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# Assessing the implications of K isotope cosmochemistry for evaporation in the preplanetary solar nebula

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**Abstract**

Homogeneity in $^{41}K/^{39}K$ among Earth, Moon, chondrites, and achondrites has been cited as evidence that evaporation of protoplanetary dust could not have caused variability in the mass of moderately volatile elements among Solar System planets and meteorite parent bodies. Herein, consideration of a simple physical model for evaporation of mineral grains with finite K diffusivities shows that measured $^{41}K/^{39}K$ do not preclude extensive mass loss by evaporation of solid mineral grains in the preplanetary nebula. Instead the data constrain the grain size, temperature, and duration attending grain evaporation through the effects that these factors have on the evaporative–diffusive Peclet number. It is proposed that evaporation of solid dust comprising the precursors to planets can not be ruled out as a first-order mechanism for controlling the elemental composition of the rocky planets and asteroids. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The finding that $^{41}K/^{39}K$ among the terrestrial planets, meteorites, and the Moon is uniform to within approximately 2‰ or less (Humayun and Clayton [1]) has been cited as evidence that evaporation could not have played an important role in determining the compositions of planets and meteorite parent bodies (Humayun and Clayton [1]; cf. Esat [2]). Condensation rather than evaporation[1], it is argued, was the principal mechanism for elemental fractionation between terrestrial planets and the asteroids. Here this conclusion is questioned on the basis that: (1) major rock-forming elements, including K, entered the circumstellar accretion disk comprising the early solar nebula in solid form; (2) evaporation of a heterogeneous mixture of crystalline solids could have caused elemental depletion patterns similar to those observed in Solar System bodies; and (3) evaporation of crystalline solids would result in uniform K isotope ratios like those observed.

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[1] Evaporation is used as a general term encompassing volatilization of a condensed phase either from the liquid or solid state, in keeping with usage of the term in the astronomical and cosmochemical literature.

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Table 1
Elemental abundances and fractional depletions in the diffuse ISM

| Element | $(N_x/N_H)^a_\odot$ | $(N_x/N_H)^b_{\zeta Oph}$ | $\delta(x)^\odot_{\zeta Oph}{}^c$ | $(N_x/N_H)^d_{comp}$ | $\delta(x)^\odot_{comp}{}^c$ |
|---|---|---|---|---|---|
| O | $7.4\times10^{-4}$ | $1.7\times10^{-4}$ | 0.77 | $5.4\times10^{-4}$ | 0.27 |
| Si | $3.5\times10^{-5}$ | $8.9\times10^{-7}$ | 0.97 | $8.2\times10^{-7}$ | 0.98 |
| Mg | $3.8\times10^{-5}$ | $1.2\times10^{-6}$ | 0.97 | $1.0\times10^{-6}$ | 0.97 |
| Fe | $3.2\times10^{-5}$ | $3.0\times10^{-7}$ | 0.99 | $2.7\times10^{-7}$ | 0.99 |
| Ca | $2.3\times10^{-6}$ | $4.6\times10^{-10}$ | 1.00 | – | – |
| Al | $3.0\times10^{-6}$ | $4.6\times10^{-9}$ | 1.00 | – | – |
| Na | $2.1\times10^{-6}$ | $2.4\times10^{-7}$ | 0.89 | $2.1\times10^{-7}$ | 0.90 |
| K | $1.3\times10^{-7}$ | $8.0\times10^{-9}$ | 0.94 | $1.0\times10^{-8}$ | 0.92 |

[a]Solar data from Anders and Grevesse [45].
[b]ζ Ophiuchi sight line, data from [5,6].
[c]Fractional depletion as defined in the text.
[d]Composite of several sight lines, data from Duley [46].

## 2. Origin of rock-forming elements in the Solar System

Astronomical observations show that the major rock-forming elements most likely entered the nascent Solar System in solid form and that at least some of these solids were crystalline. The solid provenance of these elements places constraints on the processes that could have affected elemental abundances in Solar System bodies.

The major rock-forming elements (lithophile elements) are depleted in the gas phase of the diffuse interstellar medium (ISM) relative to solar abundances [3]. The paucity of these elements in the gaseous ISM is usually expressed as a fractional depletion $\delta(x)$[2] for element $x$:

$$\delta(x) = 1-10^{D(x)} \tag{1}$$

where $D(x)$ is the depletion index:

$$D(x) = \left[\frac{x}{H}\right] = \log\left(\frac{N_x}{N_H}\right)_{\text{ISM gas}} - \log\left(\frac{N_x}{N_H}\right)_\odot \tag{2}$$

and $N_x$ and $N_H$ refer to numbers of atoms for element $x$ and hydrogen, respectively. The missing material is thought to reside in interstellar dust [4]. With the assumption that the interstellar environment in total has cosmic (i.e., solar) abundances of the elements, the depletion index, $\delta(x)$, specifies the fractional amount of a given element sequestered in dust in the diffuse ISM:

$$\delta(x) = \frac{\left(\frac{N_x}{N_H}\right)_{\text{ISM dust}}}{\left(\frac{N_x}{N_H}\right)_\odot} \tag{3}$$

When $\delta(x)$ is 0, there is no depletion and the element $x$ is entirely in the gas phase. When $\delta(x)$ is 1, the element $x$ is absent from the gas phase and must reside entirely in the dust. Table 1 shows fractional depletions for rock-forming elements along the well-studied line of sight toward the luminous star ζ Ophiuchi [5,6] as well as depletions for a composite of several sight lines. Depletions for Si, Mg, Ca, Al, Fe, Na, and K are all $\geq 0.89$ and for most the values exceed 0:96, indicating that these elements are present primarily as solids in the ISM. The extent to which solar abundances of elements are truly representative of 'cosmic' abundances has been challenged, but use of alternative cosmic abundances does not substantially change the fractional depletions shown in Table 1 [7].

