

EXCESS AIR IN GROUNDWATER AS A POTENTIAL INDICATOR OF PAST ENVIRONMENTAL CHANGES

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Abstract. Dissolved noble gases in groundwater are used to reconstruct paleotemperature, but also yield information about "excess air", a component of dissolved gases in excess of solubility equilibrium, derived from dissolution of trapped air in the ground. A good characterization of the excess air component is necessary not only to obtain reliable noble gas temperatures, but also to investigate the potential of excess air as a proxy for past environmental conditions. Two excess air related quantities can be derived from groundwater noble gas data sets: The initial air/water ratio and the pressure exerted on the entrapped air. Under recharge conditions typical for many aquifers, the excess of dissolved gases, expressed by the relative Ne excess ΔNe , is mainly determined by the hydrostatic pressure on the entrapped air. Thus, we suggest that ΔNe is essentially a measure of the amplitude of water table fluctuations in the recharge area. Comparing data sets from three aquifers in temperate, humid latitudes and three aquifers in tropical, semi-arid regions, we find that ΔNe is generally higher in the tropical aquifers, possibly related to larger water table fluctuations in these aquifers characterized by deep unsaturated zones. Whereas ΔNe shows little temporal variation in the mid-latitude aquifers, there is a strong signal of higher ΔNe in the paleowaters of the tropical aquifers as compared to water recharged under modern climate conditions. This finding may indicate a higher variability of recharge in the past at the studied tropical sites.

1. INTRODUCTION

The temperature dependence of noble gas solubilities in water has successfully been used to reconstruct ground temperatures during the last glacial maximum (LGM) from noble gas concentrations in groundwaters (see [1, 2] for reviews). In comparison to other paleoclimate proxies, the noble gas paleothermometer has the advantage of providing absolute temperature estimates, but the disadvantage of low temporal resolution which is inherent to the groundwater archive. The importance of the method thus lies in the quantification of the temperature shift between the LGM and the Holocene. However, the calculation of the noble gas temperature (NGT) is complicated by the empirical finding of an excess of dissolved gases relative to solubility equilibrium with the atmosphere in virtually all groundwaters. Traditionally, correction for this "excess air" [3] component has been accomplished by iterative subtraction of atmospheric air from the measured noble gas concentrations [4, 5]. In certain aquifers, this procedure does not yield satisfactory results [6, 7]. In order to derive paleotemperatures from such records, a model of elemental fractionation of the excess air by partial diffusive re-equilibration has been proposed [6].

Yet, rigorous inverse modeling has shown that even the refined model does not provide an adequate description of the data [8]. As a solution to this problem, we have proposed a model explaining excess air as the result of closed-system equilibration of groundwater with persistent entrapped air [9]. Also using an inverse modeling technique [10], we could show that the new model performed best in fitting several noble gas data sets, that it has physically

meaningful parameters, and that fits to the data yield plausible values for these parameters. These results provide a new basis for the interpretation of noble gas data, in particular with respect to the excess air component, which is increasingly being viewed as a potentially useful paleoenvironmental proxy rather than a disturbing effect in the calculation of NGTs. Relationships between the amount of excess air and the lithology of the recharge area as well as the precipitation rate have been observed [11]. A peak of excess air in an aquifer in Namibia has been attributed to the water table rise during a transition to a wetter climate [12]. Here, we first discuss the closed-system equilibration model for excess air and the physical meaning of its parameters. We then apply the model to several published and new noble gas data sets from paleogroundwaters, look for systematic patterns of the excess air parameters, and try to relate the observed patterns to plausible environmental factors.

2. THE MODEL

The traditional assumption that excess air is formed by complete dissolution of small air bubbles trapped in soil pores [1, 3] can be expressed by the following model equations for the concentrations of dissolved atmospheric gases i [10]:

$$C_i(T, S, P, A_d) = C_i^*(T, S, P) + A_d \cdot z_i \quad (1)$$

where A_d is the concentration of dissolved dry air, and z_i are the volume fractions of the individual gases in dry air. The moist air solubility equilibrium concentrations C_i^* are functions of temperature T , salinity S , and atmospheric pressure P , given by Henry's law:

$$C_i^*(T, S, P) = \frac{p_i^{atm}}{H_i(T, S)} = \frac{(P - e(T))f_i}{H_i(T, S)} \quad (2)$$

where $H_i(T, S)$ are the Henry coefficients and $e(T)$ is the saturation water vapor pressure.

