Noble gas composition in rainwater and associated weather patterns

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[1] This work represents the first comprehensive noble gas study in rainwater. It was carried out in southeast Michigan. Results show that all rainwater samples are in disequilibrium with surface conditions. Two noble gas patterns are identified. The first one, associated with low-pressure systems, presence of fog and light rainfall, displays a relative Ar enrichment together with Ne, Kr, and Xe depletion. The second one, associated with the passage of frontal systems, displays a mass-dependent depletion pattern. Precipitation is characterized by thunderstorms, heavy rainfall, and high cloud ceiling heights. A diffusion mass-transfer model suggests that noble gas patterns originate from ice. Complete re-equilibration with surface conditions should occur within hours. For the first time, this study establishes a direct correlation between the noble gas composition in rainwater and weather patterns and highlights their potential to identify timing and location of recharge in shallow aquifer systems where infiltration is rapid. **Citation:** Warrier, R. B., M. Clara Castro, C. M. Hall, and K. C. Lohmann (2013), Noble gas composition in rainwater and associated weather patterns, *Geophys. Res. Lett.*, *40*, 3248–3252, doi:10.1002/grl.50610.

1. Introduction

[2] The concentration of the atmospheric component of noble gases (He, Ne, Ar, Kr, and Xe) dissolved in the recharge area of groundwater systems is considered to be mainly a function of the ground air temperature, the mean local atmospheric pressure (altitude of the recharge area) and excess air [*Kipfer et al*., 2002; *Hall et al*., 2012]. Consequently, noble gas temperatures (NGTs) are generally assumed to record the mean annual air temperature and have been regarded as a robust indicator of past climate [*Kipfer et al*., 2002; *Aeschbach-Hertig et al*., 2002; *Sun et al*., 2010; *Castro et al*., 2012]. Calculation of NGTs assumes that rainwater at the water table, commonly referred to as air saturated water (ASW), is in equilibrium with ground air. Lack of noble gas equilibration with respect to surface conditions, however, was recently observed in a study of high-altitude springs in the basaltic Galapagos Islands [*Warrier et al*., 2012]. More specifically, the presence of a previously unknown noble gas pattern was identified, with relative Ar enrichment, together with Ne, Kr, and Xe depletion. In addition, all samples displayed atmospheric He excesses. *Warrier et al*. [2012] hypothesized that this previously unknown noble gas pattern resulted from mixing between high altitude (≥1.5 km) rainwater and low-altitude (~400 m) fog droplets.

[3] Only a few measurements of noble gas concentrations in rainwater are currently available, four in the Jordan Rift Valley, Israel [*Mazor*, 1972], and two in southeast Michigan, USA [*Warrier et al*., 2012]. Independent of geographic location, it is apparent that these scarce currently available measured noble gas concentrations in rainfall are not in equilibrium with surface conditions and show significant deviations from expected ASW values. Although disequilibrium of noble gas concentrations in rainfall with surface conditions were first observed over 40 years ago [*Mazor*, 1972], no comprehensive study of the noble gas composition in rainwater had been carried out up to the present. Such studies are critical to validate the use of the noble gas paleothermometer in sedimentary systems, in addition to potentially developing their use as tracers of groundwater circulation in fractured and karstic environments, where rainwater infiltration is rapid. Indeed, the use of noble gases as paleoclimate indicators is directly dependent on the time required for noble gases dissolved in rainwater and subsequently at the water table to equilibrate with the atmosphere. In turn, disequilibrium conditions of noble gases in rainwater and subsequently at the water table will allow noble gases to be used to identify timing and location of recharge in shallow aquifer systems where infiltration is rapid.

[4] To understand the origin of the unique noble gas pattern in high-altitude springs in the Galapagos Islands [*Warrier et al*., 2012] and to investigate processes affecting the noble gas composition in rainwater, rainwater samples were collected in southeast Michigan in 2011 during multiple precipitation events over a period of several months and analyzed for noble gas concentrations and helium isotopic ratios. Here, for the first time, noble gas patterns in rainwater are analyzed together with multiple weather data at the time of sample collection. In contrast to the historical use of noble gases as indicators of paleoclimate, such a combined analysis highlights a new application of noble gases, more specifically, as tracers of weather patterns in areas of rapid rainwater infiltration.