A shortfall in the flux of dust from stellar sources relative to the rate of destruction in the diffuse ISM implies that grains grow and regrow in interstellar space in a process of cyclical conversion from solid to vapor and back again [8]. Much of

[2] In this section the symbol $\delta$ refers to fractional depletion of elemental abundances. Throughout the remainder of the paper $\delta$ is used to express isotopic abundances. The two meanings of the symbols should be clear from the context.

the growth apparently occurs in the denser molecular clouds [9,10]. Once solids of the ISM enter a molecular cloud they are protected from exposure to the destructive forces like shock waves and sputtering that prevail in the diffuse phases of the ISM [8,9]. As a result, rock-forming elements should be retained as solids in molecular clouds.

The Solar System formed from an accretionary disk of rotating gas and dust that collapsed from a molecular cloud [11]. Support for this description of the early solar nebula comes from observations of circumstellar disks associated with young stars [12]. Astronomical observations of molecular cloud cores and accretion disks suggest that grains (including crystalline olivine and pyroxene) in these environments are larger on average than typical grains in the diffuse ISM [13]. Grain sizes in disks range from $\leq 1$ μm to $> 10$ cm [13,14]. New infrared spectroscopic data confirm that silicates and ices are important constituents of accretion disks during the earliest stages of low-mass star formation [15]. Grain size and crystallinity in protoplanetary accretion disks apparently increase by coagulation and annealing at temperatures below 250 K [16].

The implication of these observations is that rock-forming elements persist in solid form in the diffuse ISM, in molecular clouds, and in circumstellar accretion disks. Although the nature of the solid grains may be altered to varying degrees in each environment by cyclical growth, annealing, and devitrification, the preponderance of evidence is that elements like Si, Mg, Ca, Al, Fe, Na, and K entered the protoplanetary disk surrounding the nascent Sun as solids.

## 3. Processing solids in the early solar nebula

Elements comprising rocky objects of the Solar System were separated according to their volatilities [17]. Since the rock-forming elements apparently entered the nebula in solid form, transfer of these elements between condensed and vaporous phases must have occurred primarily within the nebula. Separation of elements according to volatility can occur by either incomplete evaporation or incomplete condensation. In general, partial condensation suggests that the elements evolved from high to low temperatures while partial evaporation suggests the material evolved from low to high temperatures. The meaning of 'high' and 'low' in this context depends upon the elements involved in the partitioning (Section 4).

Temperatures and pressures in the accretion disk were highest near its center and decreased with radial distance [18]. Astronomical observations of young stellar objects and mathematical simulations suggest that early in its evolution the protosun accreted at a rate of $\sim 1 \times 10^{-5}$ $M_\odot$ $yr^{-1}$ [11]. The disk is expected to have acted as a steady-state source for the growing nebular core for tens of thousands of years [18]. Material within 2 AU of the growing star would have been consumed every 80 years based on a steady-state canonical disk mass of 0.02 $M_\odot$. As the protosun entered its T Tauri phase, accretion is expected to have slowed, by analogy with T Tauri stars, eventually settling to a rate of $\sim 1 \times 10^{-8}$ $M_\odot$ $yr^{-1}$ that persisted for perhaps several million years [11]. The material comprising the inner 2 AU of a 0.02 $M_\odot$ disk would have been consumed every 80 000 years during this interval. These estimates for accretion rates suggest that the material from which planets were made came from distal regions of the accretion disk (heliocentric distances beyond the present-day positions of planets) as a result of radial drift.

Hydrodynamical calculations provide estimates for pressures and temperatures in the accretion disk that gave rise to our Solar System [18–20]. Based on these models, one can infer that the maximum midplane temperature attained at the present-day median position of the asteroid main belt (2.7 AU) was approximately 1000 K. At 1 AU temperatures may have been as high as 1500 K. Accretion could have sustained such high temperatures for perhaps 20 000 years [20]. Pressures are expected to have been $\leq 10^{-5}$ bar at positions $\geq 1$ AU.

Evidently, for perhaps tens of thousands of years, solid silicates and oxides should have been subject to partial evaporation upon drifting from cool distal regions of the nebula to the warmer region that lay between 3 and 1 AU from the protosun [21,22]. The bulk of the dust

was ferromagnesian in composition [13]. There is little evidence that temperatures were sufficiently high in this region to cause complete evaporation of ferromagnesian solids (>1500 K, [21]). Partially evaporated grains that eventually drifted closer to the nebular core would have been replaced by fresh in-falling solids coming from cooler regions beyond 3 AU and from above and below the midplane of the disk. Separation of elements in the gas and solid phases is thought to have occurred by a net outward flow of pressure-supported gas relative to the in-falling grains [23]. Chondrules in chondrites record temperatures in excess of 1500 K but are widely acknowledged to be the products of transient heating events such as localized collisions or collision-induced shock waves [24].

## 4. Partitioning of elements by volatility

Elemental abundances normalized to Ca and CI carbonaceous chondrite are used throughout this paper. Concentrations normalized to Si and CI are used in cosmochemistry by convention. Normalization to Ca is preferred because silicon-normalized concentrations obfuscate the nature of volatilization reactions. Silicon is not conserved in the condensed phase during volatilization at the temperatures of interest [25]. Ca, on the other hand, is retained in the condensed phase during volatilization [25].