The conceptual idea of our model for the formation of excess air [9] is that during a rise of the water table bubbles of soil air are trapped in some pores and pressurized by hydrostatic overload and surface tension. However, this entrapped air does not completely dissolve, but instead reaches solubility equilibrium with the surrounding water under the enhanced pressure. The water eventually reaches the fully saturated zone, whereas the gas bubbles remain trapped in their pores. During fluctuations of the water table, the gas phase is periodically replaced by soil air, which is assumed to be identical to atmospheric air.

In the initial situation we have a water volume V_w with gas concentrations $C_i^*(T, S, P)$, i.e., in atmospheric solubility equilibrium at the conditions in the recharge area. The finite trapped gas volume V_g^0 contains moist air under a total pressure $P_g > P$. The STP-volume of dry air in the trapped gas per unit mass of water is given by:

$$A = \frac{V_g^0}{\rho(T, S)V_w} \cdot \frac{P_g - e(T)}{P_0} \quad (3)$$

where P_0 is the standard pressure (1 atm). In summary, the initial state of the system is completely described by five parameters: T , S , P , P_g , and V_g^0/V_w . Note that only the ratio V_g^0/V_w is relevant, not the absolute volumes.

Complete dissolution of the entrapped air A would lead to an unfractionated excess air component corresponding to A_d in eq. 1. However, if the trapped air is only partly dissolved, a

final state is reached in which a gas volume V_g remains, which is in solubility equilibrium with the constant water volume V_w under the constant total pressure P_g . Thus, in the final state the partial pressures p_i of all gases in V_g are related to the dissolved gas concentrations C_i in V_w by Henry's law:

$$p_i = H_i(T, S) \cdot C_i \quad (4)$$

Since we describe a finite, closed system ($V_w + V_g$), the total number of moles n_i of all gases within the system must be the same in the initial and the final state:

$$n_{i,w}^0 + n_{i,g}^0 = n_{i,w} + n_{i,g} \quad (5)$$

In order to derive an equation for the dissolved gas concentrations in the final state from this condition of mass conservation, it is useful to introduce the following definitions:

$$v \equiv \frac{V_g}{V_g^0}, \quad q \equiv \frac{P_g - e}{P - e}, \quad \text{and} \quad F \equiv \frac{v}{q}, \quad (6)$$

where v is the ratio of the gas volumes in the final and initial state, q is the ratio of the dry gas pressure in the trapped gas to that in the free atmosphere, and F describes the reduction of the volume of entrapped air (A) due to partial dissolution (v) and compression ($1/q$). By spelling out eq. 5, using eqs. 2, 3, 4, and 6 as well as the ideal gas law, we obtain the model equations that describe the final gas concentrations in the water phase:

$$C_i(T, S, P, A, F) = C_i^*(T, S, P) \cdot \frac{1 + Az_i/C_i^*}{1 + FAz_i/C_i^*} = C_i^* + \frac{(1 - F)Az_i}{1 + FAz_i/C_i^*} \quad (7)$$

Note that only the combined parameter $F = v/q$ is needed to define the excess air component, not v and q individually. From the physical requirement that the sum of the partial pressures of all gases in the trapped volume equals the total pressure, we can derive (by using eqs. 2, 4, 6, and 7) an implicit equation that couples the parameters q , v , and A :

$$q = \sum_i z_i \frac{1 + A \frac{z_i}{C_i^*}}{1 + \frac{v}{q} A \frac{z_i}{C_i^*}} \quad (8)$$

Once F is determined from fitting eq. 7 to the data, both q and v can be calculated from eq. 8. Any pair of the parameters A , F , q , and v fully determines the amount and composition of excess air, the most intuitive choice being A (\approx volume of entrapped air) and q (\approx pressure exerted on the entrapped air).

