental artifacts associated with the nature of the mesostases in these chondrules. For instance, in Bishunpur the chondrule with the widest variation had pitted mesostasis, due to loss of some of the glass, presumably during the making of the section (Alexander et al. 2000).

Whatever the reason for the range of measured K isotopic

Table 3. Analyses by electron microprobe of mesostasis in two zoned chondrules from Semarkona. Points are arranged in order of increasing Na₂O. Also shown are analyses of four mesostasis inclusions in olivine grains. Except for the four inclusions in chondrule A, coexisting CPX analyses are listed in Table 4.

	Dist. ^a	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P_2O_5	Cl	K ₂ O	CaO	TiO ₂	Cr ₂ O ₃	MnO	FeO	Total
Point	μm	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Zoned c	hondrule	А												
15	175	0.40	6.63	20.3	48.9	n.d.	n.d.	n.d.	17.0	0.91	0.43	0.11	0.36	95.0
7	117	0.55	4.92	20.2	52.0	n.d.	0.02	0.01	17.0	0.97	0.46	0.12	0.38	96.6
12	157	0.89	5.16	19.4	56.5	n.d.	n.d.	0.01	15.3	0.70	0.45	0.22	0.32	98.9
14	98	0.97	4.94	20.2	54.6	n.d.	n.d.	0.02	14.8	0.68	0.42	0.15	0.26	97.0
4	94	1.39	4.89	21.7	53.8	0.02	0.01	0.01	15.7	0.74	0.35	0.11	0.25	99.0
3	27	1.50	4.02	20.9	56.9	0.02	0.01	0.06	13.4	0.27	0.26	0.10	0.33	97.8
6	63	1.62	5.06	20.6	53.8	0.02	n.d.	0.03	14.2	0.65	0.32	0.21	0.30	96.8
11	98	1.66	4.31	19.5	55.6	0.02	n.d.	0.07	14.8	0.79	0.41	0.15	0.39	97.6
10	71	2.48	4.09	19.7	54.3	0.02	n.d.	0.24	12.1	0.27	0.32	0.20	0.48	94.2
5	16	3.61	4.81	21.6	56.7	0.02	n.d.	0.22	11.7	0.35	0.12	0.11	0.56	99.8
2	8	4.06	3.93	21.7	55.3	n.d.	n.d.	0.21	11.7	0.36	0.18	0.12	0.94	98.5
8	8	4.34	5.38	19.7	55.3	n.d.	n.d.	0.26	12.2	0.27	0.24	0.17	0.69	98.5
9	24	4.50	4.46	19.8	54.4	n.d.	n.d.	0.26	11.3	0.36	0.06	0.07	0.50	95.6
13	20	4.80	4.17	20.6	56.2	0.02	n.d.	0.28	10.9	0.24	0.22	0.22	0.49	98.1
1	12	5.88	3.48	21.0	56.8	n.d.	0.03	0.35	9.4	0.21	0.05	0.05	1.27	98.5
Incl. 1		0.46	6.82	20.5	48.2	n.d.	n.d.	0.01	16.1	0.83	0.44	0.07	0.31	93.7
Incl. 2		1.74	4.04	19.9	48.8	0.03	n.d.	0.04	16.7	0.83	0.48	0.10	0.35	93.0
Incl. 3		1.17	3.98	19.8	47.4	0.04	n.d.	0.01	16.3	0.81	0.50	0.14	0.29	90.5
Incl. 4		1.24	9.12	18.8	45.5	0.02	n.d.	0.02	13.9	0.81	0.44	0.16	0.44	90.5
Zoned c	hondrule	В												
1	97	4.32	3.14	20.6	59.2	n.d.	0.02	0.37	7.54	0.41	0.19	1.00	1.41	98.2
4	148	5.74	4.10	19.4	56.5	0.02	0.01	0.28	9.78	0.54	0.37	0.98	1.41	99.1
2	11	8.23	3.52	18.8	58.2	n.d.	0.02	0.48	7.60	0.41	0.15	0.42	0.70	98.5
3	18	8.84	2.78	19.9	61.2	0.02	n.d.	0.61	5.42	0.36	0.14	0.48	0.57	100.3