Normalization to Ca and CI yields quantities that are equivalent to masses relative to a CI precursor if volatilization controlled elemental concentrations. This useful property is revealed by first considering the ratio of the concentration of element $x$ in an object before and after volatilization:

$$\left(\frac{c^x}{c_0^x}\right) = \frac{m^x}{m_0^x}\frac{M_0}{M} \tag{4}$$

where $c^x$ is the concentration of element $x$ in the condensed phase, $m^x$ is the mass of element $x$ in the condensed phase, $M$ is the total mass of the condensed phase, and the subscript 0 refers to the initial quantities. From Eq. 4 it is evident that changes in concentration arise from changes in total mass as well as from changes in the mass of the element of interest. Concentration ratios alone do not distinguish one effect from the other. It is for this reason that results of some evaporation experiments have been reported in terms of extensive mass loss rather than as changes in concentrations [25].

For unambiguous comparisons between experimentally determined volatilities of the elements and the elemental abundances in Solar System objects, it is useful to remove the effects of total mass on the concentration data and instead examine the masses of the elements relative to their initial values. This is possible by recognizing that Ca, a refractory lithophile element, is effectively non-volatile under the relevant conditions [25–27]. Assuming that the compositions of CI meteorites are representative of the original compositions of planetary and asteroidal precursors (i.e., solar abundances apply), the ratio of the Ca concentration in CI meteorites ($c_{\mathrm{CI}}^{\mathrm{Ca}}$) to the concentration of Ca in a given object $j$ ($c^{\mathrm{Ca}}{}_j$) is equal to the total mass of the object relative to its mass when it had a CI composition, or $M_j/M_{\mathrm{CI}}$, so long as volatility controlled fractionation:

$$\left(\frac{c_{\mathrm{CI}}^{\mathrm{Ca}}}{c_j^{\mathrm{Ca}}}\right) = \frac{m_{\mathrm{CI}}^{\mathrm{Ca}}}{m_j^{\mathrm{Ca}}}\frac{M_j}{M_{\mathrm{CI}}} \simeq \left(\frac{M_j}{M_{\mathrm{CI}}}\right) \tag{5}$$

Multiplying Eq. 4 by Eq. 5 yields:

$$\left(\frac{c_j^x}{c_{\mathrm{CI}}^x}\right)\left(\frac{c_{\mathrm{CI}}^{\mathrm{Ca}}}{c_j^{\mathrm{Ca}}}\right) = \frac{m_j^x}{m_{\mathrm{CI}}^x}\frac{M_{\mathrm{CI}}}{M_j}\frac{M_j}{M_{\mathrm{CI}}}\frac{m_{\mathrm{CI}}^{\mathrm{Ca}}}{m_j^{\mathrm{Ca}}} \simeq \left(\frac{m_j^x}{m_{\mathrm{CI}}^x}\right) \tag{6}$$

where $m_j^x$ is the mass of element $x$ in reservoir $j$. Eq. 6 permits calculation of the mass of an element $x$ in reservoir $j$ representing a planet or parent body relative to the mass of $x$ in the original CI-like precursor. Concentrations transformed in this way are extensive in so far as the original mass of Ca (i.e., numbers of Ca atoms) was unchanged during elemental fractionation. It is important to realize that the right hand side of Eq. 6 applies to an aliquot of the CI reservoir what ever the original size of that aliquot. The only assumption is that reservoir $j$ began with relative elemental abundances equal to those of the CI reservoir.

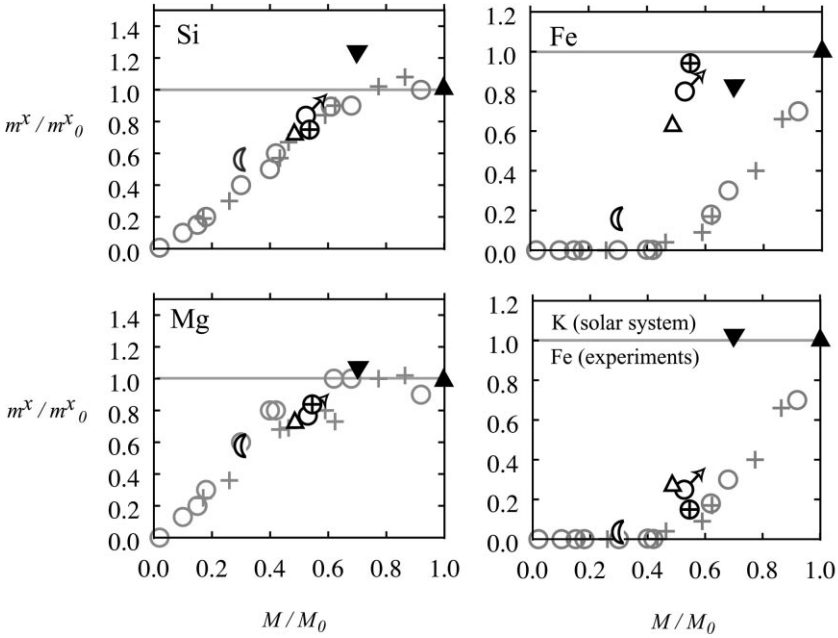


Fig. 1. Fractional mass depletions in Si, Mg, Fe, and K plotted against fractional reductions in total mass for Solar System bodies (black symbols) and residues of partial evaporation in the laboratory (gray symbols). Values for Solar System bodies were calculated using Eqs. 5 and 6. Standard symbols are used for Earth, Mars (SNC), and Moon. Additional symbols are: filled triangle = CI carbonaceous chondrite, upside down filled triangle = L ordinary chondrite, and open triangle = CV carbonaceous chondrite. Data for Earth, Mars, and chondrites are from Wänke and Dreibus [28], Wasson and Kallemeyn [41], and McDonough and Sun [29]. Those for the Moon are from Taylor [42]. Gray crosses show residues of evaporated molten CV3 chondrite [25]. Gray circles represent residues of evaporated melts with CI compositions [26]. Since K was not reported for the experiments, K in the Solar System objects is compared with Fe from experiments because the two are crudely comparable in their volatilities with respect to refractory lithophile elements.