The decomposition of F into v and q is of interest for the physical interpretation of the excess air parameters. To illustrate this, it is useful to examine some limiting cases. A trivial case is $F = 1$, when eq. 8 implies also $q = v = 1$. This means that there is no pressure excess and no dissolution, thus, no excess air at all. Another simple case is $F = 0$, when eq. 7 reduces to eq. 1, i.e., complete dissolution. The important point to note is that for any given concentration of entrapped air (any value of A), eq. 8 prescribes the pressure q that is needed to achieve

complete dissolution ($v = F = 0$). This limiting pressure is essentially the pressure needed to hold all nitrogen contained in V_g^0 in solution in the water volume V_w .

Another, not so obvious but very interesting, limiting case is that A approaches infinity (very large reservoir of entrapped air). In this case, we find from eq. 8 that v approaches 1, i.e., the gas volume remains constant independent of the pressure q . Eq. 7 reduces to:

$$C_i = C_i^* \frac{1}{F} = q C_i^* = \frac{P_g - e}{P - e} C_i^* = C_i^*(T, S, P_g) \quad (9)$$

This means that all concentrations are enlarged by the constant factor q , corresponding to atmospheric equilibrium at the increased pressure P_g . Thus, eq. 9 describes a pressure effect, or equilibration with an infinite air reservoir (e.g., the free atmosphere) at increased pressure. Apparently, eq. 7 is a very general description of the concentrations of dissolved gases in groundwater, describing all possible cases between no excess air ($F = v = q = 1$), pure excess air ($F = v = 0$, A and q linked by eq. 8), and a pure pressure effect ($A = \infty$, $v = 1$).

Interestingly, noble gas data from groundwater samples can often be described quite well by a pressure effect, i.e., using only T and P as free parameters. However, the solutions obtained from a pure pressure model tend to yield unrealistically high values for T and P . In contrast, the closed-system equilibration model (eq. 7) with T , A , and F as free parameters usually yields realistic values for all parameters. Sometimes, however, the fitting procedure converges to the "pressure effect" solution with large A . Fits with large A tend to behave numerically unstable, because any large value of A produces a similarly good fit (measured by χ^2), and because of a strong correlation of the parameters A and T . Empirically we find these problems for solutions with $A > 0.1 \text{ cm}^3\text{STP/g}$ (corresponding to an air/water volume ratio $> 1:10$ at STP). Although such solutions provide the best fit to the data, they appear to be rather accidental, because usually slightly worse but still acceptable fits with lower and more realistic A -values exist. Care should therefore be taken in interpreting results with large values of A . In the literature, the excess air component is often expressed by the relative Ne excess, ΔNe (%) = $(C_{\text{Ne}}/C_{\text{Ne}}^* - 1) \cdot 100$. In the case of complete dissolution of entrapped air (eq. 1), ΔNe is directly related to the excess air parameter A_d . In general, however, the relationship between ΔNe and A is not straightforward. Nevertheless, ΔNe is a very useful measure of the size of the excess air component. In particular, it is practically an observable quantity, nearly independent of the choice of the correct model for excess air and the exact calculation of T , because the equilibrium concentration C_{Ne}^* does not strongly depend on temperature.

3. RESULTS AND DISCUSSION

In order to investigate systematic patterns of the excess air parameters, we applied the closed-system equilibration model to six groundwater noble gas data sets, three of them representing temperate northern latitudes, and three representing semi-arid tropical locations. These paleorecords originate from: 1) Belgium, Ledo-Paniselian aquifer, about 51°N, 4°E; 2) France, Miocene aquifer in the Valreas Basin, about 44°N, 5°E [13]; 3) USA, Maryland, Aquia aquifer, about 39°N, 77°W [14, 15]; 4) Niger, Continental Terminal aquifers in the Basin of Iullemeden, about 13°N, 3°E; 5) Brazil, Piauí Province, Serra Grande and Cabeças aquifers, about 7°S, 41°W [6]; 6) South Australia, J-K aquifer in the southwestern Great Artesian Basin, about 27°S, 134°E [16]. With the exception of the classical data set from Brazil, taken from [6], these are unpublished data. Full accounts of the paleoclimatic implica-

tions of these data sets will be given elsewhere. Here, we focus on the excess air component and its possible relationship to environmental conditions.

