Noble Gas Composition in Rainwater and Associated Weather Patterns

Supplementary Text 3: Diffusive mass transfer of noble gases in a raindrop and calculation of average raindrop sizes from measured noble gases in rainwater

1. **Introduction**

    Overall mass-dependent noble gas patterns for rainwater samples from southeast Michigan display simultaneous atmospheric He excesses and Ne, Ar, Kr and Xe depletion with respect to ASW (Fig. 1c, main text). As mentioned in section 5 of the manuscript, these patterns cannot originate from liquid rainwater that equilibrated at higher altitudes. Instead, they can be accounted for if precipitation originates as ice (cf. Section 5, Fig. 2, main text). Multiple lines of weather evidence, including observations of hail (direct observation of hail was observed for samples nr10-1 and 13 while weather data indicate hail for samples nr4-1,4-2,5-2,6,9,10-2,12 and 13; see Text S1, Table S2) during sample collection as well as examination of probable condensation altitudes (cf. Text S1) suggest that precipitation originating as ice is likely in southeast Michigan. Below, in section 2, we first describe a simple mass-transfer model involving diffusion in a sphere (raindrop), which is used to qualitatively show that noble gas patterns in Michigan rainwater samples originate from ice (Fig. 2, section 5, main text). Subsequently, in section 3 below, we use this diffusion model and a more rigorous quantitative approach, to evaluate the time-dependent evolution of noble gas patterns in raindrops assuming a constant equilibrium boundary condition and noble gas diffusion coefficients. In section 4 below, the time-dependent evolution of noble gas patterns in raindrops is discussed in the context of varying equilibrium boundary conditions and noble gas diffusion coefficients used in the model. The effects of boundary conditions and diffusion coefficients assumed in sections 2-4 on the rate of noble gas incorporation into a raindrop are compared in section 5. Finally, in section 6, a novel application of dissolved noble gases in rainwater is demonstrated. Specifically, a procedure for estimating average raindrop sizes using the diffusion model together with measured rainwater noble gas concentrations is outlined.

2. **Diffusive Mass-Transfer in Raindrop Model Description and Calculation of Isothermal Equilibrium Stages of Noble Gases in a Raindrop**

    Diffusion of noble gases into a raindrop can be simulated using a simple mass-transfer model in a sphere. The total amount of noble gases diffusing into or out of a sphere with a constant concentration at the surface is given by the infinite series solution [*Crank*, 1975]:

$$F_i = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 X\right) \qquad (1)$$

or,

$$F_i = 6X^{0.5}\left\{\pi^{-0.5} + 2\sum_{n=1}^{\infty} ierfc\frac{n}{\sqrt{X}}\right\} - 3X \qquad \text{, if } X<0.182873063 \quad (2)$$

where F_i is the fraction of noble gas 'i' (where, 'i'=He, Ne, Ar, Kr and Xe) transferred at any given time 't', parameter $X=Dt/a^2$, where 'a' is the radius of raindrop, 'D' is the diffusion coefficient of noble gases and 'n' is the nth term of the infinite series solution. Equations (1) and (2) provide the basis to calculate diffusive mass transfer in a raindrop of a particular size. If one assumes that: a) noble gas concentrations in raindrops start as ice (see section 5 of main text) and; b) noble gas concentrations of ice crystals within clouds are similar to the average ice concentrations in Lake Vida, Antarctica [see section 5 of main text, *Malone et al.*, 2010], expected noble gas patterns as mass transfer proceeds within a raindrop starting from ice and reaching different stages of isothermal equilibrium (=1; assuming ASW at 0˚C) can be calculated (Fig. 2, main text) by:

$$F_i = \frac{\left(\dfrac{C_m}{C_{eq}} - \dfrac{C_{ice}}{C_{eq}}\right)}{\left(1 - \dfrac{C_{ice}}{C_{eq}}\right)} \qquad (3)$$

or, Equation (3) may also be written as:

$$C_m = F_i \times \left(C_{eq} - C_{ice}\right) + C_{ice} \qquad (4)$$

where F_i is the fraction of noble gas 'i' as defined earlier (equations 1, 2), C_m, C_{eq}, C_{ice} are the measured, equilibrium and average ice noble gas concentrations. Using equation (3), model expected noble gas patterns (C_m/C_{eq}; green dotted lines, Fig.2, main text) can be calculated for various stages of equilibration (F_i values between 0-100%) using initial average ice concentrations, C_{ice}/C_{eq} equal to 1.383, 0.825, 0.097, 0.064 for He, Ne, Ar, Kr and Xe (solid green line, Fig.2, main text; *Malone et al.*, 2010). For example, to derive the expected noble gas patterns for 50% equilibrium (green dotted lines, Fig.2, main text), C_{ice}/C_{eq} values from *Malone et al.* [2010] is used for each noble gas with F_i=0.5 in equation (3) to calculate (C_m/C_{eq}). This yields model values (C_m/C_{eq}) of 1.192, 0.913, 0.549, 0.532 and 0.525 for He, Ne, Ar, Kr and Xe respectively and is plotted as the 50% equilibrium line (green dotted lines, Fig.2, main text). Model expected noble gas patterns are similarly derived for various stages of equilibration assuming initial average ice concentrations from *Malone et al.* [2010] and F_i values between 0-100%. It is important to note here that model noble gas patterns derived in Figure 2 (main text) is time-independent and represents a simple, qualitative analysis of the evolution of noble gas patterns from ice to equilibrium values. Actual noble gas concentrations within a raindrop are expected to evolve at different rates as discussed in section 3 of this supplementary text.

Such a qualitative comparison of model-expected and measured noble gas patterns (cf. Fig.2, main text) suggests that this simple model is capable of reproducing atmospheric He excesses together with Ne, Ar, Kr and Xe depletion patterns observed in our Michigan rainwater samples when they are assumed to evolve from ice. For example, sample nr4-2 indicates measured He and Ne concentrations within 50%-60% of equilibrium with the atmosphere while Ar, Kr and Xe point to equilibration values between 60% and 70% (Fig. 2, main text). Ar, Kr and Xe point to greater equilibration values than He and Ne due to increased dissolution of the heavier noble gases in rainwater resulting from heat transfer, a process which is not accounted for in our simple

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diffusive mass-transfer model. Indeed, evaporation of a falling raindrop lowers the droplet's surface temperature compared to its surroundings leading to greater dissolution of the more temperature sensitive heavier noble gases Ar, Kr and Xe [see, e.g., *Elperin et al.*, 2007]. A comprehensive treatment of transient, coupled heat and mass transfer of noble gases within a falling raindrop is out of the scope of the present manuscript. However, our simple diffusion mass transfer model qualitatively shows that mass-dependent noble gas patterns are expected in rainwater if the latter is assumed to start as ice. To further support our conclusion, we use a more rigorous quantitative approach and evaluate the time-dependent evolution of noble gases within a raindrop as described below.

3. Time-dependent evolution of noble gas patterns within a raindrop assuming a constant equilibrium boundary condition and noble gas diffusion coefficients

The time-dependent evolution of noble gas patterns within a falling raindrop is simulated using the diffusive mass transfer model for a sphere discussed earlier (equations 1-3, supplementary text 3) in addition to the following assumptions: a) noble gas concentrations in raindrops start as ice (see section 5 of the main text) and; b) noble gas concentrations of ice crystals within clouds are similar to the average ice concentrations in Lake Vida, Antarctica [*Malone et al.*, 2010]. Expected noble gas patterns (C_m/C_{eq}) within a raindrop starting from ice can be determined at any given time 't' by first calculating parameter 'F_i', which is the fraction of noble gas 'i' (where, 'i'=He, Ne, Ar, Kr and Xe) transferred at any given time 't' using equations (1) and (2). Subsequently, using equation (3) and initial average ice concentrations, C_{ice}/C_{eq} equal to 1.383, 0.825, 0.097, 0.064 for He, Ne, Ar, Kr and Xe (solid green line, Fig. S9a; *Malone et al.*, 2010) model expected noble gas patterns (C_m/C_{eq}) for any time 't' may be derived (blue, red lines, Fig. S9a).