By applying Eqs. 5 and 6 it is possible to compare directly the elemental abundances of Solar System objects with abundances in residues from evaporation experiments. Fig. 1 shows the masses of Si, Mg, Fe, and K for Earth, Mars (SNC meteorites and the assumption that all elements less volatile than Na are present in CI concentrations [28]), Moon, L ordinary chondrite, and CV carbonaceous chondrites relative to CI plotted against the total mass ratio on the basis of constant Ca abundance. Also shown are published experimental data obtained by evaporating molten samples of the Allende CV3 meteorite [25] and molten synthetic samples with CI abundances of Si, Mg, Al, Ca, Fe, and Ti [26].

The rocky bodies of the Solar System have elemental depletion patterns similar to the residues from the evaporation experiments (Fig. 1), although the data for Fe are systematically displaced from the experimental results. The similarity confirms that volatility was the first-order control on the relative abundances of the major rock-forming elements and provides a benchmark for assessing the magnitudes of the depletions.

Fig. 1 shows that the rocky bodies for which bulk compositions are known are depleted not only in moderately volatile elements like K, but also in the more refractory lithophiles Si and Mg (Si and Mg are transitional in volatility between refractory lithophiles and moderately volatile lithophiles), and that the extent of depletion is to be expected based on the total mass loss for these bodies relative to CI progenitors. Depletions in the moderately refractory lithophiles are not evident when normalizing to Si by definition (e.g., [28]). The ambiguity that arises when using Si is evident from Eq. 6 when Ca is replaced by Si. In this case the relation $m_j^{\mathrm{Si}} = m_{\mathrm{CI}}^{\mathrm{Si}}$ can not be as-

sumed to hold (cf. Fig. 1) and differences in concentrations normalized to Si reflect differences in the mass of Si as well as differences in the mass of the element of interest ($x$). If Ca was not completely conserved by virtue of its proven refractory nature, the points representing Solar System bodies in Fig. 1 would be shifted somewhat along the positive slope of the depletion trend (both abscissa and ordinate are similarly affected), but the overall pattern is robust. Depletion of Si and Mg in bulk Earth relative to CI chondrites has been observed previously [29]. When Ca is treated as a conserved element, it appears that rocky bodies in the Solar System are depleted in not only the moderately volatile lithophiles like K, but in the more refractory rock-forming elements like Si and Mg as well.

Depletion in the more refractory elements constrains the thermal regime in which vapor and solids coexisted in the vicinity of terrestrial planet and asteroid accretion. In order for the pattern in Fig. 1 to result from partial condensation, temperatures would have to have been higher than condensation temperatures for the prevalent ferromagnesian silicates ($>1500$ K, [21]) so that the moderately refractory lithophile elements that comprise these phases could have been primarily in the gas phase. Otherwise these elements could not have condensed from the gas to form the solids because they would not have been present in the gas in the first place. Conversely, if the pattern in Fig. 1 is the result of partial evaporation, temperatures must have approached, but not exceeded, at least for long, ferromagnesian silicate condensation temperatures ($\leq 1500$ K) in the region of terrestrial planet formation to allow for an appreciable rate of Si and Mg evaporation (evaporation rates are proportional to equilibrium vapor pressures) at the present-day position of Earth and Moon (1 AU) without completely volatilizing the solids. As described in Section 3, the temperature structure implied by evaporation of moderately refractory lithophile elements is consistent with our present understanding of the thermal structure of protoplanetary disks of Solar System mass while condensation of these elements from a gas implies a hotter environment.

## 5. K isotope fractionation – previous work

On the basis that evaporation would lead to kinetic K isotope fractionation according to the Rayleigh fractionation law, Humayun and Clayton [1] concluded that their measurements showing uniformity in $^{41}K/^{39}K$ for terrestrial and meteoritical materials within approximately 2‰ requires that evaporation was not an effective agent for volatile element depletion relative to CI chondrite. This conclusion has influenced subsequent work on the evolution of the early solar nebula. For example, Cassen [30] cited the conclusions of Humayun and Clayton as important evidence that the inner portion of the solar circumstellar disk must have been sufficiently hot for complete vaporization of silicate minerals. Based on this premise, Cassen showed that partial condensation triggered by a slowing of stellar accretion rate and reductions in disk opacity attending grain aggregation could have caused depletions in moderately volatile elements resembling those exhibited by some carbonaceous chondrites in the region between 1 and 3 AU.

However, Esat [2] questioned the conclusion that K isotope homogeneity is evidence for partial condensation. Esat argued that Rayleigh fractionation is an ideal circumstance that may not have characterized evaporation in the early solar nebula. He also asserted that condensation, like evaporation, should lead to kinetic isotope fractionation. Esat and Williams [31] later demonstrated the veracity of the latter argument by showing that condensation of gaseous K derived from volatilization of K-rich glass results in enrichments in $^{41}K$ relative to $^{39}K$ of 1–11‰ in the laboratory.

Humayun and Clayton expressed their results in terms of mass of K relative to initial mass. As a result, their analysis of the range of possible mechanisms for evaporative K loss and $^{41}K/^{39}K$ fractionation was incomplete. Implicit in the conclusion reached by Humayun and Clayton is the assumption that the diffusivity of K in the evaporating material was sufficiently rapid that the $^{41}K/^{39}K$ was effectively uniform in the residual condensed phase, as noted by Esat [2]. By comparing measured $\delta^{41}K$ with a Rayleigh fractionation model, Humayun and Clayton made the tacit

assumption that separation of elements and isotopomers by evaporation of protoplanetary materials could only have taken place if the latter were molten.