The six data sets comprise a total of 188 samples from 164 wells. 18 of these samples could not well be fitted by eq. 7 ($p < 0.01$ in the χ^2 -test), apparently mostly due to degassing during sampling. The remaining data were checked for outliers of A , F , v , q , or ΔNe . Samples for which one of these quantities deviated by more than three standard deviations from the mean of the respective data set were excluded. This step eliminated 7 samples with very high ΔNe ($\approx 200\%$ and higher) that are likely the result of air contamination, and 4 samples with high values of A ($\approx 0.2\text{ cm}^3\text{STP/g}$ and higher) that may be artefacts of the fitting procedure. Yet, still 9 samples with $A > 0.1\text{ cm}^3\text{STP/g}$ remained, that exhibited the problems described above (large correlation and uncertainty for A and T). We also excluded these samples in order to avoid a possibly artificial bias.

Thus, we are finally left with 150 samples from six different sites as a basis for our analysis of the excess air systematics. The results are summarized in Table I and visualized in Figs. 1 and 2. An intriguing pattern is revealed by Fig. 1, showing ΔNe as a function of A . The samples from the semi-arid tropical sites align close to the line for unfractionated excess air ($F = 0$) and are characterized by low values of A and F , but high values of ΔNe . In contrast, the samples from aquifers in temperate regions tend towards high A and F but low ΔNe . This pattern is also evident in the mean values of the parameters for the different sites (Table I).

Table I. Mean values of excess air parameters for the studied aquifers

Data set	N	A	F	q	v	ΔNe
Belgium	23	0.042 ± 0.030	0.65 ± 0.28	1.15 ± 0.08	0.76 ± 0.32	19 ± 10
France	22	0.018 ± 0.008	0.57 ± 0.16	1.23 ± 0.09	0.69 ± 0.17	35 ± 14
USA	26	0.035 ± 0.017	0.76 ± 0.05	1.16 ± 0.04	0.87 ± 0.06	21 ± 4
Niger	34	0.017 ± 0.008	0.41 ± 0.13	1.48 ± 0.24	0.57 ± 0.13	64 ± 33
Brazil	19	0.016 ± 0.005	0.37 ± 0.16	1.51 ± 0.22	0.53 ± 0.17	71 ± 34
Australia	26	0.018 ± 0.013	0.34 ± 0.23	1.41 ± 0.20	0.48 ± 0.29	57 ± 26

Mean values and standard deviations of the results for the individual samples are listed.

N is the number of accepted samples.

A is given in $\text{cm}^3\text{STP/g}$, ΔNe in %, the other parameters are dimensionless.

The results for Belgium, USA, and Brazil slightly differ from those listed in [9], because a more rigorous data selection has been applied here.

Figure 1 clearly shows that there is no simple relationship between ΔNe and A . In contrast, Fig. 2 reveals a strong linear link between ΔNe and q . The explanation for these observations is that the effective excess of dissolved gases (e.g., ΔNe) is not limited by the available reservoir of entrapped air (A), but by the pressure exerted on this reservoir (q). In most cases, the pressure appears to be too low to induce complete dissolution ($F = 0$ line in Fig. 1). In fact, if entrapped air occupies 1 % of the pore space ($A \approx 0.01\text{ cm}^3\text{STP/g}$), an excess pressure of about 0.5 atm ($q = 1.5$) is needed to induce complete dissolution (at $12\text{ }^\circ\text{C}$). The data of Table I show that typical values of A range between 0.02 and $0.04\text{ cm}^3\text{STP/g}$. Thus, excess pressures up to 2 atm would be needed to completely dissolve this entrapped air. Surface tension can produce such pressures only for bubble sizes $< 1\text{ }\mu\text{m}$. For a typical sandy aquifer, capillary forces are of minor importance, and the pressure excess can be interpreted as due to hydrostatic overload. Thus, water level rises of up to 20 m would be needed for complete dissolution, which are obviously impossible in many recharge zones where water tables are only a few meters below the surface.

Hence, if the A -values found in this study are typical, we have to conclude that partial dissolution is the rule rather than the exception compared to complete dissolution or even the model of diffusive re-equilibration, which often implies very large initial excesses of dissolved gases. The literature on air entrapment in soils [17-20] suggests that entrapped air typically occupies several percent of the pore space, with some values ranging as high as 50%. The perhaps most reliable data from careful experiments suggest that only a few percent of the pore space contain immobile air that can persistently be trapped [20]. This result is consistent with the A -values found here.