2. Regional Setting and Climate

[5] Located in Midwestern United States (Figure S1), southeast Michigan has a continental type of climate with warm summers (May–Sep; mean = 19.5 ± 1.7°C; Figure S2a) and cold winters (Oct–Apr; mean = 2.7 ± 0.9°C; Figure S2a). Regional precipitation (Figure S2b) is strongly influenced by the movement of high and low-pressure systems across the North-American continent. Although precipitation is reasonably well distributed throughout the year, peak precipitation occurs during summer months, mostly as thunderstorms under the influence of southerly air masses from the Gulf of Mexico.

Additional supporting information may be found in the online version of this article.

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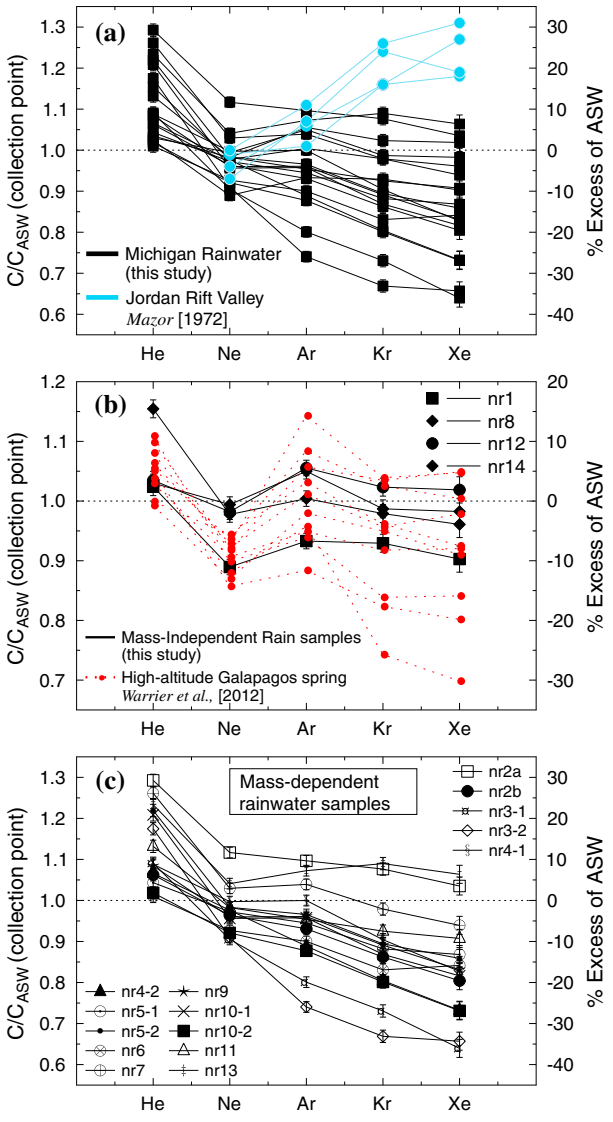

Figure 1. Measured noble gas concentrations in rainfall normalized to air saturated water corresponding to measured surface air temperature and altitude at the time and location of sampling. Right *Y* axis represents normalized values as % excess relative to ASW (a) Measured noble gas patterns in rainwater for all samples collected in southeast Michigan (black lines, this study) and samples from Jordan Rift Valley, Israel (blue lines, *Mazor* [1972]). (b) Mass-independent subset of noble gas patterns in Michigan rainfall and (c) mass-dependent subset of noble gas patterns observed in rainwater from Michigan.

By contrast, cold air masses from the northwest Pacific and Canada are stronger from mid-autumn to late spring [*Shadbolt et al*., 2006]. In addition, prevailing westerly winds bring some lake effect precipitation to the area during late fall and early winter.

3. Sample Collection and Measurements

[6] Nineteen rainwater samples were collected from Ann Arbor (42.28°N, 83.77°W) and Milan (42.08°N, 83.68°W) in southeast Michigan between May and September 2011 (Figure S1; Table S1). Most rainwater samples were collected as runoff from rooftops in bottles and/or jugs. A few samples were collected directly from rainfall. Rainwater samples were subsequently transferred into copper tubes for analysis of noble gases. He, Ne, Ar, Kr, and Xe concentrations, as well as all isotopic ratios, were measured at the University of Michigan using a MAP-215 mass-spectrometer following analytical procedures described in *Hall et al*. [2012]. Standard errors for He, Ne, Ar, Kr, and Xe concentration measurements are 1.5, 1.3, 1.3, 1.5, and 2.2%, respectively.