Young et al. [32] showed that oxygen isotope fractionation can be detected in the bulk residues of evaporated crystalline silica and that the magnitude of observable fractionation depends upon the rate of sublimation relative to the rate of diffusion. The mathematical model describing evaporation in terms of relative rates of ablation and diffusion used by Young et al. has proven applicable to other systems. For example, Davis et al. [33] measured the fractionations of Si, Mg, and O isotopes attending evaporation of molten forsterite and found that purely kinetic fractionation factors, expected to apply during free (Langmuir) evaporation, could not be used in combination with a Rayleigh fractionation model to account for the data. The authors noted that the Rayleigh model may not be valid because diffusivities of Si, Mg, and O in the melt are insufficient to maintain a homogeneous residue. The data of Davis et al. are modeled successfully using purely kinetic fractionation factors when the relative rates of ablation and diffusion are considered [32]. Competing rates also explain the different behaviors of dissimilar solid materials during evaporation. Crystalline $SiO_2$ (cristobalite), unlike crystalline $Mg_2SiO_4$ (forsterite), exhibits discernible oxygen isotope fractionation upon free evaporation in the laboratory because it volatilizes more slowly than forsterite. The fact that different crystalline solids evaporate at different rates has not been included in evaluations of the significance of the K isotope data until now.

## 6. Physical model for evaporation

### 6.1. Isotope fractionation

The present work addresses the possibility that volatilization of K occurred by evaporation of solids with limited capacity for K diffusion rather than the infinite K diffusivity implied by the Rayleigh model. The mathematical treatment has been described previously [32].

The isotopic and elemental effects of evaporation of mineral dust are simulated by equations for kinetic fractionation at the surface of a shrinking sphere coupled with those for diffusional transport within the sphere. The model sphere is taken as an analogue for a mineral grain evaporating in the early solar nebula.

Kinetic theory predicts that there will be fractionation of isotopes at the surface of a volatilizing mineral grain according to the equation:

$$\alpha = \sqrt{\frac{m}{m'}} \tag{7}$$

where $\alpha$ is the isotope fractionation factor, $m$ is the mass of the light isotopomer, $m'$ is the mass of the heavy (rare) isotopomer, and negligible quantum effects have been ignored. The fractionation factor describes the reaction rate for the heavy isotopomer relative to that for the light. In the case of volatilization of $K$, $\alpha$ is 0.9753 [1]. Alternative formulations for $\alpha$ involve evaluation of vibrational frequencies in the crystalline phase [32].

The Peclet number for ablative and diffusive transport, $\beta$, controls the degree to which isotope fractionation at the surface of a condensed phase is recorded in evaporative residues. It is defined in terms of the initial radius of the volatilizing object (assuming a spherical symmetry) $r°$, the rate of shrinkage due to mass loss $\dot{r}$ ($\partial r/\partial t$, where $t$ is time), and the diffusivity of the element of interest $D$ such that

$$\beta = -r^{\circ}\frac{\dot{r}}{D} \tag{8}$$

In general, values $> 50$ preclude detectable isotope fractionation signals in the bulk material because fractionation at the ablating grain surface is not transported into the interior of the grain by diffusion before it is removed by ablation. In this formulation, $\dot{r}$ is constant, in accord with experimental data for free evaporation [32,34].

Equations based on $\alpha$ and $\beta$ [32] were solved numerically to obtain radial profiles of $\delta^{41}K$ in evaporating materials. The profiles were integrated to obtain bulk $\delta^{41}K$ values at different fractional weight losses.

### 6.2. Elemental fractionation

The mathematical treatment of elemental fractionation is identical to that of isotope fractionation if $\alpha$ is redefined. For elemental fractionation $\alpha$ is the ratio of K concentration in vapor to that in evaporating solid, a reflection of the volatility of K relative to the remainder of the body. The precise composition and state of the material that comprised protoplanetary dust is uncertain, but estimates of the vapor pressure of K relative to other more refractory components in chondrites and basalts suggest $\alpha$ is greater than 10 and perhaps as high as 1000 [35]. The precise value for $\alpha$ is not critical, however. From asymptotic solutions to the equations of Young et al. [32] where time ($t$) is sufficiently long, it can be shown that depletion at the surface of the evaporating sphere is limited by movement of the boundary according to the relation

$$\lim_{t\to\infty}\frac{c^{\mathrm{K}}}{c^{\mathrm{K}^\circ}}=\frac{1}{\alpha} \tag{9}$$

such that differences in depletion with $\alpha=10$ and $\alpha=1000$ are negligible. A value of 100 was used for the calculations presented below.