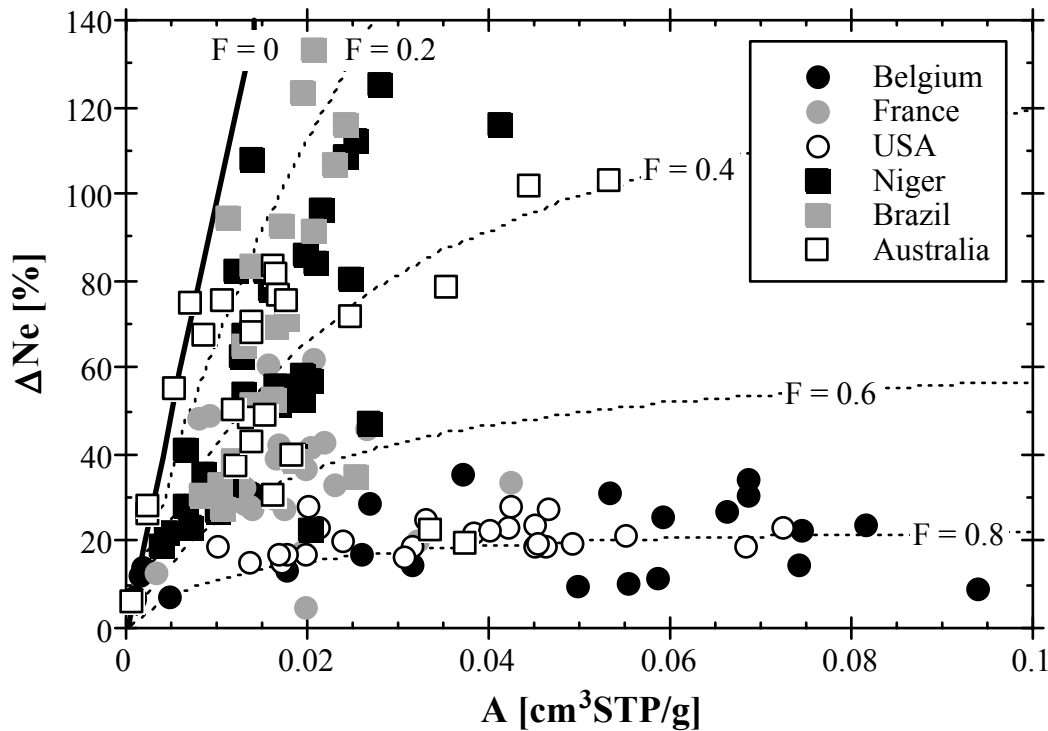


FIG. 1. The relative Ne excess ΔNe versus the initial concentration of entrapped air (A). The (dashed) lines represent solutions of eq. 7 for the indicated values of F , and $T = 20^\circ\text{C}$, $P = 1 \text{ atm}$, $S = 0\%$. Most samples have $F > 0$, indicating only partial dissolution of the entrapped air. Samples from aquifers at temperate latitudes are indicated by circles, samples from tropical aquifers by squares.

The most important conclusion from Fig. 2 is that the observable quantity ΔNe obtains a direct physical interpretation: it is essentially a measure of the pressure in the entrapped air. This pressure is always larger than the atmospheric pressure ($q > 1$), and if the overpressure is ascribed to the hydrostatic load of infiltrating water, then ΔNe should be a measure of the amplitude of water table fluctuations. This interpretation sheds new light on the observed differences between tropical and temperate sites. Typical q -values are ≈ 1.2 for the aquifers from temperate, humid regions, and ≈ 1.5 for the aquifers from semi-arid, tropical sites (Table I). Explaining these values by hydrostatic pressure due to water table rises implies typical fluctuations of 2 and 5 m, respectively. Although we have no records of the water levels at our study sites, there are arguments for larger fluctuations in the semi-arid aquifers. On the one hand, recharge in such climates is episodic, on the other hand, the unsaturated zone tends to be much deeper than in humid regions, offering a higher potential for large water table rises. An open question is whether ΔNe might be especially sensitive to water table fluctuations of a particular periodicity (e.g., seasonal or interannual).