4. Noble Gas Patterns and Associated Weather Data

[7] Noble gas concentrations for all Michigan rainwater samples (black squares, Figure 1a) deviate from expected ASW values ($C/C_{ASW} = 1$) corresponding to measured surface air temperature and altitude at the time and location of sampling. Specifically, all rainwater samples present He excesses (1%–29%) with respect to ASW that are atmospheric in origin as indicated by the measured He isotopic ratios (Table S1). Similar atmospheric He excesses (≤22%) are observed in springs in the Galapagos [*Warrier et al*., 2012]. In contrast, Ne, Ar, Kr, and Xe concentrations for most samples are depleted with respect to ASW (black squares, Figure 1a). Specifically, while Ne concentrations display a maximum depletion of 11%, Ar, Kr, and Xe display maximum depletions of 26%, 33%, and 36% with respect to ASW. Deviations of measured concentrations from expected ASW values indicate that Michigan rainwater is not in equilibrium with surface conditions. Lack of rainwater equilibration with surface conditions was first observed in the Jordan Rift Valley in Israel [*Mazor*, 1972]. However, noble gas patterns observed in this study are distinct from those previously observed by *Mazor* [1972]. While He was not reported and Ne concentrations were shown to be depleted (≤−7%) in the Jordan Rift Valley as also observed in Michigan, Ar, Kr, and Xe concentrations in rainfall were in excess of ASW for all samples by up to 11%, 26% and 31%, respectively (blue circles; Figure 1a; *Mazor*, 1972). Depleted Ar, Kr, and Xe concentrations in rainwater in southern Michigan are thus in sharp contrast to excesses observed for these same gases in Israel, and indicate that noble gas concentrations in rainfall are not uniform throughout the world. These observations further suggest that the mechanism of incorporation of noble gases in rainwater at these two locations is distinct (cf. section 5). Overall, two groups of rainwater samples can be identified in Michigan: (a) a group displaying mass-independent noble gas patterns with relative Ar enrichment and Ne, Kr, and Xe depletion represented by samples nr1, 8, 12, and 14 (black markers, Figure 1b), (b) a group displaying a mass-dependent pattern with greater depletion of the heavier noble gases Kr and Xe as compared to the lighter ones Ne and Ar (Figure 1c) represented by all the remaining samples.

[8] Distinct noble gas patterns collected from rainfall at the same location suggest a likely association with local weather conditions. Mass-independent patterns with relative Ar enrichment and Ne, Kr, and Xe depletion displayed by southern Michigan rainwater samples are remarkably similar to the previously unknown pattern observed in high-altitude spring samples in the Galapagos Islands (red circles, Figure 1b). *Warrier et al*. [2012] previously showed that mixing between rainwater that equilibrated at high altitudes (≥1.5 km) in the atmosphere together with low-altitude (~400 m) fog droplets

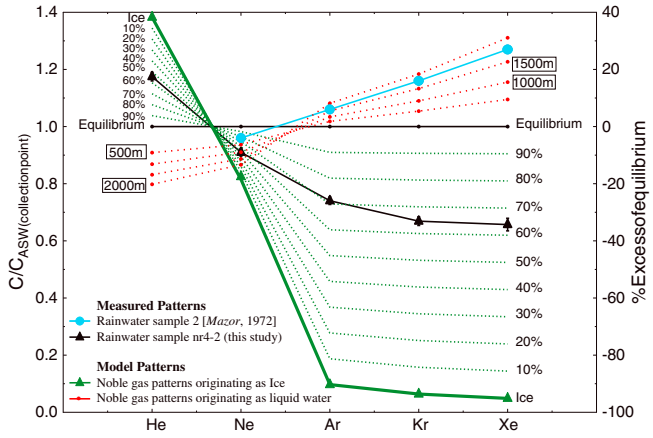

Figure 2. Comparison of measured noble gas patterns in rainwater from Michigan (nr4-2, this study, black triangle) and Israel (sample 2 of *Mazor* [1972], blue circle) together with expected rainwater patterns originating as a liquid in equilibrium at higher altitudes (red circles) and ice (green triangles). Both rainwater samples are normalized to ASW at respective measured surface conditions. Expected noble gas patterns for various isothermal equilibrium stages (0–100%) in a raindrop (green dotted lines) are also indicated. These expected patterns shown here are time-independent and do not correspond to potential concentration profiles within a raindrop (supplementary text 3).