## 7. Results

Four curves reflecting a range of possible effects on K and $^{41}K/^{39}K$ upon evaporation are shown in Fig. 2, upper panel. The plot is entirely analogous to figure 5 of Humayun and Clayton [1] and the two can be compared directly. The abscissa is the mass of K relative to the initial mass of K as it must be in order for comparisons with Rayleigh fractionation. The ordinate is the calculated shift in $^{41}K/^{39}K$ expressed as per mil deviations from the initial ratio. The largest effects occur for Rayleigh (or perfect) fractionation, corresponding to a Peclet number ($\beta$) of 0. With larger $\beta$ the isotopic shifts for a given mass loss of K decrease sharply. Fig. 2, lower panel is a magnification along the ordinate of the plot in Fig. 2, upper panel, in which some of the Solar System bodies analyzed by Humayun and Clayton [1] are compared with

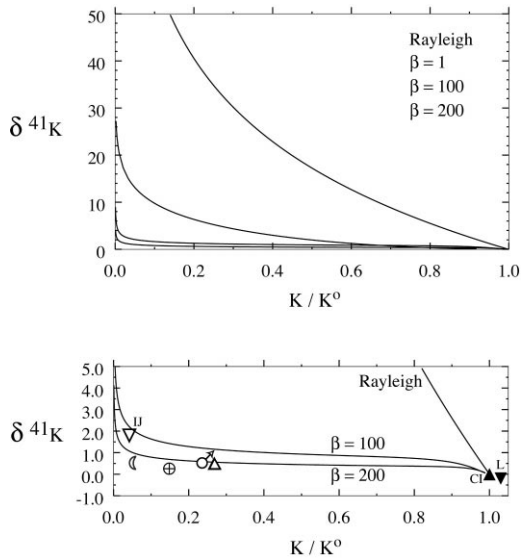


Fig. 2. (Upper panel) Plot of $\delta^{41}K$ (relative to initial $^{41}K/^{39}K$ ) vs. mass fraction of K remaining upon evaporation. Curves reflect different values for the evaporative–diffusive Peclet number $\beta$ defined in the text. Rayleigh fractionation (upper curve) corresponds to $\beta=0$. Note suppression of isotope effects with increasing $\beta$. The kinetic isotope fractionation factor is 0.9573 for all curves. (Lower panel) Magnified scale showing high-$\beta$ curves relative to Solar System bodies. The $\delta^{41}K$ values for the bodies are those of Humayun and Clayton [1]. The abscissa values for Earth, Mars, and chondrites (CV, CI, L) were calculated as described in the text from data in Wänke and Dreibus [28], Wasson and Kallemeyn [41], and McDonough and Sun [29]. The eucrite datum (IJ) represents the median of data for Ibitira (high Ca, high $\delta^{41}K$) and Juvinas (low Ca, low $\delta^{41}K$). The abscissa values for the eucrites were calculated from data in Wäanke et al. [43] and Morgan et al. [44] and those for the Moon from Taylor [42].

the evaporation curves. In constructing Fig. 2, lower panel, it was assumed that the initial chemical composition of the planetary precursor material was that of CI chondrite. The mass ratio of K relative to the CI abundance was obtained using Eq. 6. The mass of K relative to CI and the $^{41}K/^{39}K$ measurements of Humayun and Clayton [1] were then used to place each of the Solar System bodies on the plot. Humayun and Clayton used Si and La, rather than Ca, as normalizing elements. Lanthanum provides an appropriate means for calculating mass ratios of K and yields

values comparable to those based on conservation of Ca (Ca and La are both highly refractory [26]) while use of Si introduces errors as described in Section 4.

The calculations show that evaporation characterized by $\beta$ values of approximately $200 \pm 100$ are consistent with the measured $\delta^{41}$K values for eucrites, bulk Earth, SNC meteorites (Mars), CV carbonaceous chondrites, ordinary chondrites (e.g. L), and CI carbonaceous chondrites. The curves in Fig. 2, lower panel, apply to the ratios of $r°$, $\dot{r}$, and $D$ regardless of the actual values for the parameters.

## 8. Discussion

### 8.1. K isotope fractionation

The simple physical model for mineral evaporation shows that homogeneity in $^{41}$K/$^{39}$K among Earth, Moon, chondrites, and achondrites does not preclude volatilization of K in the early solar nebula. Homogeneity in $^{41}$K/$^{39}$K does place constraints on the evaporative–diffusive Peclet number, and thus grain size, temperature, and duration attending volatilization by virtue of the effects that these factors have on $\beta$.

High $\beta$ values apply to all objects, solid or liquid, once they reach asteroid size ($r°$ dominates). The constraint that $\beta$ was $\geq$100 therefore has greatest significance for the processing of condensed phases in the early solar nebula prior to accretion of asteroidal-sized objects when the characteristic size was on the order of centimeters or less [23].

### 8.2. K concentrations

High-$\beta$ evaporation could have occurred either by evaporation of solids or, under the right conditions, by evaporation of liquids. In the case of liquids there are two ways to achieve high $\beta$ numbers. One is if the initial sizes of the liquid objects were on the order of many tens of centimeters, a constraint imposed by the diffusivities of elements in silicate melts. This would require that the objects were much larger than chondrules and calcium aluminum-rich inclusions (CAIs) in chondrites. Chondrules and some CAIs are the only objects known to have been molten in space in the early solar nebula and there is no evidence that they were ever this large. The other way that silicate liquids might have evaporated at high $\beta$ is if the objects were similar in size to chondrules and CAIs but evaporated at rates that exceed free evaporation rates by a factor of 100 or more. This occurs in the laboratory when ambient pressures approach 100 kPa [36].

The extent to which high-$\beta$ evaporation of liquids could have altered K concentrations in protoplanetary material depends on complicated interactions among $\beta$ and the $\alpha$ values for all of the elements involved. In general, extreme values for $\alpha$, of order 0.1 or less for a refractory element like Ca for example, can produce large effects for concentrations even at a $\beta$ of $\geq 100$. Modeling such effects requires variable $\alpha$ and $\dot{r}$ (to see this consider what happens when concentrations of the most refractory elements approach unity). The range of possibilities involving diffusion-limited evaporation of liquids is currently under investigation [37].