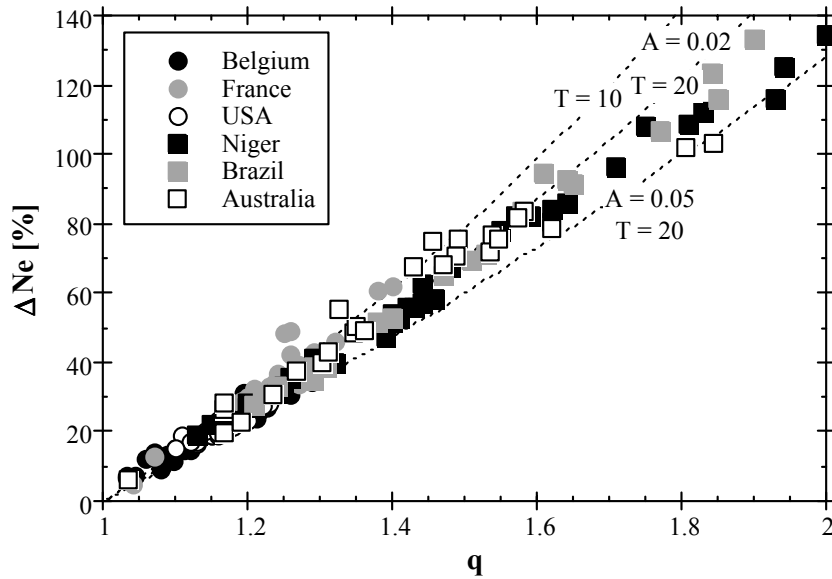


FIG. 2. The relative Ne excess ΔNe versus the pressure on the entrapped air relative to the atmospheric pressure (q). The dashed lines represent solutions of eq. 7 for the indicated values of A (in $\text{cm}^3\text{STP/g}$) and T (in $^\circ\text{C}$), as well as $P = 1 \text{ atm}$, $S = 0 \text{ ‰}$. ΔNe depends mainly on q , and only to a much lesser extent on A and T .

If ΔNe is related to water table fluctuations, it may be a proxy for the variability of recharge, and hence of precipitation, in the past. This interpretation provides a theoretical foundation for the attribution of a peak in the record of ΔNe in an aquifer in Namibia to the water table rise during a transition to a wetter climate [12]. In our data sets, we also find some systematic variations of ΔNe with groundwater age. As an example, Fig. 3 shows NGT and ΔNe as functions of the concentration of radiogenic He for the study site in France. A strong correlation between He and ^{14}C -ages [13] shows that He is a good proxy for age in this system. The samples with radiogenic He concentrations above about $4 \cdot 10^{-8} \text{ cm}^3\text{STP/g}$ are of Pleistocene age, as indicated also by a colder NGTs. The Holocene samples have ΔNe -values varying between 5 and 40 %, whereas the range for the Pleistocene samples is 30 to 65 %. Although the variability in both groups is quite high and the two ranges overlap, it is possible that the difference reflects actual changes of the recharge conditions, such as higher variability during the late Pleistocene. An interesting detail is that the highest ΔNe -values seem to form a peak, reminiscent of the stronger peak observed in Namibia [12]. Although not exactly at the same time, the peaks occur close to the time of the climatic transition in both records. However, similar features were not found in the other records studied here.

Although a detailed discussion of each record is not possible here, a general indication of climatic effects on the excess air may be obtained from correlations between NGT and ΔNe (Fig. 4). It is not expected that NGT directly influences ΔNe , but it can serve as a proxy for overall climatic conditions and to discern between Holocene and Pleistocene samples. In general, within each record high NGTs correspond to Holocene samples and low NGTs to Pleistocene samples, although there are some exceptions (e.g., the record from Australia may span several glacial-interglacial cycles [16]). Figure 4 shows that for the records from temperate regions, the correlations between NGT and ΔNe are rather weak and have different signs. In contrast, all three tropical sites show strong and very similar decreases of ΔNe with NGT, presumably reflecting climate-related changes in recharge conditions, such as higher and/or more variable precipitation during cooler climate periods in the past.