is at least partially capable of producing the observed noble gas patterns in these samples. A combined analysis of multiple weather data at the time of sample collection for all four rainwater samples displaying mass-independent patterns points to the presence of mist/fog, light to moderate rainfall, and low cloud ceiling heights (~300 m) under a low-pressure system (Text S1). Strikingly similar noble gas patterns observed in two distinct geographic locations specifically during the occurrence of fog and light rain suggest that dissolved noble gas concentrations in fog might be at least partly responsible for this unique noble gas pattern of relative Ar enrichment, together with Ne, Kr, and Xe depletion. Noble gas measurements in fog have never been carried out. We thus lack an understanding of the underlying physical processes in these systems leading to disequilibrium and mass-independent patterns. Nevertheless, gas/aqueous-phase concentrations of pollutant species in fogs such as low molecular weight organic acids, ammonia, H_2O_2, sulfur S (IV), and nitrite are also observed to be in phase disequilibrium (both supersaturated and undersaturated) with surface conditions based on Henry's law [e.g., *Munger et al.*, 1983]. Inhomogeneous pH among individual fog drops [*Pandis and Seinfeld*, 1991], vertical in-cloud variation of gas phase concentrations [*Bott and Carmichael*, 1993], and mass transport limitations due to the presence of organic films [*Moore et al.*, 2004] are some of the processes proposed to account for deviations from instantaneous phase equilibrium in fog with respect to ASW. This active area of research highlights the complexity of processes involved in gas phase dissolution of fog and suggests that a full understanding of noble gas patterns in rainwater will also require a comprehensive understanding of noble gas behavior in fog.

[9] In contrast, samples with mass-dependent patterns (Figure 1c) were collected during the passage of more active systems such as cold, warm, or stationary fronts. Precipitation was characterized by thunderstorms, heavy rainfall, and high cloud ceiling heights (>1 km; Text S1). Except for collection of sample nr5-1, during which some brief initial fog activity existed during a thunderstorm approach, total absence of fog was registered during collection of all samples displaying mass-dependent noble gas patterns for which precipitation characteristics were available (Text S1). As discussed above, in addition to other weather attributes, presence or absence of fog might thus be a critical parameter in determining observed noble gas patterns in rainwater. In addition to fog, these weather attributes include rainfall intensity and cloud ceiling heights. In turn, these distinct weather attributes relate to microphysical aspects of precipitation, including drop size distribution [e.g., *Marshall and Palmer*, 1948], droplet growth mechanism (diffusional condensation versus collision and coalescence, e.g., *Rogers and Yau*, [1989]), and dominant mass-transfer processes within raindrops (convective diffusion versus turbulent mixing, e.g., *Amokrane and Caussade*, [1999]). While a detailed analysis of raindrop microphysics is out of the scope of the current manuscript, a simple first order model is utilized below to explain the origin of some of the observed noble gas patterns in mass-dependent rainwater samples.

5. Origin of Noble Gases in Raindrops

[10] Noble gas patterns for rainwater sample nr4-2 from Michigan (this study) and sample 2 from Israel [*Mazor*, 1972] (closed black triangles and blue circles, respectively, Figure 2) are compared with expected noble gas patterns if liquid rainwater had equilibrated at higher altitudes (500–2000 m; red circles, Figure 2) assuming a surface temperature of 18°C [*Mazor*, 1972] and an average lapse rate of 6.5°C/km [*Moore*, 1956]. Because of lower pressures at high altitude, He and Ne concentrations are lower than ASW values at the surface as these gases are mostly sensitive to pressure. 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 surface ASW values (red circles, Figure 2). Expected Ar, Kr, and Xe patterns for liquid rainwater in approximate equilibrium with air for altitudes varying between 1500 and 2000 m are similar to the pattern displayed by sample 2 in Israel (red and blue circles, Figure 2) and suggest that precipitation in-cloud in this region originates as liquid water in equilibrium with the atmosphere at these high altitudes. However, such an origin cannot explain the simultaneous atmospheric He excesses and depletion of Ne, Ar, Kr, and Xe observed in most rainwater samples from southeast Michigan (black squares; Figure 1a, this study). It is possible that the Wegener-Bergeron-Findeisen process of rain formation, originating as ice crystals in mixed phase clouds, is responsible for our observed noble gas patterns [*Wegener*, 1911; *Bergeron*, 1935; *Findeisen*, 1938]. Indeed, the presence of hail and high altitude condensation levels below freezing recorded for most of our rainwater samples strongly suggests that precipitation in southeast Michigan starts as ice (Text S1), a finding that was also previously suggested by *Bernstein et al.* [2007]. While noble gas concentrations

