Noble gases and stable isotopes in a shallow aquifer in southern Michigan: Implications for noble gas paleotemperature reconstructions for cool climates

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[1] Noble gas data from the Glacial Drift, the shallowest aquifer in southern Michigan confirm findings by Ma et al. (2004) that modern noble gas temperatures (NGTs) are systematically below the current mean annual air temperature (MAAT) which, in turn, is similar to the ground temperature of these recharge waters. By tracking noble gas concentrations as well as stable isotope ratios through an autumn, winter, spring and into summer, we show that although water in this aquifer is modern, noble gases do not track the atmosphere on a short time scale. Specifically, excess ^{3}He and ^{4}He indicate that the gas environment at the water table is integrating conditions over years or decades rather than weeks or months. Our results are interpreted using various NGT interpretational models and possible mechanisms for the production of low apparent NGTs are discussed. **Citation:** Hall, C. M., M. C. Castro, K. C. Lohmann, and L. Ma (2005), Noble gases and stable isotopes in a shallow aquifer in southern Michigan: Implications for noble gas paleotemperature reconstructions for cool climates, *Geophys. Res. Lett.*, *32*, L18404, doi:10.1029/2005GL023582.

1. Introduction

[2] Because non-radiogenic isotopes of noble gases (Ne, Ar, Kr, and Xe) are conservative tracers and their concentrations in groundwater are sensitive, among other factors, to temperature for a given recharge location, NGTs are regarded as a potentially robust indicator of past climate [*Stute and Schlosser*, 1993]. NGT records have become an important and increasingly used tool to reconstruct continental paleoclimate in permanently ice-free regions. Paleoclimatic reconstructions using NGTs in ice-covered regions, however, are scarce. One such example is a NGT record derived mostly from the Marshall aquifer in southern Michigan [*Ma et al.*, 2004]. The latter has identified major global climatic oscillations since the Last Glacial Maximum (LGM), and suggests that groundwater recharge occurred under the Laurentide Ice Sheet (LIS) cover during the LGM and early deglaciation periods.

[3] The study by *Ma et al.* [2004] has, however, left unresolved questions in relation to NGT estimates in the proximity of the recharge area. Indeed, samples located close to the Marshall subcrop recharge areas, yielding modern ^{14}C ages, present significantly lower NGTs (2–5°C) than the current local MAAT of 9.1°C [*Ma et al.*, 2004]. ^{14}C temporal resolving power did not preclude the possibility that the youngest water samples were not truly indicative of the current climate. The question thus remained whether these samples are representative of current climate and, if so, what is the nature of the mechanisms responsible for a significant reduction of their estimated NGTs. By examining the noble gas and stable isotope characteristics of the Glacial Drift waters which overly and directly recharge the Marshall subcrop, as well as that of snow, ground ice and rainfall in the area, we now address these issues. Specifically, these tracers' behavior were followed over the course of 269 days, spanning autumn, winter and the spring melt of snow and ice which covers southern Michigan for much of the winter. Our new data set suggests that recharge water estimated NGTs are indeed significantly below the current MAAT in S. Michigan due to unexpectedly high measured noble gas concentrations. This new data set is analyzed in the light of differing NGT interpretational models and outline possible mechanisms that can give rise to this apparent offset with current MAAT.

2. Sample Collection and Measurements

[4] A single shallow well (~19 m screen, ca. 3 m below the water table) in the unconfined Glacial Drift aquifer located in Ann Arbor, MI (42°18.494′N, 83°45.998′ W) was used in this study as it allowed for easy routine access and continuous sampling. The well site, in the vicinity of a small hill (~275 m) is located in the Ft. Wayne terminal moraine that consists of unconsolidated sediments, mostly sands and gravels. Groundwater flows gravitationally with a WNW direction and discharges into the Huron River (~240 m). For the purposes of calculating NGTs, we assume a standard recharge altitude of 300 m. The long term MAAT for Ann Arbor is indistinguishable to that reported by *Ma et al.* [2004], with an average temperature of 9.1°C for the U. of Michigan Ann Arbor weather station over the period of 1854 to 1996.

