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Reply to comment on 'Assessing the implications of K isotope cosmochemistry for evaporation in the preplanetary solar nebula' by E. Young

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Abstract

Humayun offers several criticisms of the analysis of K isotope cosmochemistry by Young. Although Humayun's comments provide a useful description of diffusion-limited evaporation, they are not relevant to the mechanism for volatile element depletion put forward by Young. The mechanism described by Young is evaporation of a 'heterogeneous mixture of crystalline solids'. In presenting his model Young made four essential assertions: (1) the truism that the more volatile minerals are composed of the more volatile elements; (2) most rock-forming elements likely entered the early solar nebula in solid form; (3) dust in the early solar system was unlikely to be uniform in composition on the scale of individual grains; and (4) partial evaporation of crystalline solids has little effect on the isotopic composition of the residues. Humayun expresses concerns about the relevance of the last assertion but does so without the vital context provided by assertions (1)–(3). There are two underpinnings to Humayun's comments. First is the tacit assumption that dust in the early solar system was composed of grains with identical chemical compositions, effectively ignoring Young's proposed mechanism for volatile element depletion. Second is the notion that the mass fractions used by Young are extensive parameters that have little to do with the original paper by Humayun and Clayton. The first issue of whether or not solids in the early solar system were uniform in composition at the grain scale is open for debate. Young's model assumes that the grains were not all identical in composition. The second issue of whether or not Humayun and Clayton and Young used comparable methods for depicting depletion of K in solar system bodies should not be a matter for debate because the normalized concentration ratios used by Humayun and Clayton are equivalent to the *intensive* mass fractions used by Young, as shown again below.

1. Young's mechanism for selective depletion of volatile elements – a mixed population of mineral grains

Young [1] proposed that mineral grains of different chemical compositions could evaporate at different rates, and that this evaporation would naturally lead to volatile element depletion in the solids that remain while preserving the isotopic composition of the solids. This proposition appeals to the fact that minerals that comprised dust in the early solar system evaporated at rates that depended upon the volatility of their constituent elements. It also appeals to the fact that

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evaporation of crystalline solids is characterized by a high value for what was called the 'evaporative-diffusive Peclet number' (β).

All of Humayun's comments regarding the nature of high-β (i.e. diffusion-limited) evaporation are correct. He correctly states that high-β evaporation can not lead to reductions in K concentrations for a uniform starting material (i.e. a population of objects that are all chemically identical to one another). However, Young introduced his model by stating that the starting material was not uniform. As described in the paper, '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' (Section 8.2, top of p. 330, emphasis added).

The contention that minerals of different chemical compositions evaporate at different rates, and that those composed of more volatile elements evaporate at higher rates was illustrated with calculations in [1]. For this purpose, Young [1] showed that a feldspar will evaporate orders of magnitude faster than a forsterite of comparable size (Young's figures 3 and 4). Indeed these calculations show that at even moderate nebular temperatures of 800 K, a grain of feldspar with a diameter of 100 μm would survive for just a few hundred years while a grain of forsterite of the same diameter would survive essentially indefinitely (Young's figures 3 and 4). It was not Young's purpose to propose that K entered the early solar system as feldspar (as stated in [1] Section 9: 'The actual source of the potassium is of course speculative in the absence of more detailed astronomical data…'). Instead the calculations were presented to quantify the suggestion that the solid hosts for K may have evaporated more rapidly than the primary solid hosts of Mg, for example. The nature of the solids that entered the early solar nebula was discussed at length in [1].

Humayun in his comment correctly points out that the model proposed by Young goes beyond K cosmochemistry and is indeed a model for volatile element depletion in general. It is based on the simple principle that evaporative flux J is proportional to the vapor pressure P according to the equation:

$$J = \frac{1}{N_A}\frac{P}{\sqrt{2\pi kT}} \tag{1}$$

where N_A is Avagadro's constant, T is temperature, and k is Boltzmann's constant. If volatile elements comprise a mineral, the vapor pressure tends to be high and the evaporation rate also tends to be high. Eq. 1 is an oversimplification to be sure (the retarding effects of the evaporation coefficient α, evaluated empirically by experiments, are excluded here) and this is why Young presented calculations based on published experimental data that confirm the general concept embodied by Eq. 1 (figures 3 and 4 in [1]).