For example, Figure S9a shows the evolution of noble gas patterns within a raindrop starting from ice (green markers, Fig.S9a) and reaching isothermal equilibrium (=1; assuming ASW at 0˚C) at various times 't' for a 5mm droplet derived using equations 1-3 (blue, red markers, Fig. S9a). However, equations 1 and 2 require knowledge of the diffusion coefficients of noble gases 'D'. Because the raindrop simulations represent a phase transition from solid ice to liquid water, model noble gas patterns are calculated using noble gas diffusion coefficients in both liquid water (blue markers, Fig.S9a) and solid ice (red markers, Fig.S9a). Liquid water noble gas diffusivities were assumed at a temperature of ~0˚C because diffusion in liquid water is slowest at 0˚C and this will yield maximum time to equilibration. However, because noble gas diffusion coefficients in liquid water are only well known between 5 and 35˚C [*Jähne et al.*, 1987], values at 0˚C were approximated by the following temperature dependency [*Eyring*, 1936]:

$$D_i = A_i \times \exp\left(E_a/RT\right) \qquad (5)$$

where D_i is the diffusion coefficient for noble gas 'i' (where i=He, Ne, Ar, Kr, Xe) at any temperature 'T' (ºK), 'R' is the universal gas constant of 8.314 J/K-mol, 'E_a' and 'A' are fit parameters for each noble gas given by *Jähne et al.* [1987]. Noble gas diffusivities in solid ice were calculated by mass-scaling the diffusion coefficient of CO_2 in ice from Antarctica (D_{CO2}= 7.24x10^{-11} m^{2}s^{-1} at -25.4°C; *Ahn et al.*, 2008) as follows:

$$D_{ice} = D_{CO_2} \times \left(M_{CO_2} \Big/ M_i \right)^{1/2} \qquad (6)$$

where D_{ice} is the diffusion coefficient for noble gas 'i' (where i=He, Ne, Ar, Kr, Xe) in ice and M_{CO2} and M_i are the mass of CO_2 and respective noble gas 'i'. Noble gas diffusion coefficients thus calculated in liquid water are ~1 or more orders of magnitude faster than in solid ice and are likely to represent extreme values (Table S3). Because of large variations in noble gas diffusion coefficients, the evolution of rainwater noble gas patterns are calculated at various times 't' for both diffusivity values in ice (red markers, Fig.S9a; t=200s, 1000s, 5000s, 50000s) and liquid water (blue markers, Fig. S9a; t=200s, 500s, 1000s, 5000s) using equations 1-3.

Figure S9a compares model-expected (red, blue markers) evolution of noble gas patterns in a raindrop with measured rainwater noble gas pattern for sample nr4-2 (black triangles). Such a comparison confirms results from our qualitative analysis (section 2, text S3) and indicates that mass-dependent noble gas patterns are expected in rainwater if the latter is assumed to start as ice. Specifically, this comparison shows that measured He and Ne concentrations for nr4-2 fall within the domain of model rainwater patterns for t=1000s assuming diffusion coefficients in liquid water and ice (shaded region, Fig. S9a) while measured Ar, Kr and Xe concentrations for nr4-2 are marginally greater than model-prediction for t=1000s assuming diffusivity of liquid water (blue marker dashed line, Fig. S9a) by 6%, 11% and 16%, respectively. As previously mentioned in section 2, the diffusive model under-predicts measured Ar, Kr and Xe concentrations due to increased dissolution of the temperature-sensitive heavy noble gases in rainwater resulting from cooling of droplet surface by evaporation of a falling raindrop, a process which is not accounted for in our simple diffusive mass-transfer model. In addition, Fig.S9 also shows that the evolution of rainwater noble gas patterns is faster when noble gas diffusivity values in liquid water (blue marker, Fig.S9a) are assumed as compared to ice (red marker, Fig.S9a). Nevertheless, irrespective of the absolute time taken, rigorous calculation of time-dependent evolution of noble gas patterns in rainwater confirms that mass-dependent rainwater noble gas patterns originate from ice.

