

VOLATILE DEPLETION IN THE INNER SOLAR SYSTEM: RAYLEIGH DISTILLATION AND POTASSIUM ISOTOPES; Tezer M. Esat, Research School of Earth Sciences, Australian National University, Canberra 0200, Australia.

The rocky planets, the Moon and some meteorites are depleted in elements that are volatile at temperatures below about 1200 K. Large variations in condensation or vaporisation temperatures can be invoked to account for the segregation of volatile from refractory elements. Starting with an initial hot nebula, incomplete condensation and removal of uncondensed volatiles is one alternative; partial vaporisation and removal of volatiles by heating of cold nebular material is another possibility. Incomplete mass transport across spatial temperature gradients can cause mass dependent variations in isotopes, in particular, of light mass elements. If high temperature vaporisation occurs across a liquid-vacuum interface (Rayleigh distillation), mass flow is unidirectional, resulting in complete removal of vaporised material. In a gaseous envelope mass transport could occur bidirectionally through vaporisation as well as collisional capture such that, in the limiting case, the system will approach equilibrium with no net isotope fractionation. Similarly, during condensation or nucleation sticking probabilities can be less than unity and any isotope effects will be correspondingly diluted. Humayun and Clayton [1] have addressed the causes of volatile depletion in planetary materials by searching for mass dependent isotope fractionation in the moderately volatile element potassium. Samples investigated include chondrites, achondrites, lunar samples and two Ca-Al-rich inclusions (CAI). The data show normal isotope compositions except for confirming the effects in lunar soils which were first noted during the early 70's. Based on this data, Humayun and Clayton [1] rule out Rayleigh type distillation as the cause of volatile depletion. They extrapolate from this point and exclude the possibility of any mass loss due to vaporisation. Furthermore, they declare a distinction between "kinetic", Rayleigh type distillation and condensation; asserting that condensation only proceeds through an equilibrium process and with minimal isotope effects. On this basis, they attribute volatile depletion to partial condensation from an initially hot solar nebula. In this abstract, after considering the required conditions for Rayleigh type isotope fractionation, I will argue that both condensation and vaporisation are expected to produce similar outcomes and cannot be used to exclude one process over the other as the cause of volatile depletion. In fact, the distinction may be irrelevant as both incomplete vaporisation and incomplete condensation, of a type more general than the restrictive Rayleigh process, may have played a role in the early solar system.

Chemical procedures as well as isotope ratio measurements can cause mass dependent shifts in isotopes. High precision techniques, such as double spiking can discriminate between instrumental and natural mass dependent isotope fractionation. These methods cannot be used for K as at least four stable isotopes are required. For example, Russell et al., [2] found remarkably uniform and normal Ca isotopic composition in terrestrial, lunar and bulk meteoritic samples. Similar comments can be made for Ti and Mg. Isotope fractionation was only detected in CAI's where large effects occur in O [3], Mg [4,5], Ca [6] and to lesser extent in Ti [7] and Cr [8]. Except for light elements (H, O) isotope fractionation in nature appears rare and limited to cases where kinetic effects operate.

In the laboratory, vacuum vaporisation of molten silicate samples can duplicate the fractionation effects in CAI's [9,10]. The shift in isotope ratios with mass loss fits the Rayleigh process and is logarithmically proportional to inverse square root ratio of the masses. Rayleigh distillation demands the existence of a well mixed reservoir and the complete removal of the vaporised material kinetically. For silicates this can only be achieved for molten samples in a low pressure (vacuum) environment. In intermediate cases, within gaseous envelopes, quasi-equilibrium or full equilibrium conditions may prevail and mediate the outcome for isotope fractionation. For example, partial distillation in vacuum by heating from the solid state, without melting, shows minimal mass fractionation [10]. Meteors entering the atmosphere keep their interiors cool and intact by shedding hot molten outer skin. There is mass loss at high temperature but no significant isotope fractionation in the ablated outer skin of meteorites [11,1]. Tektites behave similarly. Aerodynamic, flanged button type tektites were presumably shaped by exposure to high temperatures and mass loss. Analyses of the extremities show no significant isotope effects in Mg or K [12,1]. Again the dominant process is mass loss and cooling by ablation, possibly under quasi-equilibrium conditions influenced by the surrounding hot plasma boundary layer and the atmosphere. Molini-Velsko et al. [13] used a solar furnace to rapidly vaporise glass and basalt. Distillation in a solar furnace is an uncontrolled process; rapid evaporation and high temperature gradients can be expected. Silicon isotopes in the residues were minimally fractionated from 0 to 1.4‰ per mass unit for up to 80% mass loss. Subsequent experiments [10], under controlled conditions, with molten silicate samples and gradual increments in temperature revealed isotope fractionation in accord with Rayleigh predictions (15‰ per amu fractionation in Si for 88% mass loss). Rapid vaporisation of part of a sample does not necessarily imply loss of all elements. Depending on the amount of available energy the more