[5] Water samples for noble gas analysis were collected in 3/8″ Cu tubes clamped at both ends and analyzed for He, Ne, Ar, Kr and Xe isotopes using an automated noble gas extraction system connected to a MAP215 mass spectrometer which has been modified to have sufficient mass resolution for measuring ^{3}He/^{4}He ratios. Noble gases as well as δ^{18}O and δD were analyzed at the University of Michigan. Sampling and measurement procedures are those as reported by *Ma et al.* [2004] with further details on noble gas procedures given by *Saar et al.* [2005]. With the exception of He, all other noble gas isotope ratios were

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identical to air within measurement precision. Detailed data tables for this study are provided elsewhere[1].

3. Results and Discussion

[6] Stable isotope results are summarized in Figure 1. All δD and $\delta^{18}O$ lie close to both the global [*Craig*, 1961] and local (Simcoe, Ont., Canada) meteoric water lines, a trend previously observed by *Ma et al.* [2004] in the Marshall aquifer. Except for a sample collected at day 138 (relative to Oct. 1, 2004) immediately following a significant snow melting event where elevated temperature was accompanied by rain, all other well water data are tightly clustered, with an average $\delta^{18}O$ value of $\sim -9.5‰$, similar to that also observed in the Marshall aquifer (Figure 1) [*Ma et al.*, 2004]. The former has $\delta^{18}O$ of $\sim -15.6‰$ and plots between the clustered data and three snow samples collected at the well site. Also plotted are rain water samples collected during storms with $\delta^{18}O$ ranging from -2.2 to $-6.8‰$. Although average well water values appear to be the result of mixing between rain water and snow, it is apparent that a major sudden influx of snow melt can briefly change the local isotopic composition of groundwater.

[7] Figure 2 shows fitted NGTs, measured pH, water well T and $\delta^{18}O$ as a function of time. Water temperatures vary slightly, but generally cluster very close to the MAAT. The NGT values were calculated using two different models: the unfractionated air (UA) model which assumes that groundwater has equilibrated at 100% relative humidity and any excess noble gas derived from the incorporation of air bubbles has atmospheric composition [*Stute and Schlosser*, 1993]; and the continuous equilibration (CE) model of *Aeschbach-Hertig et al.* [2000] which allows for partial dissolution of trapped air, thereby leading to noble gas fractionation. UA and CE NGT models yield average temperatures of 5.1 and 6.6°C respectively, which are significantly lower than the MAAT, the latter being indistinguishable from the measured water well T during sampling. UA NGTs systematically lower than MAAT were previously found in groundwaters in Germany [*Stute and Sonntag*, 1992] and were attributed to the effect of vegetation cover, presumably due to depressed ground T. This is clearly not the case in S. Michigan as groundwater T and MAAT are very similar.

[8] Significant NGT scatter is apparent (Figure 2), even for replicate samples. This scatter is much greater than for laboratory-produced samples, which are perfectly modeled within measurement error using the UA model. The UA fits used the method of *Ballentine and Hall* [1999] and this inversion technique was also adapted to perform constrained CE model fits (non-negative air and $0 \leq F \leq 1$). Details of the fits are given in Tables S2 and S3, see auxiliary material. Overall, CE model fits typically have χ^2 values below 1 and fit the measured noble gas volumes more successfully than the UA model. However, the estimated error is typically twice as large for CE fits than UA fits. No significant NGT variation is observed with time.

