1 **Paper# 2012GLXXXXXX**
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3 **Noble Gas Composition in Rainwater and Associated Weather Patterns**

4 **Supplementary Text 4**: **Time taken for noble gas disequilibrium patterns in rainfall**
5 **to re-equilibrate at the surface**
6
7 **1. Introduction**
8
9   Measured He, Ne, Ar, Kr and Xe concentrations in all rainwater samples from
10 southeast Michigan are not in equilibrium with surface conditions and deviate from
11 expected ASW values. Specifically, rainwater samples display a maximum deviation of
12 29%, -11%, -26%, -33% and -36% with respect to ASW for He, Ne, Ar, Kr and Xe ,
13 respectively (cf. Section 4, main text). Rainwater is typically assumed to re-equilibrate at
14 surface conditions on the order of a few minutes [see e.g., *Mazor,* 1972; *Klump et al.*,
15 2007]. While *Mazor* [1972] did not provide any calculations for this assumption, *Klump*
16 *et al.* [2007] utilize a simple calculation based on diffusive length of noble gases to show
17 that a water film of several millimeters in thickness would be in equilibrium with the
18 atmosphere within 10 min. However, neither study used actual rainwater measurements
19 to calculate the time taken by noble gases in rainwater to re-equilibrate at the surface.
20 Below, we utilize a detailed model of diffusion in a plane sheet of water to calculate the
21 time required for our measured maximum disequilibrium patterns in rainwater to re-
22 equilibrate at surface conditions using realistic water depth values from precipitation data
23 in Michigan.
24
25 **2. Model Description**
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27   The total amount of noble gases diffusing into or out of a plane sheet of water is
28 given by the infinite series solutions [*Crank*, 1975]:
29

30 $$F_i = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left\{-(2n+1)^2 \pi^2 X \middle/ 4\right\} \qquad (1)$$

31
32 or,

33 $$F_i = 2(X)^{0.5}\left\{\pi^{-0.5} + 2\sum_{n=1}^{\infty}(-1)^n ierfc\left(\frac{n}{\sqrt{X}}\right)\right\} \qquad \text{if X<0.6465} \quad (2)$$

34

35 $$where, \quad X = \frac{Dt}{l^2} \qquad (3)$$

36 F_i is the fraction of noble gas 'i' (where, 'i'=He, Ne, Ar, Kr and Xe) transferred at any
37 given time 't', 'l' is the depth of water (or thickness of water film), D is the diffusion
38 coefficient of noble gases and 'n' is the nth term of the infinite series solution. Equations
39 (1), (2) and (3) can be utilized to solve for parameter 'X' by setting F_i=29%, -11%, -26%,
40 -33% and -36% for He, Ne, Ar, Kr and Xe, respectively. From calculated vales of 'X',
41 the time 't' taken to re-equilibrate can be obtained from equation (3) given the diffusion

42 coefficient 'D' of noble gases and water depth or thickness of water film 'l'. Diffusion
43 coefficients at a temperature of 25˚C were used in our calculations because it is close to
44 the mean measured surface air temperature at the time of collection of rainwater samples
45 (Table S1). Values for noble gas diffusion coefficients at 25˚C are given by *Bourg and*
46 *Sposito* [2008]. In addition, water depth or thickness of water film 'l' was chosen based
47 on measured hourly precipitation data from the Ann Arbor weather station during the
48 period of sample collection (May-September, 2011). During the period of sample
49 collection, precipitation as high as 8.2cms was recorded in one hour. While this
50 represents an extreme value, multiple rainfall events record precipitation of 1cm or more
51 in one hour during this time period. Consequently, we utilize a water depth of 1cm to
52 calculate the time 't' required for noble gases in rainwater to re-equilibrate using equation
53 (3). Results of these calculations are presented below.
54
55 **3. Model Results and Discussion**
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57 Considering a water depth of 1 cm, the maximum measured He excess of 29% in rainfall
58 would take 900.5s (or ~15 minutes) at 25˚C to reach equilibrium with surface conditions.
59 Similarly, maximum deviations of -11%, -26%, -33% and -36% for Ne, Ar, Kr and Xe
60 measured in rainfall would take ~3.3mins, ~34mins, ~72mins and ~108mins,
61 respectively, to reach equilibrium with surface conditions for a water depth of 1 cm and
62 25˚C. Our calculations show that re-equilibration is faster for the lighter noble gases He
63 and Ne as compared to the heavier noble gases Ar, Kr and Xe due to both their higher
64 diffusion coefficients and lower initial disequilibrium levels with respect to surface
65 conditions. In addition, it should be noted that a smaller water depth 'l' would also lead to
66 shorter re-equilibration times for all noble gases, in addition to processes such as
67 turbulent mixing, if present. Nevertheless, our calculations show that the typical
68 assumption that re-equilibration of rainwater at the surface is completed within a few
69 minutes [see e.g., *Mazor,* 1972; *Klump et al.*, 2007] is more applicable for lighter noble
70 gases and smaller water depths (<1cms) while heavier noble gases and greater water
71 depths require re-equilibration times on the order of hours.
72   Noble gas concentrations of rainfall and fog will thus be recorded in groundwater
73 systems if the time taken to re-equilibrate with surface conditions is greater than the time
74 taken to reach the water table. This is likely the case at high altitudes of the Galapagos
75 Islands where rapid water infiltration due to the presence of fractures or thin soil cover
76 [*Warrier et al.*, 2012] allows little time for noble gas to re-equilibrate at the surface.
77 However, sedimentary aquifer systems typically have thicker unsaturated zones and
78 longer infiltration times allowing sufficient time for rainwater to re-equilibrate with
79 ground air. This, in turn, allows the use of noble gases in paleoclimate reconstructions
80 (e.g. *Kipfer et al.*, 2002, *Castro et al.*, 2007, 2012, *Alvarado et al.*, 2009).
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