^aDistance from the point to the surface of the chondrule as measured in the thin section.

n.d. = not detected. Detection limits were: $K_2O = 0.008$ wt%, $P_2O_5 = 0.015$ wt%, and Cl = 0.009 wt%.

compositions, the single most important result is that there is not a systematic correlation between K isotopes and (K/Al)_L ratio. The absence of a Rayleigh-like relationship between K isotopic composition and elemental abundance in chondrules (Fig. 4) exhibiting such a wide range of alkali abundances (Fig. 1 and 4) is problematic. Experimentally measured evaporation rates (Yu et al. 2003) suggest that one cannot simply appeal to heterogeneous precursors to explain the range of alkali abundances. The measured rates suggest that under currently accepted conditions and time scales for chondrule formation, K should have experienced significant evaporation and isotopic fractionation whatever its starting abundance. Indeed, the more refractory the chondrule, the higher the maximum temperature it is likely to have experienced and, therefore, the greater the degree of K loss and isotopic fractionation that is expected.

In addition, equilibrium calculations suggest that at near liquidus conditions alkali abundances would have been much lower than now found in chondrules, even in highly dust enriched systems (Ebel and Grossman 2000). If chondrules approached the predicted equilibrium alkali abundances at near liquidus temperatures, which experimental evaporation rates suggest they probably would have, then the alkalis must have re-entered chondrules. When did this occur? The two possibilities are during chondrule cooling and/or during parent body processing. Although Semarkona has probably not experienced significant metamorphism, parent body modification of alkali abundances and isotopic compositions in chondrules may still be a factor.

Alkali Contents of Chondrules During Growth of CPX

Many chondrules contain CPX that formed late in their crystallization. Experiments suggest that CPX would have formed in chondrules below 1373 K if they cooled at rates of ≤ 100 K/hr (DeHart and Lofgren 1996). Equilibrium calculations also suggest that CPX should form below ~1400 K (Ebel and Grossman 2000), in reasonable agreement with the experiments. Thus, the CPX should record the alkali contents of the chondrule melt shortly before final solidification.

The equilibrium calculations also suggest that at a given total pressure, the equilibrium Na contents of the melt during CPX formation will depend on the temperature and dust/gas ratio: at 1400 K and $P_{tot}=10^{-3}$ bars, the predicted Na₂O contents are 0.04 wt% and >2 wt% for dust/gas ratios of 100

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P_2O_5	CaO	TiO ₂	Cr ₂ O ₃	MnO	FeO	Total
Point	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Zoned c	hondrule A										
15	(no CPX	present)									
7	0.04	18.6	10.1	48.1	n.d.	20.1	1.54	0.79	0.13	0.33	99.8
12	0.03	15.4	11.0	48.4	0.03	22.8	1.15	0.91	0.15	0.31	100.2
14	0.06	14.5	11.8	47.8	n.d.	23.5	1.28	0.91	0.11	0.27	100.3
4	0.03	13.3	14.3	46.0	n.d.	23.7	1.36	0.97	0.11	0.27	100.1
3	0.06	15.4	11.5	47.3	0.03	22.6	1.19	0.90	0.13	0.43	99.5
6	0.04	17.3	9.6	49.4	n.d.	21.3	1.38	0.95	0.18	0.36	100.4
11	0.09	15.2	10.2	48.2	0.03	23.5	1.44	0.87	0.18	0.26	99.9
10	0.04	17.8	7.3	49.5	n.d.	21.1	1.20	0.87	0.20	0.73	98.9
5	0.04	20.5	6.7	51.5	n.d.	19.2	1.32	0.81	0.22	0.64	100.9
2	0.05	16.9	10.6	48.5	n.d.	21.5	1.45	0.96	0.18	0.85	100.9
8	0.04	19.5	6.9	50.6	n.d.	19.9	1.21	0.79	0.30	0.82	99.9
9	0.03	18.6	7.5	50.3	n.d.	20.7	1.19	0.73	0.21	0.47	99.8
13	0.04	21.8	5.2	52.3	n.d.	18.0	1.11	0.82	0.34	0.81	100.5
1	0.02	20.0	6.5	51.2	n.d.	19.8	1.22	0.79	0.26	0.88	100.6
Zoned c	hondrule B										
1	0.16	19.1	5.1	51.0	0.02	18.9	0.58	1.77	1.09	1.01	98.6
4	0.16	18.8	6.1	50.1	n.d.	19.0	0.71	2.12	1.02	1.34	99.3
2	0.21	19.4	5.5	51.3	n.d.	18.8	0.73	1.89	1.33	1.45	100.7
3	0.18	22.6	2.7	53.2	n.d.	16.0	0.38	1.40	1.74	1.53	99.8