[9] Both the CE and UA models allow one to estimate the amount of ^{3}He and ^{4}He that would result from air saturated water (ASW) and dissolved excess air if all He present in the water had an atmospheric origin [see, e.g., *Saar et al.*, 2005]. It is clear that all well water samples display significant excess ^{3}He and ^{4}He with total He volumes greater than predicted with respect to ASW and excess air components by at least 1×10^8ccSTP/g (Figure 2a and Tables S2 and S3). In addition, R/R_a well water values where R is the measured ^{3}He/^{4}He ratio and R_a is the atmospheric ratio, range from 1.18 to 1.40 indicating excess ^{3}He volumes equivalent of 10–15 TU if one assumes that excess ^{3}He results entirely from natural and/or bomb ^{3}H decay. An anthropogenic origin for most of the excess ^{3}He in southern Michigan recharge waters is consistent with previous measurements in the area (see discussion by *Ma et al.* [2005]). Although our data set indicates that directly measured $\delta^{18}O$, δD and pH respond quickly to the large water influx from snow melting at the end of winter (Figure 2), the presence of significant excess ^{3}He and ^{4}He indicate that these gases are not in equilibrium with the atmosphere. Similar He excess in shallow aquifers were found by *Solomon et al.* [1996]. Water samples from the Marshall aquifer [*Ma et al.*, 2004] have also been analyzed for He and display a significant build up of both ^{3}He and ^{4}He [*Ma et al.*, 2005]. He build up in the Marshall is much greater than could be sustained by in situ decay of U and Th, and is due to external production (e.g. sedimentary sequence below the Marshall and crystalline basement). Preliminary calculations based on He concentrations in the Glacial Drift (this study), in situ production rates in a predominantly sand/sandstone environment, and He fluxes within the Michigan Basin [see, e.g., *Ma et al.*, 2005] indicate that most of the well He excess has an origin external to the aquifer and suggest a groundwater residence time within the Glacial Drift of ~30yrs. Based on He considerations, it is thus apparent that noble gases dissolved in the Glacial Drift recharge waters are not in equilibrium with the atmosphere, but instead reflect groundwater-air interactions over at least a few decades.

[10] In addition to well water samples, ground ice that remained at the end of winter was also analyzed. This clear ice was typical of the remnants of the winter snow cover. Ice was coarsely crushed, kept frozen, put into the noble gas extraction system and after evacuation to a pressure of less than 1×10^{-4} Torr, the ice was allowed to melt and noble gas extraction could proceed normally. Results of all noble gas measurements are given in Table S1, see auxiliary material. Our ground ice samples had very low Ne, Ar, Kr and Xe concentrations. By contrast, He concentrations were significantly enriched over that expected for ASW, results that are in very good agreement with findings by *Top et al.* [1988] for noble gases in sea ice. It is conceivable that some of the ^{4}He seen in water samples could derive from mixing with melted ice which has not equilibrated with air, but the ice samples' low Ar, Kr and Xe concentrations would tend to increase apparent NGT values which is the opposite effect needed to explain the measured offset from MAAT. Ground ice ^{3}He/^{4}He ratios are identical to air (Table S1), showing that excess ^{3}He cannot result from ice and likely has an anthropogenic origin from ^{3}H decay as previously discussed.

[11] *Stute and Schlosser* [1993] discussed many of the assumptions that go into producing an accurate NGT

[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2005GL023582.

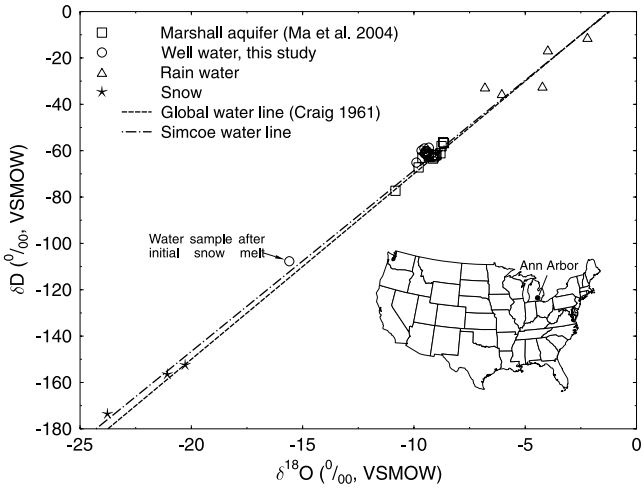

Figure 1. δD vs. $\delta^{18}O$ in the Glacial Drift well waters, snow and rain samples (this study), as well as the Marshall aquifer [*Ma et al.*, 2004]; Global and Simcoe water meteoric lines from *Craig* [1961] and http://isohis.iaea.org/, respectively. Inset: sampling location.