For the sake of simplicity, the diffusive model calculations used so far assumed a constant equilibrium boundary condition with noble gas composition in raindrops going from ice to ASW at 0˚C (sections 2, 3). However, in reality, raindrops experience variations in temperature and pressure as they fall through the atmosphere. In the next section, we discuss the time dependent evolution of rainwater noble gas patterns assuming variable equilibrium boundary conditions and diffusion coefficients in the context of varying temperature and pressure experienced by a falling raindrop.

4. Time-dependent evolution of noble gas patterns in a raindrop assuming variable equilibrium concentrations and diffusion coefficients

In sections 2 and 3 of this supplementary text, the evolution of noble gas patterns within a raindrop was calculated using the simplifying assumption of a constant equilibrium boundary condition at the surface of a droplet (ASW at 0˚C) as well as constant noble gas diffusion coefficients. However, in reality, raindrops experience variations in temperature and pressure (altitude) as they fall through the atmosphere.

Because noble gas concentrations are dependent on temperature and altitude (partial pressure), equilibrium noble gas concentrations at the surface of a falling rain droplet will vary (red circles, Fig.2, main text). As previously mentioned in section 5 of main text, because of lower pressures at high altitude, equilibrium He and Ne concentrations are lower than ASW values at the ground surface as these gases are mostly sensitive to pressure (red circles, Fig.2, main text). In contrast, the heavier noble gases Ar, Kr and Xe are particularly sensitive to temperature and the impact of low temperatures at altitude dominates over that of low pressures leading to expected concentrations at higher altitudes higher than ground surface ASW values (red circles, Fig.2, main text). In addition, variations in temperature will also affect the noble gas diffusion coefficients (cf. equation 5, Text S3). Specifically, an increase in ambient atmospheric temperature with decreasing altitude leads to faster noble gas diffusion coefficients (cf. equation 5, Text S3). Below, we investigate the time-dependent evolution of noble gas concentrations within a raindrop when equilibrium noble gas concentrations as well as noble gas diffusion coefficients are varying during droplet fall.

Because equilibrium noble gas concentrations and diffusion coefficients vary as a function of temperature and altitude, the evolution of noble gas patterns within a well-mixed falling raindrop is computed at discrete, multiple time steps using the diffusive mass transfer model for a sphere (equations 1-3, Text S3) together with assumptions on the noble gas composition of ice crystals within clouds discussed earlier (sections 2, 3, Text S3). At each time step 't' (time interval=0.01s), noble gas diffusion coefficients are first calculated based on the ambient temperature of the atmosphere at that altitude using equation (5). Calculated noble gas diffusion coefficients are used to determine parameter F_i, which is the fraction of noble gas 'i' (where, 'i'=He, Ne, Ar, Kr and Xe) transferred at any given time 't' using equations (1) and (2) that are derived for a constant boundary condition. A constant boundary condition approximation is valid here because within the small time interval modeled (t=0.01s corresponding to ~10m drop in altitude for a 5mm raindrop), large transient variations in equilibrium atmospheric noble gas concentrations are not expected. Subsequently, model expected noble gas patterns (C_m) for any time 't' is derived using equation (4) together with initial average ice concentrations (C_{ice}; see sections 2, 3, Text S3) and equilibrium noble gas concentrations corresponding to a particular altitude and temperature (C_{eq}). This procedure is illustrated through a specific example below.