Table 4. Electron microprobe analyses of clinopyroxene in two zoned chondrules from Semarkona. Coexisting mesostasis analyses are listed in Table 3.

n.d. = not detected. Detection limit for $P_2O_5 = 0.015$ wt%.

times and 1000 times solar, respectively (Ebel and Grossman 2000). The equilibrium calculations include formation of feldspar that is rarely found in ferromagnesian chondrules. How the suppression of feldspar crystallization will affect the calculated CPX formation temperature and Na₂O contents of the melt remains to be seen. Nevertheless, the alkali contents of mesostasis that is in equilibrium with CPX could ultimately provide useful constraints for P_{tot} and the dust/gas ratios during chondrule formation.

In type I chondrules, CPX often contains Na in abundances (Fig. 6a) that suggest that it crystallized from a melt with a composition that was very similar to the present composition of the mesostasis (Jones 1994; Libourel et al. 2003). However, our new data on zoned chondrules reveal a level of complexity that was not previously understood. The CPX in the two zoned chondrules we have studied in detail have uniform Na contents, regardless of the Na content of adjacent mesostasis. Mesostasis in the chondrule cores have compositions that are consistent with igneous partitioning of Na between glass and CPX, but all of the excess Na in the outer parts of zoned chondrules must have been introduced after CPX crystallized. This is supported by the observations of Grossman et al. (2002), who found that halogens and water were associated with alkali zonation. Thus there are two temperatures/times at which alkalis may have re-entered chondrules: at high temperature prior to CPX crystallization, and at low temperature during alteration or metamorphism of solid chondrules. In unzoned chondrules, either or both of these processes may have occurred.

Although the CPX and mesostasis compositions in the cores of many type I chondrules seem to conform quite well to experimental measurements of the Na distribution coefficient, the agreement is not so good for type II chondrules (Fig. 6b). Some type II chondrules do lie on the extension of the type I array, but most lie well above it. The experimental measurements of the distribution coefficients were all conducted in the Fe-free diopside-albite system (Blundy et al. 1995). For experiments conducted at high pressure, the dioside-albite system produced consistently lower Na distribution coefficients than for natural systems (Blundy et al. 1995), showing that composition can influence the Na distribution coefficient. In their thermodynamic modeling of the Na distribution coefficient, Blundy et al. (1995) conclude that the compositional dependence is due to non-ideality in the dioside-albite melt and that any compositional dependence would be much less in multicomponent systems, although their treatment does not include the influence of FeO. The variations in CPX and mesostasis compositions within and between type I and type II chondrules are gradational, and there are no apparent systematic variations in the Na distribution coefficients with composition. There must be another cause for the differences between type I and type II chondrule CPX-melt Na distribution coefficients.

No alkali zoning has been reported in type II Semarkona chondrules, but Grossman and Brearley (2005) found evidence of alkali exchange between chondrules and matrix even in some highly unequilibrated ordinary chondrites and



Fig. 6. a) The Na contents of mesostasis and CPX pairs in type I chondrules, including the two alkali zoned chondrules (Tables 3–6). The line is the experimentally determined equilibrium line for the albite-diopside system (Blundy et al. 1995). The Na contents of mesostasis and CPX in most chondrules are roughly consistent with the CPX growing near equilibrium from the mesostases. However, in the two zoned chondrules the CPX compositions are roughly constant, but the Na contents of the mesostasis increases towards the edge of the chondrules. Clearly, the Na responsible for the zoning entered the chondrules after CPX formation. b) Comparison of Na contents of CPX and mesostasis in type I and II chondrules (Tables 5–8). The Jones (1990, 1996) type II data have systematically lower Na₂O contents than those reported here, suggesting some loss of Na₂O during analysis. Some type II chondrules lie on the extension of the type 1 array, but most lie above the type I array. The apparently higher Na distribution coefficients in most type II chondrules suggests that their CPX formed at lower temperatures than CPX in most type I chondrules.