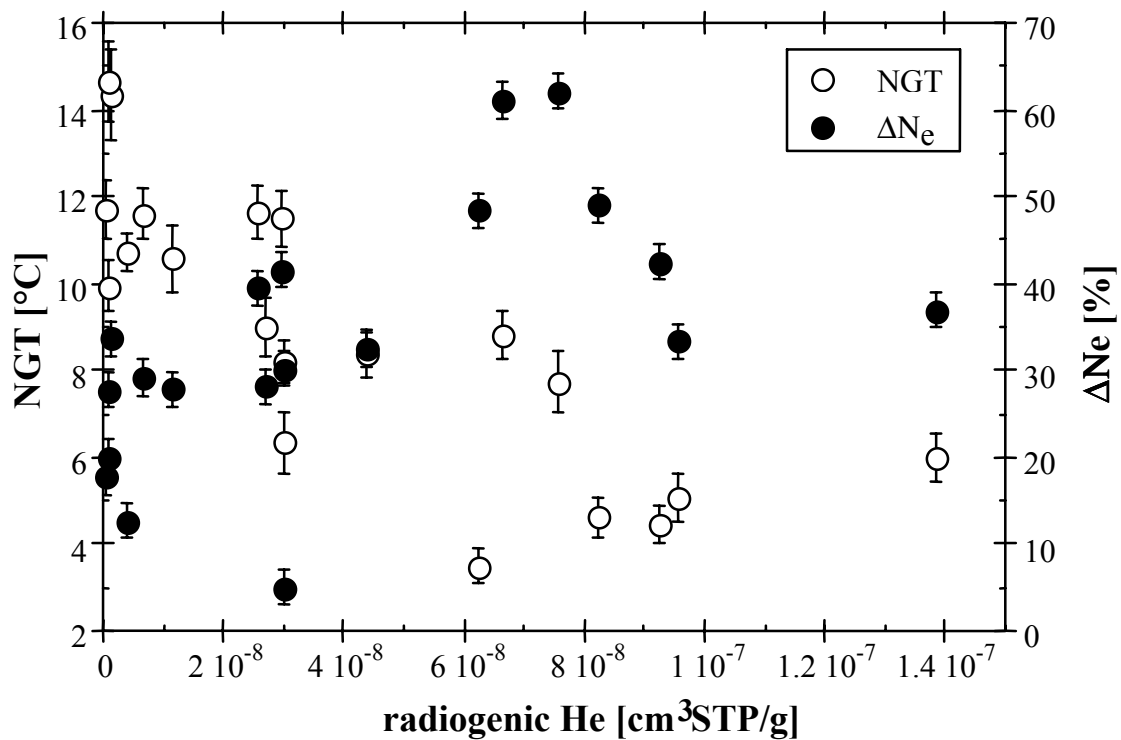


FIG. 3. Noble gas temperature (NGT) and Ne excess (ΔNe) in the aquifer from France (Valreas Basin) as functions of radiogenic He (a proxy for groundwater age). The transition between Holocene and Pleistocene samples occurs around $4 \cdot 10^{-8} \text{ cm}^3 \text{STP/g}$ [13].

