CAN LUNAR FORMATION THEORIES BE TESTED WITH K ISOTOPES? N. Dauphas[1], M. Meheut[2], M. Blanchard[2], H. Zeng[1], G. Galli[3,4], R.N. Canup[5], C. Visscher[6], N. Nie[1], [1]Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago (dauphas@uchicago.edu), [2]Géosciences Environnement Toulouse, Observatoire Midi-Pyrénées, CNRS UMR 5563, Université Paul-Sabatier, [3]Institute for Molecular Engineering, The University of Chicago, [4]Materials Science Division, Argonne National Laboratory, IL, [5]PSD, Southwest Research Institute, Boulder, [6]Dordt College, Sioux Center.

Introduction: The chemical compositions of lunar rocks differ in several respects from those of terrestrial rocks [1]. Among those distinguishing features is the depletion in volatile element K in the Moon relative to the Earth. The abundance of K is most often normalized to that of U because both elements have incompatible behaviors during magmatic processes but U is highly refractory, so the K/U is a simple and direct measure of depletion in volatile element K in planetary bodies (e.g., see Fig. 3 of ref. [2]). Relative to CI chondrites, the Earth is depleted in K by a factor of ~6 while the Moon is depleted by a factor of ~28. For comparison, angrites are depleted in K by a factor of ~110 while chondrites span a range from 0.8 (*i.e.*, an enrichment) for EL to ~4 for CV.

The reason for this depletion is poorly understood. It could have arisen from collision of an ultra-depleted impactor with the protoEarth only if over 80% of the Moon was derived from the impactor, which is achieved in some canonical impact models. If 70% of the Moon came from a K-depleted impactor like angrites [3], the inherited depletion factor in the Moon would have been ~18 [1/(0.7/110+0.3/6)], falling short of explaining the K depletion seen in the Moon. Advocating a high impactor contribution in the Moon (>80%) makes the problem of the Earth-Moon isotopic similarity in O, Ti and W more acute. This suggests that the giant impact event must have induced some loss of K.

Vaporization and condensation are processes that are known to induce equilibrium and kinetic isotopic fractionations. Early K isotope measurements showed that lunar rocks had the same isotopic compositions as Earth and chondrites [4] but the precision of those measurements was limited. A recent study revisited this question and found that lunar rocks were enriched in the heavy isotopes of K by +0.4 ‰ [5]. Wang and Jacobsen [5] used this observation to question the canonical giant impact scenario and argued that this was entirely consistent with a high-energy impact scenario involving near-complete homogenization of the Moon and Earth [6-7]. They however did not examine all plausible scenarios for fractionation of K isotopes during impact.

Two important processes can fractionate K isotopes during either vaporization or condensation [8 and references therein]. One is kinetic isotopic fractionation, which stems from the kinetic theory of gases through the Hertz-Knudsen equation. This fractionation follows from the consideration that light atoms or molecules tend to impinge surfaces at a higher rate than heavier species. The implication is that evaporation tends to enrich the solid/liquid residue in the heavy isotopes while condensation tends to enrich the condensed phase in the light isotopes. The second process is equilibrium, which leads to enrichments in the heavy isotopes in the phases that forms the strongest bonds. In the case of equilibrium between condensed phase and gas, the former will usually have heavy isotopic composition relative to the latter. The extent to which K depletion will be accompanied by K isotopic fractionation will depend on the role played by these various processes. Very few laboratory experiments have studied K isotopic fractionation during vaporization but important insights can be gained based on theoretical considerations.

Below, we evaluate how equilibrium and kinetic processes could have shaped K isotopic fractionation in the terrestrial and lunar rocks, and discuss implications for Moon-formation theories.
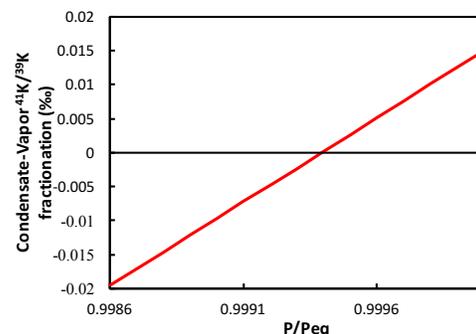
Fig. 1. Instantaneous K isotopic fractionation during condensation (see text and refs. 12 and 13 for details).