could not rule out the possibility that this process occurred even in Semarkona. During electron probe analysis, Na is much more mobile in type II glasses than in type I glasses. The apparently higher mobility of Na in type II chondrule glasses allows for the possibility that some type II chondrules have completely exchanged with the matrix. Postcrystallization addition of Na to the mesostasis would not explain the differences between type I and type II chondrules



Fig. 7. Comparison of the L-chondrite normalized Na/Al ratio versus SiO₂ (top) and Al₂O₃ (bottom) contents (wt%) in type IA Semarkona chondrule mesostases from Jones and Scott (1989) with the mesostasis compositions predicted by MELTS assuming closed system fractional crystallization of olivine, OPX, and CPX. MELTS reproduces the compositional trends seen in the chondrule mesostases, but not their actual compositions.

Table 5. Analyses by electron microprobe of mesostasis in type I chondrules from Semarkona. Coexisting CPX analyses are listed in Table 6.

	Txt ^a	Na ₂ O	MgO	Al_2O_3	SiO ₂	P_2O_5	Cl	K ₂ O	CaO	TiO ₂	Cr ₂ O ₃	MnO	FeO	Total
Point	mol%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
2	IA	0.55	2.09	29.0	46.6	n.d.	0.03	n.d.	17.2	0.11	0.11	0.04	0.09	95.8
3	IAB	2.29	6.21	20.0	49.1	0.02	0.05	0.10	13.4	0.43	0.37	0.16	3.47	95.6
4	IB	5.54	3.25	15.3	57.7	n.d.	0.02	0.42	8.45	0.43	0.39	1.11	1.92	94.6
5	IB	6.42	1.21	14.6	65.5	n.d.	0.02	0.60	4.90	0.46	0.05	0.95	2.51	97.3
7	IAB	9.90	0.98	20.4	66.1	0.06	0.02	0.80	0.77	0.50	0.04	0.13	2.11	101.8
9	IAB	0.33	2.57	28.6	48.6	n.d.	0.04	n.d.	17.4	0.22	0.02	0.01	1.85	99.6
10	IAB	1.31	2.62	27.0	48.1	0.04	0.01	0.04	16.5	0.20	0.20	0.04	0.37	96.5
11	IAB	1.10	7.21	21.4	45.5	n.d.	0.03	0.03	15.6	0.60	0.43	0.20	2.32	94.5
12	IAB	3.36	4.63	20.9	51.8	n.d.	n.d.	0.22	11.6	0.37	0.47	0.49	0.38	94.2
13	IA	0.59	7.42	16.9	56.6	0.02	0.01	0.02	14.7	0.53	0.55	0.14	0.51	97.9
14	IAB	2.12	4.86	21.2	55.4	0.02	0.01	0.04	12.6	0.36	0.37	0.30	0.31	97.6
15	IAB	4.98	3.88	22.2	50.7	0.02	0.01	0.27	10.7	0.19	0.30	0.47	0.82	94.5
16	IB	6.83	1.49	15.9	59.3	0.02	n.d.	0.75	4.06	0.50	0.02	0.55	3.23	92.6
17	IA	2.35	3.33	21.3	54.5	0.03	0.02	0.09	13.1	0.29	0.37	0.16	0.73	96.3

^aTexture using the Scott and Taylor (1983) classification.

n.d. = not detected. Detection limits were: $K_2O = 0.008$ wt%, $P_2O_5 = 0.015$ wt%, and Cl = 0.009 wt%.

because it is the Na contents of the type II CPX that is too high, not the mesostasis. Loss of Na from the mesostasis is a potential explanation, but it seems unlikely as it requires that the original Na contents of some type II chondrule mesostases would have been unreasonably high (up to 20 wt% Na₂O).