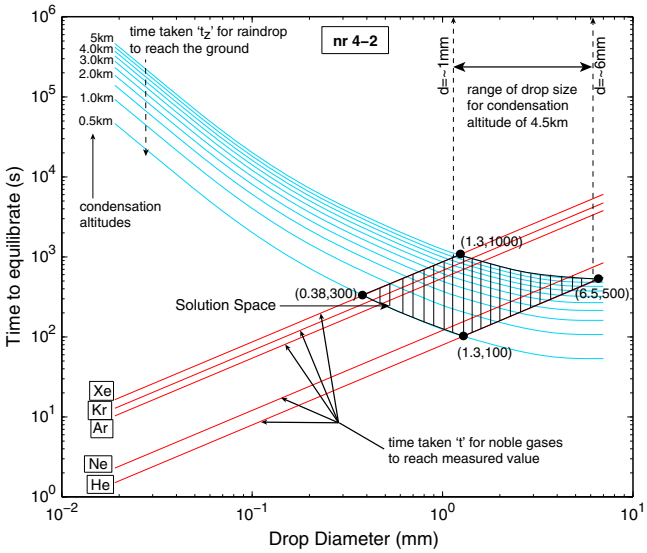

Figure 3. Calculation of raindrop sizes for precipitation event corresponding to sample nr4-2. Comparison of time (y axis) taken by noble gases to reach measured values in raindrops of different sizes (x axis) and time taken for a drop to fall from cloud base to ground surface yields a solution space (shaded area) of time and droplet diameters. Range of droplet sizes constrained by observed condensation altitude for this precipitation event is also indicated.

in ice within clouds have not been measured, overall mass-dependent noble gas patterns in Michigan rainwater (Figure 1c) are very similar to average measured noble gas patterns in Antarctica ice (*Malone et al*., 2010; green triangles, Figure 2). In particular, average noble gas composition in ice is enriched in He and depleted in Ne by 38% and 18%, respectively, while the heavier noble gases Ar, Kr, and Xe are extremely depleted, by 90%, 94%, and 95% with respect to equilibrium conditions, respectively (green triangles, Figure 2, ASW at 0°C, *Malone et al*., 2010). Laboratory experiments show that the unique noble gas patterns observed in ice are due to the ability of smaller atoms such as He to be incorporated into the ice structure as freezing progresses, as opposed to larger atoms such as Ar, Kr, and Xe which are entirely excluded from the ice structure, while Ne remains in ice at low concentrations [*Top et al*., 1988]. Indeed, these experimental results agree well with noble gas measurements of two Arctic sea ice samples [*Top et al*., 1988].

[11] A simple mass-transfer model (Text S3) involving diffusion in a sphere (raindrop) was first used to investigate whether noble gas patterns in Michigan rainwater can originate from ice, assuming that noble gas concentrations in ice crystals within clouds are similar to those of Antarctic ice. Expected noble gas patterns corresponding to different stages of isothermal disequilibrium starting from ice and assuming ASW at 0°C as diffusive mass transfer proceeds within a raindrop are shown (green dotted lines, Figure 2). While these patterns shown in Figure 2 are time-independent, actual noble gas concentrations within a raindrop are expected to evolve at different rates (Text S3). Comparison of expected and measured noble gas patterns suggests that such a model is capable of reproducing the various degrees of atmospheric He excesses together with Ne, Ar, Kr, and Xe depletion levels observed in our Michigan rainwater samples. 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% (Figure 2). 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 diffusive mass-transfer model (cf. Text 3). 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]. While 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, an analysis of the time-dependent evolution of noble gas patterns in a raindrop is undertaken (Figure S9, Text S3). Results from the analysis agree well with the results from a simple diffusion mass-transfer model and clearly show that mass-dependent noble gas patterns are expected in rainwater if the latter is assumed to start as ice. This, in turn, strongly suggests that ice is the starting point of rainwater formation in southeast Michigan (this study, see also *Bernstein et al*., 2007).