estimate. One of these is that the composition of the soil gas in the unsaturated zone is identical to air with 100% relative humidity. If, instead, a significant atmospheric component like O_2 is consumed via biological activity without an equivalent production of gaseous CO_2, then all of the noble gas partial pressures will be elevated, leading to low apparent NGTs [*Stute and Schlosser*, 1993]. This is equivalent to assuming a recharge altitude below its true value. Given the high solubility of CO_2 in cold water, it is not inconceivable that this "oxygen depletion" (OD) model may be at least partially responsible for the bias to low NGTs that is seen in this study. O_2 depletion as high as 50% of the atmospheric value has been documented for a shallow aquifer in Canada [*Miller et al.*, 1985]. An additional NGT model that was considered was the negative pressure (NP) theory of *Mercury et al.* [2004]. In this model, noble gas solubility is enhanced by capillary action due to a change in water surface tension.

[12] The above models assume at least approximate equilibrium conditions between gas and water in the unsaturated zone at mean ground temperature. However, given the extremely inefficient nature of noble gas transport due to diffusion, this may be an inaccurate assumption in some cases. It is possible to model the data set as a simple mixture of ~40% ASW at 0°C (snow melt) with ~60% at the MAAT (rain), a mixture that would be roughly compatible with the stable isotope data. However, significant shifts in NGTs in the spring would then be expected and these are not observed. Alternatively, partial loss of excess air can be modeled using the diffusive loss model of *Stute et al.* [1995], referred to here as the DIF model.

[13] We performed a χ^2 analysis of the various NGT models using our complete noble gas data set and the results are shown in Figure 3. In the analysis, NGT plus at most one other parameter was varied and excess air was estimated individually for each of the 20 measurements to yield the best fit to all of the data for that set of parameters. For the UA model, only NGT was varied and the second varied parameter for the other models were: effective altitude for OD; fractionation factor F for CE; capillary pressure for NP; and the natural logarithm of the diffusive fractionation factor F for DIF. The expected χ^2 value if all the data are consistent with a single NGT (and auxiliary parameter) would be ~58 and none of the models' minima is that low. As can be seen from Figures 3a and 3c, the UA and CE models with an assumed altitude of 300 m are not compatible with the MAAT.

[14] The NP model can be compatible with MAAT, but its very elongated minimum does not define a unique NGT value. The NP model minimum near the MAAT is at a pressure of ~−90 bars which corresponds to a relative humidity of ~94% in the unsaturated zone [*Mercury et al.*, 2003]. One possible mechanism that could lower relative humidity in the unsaturated zone during the winter is the presence of ice on the surface which could effectively act as a "cold trap", drawing water vapor from below and depressing the local relative humidity. The DIF model (Figure 3e) has a broad minimum from 5° to 10°C and could be compatible with the MAAT at an altitude of 300 m with a fractionation factor F of ~0.1.

[15] The OD model may be the most successful at reconciling our data with the MAAT (Figure 3b). It is interesting to note that at the χ^2 minimum along the MAAT line at an effective altitude of ~−1000 m, the excess air values for most of the samples nearly disappear, suggesting