Humayun's equations (2a) and (2b) do not address the model proposed by Young [1]. In order to relate Humayun's equations to Young's model, one must consider a mixture of grains, including some that are K-rich and some that are K-poor. The amount of K in the physical mixture of solids at any particular time is determined primarily by the mass of K-rich grains, or $m_{\mathrm{K-rich}}$. Similarly, the mass of Si would be determined by the mass of grains containing most of the Si, or $m_{\mathrm{Si-rich}}$. After a specified duration of evaporation, K/Si for the reservoir composed of these grains will evolve according to the relative changes in $m_{\mathrm{K-rich}}$ and $m_{\mathrm{Si-rich}}$. The element ratio normalized to the initial condition (specified by the o subscript) is:

$$\frac{(\mathrm{K/Si})}{(\mathrm{K/Si})_o} = \frac{(m_{\mathrm{K-rich}}/m_{\mathrm{K-rich,o}})}{(m_{\mathrm{Si-rich}}/m_{\mathrm{Si-rich,o}})}. \tag{2}$$

If the mass of the K-rich grains decreases more rapidly than the mass of the Si-rich grains we have:

$$\frac{m_{\mathrm{K-rich}}}{m_{\mathrm{K-rich,o}}} < \frac{m_{\mathrm{Si-rich}}}{m_{\mathrm{Si-rich,o}}} \tag{3}$$

and therefore:

$$\frac{\mathrm{K}}{\mathrm{Si}} < \left(\frac{\mathrm{K}}{\mathrm{Si}}\right)_o. \tag{4}$$

This is Young's model cast in the terms used by Humayun in his comment. Young's contention is that the inequality in Eq. 3 is likely to have been the case in the early solar system.

2. K/K_o is the measure of K deficit used by Humayun and Clayton and by Young

Humayun argues that Humayun and Clayton [2] used the concentration before and after evaporation as the measure of K depletion in constructing their figure 5 while Young [1] uses the mass of K before and after evaporation in constructing his figure 2. In fact, Young uses the mass fraction (not mass), and this mass fraction is the same parameter used by Humayun and Clayton.

Young pointed out that the abscissa values in Humayun and Clayton's figure 5 and Young's figure 2 are proxies for the mass fractions of K and not K concentrations (Section 4 in [1]). Therefore, the curves in Young's figure 2 (to be compared with figure 5 in [2]) say nothing about the concentration of K in the residue. They simply illustrate that high-β evaporation could lead to a reduction in the mass of K in the residues without affecting the isotopic composition of K in the residue (at the 1‰ level). In the context of Young's proposed mechanism for volatile element depletion, the high-β curves in his figure 2 apply only to those K-bearing grains of dust in the early solar nebula that were subjected to partial evaporation. They have no bearing on the fate of material that did not contain K and no bearing on grains that completely evaporated (neither of which effects the isotopic composition of K in the residue). The same is true of the Rayleigh fractionation curve ($\beta = 0$) in both figures. The Rayleigh equation applied to the evolution of $^{41}K/^{39}K$ does not tell us explicitly how the other elements behave while $^{41}K/^{39}K$ goes up and K/K_o goes down.

Humayun is incorrect in his assertion that a mass fraction is an extensive variable. Extensive variables depend upon absolute amount and are never dimensionless. Since mass divided by mass is dimensionless, mass fraction is clearly an intensive variable. In the present context mass fraction of K means the mass of K divided by the mass of K when the reservoir of interest (no matter the size) had a composition like that of the CI meteorites. It is vital to understand, but perhaps easily overlooked, that it is valid to compare mass fractions of K remaining in reservoirs that started out with different total masses so long as each had a CI chemical composition to begin with (mass fraction is intensive). Humayun correctly points out that the initial sizes of the reservoirs (e.g. initial masses of potassium, or K_o) that went to make the terrestrial planets and other rocky bodies are inherently unknowable, but Young [1] shows that the mass fraction of an element, e.g. K/K_o, is knowable.

Humayun is mistaken in suggesting that 'mass fraction [of K] remaining' and F in the Rayleigh equation are both measures of the concentrations of K normalized to the concentrations prior to fractionation. The fact that F in the Rayleigh equation is a mass fraction, i.e. K/K_o (mass or atom fraction of K remaining), and not a concentration ratio is established unequivocally by deriving the Rayleigh equation for the purpose at hand. The derivation is provided in the Appendix for the interested reader. The derivation establishes beyond argument that F in the present context is K/K_o. The derivation also shows that F in the Rayleigh equation will always be the ratio of the denominators of the concentrations or isotope ratios being monitored. The parameter F is never a concentration ratio and does not reflect concentration because it monitors only the element of interest. The fractional loss of K is described by F regardless of the value of β, the concentration of K in the residue, and the initial mass of the starting material.