Figure S9b compares measured noble gas concentrations of sample nr4-2 together with the time-dependent evolution of noble gas patterns from ice for a 5mm droplet assuming variable equilibrium concentrations and diffusion coefficients. The raindrop is assumed to fall from an altitude of ~4500m through an atmosphere with a temperature lapse rate of 6.072˚C/km. Likely altitude of condensation (~4500m) and lapse rate were determined from sounding data (cf. Text S1) as well as from the measured surface temperature for nr4-2 at the time of collection (26˚C; Table S1). Fig. S9b shows the effect of varying temperature and altitude on equilibrium noble gas concentrations (C_{eq}; red markers). Model expected noble gas patterns (C_m) are calculated using the procedure outlined above for every second. Figure S9b shows the evolution of noble gas patterns within the raindrop from ice at 50s, 100s, 200s, 300s, 400s and 443s, at which point the raindrop reaches the ground based on our assumptions of droplet size and condensation altitude. Comparison of model evolution of noble gas patterns in a raindrop (green dotted

markers, Fig. S9b) with measured rainwater noble gas pattern for sample nr4-2 (black triangles) confirms our previous results from section 2 and 3 of this supplementary text and indicates that mass-dependent noble gas patterns are expected in rainwater if the latter is assumed to start as ice. Indeed, Fig. S9b shows that measured He and Ne concentrations for nr4-2 compare well with model rainwater patterns (C_{model}-C_{meas}<5%) while measured Ar, Kr and Xe concentrations for nr4-2 are marginally greater than model-prediction for t=443s by 9%, 11% and 15%, respectively. As previously mentioned in sections 2 and 3 the diffusive model under-predicts measured Ar, Kr and Xe concentrations due to increased dissolution of the heavier noble gases in rainwater resulting from surface cooling during evaporation of a falling droplet, a process which is not accounted for in our simple diffusive mass-transfer model. Results of evolution of noble gas concentrations within a raindrop obtained using variable equilibrium noble gas concentrations and diffusion coefficients are similar to the results obtained by using a constant equilibrium boundary condition (sections 2, 3, Text S3). Thus, irrespective of the boundary condition used, our calculations show that mass-dependent rainwater noble gas patterns clearly originate from ice. These results are in agreement with multiple lines of weather evidence, including direct observations of hail for samples nr10-1 and 13, weather data during sample collection which indicate hail for samples nr4-1,4-2,5-2,6,9,10-2,12 and 13 (see Text S1, Table S2) as well as examination of probable condensation altitudes (cf. Text S1) that suggest precipitation originating as ice is likely in southeast Michigan.

5. Comparison of the effects of boundary conditions and noble gas diffusion coefficients assumed on the rate of noble gas incorporation into a raindrop

While all the different boundary conditions and noble gas diffusion coefficients investigated in sections 2-4 clearly point to an ice origin of mass-dependent rainwater noble gas patterns, the different assumptions yield varying rates of noble gas incorporation into a raindrop. Figure S10 compares the time evolution of individual noble gases within a raindrop of size 5mm based on the assumed boundary conditions and diffusion coefficients used in sections 2-4. If a constant equilibrium boundary condition is used (sections 2 and 3), equilibration of all noble gases within the raindrop is faster assuming diffusion coefficients for liquid water (red line, Fig. S10) as compared to solid ice (green line, Fig. S10). This is because noble gas diffusion coefficients in liquid water are 1-2 orders of magnitude faster than in solid ice (cf. Table S3). However, when a variable equilibrium condition is used together with varying liquid water diffusion coefficients (section 4; blue line, Fig.S10), evolution of all noble gases except Ne is faster as compared to constant boundary condition (red line, Fig.S10). Such a pattern cannot only be due to the temperature-effect of noble gas diffusion coefficients because they tend to be faster at higher temperatures and lower altitudes for all noble gases (cf. equation 5). Instead, faster equilibration of all noble gases except Ne is observed when a variable equilibrium condition is used because model expected noble gas values (C_m) at any time 't' is dependent on the term (C_{eq}- C_{ice}) as shown in equation (4). For all noble gases except Ne, the term (C_{eq}- C_{ice}) is greater when a variable equilibrium condition is used (red circles, green triangles, Fig.S9b) as compared to constant equilibrium condition (solid black line, green triangles, Fig. S9b). By contrast, (C_{eq}- C_{ice}) for Ne is lower when

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a variable equilibrium condition is used (red circles, green triangles, Fig.S9b) as compared to constant equilibrium condition (solid black line, green triangles, Fig. S9b). This leads to a slightly slower equilibrium of rainwater noble gas patterns for Ne assuming a variable boundary condition as compared to a constant boundary condition.