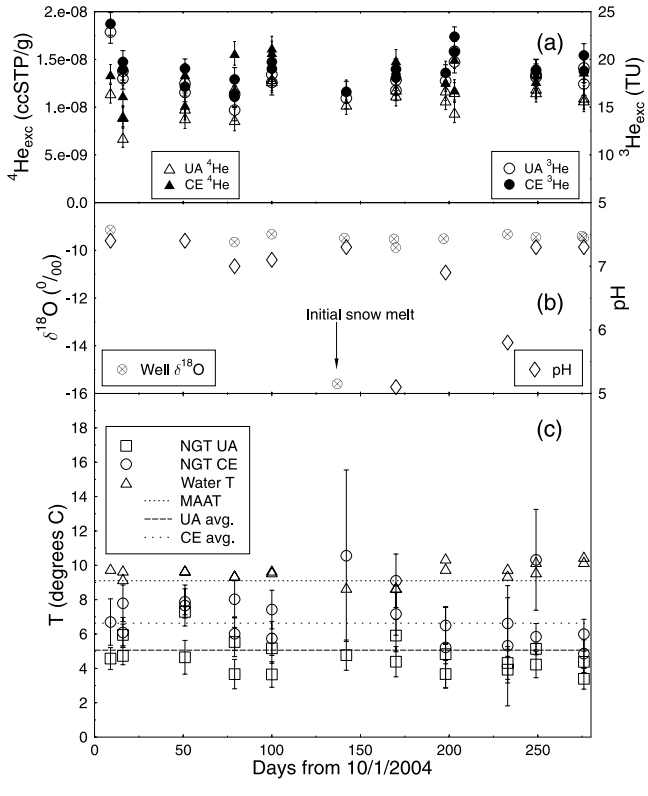

Figure 2. Data plotted as a function of time. (a) $^4He_{excess}$ (triangles, left) and $^3He_{excess}$ (circles, right); (b) $\delta^{18}O$ (cross, left), pH (diamond, right); (c) NGTs and measured water T. All errors ±1σ.

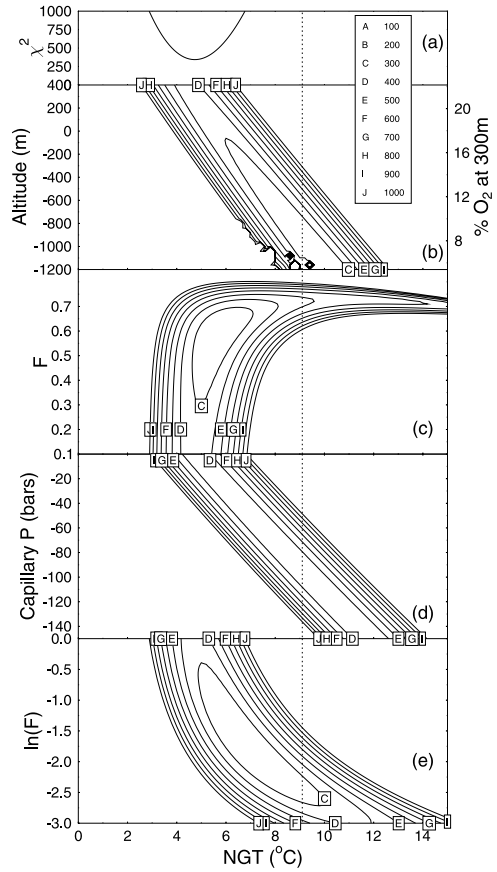

Figure 3. χ^2 for fits to complete noble gas data set using the following models: (a) UA; (b) OD; (c) CE; (d) NP; (e) DIF. Contour interval = 100. Vertical dashed line is MAAT. See text for details.

that if this model is approximately correct, excess air may be routinely over-estimated using standard techniques.

4. Conclusions

[16] The rapid response of pH and $\delta^{18}O$ to the end of winter snow melt indicates that water in this shallow Glacial Drift aquifer is modern, but the presence of large amounts of excess ^3He and ^4He suggests that the gas environment at the water/gas interface can remain out of equilibrium with the atmosphere for years or decades. The standard UA model for NGT underestimates the actual average air and ground temperatures by $\sim$4°C and the CE model is too low by $\sim$2.4°C. He enrichment in ice could supply some excess ^4He, but it cannot explain the significant excess ^3He seen in this aquifer. The latter is likely to have an anthropogenic origin from ^3H decay.

[17] Mechanisms which can reconcile the standard UA model with the MAAT include: partial diffusive loss of excess air (DIF model); an increase in noble gas solubility due to a drop in relative humidity in the unsaturated zone (NP model); and/or an increase in noble gas partial pressure at the gas/water interface above that expected for the aquifer's altitude, due to reduction of O_2 without an equivalent increase in CO_2 (OD model). At present, there is no unique solution and further studies are needed to clarify the mechanisms at the origin of the observed offset between NGTs and MAAT.

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