Table 2
Total masses and elemental masses relative to CI precursors

| Body $j$ | $M_i/M_{CI}^{a}$ | $m_j^{Si}/m_{CI}^{Si\,b}$ | $m_j^{Mg}/m_{CI}^{Mg\,b}$ | $m_j^{Fe}/m_{CI}^{Mg\,b}$ | $m_j^{Rb}/m_{CI}^{Rb\,b}$ | $m_j^{K}/m_{CI}^{K\,b}$ |
|---|---|---|---|---|---|---|
| Moon | 0.29 | 0.56 | 0.57 | 0.16 | 0.04 | 0.04 |
| Earth | 0.54 | 0.73 | 0.85 | 0.97 | 0.12 | 0.15 |
| Mars (SNC) | 0.53[c] | 0.82[c] | 0.78[c] | 0.80[c] | 0.20[c] | 0.23[c] |
| CV | 0.48 | 0.72 | 0.72 | 0.63 | 0.27 | 0.27 |
| L | 0.70 | 1.24 | 1.08 | 0.83 | 0.98 | 1.03 |

[a]Eq. 5 and data from [28,29,41,42].
[b]Eq. 6 and data as above.
[c]Based on the assumption that Ca, Si, and Mg concentrations are identical to CI [28].

Although high-$\beta$ evaporation of liquids is feasible under special circumstances, it is normal for evaporation of crystalline solids. If the lithophile elements in the early solar nebula resided in a heterogeneous population of solids, then elemental fractionation by evaporation should have occurred since solids with different chemical compositions and different structures evaporate at different rates. If this heterogeneous material was crystalline, it would have evaporated with high $\beta$, causing elemental fractionation but not isotope fractionation.

## 9. Evaporation of heterogeneous crystalline solids

The progenitor planetary material that hosted K in the early solar nebula is unknown. However, alkalis could have been present in solids other than the abundant ferromagnesian phases evidenced in astronomical observations. Solids in the diffuse ISM are largely amorphous and evaporation of feldspathic glass is almost certainly a low-$\beta$ process with respect to K ($\beta < 1$) because of the high diffusivities of alkalis in the glass [38]. However, there is evidence for annealing of amorphous material to produce crystalline phases in protoplanetary disks [16] and crystalline feldspars can evaporate with high $\beta$. The effects of volatilizing a multimineralic reservoir of crystalline solids can be illustrated by comparing the evaporation rates of feldspar, an analogue for the unknown K host in the early solar nebula, and forsterite, representing the ferromagnesian phases in the nebula. The choice of feldspar as the analogue for the K carrier is based on the observation that some primitive materials like interplanetary dust particles contain feldspar as a host for alkali elements [39]. The actual source of the potassium is of course speculative in the absence of more detailed astronomical data bearing on the identity of mineral grains surrounding young stellar objects.

Precise measurements of feldspar evaporation rates have not been made, but the maximum rate of free evaporation (Langmuir evaporation) can be estimated from Knudsen cell measurements of plagioclase vapor pressures [27,35] using

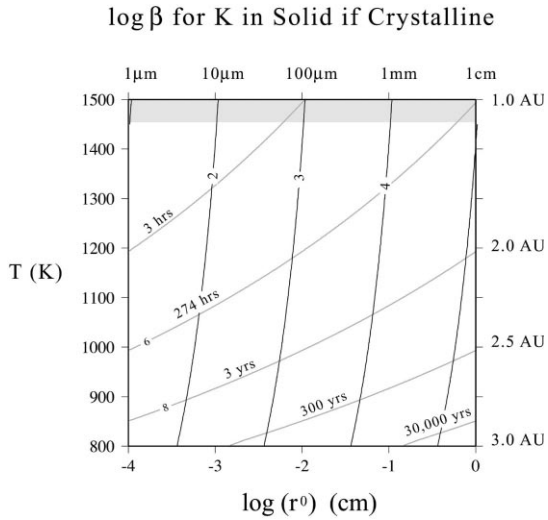


Fig. 3. Contours (solid lines) of log $\beta$ for K in crystalline feldspar as a function of temperature and grain size based on parameters in Table 3. Also shown are contours (gray lines) for log$\tau$ where $\tau$ (s) is the life span of an evaporating grain of feldspar assuming a spherical geometry.

the expression:

$$J_{\text{evap}} = \frac{1}{N_{\text{A}}} \frac{P}{\sqrt{(2\pi mkT)}} \tag{10}$$

where $J_{\text{evap}}$ is the evaporative flux in mol/(m$^2$ s), $N_{\text{A}}$ is Avagadro's constant, $P$ is the vapor pressure (Pa), $m$ is the mass of the evaporating species (kg), $k$ is Boltzmann's constant, and $T$ is temperature (K). Nagahara and Kushiro [27] found that plagioclase evaporates (sublimes) incongruently to yield a non-stoichiometric product rich in Ca and Si at grain margins. Based on their analysis, the reaction for plagioclase evaporation is:

$$[\text{Ca}_{1-x}\text{Na}_x\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8]_{\text{s}} \rightharpoonup x\text{Na}_{\text{v}} + x\text{Al}_{\text{v}} + x\text{SiO}_{\text{v}} + \frac{3x}{2}\text{O}_{2_{\text{v}}} + [\text{Ca}_{1-x}\text{Al}_{2-2x}\text{Si}_2\text{O}_{8-4x}]_{\text{s}} \tag{11}$$

where subscripts s and v signify solid and vapor, respectively. The gas phase in this reaction has the stoichiometry of nepheline. An Arrhenius-type rate equation for plagioclase evaporation (Table 3) is defined by the average mass for the gaseous species in Eq. 11, the vapor pressures of $1 \times 10^{-3}$