The thermodynamic model for calculating Na distributions developed by Blundy et al. (1995) suggests that there should be a significant temperature dependence to the distribution coefficient. At low pressures, the model predicts that the Na distribution coefficient would increase from 0.04

at ~1573 to 0.1 at ~1273 and 0.2 at ~1173 K. At present, the best explanation for the differences between type I and type II chondrule distribution coefficients is that the CPX in many type II chondrules formed at lower temperatures than type I chondrules.

The Elemental Compositions of Chondrule Mesostases

While temperature and dust/gas ratios may have been important factors in determining alkali abundances in

	Na ₂ O	MgO	Al_2O_3	SiO ₂	P_2O_5	CaO	TiO ₂	Cr ₂ O ₃	MnO	FeO	Total
Point	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
2	0.07	18.6	3.78	52.2	n.d.	19.9	1.88	1.31	0.47	0.71	99.0
3	0.06	14.6	12.1	46.8	n.d.	22.5	1.46	1.79	0.20	0.57	100.1
4	0.14	19.0	3.24	52.4	n.d.	20.3	0.64	1.47	1.34	1.17	99.7
5	0.23	17.8	3.02	51.8	0.03	19.1	0.54	2.22	1.38	2.73	98.9
7	0.90	16.5	5.27	52.5	0.03	17.9	0.69	1.54	0.55	3.23	99.1
9	0.20	17.8	9.91	49.3	n.d.	20.2	1.14	0.93	0.62	0.57	100.7
10	0.09	20.3	4.83	52.9	n.d.	19.4	0.73	0.97	0.20	0.47	99.9
11	0.03	18.6	8.23	49.1	n.d.	20.6	1.17	0.79	0.23	0.46	99.2
12	0.11	17.1	9.48	48.7	n.d.	21.1	0.98	1.39	0.51	0.36	99.6
13	0.04	19.0	7.32	50.6	n.d.	20.2	1.31	1.02	0.12	0.32	99.9
14	0.05	17.5	8.40	48.8	n.d.	20.7	1.20	1.15	0.27	0.49	98.5
15	0.05	25.4	4.77	53.7	n.d.	12.9	0.56	0.96	0.64	0.74	99.7
16	0.28	17.8	3.35	51.8	n.d.	18.3	0.77	1.66	1.17	4.11	99.2
17	0.07	16.4	8.71	49.2	n.d.	22.6	1.24	1.06	0.17	0.92	100.5

Table 6. Electron microprobe analyses of clinopyroxene in type I chondrules from Semarkona. Coexisting mesostasis analyses and olivine compositions are listed in Table 5.

n.d. = not detected. Detection limit for $P_2O_5 = 0.015$ wt%.

Table 7. Analyses by electron microprobe of mesostasis in type II chondrules from Semarkona. Coexisting CPX analyses are listed in Table 8.