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refractory phases will be retained, thus effectively segregating volatile from refractory components. Failure to find mass fractionation in planetary materials only rules out Rayleigh distillation into vacuum, but other modes of high temperature vaporisation in vacuum or vaporisation in relatively high pressure, gaseous envelopes is not excluded. Humayun and Clayton [1], having ruled out vaporisation as the cause of volatile depletion, invoke partial condensation as the most likely candidate on the assumption of equilibrium processes in condensation as opposed to kinetic effects in distillation. There is no a priori reason to make such a distinction but every reason to assume that isotope effects in partial condensation and vaporisation are reversibly identical. Obviously, equilibrium condensation can take place but only under specific circumstances, such as approximately constant temperatures and mixing through bidirectional mass flow.

Uyeda et al., [14] have investigated Mg isotope fractionation during condensation of silicate vapour generated by vaporising forsterite at 1500 °C in an ambient atmosphere of H₂ at nebular partial pressures. The material condensed at various temperatures showed Mg isotope fractionation ranging from -2.6% to +0.7% per mass unit; a total range of 3.3% per mass unit. The results of these experiments are unambiguous: mass dependent isotope fractionation can occur as a direct result of condensation of hot silicate vapour with a magnitude related to temperature at the time of condensation. Large mass dependent isotope fractionation can also occur in condensation during snowfall at a rate proportional to cloud temperature [15]. These are dramatically apparent in the Greenland, GRIP ice core depth profile of oxygen isotopes [15]. The magnitude of the effect ($\delta^{18}\text{O}$) is -35‰ for the Holocene and the transition from the last Glacial to Holocene is represented by a shift of about 7‰. Thus, kinetic effects in condensation do occur naturally and can be demonstrated in laboratory experiments. On this basis, models requiring volatile loss by vaporisation cannot be excluded in favour of partial condensation from a hot nebula as argued for by Humayun and Clayton [1].

How then can we reconcile the absence of isotope fractionation with extensive volatile depletion? A possible mechanism can best be illustrated by a specific example. The current model for the formation of the Moon involves a giant Earth impact with a Mars sized impactor [16,17]. Temperatures as high as 8000 to 14000 K can be generated during the collision [18]. The impact will result in almost instantaneous vaporisation of material both from the impactor and Earth's mantle and bulk transfer into orbit; these are conditions which are not favourable for operation of Rayleigh type distillation. The absence of K and Mg isotope fractionation in the Moon [1,5] are in accord with such a scenario. The depletion in the Moon of very volatile elements (e.g. Cs, Pb, Tl, Bi) and water can be accommodated by assuming that these volatile elements will be the last ones to condense into the accreting proto Moon and can be swept away in bulk in the prevailing chaos around Earth orbit. The low lunar initial $^{87}\text{Sr}/^{86}\text{Sr}$ [19,20] which is similar to the solar system initial [21] requires a pre-terrestrial depletion in volatile elements. A scenario, just as described for the formation of the Moon is appropriate and coupled with repeat episodes of vaporisation and condensation possibly in localised gaseous and dusty envelopes can account for the separation of Rb from Sr and the depletion of volatile elements from the inner solar system without generating large scale isotope fractionation in numerous elements.

Rayleigh type isotope fractionation occurs under special circumstances and absence of isotope effects is not a sufficient condition to exclude episodes of high temperature vaporisation in the nebula. Uniform K isotopic composition of planetary materials do not exclude models invoking high temperature vaporisation for refractory-volatile segregation nor can it favour models involving partial condensation. Both processes may operate in some circumstances, as in the giant-impact scenario for the formation of the Moon. Causes of volatile depletion in the inner solar system probably include multiple episodes of vaporisation and condensation in a turbulent nebula in a mélange of kinetic, quasi-equilibrium and equilibrium processes followed by bulk transport of elements with low condensation temperatures. The notion of kinetic Rayleigh distillation or condensation as a dominant mechanism governing processes in the early solar system is not supported by the mass of available isotopic data on protoplanetary materials.

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