The La-CI 'double normalization' used by Humayun and Clayton (and other cosmochemists) is a proxy for $F = K/K_o$ because the ratio of element concentration ratios:

$$\frac{(C_K/C_{La})}{(C_K/C_{La})_{CI}} = \frac{m_K}{M}\frac{M}{m_{La}}\frac{M_{CI}}{m_{K,CI}}\frac{m_{La,CI}}{M_{CI}} \qquad (5)$$

reduces to the 'mass fraction remaining' of K if the reservoir that evolved to form a body began with a CI-like C_K/C_{La} (as assumed by [2]) and if the mass of La was left unchanged. The size of the reservoir is of no consequence to this argument. The mass of La is likely to have been conserved since volatility controlled the partitioning of the elements and La is essentially non-volatile [1]. In this case Eq. 5 becomes:

$$\frac{(C_K/C_{La})}{(C_K/C_{La})_{CI}} =$$

$$\frac{m_K}{M}\frac{M}{m_{La}}\frac{M_{CI}}{m_{K,CI}}\frac{m_{La,CI}}{M_{CI}} = \frac{m_K}{m_{K,CI}} = \frac{K}{K_o} = F \qquad (6)$$

because the total masses M and M_{CI}, and the masses of La, m_{La} and $m_{La,CI}$, cancel. Here lies the usefulness of normalizing to a conserved element, i.e. an element that is not affected by volatilization. Double normalization to a refractory element offers a means for estimating F and therefore comparing meteorite and planetary compositions to Rayleigh curves. It also provides a means for evaluating which elements were lost or gained within a particular reference frame (La may not be entirely conserved, but it may be more so than the other elements). Concentrations alone are inadequate in this regard [1]. Young [1] used Ca as the normalizing element in Eq. 6 because like La, it is refractory. Young's proposed mechanism for preserving the masses of non-volatile elements is to have them locked up in refractory mineral grains.

Humayun suggests that the La-CI double normalization used by Humayun and Clayton [2] is a measure of the concentration of K before and after element partitioning, or $C_K/C_{K,CI}$ (where CI refers to the initial condition), rather than the mass fraction of K remaining. However, it is clear that $(C_K/C_{La})/(C_K/C_{La})_{CI} = C_K/C_{K,CI}$ only when the concentration of La is the same in every body. This is of course not the case. Earth, Moon, and many chondrites do not have CI-like concentrations of La ([1] and references therein). The La-CI double normalization used by [2] is a measure of K/K_{CI} and not $C_K/C_{K,CI}$.

Humayun and Clayton [2] used a double normalization to Si and CI for some bodies. In this case Eq. 6 is neither F nor $C_K/C_{K,CI}$ because the concentration of Si is not the same for all bodies and the mass of Si is likely to have been altered by volatilization ([1], figure 1). This is the reason that Young [1] chose to normalize all data to Ca; Si is volatile and cannot serve as a normalizing element where volatility is important but Ca and La can because they are always refractory. In practice since K is significantly more volatile than Si, the use of Si rather than Ca or La as a normalizing element shifts the estimated values of F for solar system bodies only slightly; $(C_K/C_{Si})/(C_K/C_{Si})_{CI}$ is a crude estimate of K/K_{CI} but it is a poor estimate of $C_K/C_{K,CI}$ (because C_{Si} is so variable from body to body).

3. Some minor points

Humayun raises a host of smaller points, most of which are answered satisfactorily once the model proposed by Young is understood. Nevertheless, there remain several points that deserve direct response.

Near the end of his comment Humayun dismisses selective evaporation of mineral grains by suggesting that the alkali elements are partitioned from one another in rocky bodies. However, Young [1] (table 2) showed that the mass losses of K and Rb (based on conservation of Ca) are indistinguishable in solar system bodies. Using the published data cited in [1] one can compute values of Cs/Cs_o based on Ca normalization. For the L and CV chondrites the values match those for K and Rb (~1 and 0.25, respectively) while the values for Earth and Moon yield lower Cs/Cs_o than K/K_o and Rb/Rb_o by a factor of ~2 to ~3. The significance of these deviations is unclear. We should not dismiss the possibility, however, that our estimates of bulk trace element concentrations for planetary bodies may not be entirely accurate. In particular, Rb/Cs values for Earth and Moon have been disputed [3,4], and the possibility for selective partitioning of alkali elements into the cores of differentiated bodies at high pressures (especially Cs) limits the accuracy of estimates of bulk (as opposed to mantle+crust) concentrations [5]. In any case, understanding the reason that the relation $\mathrm{Cs/Cs_o} < \mathrm{K/K_o} \sim \mathrm{Rb/Rb_o}$ obtains for some bodies and not others will require a more thorough understanding of all sources of element partitioning in the early solar nebula and in the differentiated bodies themselves.