	u III 1001	• • •												
Name	Fa ^a mol%	Na ₂ O wt%	MgO wt%	Al ₂ O ₃ wt%	SiO ₂ wt%	P ₂ O ₅ wt%	Cl wt%	K ₂ O wt%	CaO wt%	TiO ₂ wt%	Cr ₂ O ₃ wt%	MnO wt%	FeO wt%	Total wt%
	14.6	2.04	0.74	11.0	70.7	0.76	1	0.04	0.60	0.44	1	0.10	()7	06.2
А	14.6	3.84	0./4	11.8	/0./	0.76	n.d.	0.94	0.62	0.44	n.d.	0.18	6.27	96.3
В	6.5	7.49	1.51	13.8	67.6	0.05	0.01	0.82	1.73	0.50	0.05	0.39	5.73	99.7
С	21.9	8.85	1.19	15.9	67.5	0.19	n.d.	0.88	0.88	0.63	n.d.	0.19	4.09	100.3
D	18.6	5.88	0.58	14.6	70.9	0.23	n.d.	0.99	1.53	0.44	n.d.	0.16	4.20	99.5
E	9.9	7.27	0.41	14.6	64.1	0.02	n.d.	0.74	2.14	0.47	0.03	0.37	7.44	97.6
F	22.0	4.76	0.49	14.6	68.8	0.33	0.01	0.85	0.98	0.53	0.03	0.18	5.37	96.9
G	7.3	7.08	0.87	13.0	72.3	n.d.	n.d.	0.90	0.97	0.48	n.d.	0.26	4.54	100.4
Н	13.0	2.03	0.45	13.3	71.8	0.48	n.d.	1.03	0.42	0.43	0.05	0.17	4.95	95.1
Ι	6.4	7.01	0.73	12.9	68.9	0.02	n.d.	0.94	0.82	0.44	0.03	0.29	4.88	97.0
J	15.0	5.48	0.96	14.0	67.4	0.34	0.02	0.90	0.92	0.57	0.04	0.14	4.38	95.1
L	14.8	6.23	1.70	8.9	69.3	0.67	0.01	0.69	0.93	0.37	0.02	0.27	10.6	99.7
М	9.9	8.61	0.91	15.9	63.5	0.02	0.01	0.82	1.45	0.48	0.05	0.26	5.03	97.0
Ν	13.8	5.80	1.24	9.95	68.8	0.54	0.02	0.79	0.76	0.35	n.d.	0.31	8.67	97.2
0	16.5	8.81	0.07	22.4	61.8	0.02	n.d.	0.28	4.11	0.11	0.04	0.02	0.51	98.2
Р	11.9	8.21	0.72	15.7	66.1	0.16	0.02	0.85	0.50	0.53	0.02	0.21	4.82	97.8
Q	10.1	8.76	0.23	22.1	60.5	0.03	0.01	0.28	3.95	0.37	n.d.	0.05	1.30	97.5
R	16.0	7.09	0.41	15.2	69.3	0.45	n.d.	0.98	0.96	0.52	0.04	0.11	5.00	100.0
S	4.3	7.43	2.00	19.5	58.2	0.05	n.d.	0.07	6.04	0.56	0.03	0.58	5.14	99.5
Т	19.3	8.39	0.02	23.4	59.1	0.02	0.02	0.21	4.24	0.06	n.d.	n.d.	0.20	95.6

^aFayalite content of olivine in the same chondrule; single point analysis near core of typical grain.

n.d. = not detected. Detection limits were: $P_2O_5 = 0.015 \text{ wt\%}$, Cl = 0.009 wt%, $Cr_2O_3 = 0.015 \text{ wt\%}$, and MnO = 0.016 wt%.

chondrule mesostases, were they the only factors? In particular, what are the origins of the correlations between alkali/Al ratios and glass compositions (Figs. 2 and 3)? It is unlikely that these correlations reflect chondrule precursor compositions since the alkali contents of the precursor should not survive chondrule formation.

It is possible that silica re-entered chondrules during crystallization. Type I chondrules often contain a shell of low-Ca pyroxene around an olivine-rich core, an effect that may be explained by late entry of SiO₂ (Nagahara et al. 1999; Tissandier et al. 2002). In CR chondrites, silica-rich igneous rims have been observed around type I chondrules (Krot et al. 2003), consistent with late condensation of SiO_2 onto the chondrules as the rims formed. But it is not clear why these do not occur in other chondrite groups or exactly how the rimformation process is related to chondrule formation.

We have found no compelling evidence in the compositions of the chondrule mesostases for an influx of silica in any of the chondrules studied here. If the alkali zonation in chondrules were the result of recondensation, these are the chondrules that might be expected to show the best evidence for silica recondensation as well. As found in a