6. Calculation of Droplet Sizes From Measured Noble Gas Concentrations in Rainfall

[12] Because ice is the starting point of rainwater formation in southeast Michigan (cf. section 5), a novel application of dissolved noble gases in rainwater is highlighted here. Specifically, measured rainwater noble gas concentrations are used to provide a range of raindrop sizes for corresponding rainfall events as briefly described for rainwater sample nr4-2 (see Text S3 for details). First, the time "t" taken to achieve measured noble gas concentrations in rainwater from initial ice concentrations is calculated using a diffusive mass-transfer model in a raindrop (cf. section 5) for a range of assumed droplet diameters (0.019–10 mm; red lines, Figure 3). Time "t" is then compared with time "t_z" taken for a raindrop to fall at terminal velocity from a cloud base between 0.5 and 5 km for a similar range of assumed droplet sizes (blue lines, Figure 3) yielding a solution space (shaded area, Figure 3) defined by equilibration times of 100, 300, 500, and 1000 s and droplet sizes of 0.38, 1.3, and 6.5 mm diameter. Because weather sounding data for nr4-2 indicate a condensation altitude of ~4.5 km (Table S4), drop sizes are further constrained to be between 1 and 6 mm. Drop sizes for other mass-dependent rainwater samples are similarly calculated and yield values between 0.45 and 10 mm in diameter (Table S4), which fall within the range of raindrop sizes observed in nature [*Rogers and Yau*, 1989]. Because large drop sizes are generally associated with heavy rainfall [e.g., *Marshall and Palmer*, 1948], our results indicate that heavy rainfall is expected for samples displaying mass-dependent depletion. Heavy rainfall for these samples is corroborated both by direct observations at the time of collection as well as by weather stations' data (Text S1).

7. Time Estimates for Noble Gases in Rainwater to Re-equilibrate at the Surface

[13] Our study shows that all rainwater samples, without exception, are in disequilibrium with surface conditions. However, calculation of NGTs assumes that rainwater at the water table is in equilibrium with ground air. Although noble gases in rainwater are typically assumed to re-equilibrate at surface conditions on the order of a few minutes (Text S4), a detailed analysis using actual rainwater measurements is lacking. Time taken for measured maximum deviations of noble gases in Michigan rainwater (Figure 1) to re-equilibrate at the surface is calculated using a diffusive mass-transfer model in a sheet of water considering a realistic water depth of 1 cm and an average surface air temperature of 25°C (Text S4). Our results show that maximum atmospheric He excesses of 29% in rainwater would take ~15 min to reach equilibrium, while maximum deviations of −11%, −26%, −33%, and −36% for Ne, Ar, Kr, and Xe would take ~3.3 min, ~34 min, ~72 min, and ~108 min (~2 h), respectively. Faster re-equilibration of He and Ne as compared to Ar, Kr, and Xe is observed due both to their higher diffusion coefficients and lower initial disequilibrium with respect to surface conditions. Our calculations show that the typical assumption of rainwater re-equilibration occurring within minutes is more applicable for lighter noble gases and smaller water depths (<1 cm) while heavier noble gases and greater water depths require re-equilibration time on the order of hours. Noble gas patterns in rainfall will thus be recorded in groundwater systems if the time to re-equilibrate with surface conditions is greater than the time taken to reach the water table. This is likely the case in the Galapagos Islands where rapid water infiltration due to the presence of fractures and thin soil cover [*Warrier et al*., 2012] allows little time for noble gas re-equilibration at the water table. However, sedimentary aquifer systems typically have thicker unsaturated zones and longer infiltration times allowing sufficient time for rainwater to re-equilibrate with ground air. This, in turn, validates the use of noble gases in paleoclimate reconstructions (e.g., *Kipfer et al*., 2002, *Castro et al*., 2012).

8. Concluding Remarks

[14] The first comprehensive study of noble gases in rainwater is presented here. It is shown that noble gases are consistently in disequilibrium with surface conditions and that their composition is directly linked to weather patterns. It is the first time that such a linkage is established. These findings allow not only for the development of an entirely new application of noble gases as tracers of groundwater circulation in fractured and karstic systems where infiltration is rapid, but also for the validation of the use of the noble gas paleothermometer in sedimentary systems.

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