However, irrespective of the boundary condition used, our calculations shown in sections 2-4 indicate that mass-dependent rainwater noble gas patterns clearly originate from ice and are in agreement with multiple lines of weather evidence observed for these samples. Because mass-dependent rainwater noble gas patterns originate from ice, we demonstrate a novel application of dissolved noble gases in rainwater in the next section. Specifically, we outline a procedure to estimate average raindrop sizes using the diffusion model described in section 2 together with measured rainwater noble gas concentrations.

6. Calculation of droplet size using measured noble gas concentrations in rainfall

In addition to calculating expected noble gas patterns for diffusive mass transfer of noble gases into a raindrop, the model described in section 2, can also be used to provide a range of droplet sizes for corresponding rainfall event using measured noble gas concentrations in rainwater. Similar to the assumptions in section 2, if it is assumed that: a) noble gas concentrations in raindrops start as ice and; b) noble gas concentrations of ice crystals within clouds are similar to the average ice concentrations in lake Vida, Antarctica [*Malone et al.*, 2010], the total amount of noble gases transferred (parameter F_i) can be calculated for each rainwater sample collected using equation (3). From the calculated F_i value for a given sample (equation 3), parameter X is then calculated from the inverse of F_i as follows:

$$F_i^{-1} = X = \frac{2}{\pi}\left(1 - \sqrt{1 - \left(\pi \times F_i / 3\right)}\right) - \frac{F_i}{3}, \qquad \text{if } (F_i < 0.9) \quad (7)$$

or,

$$F_i^{-1} = X = \frac{-1}{\pi^2}\log\left(\frac{\pi^2(1 - F_i)}{6}\right), \qquad \text{if } (F_i > 0.9) \quad (8)$$

Because $X = Dt/a^2$, the time taken 't' by a specific noble gas in a raindrop of size 'a' to achieve the corresponding 'F_i' value can be calculated. Since the size of raindrop 'a' is unknown, the time required for equilibration F_i value to be achieved (parameter 't' in equations 1 and 2) for a specific sample is calculated for a range of droplet diameters between 0.019 and 10mm (red lines, Fig. 3 main text) assuming liquid water diffusion coefficients for all noble gases at a temperature of 0°C (Table S3). This will yield the maximum possible equilibration times for each gas since diffusion is slowest at 0°C. The range of equilibration times (parameter 't' in equations 1, 2) calculated from measured noble gas concentrations using the above procedure for each sample (red lines, Fig. 3 main text) is further compared with the time 't_z' taken for a raindrop of specific size to fall to the ground from the cloud base (blue lines, Fig. 3 main text). 't_z' is calculated as the ratio of cloud condensation altitude and the terminal velocity 'V_t' of a droplet, which is defined as the maximum velocity of a falling raindrop at which the gravitational force equals the drag force acting on the drop [see e.g., *Testik and Barros*, 2007]. Cloud condensation altitudes between 0.5 and 5 kms (Fig. 3 main text) were

assumed based on most probable condensation altitudes from weather sounding data (Fig. S7) and terminal velocity was calculated using the formulations given by *Beard* [1976] for droplet diameters between 0.019 and 7mm (Fig. S11). Terminal velocities calculated using *Beard* [1976] formulations agree well with values obtained from empirical relations provided by *Rogers* [1989], *Atlas et al.* [1973] and *Best* [1950] for droplet sizes between 0.08 and 1.5mm, 0.6 and 5.8mm and 0.3 and 6mm respectively (Fig. S11). Comparison of the time 't' taken by a specific noble gas in a raindrop of size 'a' to achieve the corresponding 'F_i' value (red lines, Fig. 3 main text) calculated earlier and the time 't_z' taken for a raindrop of specific size to reach the ground (blue lines, Fig. 3 main text), will yield a solution space of droplet size and equilibration time corresponding to any specific event. From weather sounding data (e.g., Fig. S7), if a specific condensation altitude can be identified (Table S4), the range of droplet sizes can further be constrained. This model approach is described further below with a specific example.