Name	Na ₂ O	MgO	Al_2O_3	SiO ₂	P_2O_5	CaO	TiO ₂	Cr ₂ O ₃	MnO	FeO	Total
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
А	0.86	13.1	0.79	50.4	0.94	18.8	0.28	1.88	0.59	9.29	96.9
В	0.52	16.9	1.06	53.5	n.d.	16.0	0.30	1.63	1.01	8.19	99.1
С	0.38	18.6	1.03	53.2	0.03	12.8	0.18	1.58	0.63	9.90	98.4
D	0.68	13.8	1.59	52.5	0.03	19.8	0.51	1.59	0.41	8.91	99.8
E	0.42	16.4	1.25	51.2	n.d.	13.5	0.35	1.31	1.12	12.2	97.8
F	0.47	14.0	0.98	49.9	0.06	12.2	0.40	0.52	0.79	17.4	96.7
G	0.71	15.1	1.12	51.3	0.04	18.9	0.17	1.95	0.61	6.22	96.1
Н	1.11	12.8	0.98	51.8	0.41	19.0	0.28	2.53	0.54	8.73	98.2
Ι	0.90	15.8	1.61	53.9	n.d.	18.2	0.25	1.82	0.71	5.69	98.8
J	0.54	17.3	0.74	50.9	n.d.	12.9	0.19	1.36	0.60	12.5	97.1
L	0.58	15.3	0.31	51.4	n.d.	11.1	0.14	1.33	0.69	15.9	96.8
М	0.74	15.9	1.91	51.4	n.d.	16.3	0.38	1.75	0.92	8.35	97.6
Ν	0.84	12.2	0.63	52.4	0.08	16.2	0.40	1.10	0.81	14.1	98.7
0	1.89	13.5	7.05	50.8	0.03	14.9	0.72	1.28	0.80	9.42	100.4
Р	0.52	17.1	1.13	52.5	n.d.	13.7	0.20	1.40	0.80	11.0	98.4
Q	0.34	18.3	2.43	52.8	n.d.	14.3	0.48	1.14	1.49	8.13	99.5
R	1.03	15.6	2.51	54.5	0.02	11.3	0.26	0.77	0.69	15.0	101.7
S	0.29	18.5	3.17	50.1	0.02	15.7	0.43	2.42	0.82	4.06	95.4
Т	0.35	14.7	2.08	50.2	n.d.	17.9	0.20	1.20	0.67	9.11	96.4

Table 8. Electron microprobe analyses of clinopyroxene in type II chondrules from Semarkona. The coexisting mesostasis analyses and olivine compositions are listed in Table 7.

n.d. = not detected. Detection limit for $P_2O_5 = 0.015$ wt%.

previous study (Grossman et al. 2002), there is no consistent increase in alkalis and silica and correlated decrease in Al₂O₃ etc. in alkali-zoned chondrules. In the unzoned chondrules, their mesostasis major element compositions are qualitatively consistent with fractional crystallization, although we believe that re-entry of some or all of the alkalis must have occurred. We have used MELTS (Ghiorso and Sack 1995) to model the fractional crystallization of the type IA chondrules analyzed by Jones and Scott (1989). These chondrules exhibit the widest range of SiO₂ and Al₂O₃ concentrations. Figure 7 compares the actual and modeled mesostasis compositions when the calculations were stopped at 1273 K. Crystallization of feldspar was suppressed in the calculations because it is not present in the chondrules. As might be expected, MELTS does not reproduce the mesostasis compositions exactly. Errors both in the MELTS model and in the bulk chondrule compositions will have contributed to this. Nevertheless, MELTS does reproduce the overall inverse correlation between SiO₂ and Al₂O₃ concentrations in the chondrule mesostases, and the alkali/Al correlations with SiO₂ and Al₂O₃ concentrations (Fig. 7).

The Ca/Al variations in the mesostases (Fig. 3) cannot be due to SiO_2 recondensation and are much larger than observed in bulk chondrules, supporting the idea that the variations in mesostases compositions are the result of crystallization. What causes the apparent rough inverse correlation between Ca/Al and Na/Al ratios in the chondrule mesostases (Fig. 3)? While silicate melts are less ordered than crystals, they are not fully disordered. As a result, local charge compensation is still important in silicate melts. In peraluminous melts, the alkalis are accommodated in the