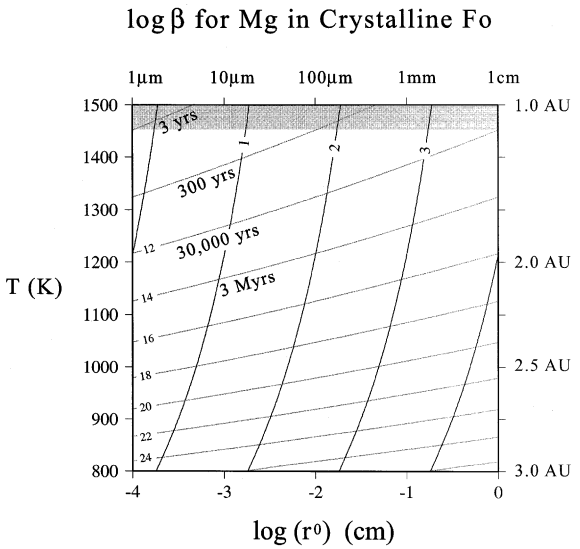


Fig. 4. Contours (solid lines) of log$\beta$ for Mg in forsterite as a function of temperature and grain size based on parameters in Table 3. Also shown are contours (gray lines) for log$\tau$ where $\tau$ (s) is the life span of an evaporating grain of forsterite assuming a spherical geometry.

and 0.1 Pa at 1373 and 1773 K, respectively cited by Nagahara and Kushiro [27] (consistent with the data in [35]), Eq. 10, and the slope and intercept for a plot of ln $J_{evap}$ vs. $1/T$.

The diffusivity of K in plagioclase can be combined with the estimated rate of plagioclase evaporation to yield values for $\beta$ as a function of grain size and temperature. Results (Fig. 3) show that grains of crystalline feldspar with diameters of 20 μm or more will evaporate with $\beta$ high enough to preclude K isotope fractionation ($\beta \geq 100$) at temperatures corresponding to the region of planet and asteroid formation in the early solar nebula. The minimum grain size consistent with high-$\beta$ evaporation can be extended downward to about 1 μm if evaporation took place further out in the nebula at temperatures of 600 K or less. High-$\beta$ evaporation of K from plagioclase is supported by the lack of K depletion in plagioclase residues following evaporation [27].

Comparing the life span of grains in Fig. 3 with the time scales for transport in the nebula (Section 3) one finds that felspar grains less than several mm in diameter could have evaporated completely at heliocentric distances as great as 3 AU (i.e., as far out as the outer limit of the present-day asteroid main belt). In this same region and under the same conditions (i.e., Langmuir evaporation) the amount of crystalline forsterite lost to the vapor phase would be minimal (Fig. 4). Further out in the nebula, beyond 3 AU, the rate of feldspar evaporation allows for significant mass loss at temperatures as low as 600 K while the elements comprising forsterite would remain entirely in the solid. It follows that appreciable amounts of alkali elements residing in crystalline feldspathic materials would have been lost to vapor in the nebula while moderately refractory elements like Si and Mg would have been retained in solids until the dust reached the region $<1.5$ AU from the Sun (Figs. 3 and 4).

Figs. 3 and 4 suggest that evaporation of ferromagnesian and feldspathic crystalline solids at distances from the protosun of $\sim 3$ AU would have resulted in loss of K and other alkalis (e.g., Rb, Table 2) relative to Ca, Si, Mg, and other more refractory lithophile elements without fractionation of the isotopes of K. Volatilization of feldspar would have moved Al from solid to vapor while leaving Ca in the solid (Eq. 11). Mobility of Al relative to Ca is a signature of feldspar–vapor reaction since it contrasts with the behavior of these elements during evaporation of molten chondritic material where Al and Ca are both retained by the condensed phase [25,33]. It has been suggested that Al may be depleted by as much as 15% relative to Ca in at least the upper portion of Earth's mantle [40]. Depletions of Al relative to Ca in mantle rocks are usually attributed to the effects of fractionation during igneous processes rather than to the composition of bulk Earth [29], but an alternative explanation could

Table 3
Arrhenius rate equations $k = A\ \exp(-E_a/(RT))$

| $k$ | $A$ | $E_a$ (kJ/mol) | Notes |
|---|---|---|---|
| $D_K^{albite}$, cm$^2$/s | $3.0\times10^{-3}$ | 242.0 | [38] |
| $\dot{r}$ plagioclase, cm/s | 82.3 | 226.4 | calculation described in text |
| $D_{Mg}^{forsterite}$, cm$^2$/s | $1.3\times10^{6}$ | 608.0 | [47] |
| $\dot{r}$ forsterite, cm/s | $4.8\times10^{8}$ | 574.4 | [22,34] |

be incongruent vaporization of feldspathic planetary precursors.

## 10. Conclusions

Consideration of a simple physical model in which mineral grains with finite K diffusivities shed mass by evaporation shows that homogeneity in $^{41}K/^{39}K$ among rocky bodies of the Solar System does not preclude extensive mass loss by evaporation relative to a CI reservoir in the protoplanetary solar nebula. Instead the data constrain the grain size, temperature, and duration attending mineral evaporation through the effects that these factors have on the evaporative–diffusive Peclet number. Significant depletion in K and other alkali elements without changes in $^{41}K/^{39}K$ among rocky bodies of the Solar System is explained if the progenitor K hosts were crystalline mineral grains that evaporate more rapidly than ferromagnesian crystalline phases. Low masses of moderately refractory rock-forming elements like Si and Mg relative to a CI chondrite reservoir in some Solar System bodies support the proposed evaporation model.

It is suggested that transfer of elements between a gaseous and condensed state varied across the early solar nebula in response to temperature and that evaporation of solid dust comprising the precursors to planets can not be ruled out as a mechanism for this transfer.

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