Equilibrium and kinetic isotopic fractionation between gas and condensate: *Equilibrium isotopic fractionation.* Knowing the phases involved and temperature of equilibration is all that is needed to calculate equilibrium isotopic fractionation. Under reasonable conditions for an impact-generated disk, K will condense in the temperature range 4000-3000 K [9-11] with gas K primarily speciated as gaseous atomic K.

For the condensed phase, we used microcline and orthoclase as model silicate compositions ($KAlSi_3O_8$). The equilibrium isotopic fractionation between coexisting phases (in ‰) is given by the difference in the logarithm of their reduced partition function ratios $1000 \ln \beta$. For an ideal monoatomic gas, $1000 \ln \beta = 0$. We calculated the value of $1000 \ln \beta$ of microcline using the DFT technique. At a temperature of 3000 K, we find an equilibrium fractionation Δeq between condensate and gas of 0.015 ‰ while a temperature of 4000 K yields a fractionation of 0.009 ‰ for the $^{41}K/^{39}K$ ratio. Huang et al. [10] previously reported K equilibrium isotopic fractionation and found values of ~0.029 and 0.017 ‰, respectively. These are higher than our calculated values by a factor of 2. Both sets of values are low in regard to the measured isotopic fractionation in lunar rocks.

Kinetic isotopic fractionation. Some high energy impact scenarios consider that sufficient equilibration must have taken place so as to allow the mantle of the Earth to have fully exchanged isotopically with the lunar disk [6,7]. It is thus likely that the vapor was either equilibrated with the condensed phase or simply inherited its composition from the Theia-protoEarth system if everything was vaporized. Any kinetic fractionation would thus most likely have taken place during condensation. Because light isotopes impinge surfaces at a higher rate than heavy isotopes, kinetic fractionation leads to an enrichment in the light isotopes of the condensate [12,13]. The extent of this fractionation is however going to depend on the degree to which the gas is supersaturated relative to thermodynamic equilibrium. If the gas is highly supersaturated (and neglecting any possible mass-dependence of the condensation coefficients), then the kinetic isotopic fractionation factor between condensate and vapor is Δki=$1000[(39/41)^{0.5}-1]$=-24.7 ‰. If the vapor pressure is equal to the equilibrium vapor pressure, then only equilibrium isotopic fractionation will be present.

Isotopic fractionation during condensation. In general, the isotopic fractionation between condensate and gas will depend on p=Peq/P (where Peq is the equilibrium vapor pressure) [14] (Fig. 1),

Δcond=$p\Delta$eq+$(1-p)\Delta$ki.

A complicating factor is whether the condensate remains in isotopic equilibrium with the vapor throughout condensation or it is effectively removed (because of kinetic barriers to isotopic exchange). These end-member scenarios can be modeled with batch or distillation models.

Discussion: The observation that needs to be explained is the ~+0.4 ‰ K isotopic fractionation between lunar and terrestrial rocks at ~80% K loss. Ki-

netic effects, because they would presumably enrich the condensates in the light isotopes, cannot explain the heavy isotope enrichment of the Moon relative to the Earth. Batch equilibrium also cannot explain this fractionation because the equilibrium fractionation factor is too small. A Distillation model does not help because the heaviest that the condensate can get is the equilibrium fractionation factor at the onset of condensation. If kinetic effects are present, the isotopic fractionation could be much higher but it would be opposite in sign. Our *ab initio* calculation and theoretical considerations suggest that to first order, the isotopic fractionation imparted to condensates in the aftermath of an energetic giant Moon-forming impact should be smaller or even opposite in sign to the observed K isotopic enrichment measured in lunar rocks. Wang and Jacobsen [5] reached an opposite conclusion because they considered evaporation as the driver for the isotopic fractionation but it is not clear what the physical setting would be for such evaporation to take place. The only way that this could work is if some condensates are re-evaporated because of decoupling with the gas but this is not a straightforward prediction of the model. Re-evaporation of condensates or moonlets after decoupling from the gas in the canonical model would also lead to heavy isotope enrichments in low-energy impact scenarios. Fundamentally, there is nothing that distinguishes high-energy impact models from the canonical model with regard to K isotopic fractionation, as both are partial condensation models.

Conclusion: The equilibrium K isotopic fractionation between condensate and vapor is too small to explain the heavy K isotopic composition of the Moon and kinetic effects make the situation worse. A heavy K isotope enrichment of the Moon is not a straightforward prediction of either high-energy or low-energy impact models.

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