For example, sample nr4-2 shown in Figure 3 of the manuscript yields F_i values of 0.5, 0.5, 0.7, 0.7, 0.6 for He, Ne, Ar, Kr and Xe based on equation (3) and measured concentrations in rainwater and assuming an ice origin of noble gases in rainwater as described above. Using equation (7), these F_i values yield X values of 0.038, 0.028, 0.078, 0.059 and 0.058 for He, Ne, Ar, Kr and Xe, respectively. Assuming raindrop diameters between 0.019 and 10mm, a range of time 't', taken to achieve the calculated X values is obtained and plotted in Fig 3 (red lines). The time 't' taken to achieve a certain value of X and consequently, F_i is faster for the lighter noble gases (He, Ne) as compared to the heavier noble gases (Ar, Kr, Xe). This can also be illustrated by the temporal evolution of noble gases in raindrops of 0.1mm and 5mm in radius at a given temperature (assumed as 0˚C here; Fig. S12). As shown in Fig. S12, the lighter noble gases He and Ne reach equilibrium faster than Ar, Kr and Xe because of their higher diffusion coefficients for a given temperature as compared to the heavier noble gases (Table S3). The time 't' taken to achieve a certain value of X (red lines, Fig. 3 main text) is then compared with the time 't_z' for a raindrop to reach the ground (blue lines, Fig. 3 main text). Comparison of these two time values yields the area indicated as "solution space" (shaded area, Fig.3, main text) defined by equilibration times of 100, 300, 500, 1000s and droplet sizes of 0.38, 1.3 and 6.5mm diameter. However, this range of drop sizes can be further constrained using weather sounding data for this sample which indicates a likely condensation altitude of ~4.5km (15000 ft; at ~0˚C; Table S4). Assuming this condensation altitude yields corresponding range of drop sizes between ~1and ~6mm for the rainfall event during the nr4-2 sample collection (Fig. 3, main text). Similarly, average raindrop sizes can thus be estimated for different samples with mass-dependent patterns. Table S4 summarizes the range of raindrop sizes estimated for all mass-dependent samples (Fig. 1.c, main text) where weather-sounding data yields an approximate condensation altitude. Estimated drop sizes for mass-dependent samples are large and range between 0.45 and 10mm in diameter. These estimated droplet sizes generally fall within the maximum critical diameter of raindrops observed in nature, which, depending on the amount of airstream turbulence, is usually between 6-8mm but may reach diameters as large as 10mm [*Rogers and Yau*, 1989]. In addition, large drop sizes are generally associated with heavier rainfall (e.g., *Marshall and Palmer* [1948]). Because large drop sizes are estimated using our calculations above for samples with mass-dependent noble gas patterns, our results imply that precipitation events for these

samples are associated with heavier rainfall. Indeed, heavy rainfall was observed both by direct observations and through surface weather station records during the collection of mass-dependent samples (Text S1).

Another interesting observation from these calculations is that small raindrops (fog) of 0.1mm or less in diameter would only take 0.39s, 0.78s, 1.27s, 2.09s, 2.76s or less to reach ~90% equilibrium for He, Ne, Ar, Kr and Xe (cf. Fig. S12). This suggests that, if only mass-dependent diffusive processes were occurring in fogs, concentrations of noble gases would be expected to be in equilibrium with the surface conditions. However, our measurements show that this is clearly not the case suggesting that additional processes that are not presently understood are affecting noble gases dissolution in fogs. Further detailed investigation, including analysis of noble gases in fogs is critical to understanding these processes. Such information is useful in the fields of meteorology, atmospheric and climate sciences, in addition to hydrology and environmental engineering.

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