Humayun suggests that in order for Young's model to be correct, we should observe residues of partial evaporation in undifferentiated meteorites. However, Young's model permits complete evaporation of the more volatile grains with virtually no evaporation of the moderately refractory grains like forsterite (see figures 3 and 4 in [1]). As a result, there may be few if any signs that individual mineral grains experienced evaporative processing. The lack of identifiable evaporative residues presents no challenge at all to Young's model. Complete evaporation of some grains preserves $^{41}\mathrm{K}/^{39}\mathrm{K}$ of the remaining grains. High-β is required only for the K-bearing grains that survived.

Humayun seems to suggest that the diffusion of alkali elements in a feldspar may not limit mixing in the grains upon evaporation. This seems unlikely as there are no experimental data to support his suggestion that a crystalline solid would evaporate with $\beta < \sim 30$ [6,7]. Nevertheless, I agree with Humayun's statement that much remains to be learned about plagioclase evaporation. Indeed, much remains to be learned about incongruent evaporation of all sorts of pertinent mineral phases. The danger is that Humayun's assertion that the 'only valid' explanation for volatile element depletion in terrestrial planets and asteroids is partial condensation will stifle investigations into the ways in which minerals (and glasses) of different compositions evaporate.

4. Concluding remarks

The fundamental issue is whether or not the propensity for volatile element depletion among many rocky bodies of the solar system was a result of partial condensation from a nebular gas or was instead inherited from partial evaporation of grains that ultimately accreted to form planetesimals. Humayun and Clayton [2] suggested that uniformity in volatile element isotope ratios required partial condensation and precluded partial evaporation. Young [1] pointed out that volatile element depletion and uniformity in isotope ratios would have been a natural consequence of evaporation of dust. As a result, uniformity in light element isotope ratios does not alone resolve this issue.

The model put forward by Young [1] has to recommend it the fact that it relies on a zero-order consequence of stellar accretion: dust drifts inwards toward higher and higher temperatures in circumstellar disks. To the extent that dust was chemically heterogeneous on the grain scale, selective losses of volatile elements from solids to gas must have occurred in the early solar system. The alternative of partial condensation, put forward by Humayun as the 'only valid explanation' for volatile element depletion in planets and chondrites, requires 'large-scale vaporization events' of entirely uncertain origin.***[AH]***

Appendix. Addendum: Derivation of the Rayleigh equation

The meaning of the F parameter in the Rayleigh equation is made clear by deriving the Rayleigh equation applicable to $^{41}\mathrm{K}/^{39}\mathrm{K}$. Begin with the definition of the isotope ratio in the condensed phase (and for simplicity ignoring the gravimetric correction 39/41):

$$^{41}R = \frac{\left(\frac{m_{^{41}\mathrm{K}}}{M}\right)}{\left(\frac{m_{^{39}\mathrm{K}}}{M}\right)} = \frac{m_{^{41}\mathrm{K}}}{m_{^{39}\mathrm{K}}} \qquad \text{(A1)}$$

where M is the total mass and m is the mass of the indicated isotope. The analogous definition for the K isotope ratio in the vapor phase is:

$$^{41}R' = \frac{\left(\frac{m'_{^{41}\mathrm{K}}}{M'}\right)}{\left(\frac{m'_{^{39}\mathrm{K}}}{M'}\right)} = \frac{m'_{^{41}\mathrm{K}}}{m'_{^{39}\mathrm{K}}} \qquad \text{(A2)}$$

where the prime superscript signifies vapor. Mass balance for ^{39}K in the condensed phase–vapor phase system yields:

$$m_{^{39}\mathrm{K}} + m'_{^{39}\mathrm{K}} = m^{\mathrm{o}}_{^{39}\mathrm{K}} \tag{A3}$$

$$\mathrm{d}m_{^{39}\mathrm{K}} + \mathrm{d}m'_{^{39}\mathrm{K}} = 0. \tag{A4}$$

Similarly for ^{41}K:

$$m_{^{41}\mathrm{K}} + m'_{^{41}\mathrm{K}} = m^{\mathrm{o}}_{^{41}\mathrm{K}} \tag{A5}$$

$$\mathrm{d}m_{^{41}\mathrm{K}} + \mathrm{d}m'_{^{41}\mathrm{K}} = 0. \tag{A6}$$

The superscript o in Eqs. A3–A6 refers to the initial masses of the isotopes for the vapor and condensed phase combined. The differentials in Eqs. A4 and A6 expand to:

$$\mathrm{d}m_{^{41}\mathrm{K}} = \mathrm{d}(^{41}R\, m_{^{39}\mathrm{K}}) = {}^{41}R\,\mathrm{d}m_{^{39}\mathrm{K}} + m_{^{39}\mathrm{K}}\mathrm{d}^{41}R \tag{A7}$$

$$\mathrm{d}m'_{^{41}\mathrm{K}} = \mathrm{d}(^{41}R'\, m'_{^{39}\mathrm{K}}) = {}^{41}R'\,\mathrm{d}m'_{^{39}\mathrm{K}} + m'_{^{39}\mathrm{K}}\mathrm{d}^{41}R' \tag{A8}$$

using the definitions of ^{41}R and $^{41}R'$ in Eqs. A1 and A2.

Consider incremental transfer of an infinitesimal amount of potassium from solid to vapor indicated by $\mathrm{d}m'_{^{39}\mathrm{K}}$ with specified isotope ratio $^{41}R'$. Since $^{41}R'$ is constant over the increment of mass transfer, by mass balance and Eq. A8:

$$\mathrm{d}m'_{^{41}\mathrm{K}} = {}^{41}R'\,\mathrm{d}m'_{^{39}\mathrm{K}}. \tag{A9}$$

From Eq. A4 we can rewrite Eq. A9 as:

$$\mathrm{d}m'_{^{41}\mathrm{K}} = -{}^{41}R'\,\mathrm{d}m'_{^{39}\mathrm{K}}. \tag{A10}$$

Substituting Eqs. A7 and A10 into the equation for mass balance Eq. A6 gives:

$$0 = -{}^{41}R'\,\mathrm{d}m_{^{39}\mathrm{K}} + {}^{41}R\,\mathrm{d}m_{^{39}\mathrm{K}} + m_{^{39}\mathrm{K}}\mathrm{d}^{41}R. \tag{A11}$$

Rearranging the above:

$$\frac{\mathrm{d}m_{^{39}\mathrm{K}}(^{41}R - {}^{41}R')}{m_{^{39}\mathrm{K}}} = -\mathrm{d}^{41}R \tag{A12}$$

$$\frac{\mathrm{d}m_{^{39}\mathrm{K}}}{m_{^{39}\mathrm{K}}} = \frac{-\mathrm{d}^{41}R}{(^{41}R - {}^{41}R')} \tag{A13}$$

or

$$\frac{\mathrm{d}m_{^{39}\mathrm{K}}}{m_{^{39}\mathrm{K}}} = \frac{-\mathrm{d}^{41}R}{(^{41}R - \alpha^{41}R)} \tag{A14}$$

where $\alpha = {}^{41}R'/{}^{41}R$ as prescribed by the kinetics of evaporation (it is this definition of α that requires the condensed phase to be well mixed). Integration of Eq. A14 leads to:

$$\ln\frac{m_{^{39}\mathrm{K}}}{m^{\mathrm{o}}_{^{39}\mathrm{K}}} = \ln\frac{^{41}R}{^{41}R^{\mathrm{o}}}(\alpha - 1)^{-1}. \tag{A15}$$

Taking the exponentials of both sides of Eq. A15:

$$\frac{m_{^{39}\mathrm{K}}}{m^{\mathrm{o}}_{^{39}\mathrm{K}}} = \left(\frac{^{41}R}{^{41}R^{\mathrm{o}}}\right)^{(\alpha-1)^{-1}} \tag{A16}$$

and finally:

$$\frac{^{41}R}{^{41}R^{\mathrm{o}}} = \left(\frac{m_{^{39}\mathrm{K}}}{m^{\mathrm{o}}_{^{39}\mathrm{K}}}\right)^{(\alpha-1)} = F^{(\alpha-1)}. \tag{A17}$$

Eq. A17 is the Rayleigh fractionation equation depicting the change in ^{41}K/^{39}K with changes in the mass of K during evaporation of a well-mixed condensed phase. The derivation clearly identifies F as the mass fraction of K remaining in the condensed phase. It also shows that F says nothing about the concentration of K in the condensed phase since the only information contained within F is the mass of K at the start and the mass of K at some other point in the process. In order to relate these masses to concentration we would need to know the masses of all of the other constituents (total mass). Eq. A17 is agnostic as to how the masses of the other elements change. This is a general result; F is always the ratio of denominators of the isotope ratio or concentration terms on the left-hand side of the equation.

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