glass structure via the coupled substitution $(Na,K)AlO_2 =$ SiO₂ (e.g., Taylor and Brown 1979). When the atomic (Na+K) > Al, the excess alkalis are accommodated in a different manner, but they are likely to be much more volatile (experimental petrologists have long known that Na in metasilicates is very volatile). Consequently, chondrule mesostases with (Na,K)/Al ratios much greater than one are unlikely to be products of chondrule formation in the nebula. Calcium in peraluminous melts will be involved in a similar substitution, $Ca_{0.5}AIO_2 = SiO_2$. Energetically, the alkali aluminate substitution is favored over the Ca aluminate (Navrotsky et al. 1982; Roy and Navrotsky 1984). Thus, as the alkalis recondense they are likely to displace the Ca on the Al bonded sites, perhaps promoting the crystallization of CPX and, therefore, explaining the rough inverse correlation between Ca/Al and Na/Al ratios in the chondrule mesostases (Fig. 3).

Melt Inclusions and Alkali Contents Prior to CPX Formation

So far, based on theoretical expectations, we have assumed that alkali/Al ratios at peak chondrule temperatures were much less than now present in chondrule mesostases. Potentially, melt inclusions may preserve a direct record of alkali abundances at higher temperatures than is recorded by the CPX. However, for this to be the case, the melt inclusions must have remained sealed from the time of their formation. This assumption now seems doubtful.

Grossman and Brearley (2005) found that in type II chondrules, where melt inclusions in olivine grains are

plentiful, K/Al ratios in the inclusions are frequently elevated in response to crystallization of albite elsewhere in the chondrule; thus, the inclusions are not sealed by their host crystals. Table 3 shows the compositions of four melt inclusions in the zoned type IAB chondrule A in Semarkona (Fig. 5). We showed above that this chondrule has experienced low temperature secondary entry of alkalis. These inclusions all have compositions similar to nearby mesostasis areas outside the host olivine and thus they too were not sealed. In two-dimensional thin sections, it can never be demonstrated that what appears to be a melt inclusion is not in fact a section through an embayment that is directly connected to the mesostasis.

The measured isotopic composition of an inclusion in chondrule Sem-28 is isotopically heavy (δ^{41} K = 11.5 ± 1.2‰). It is tempting to conclude that this inclusion has preserved a record of evaporation. A 12‰ enrichment in ⁴¹K is equivalent to ~40% K loss under Rayleigh conditions. However, the alkali/Al ratio of the inclusion is essentially identical to that of the chondrule mesostasis, which has a normal isotopic composition (δ^{41} K = 0.8 ± 0.9‰). Thus, it is likely that the measured isotopic composition of the inclusion is an artifact, perhaps because, due to its size, a significant amount of the host olivine was included in the analysis.

CONCLUSIONS

Evaporation experiments and cosmic spherules show that isotopic fractionation associated with evaporation of K behaves as predicted by Rayleigh fraction. It seems clear from the results for Bishunpur and now Semarkona chondrules that, despite a wide range in (K/Al)_L ratios, OC chondrules do not record a simple history of Rayleigh-type loss of K. There is some scatter in the measured K isotopic compositions that may be real, but the lack of systematic variations between the isotopic compositions and K/Al ratios suggests that they are probably due to instrumental artifacts. Even if all measurements are real, the isotopically fractionations are much less than would be expected from Rayleigh fractionation from an initially L-chondrite-like melt. Based on experimentally measured evaporation rates and the currently accepted chondrule formation conditions and time scales, we believe significant K evaporation from chondrules must have occurred. The scarcity of K isotopic fractionation in chondrules suggests that they exchanged with the rim/ matrix on the parent body or they exchanged with the surrounding gas when they formed. Based on the Na contents of CPX, the cores of many type I and type II chondrules in Semarkona have alkali contents that were probably established at the time of final crystallization. For these, our preferred explanation for the lack of systematic isotopic enrichments, particularly in the alkali-poor type Is, is that they exchanged with the ambient gas when they formed. For the outer parts of zoned type I chondrules and, possibly, the cores of some thoroughly altered chondrules, the alkali contents

established at high temperatures have been overprinted by a later influx of alkalis. In a previous study, it was shown that in zoned chondrules water and halogens entered the chondrules along with the alkalis. Hence, it is likely that the alkali zonation in chondrules is the result of the parent body aqueous alteration that Semarkona experienced.

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