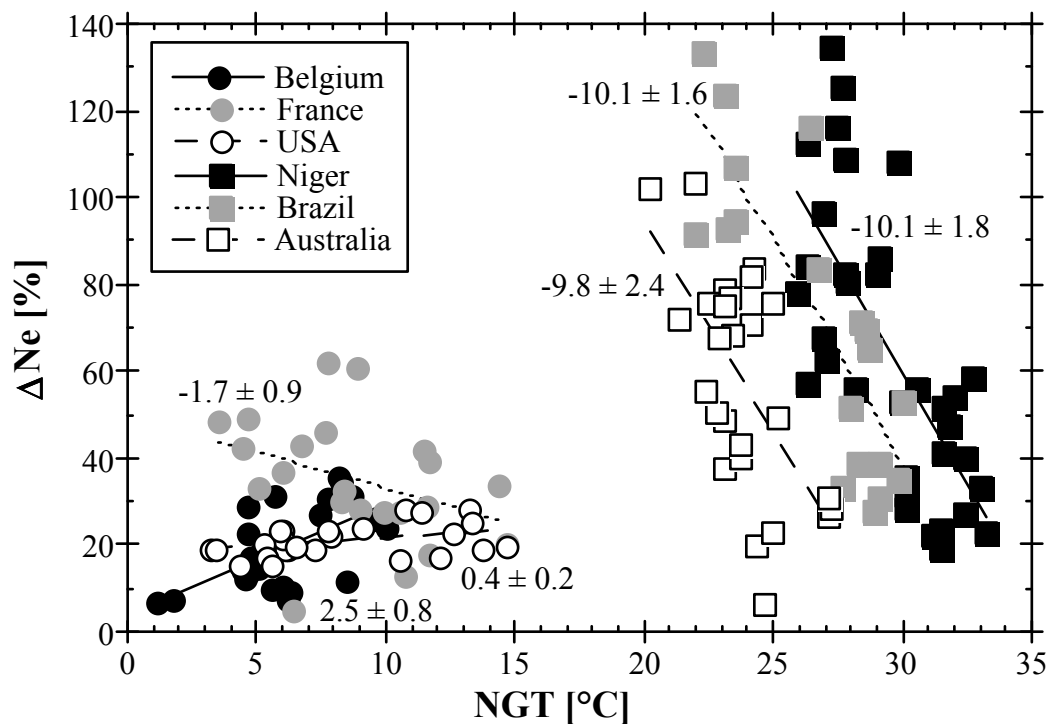


FIG. 4. Correlation between ΔNe and NGT for the different aquifers. Regression lines and their slopes (in $\% \text{ } ^\circ \text{C}^{-1}$) are indicated. All three tropical aquifers show strong correlations.

The results of Fig. 4 are in excellent agreement with the only previous study comparing excess air in different aquifers [11], which found no relationship between NGT and ΔN_e for limestone aquifers of the UK, a certain decrease of ΔN_e with NGT for a sandstone aquifer in the UK, and a strong decrease of ΔN_e with NGT for a sandstone aquifer in Niger. Thus, in particular the strong relationship between ΔN_e and some climatic factor in tropical, arid to semi-arid regions appears to be a consistent feature. The data are not conclusive as to whether this factor could be precipitation. Wilson and McNeill [11] found an increase of ΔN_e with mean annual precipitation when comparing different aquifers, but ascribed this effect to different lithologies and inferred a decrease of ΔN_e with precipitation when comparing data from the same lithologies. We think that lithology should not have a major influence on ΔN_e , because it may control A , but not q . Although the aquifers discussed in our study all have similar lithologies (sands and sandstones), they cover a large range in ΔN_e . Moreover, we expect ΔN_e to depend on water table fluctuations and thus on the variability of precipitation rather than on its mean value. However, in semi-arid climates with a distinct rainy season, higher variability of precipitation may be equivalent to higher mean precipitation.

4. CONCLUSIONS

The parameters of the model of excess air formation by equilibration of groundwater with a finite reservoir of entrapped air under increased pressure and closed conditions have a clear physical interpretation. The parameter A describes the volume of entrapped air per unit mass of water, and q describes the increase of pressure relative to the atmospheric pressure. Moreover, the widely used measure of the size of the excess air component, ΔN_e , is strongly related to q and thus is mainly a measure of pressure on the entrapped air bubbles. This leads us to the assumption that ΔN_e might reflect fluctuations of the water table and hence the variability of recharge and precipitation.

Although both A and q are quite variable in all investigated data sets, there are systematic differences between aquifers from tropical and temperate latitudes. The data from tropical aquifers yield relatively low values of A and high values of q , whereas those from temperate latitudes give high A and low q . In some data sets there are indications for differences in q between Pleistocene and Holocene samples, most prominently all aquifers from semi-arid tropical sites indicate a strong decrease of ΔN_e with NGT. A more detailed discussion of the tropical records is needed to substantiate the conjecture that the changes of ΔN_e indicate climatic changes such as a higher variability of precipitation during cooler periods in the past.

In summary, it appears that the excess air component does carry valuable information about past environmental conditions, which is however difficult to read due to natural variability and incomplete understanding of the controlling processes. Further detailed investigations both on the laboratory and field scale are needed to firmly establish relationships between excess air parameters and environmental conditions.

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