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Noble gas thermometry and hydrologic ages: Evidence for late Holocene warming in Southwest Texas

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[1] Paleoclimatic reconstruction using noble gas concentrations in the Carrizo aquifer of southwest Texas and water ages determined through simulation of groundwater age reveals abrupt late Holocene temperature increases previously unidentified through ^{14}C dating. Of particular interest is a temperature increase of up to 3.4°C in the first half of the last millennium following a cold period between ~3.7 and 0.9 Kyrs BP. Wet, cool periods in the region are associated with El-Nino dominated conditions, while warm, arid events are linked to multi-decade La-Nina dominant events. The data shows a slow decrease in temperature between ~1,200 and 200 Kyrs BP, a decrease that accelerated in the late Pleistocene and early Holocene. This decrease was followed by warming in the last millennium, that seems to be continuing today. *INDEX TERMS:* 1620 Global Change: Climate dynamics (3309); 1833 Hydrology: Hydroclimatology; 1829 Hydrology: Groundwater hydrology; 1899 Hydrology: General or miscellaneous. **Citation:** Castro, M. C., and P. Goblet, Noble gas thermometry and hydrologic ages: Evidence for late Holocene warming in Southwest Texas, *Geophys. Res. Lett.*, *30*(24), 2251, doi:10.1029/2003GL018875, 2003.

1. Introduction

[2] Paleoclimatic reconstruction through the use of noble gases dissolved in groundwater has been the object of numerous studies in recent years [e.g., *Stute et al.*, 1992; *Weyhenmeyer et al.*, 2000]. Unlike many other continental proxies noble gas temperatures (NGTs) are a direct measure of the temperature at which groundwater equilibrated with the atmosphere during infiltration [e.g., *Stute and Schlosser*, 1993].

[3] In recent years, new methods for accurately determining noble gas temperatures have been developed [*Porcelli et al.*, 2002]. Paleoclimatic reconstruction through noble gas thermometry, however, is not only an issue of accurate temperature determination but is also one of accurate water age estimation, so that correct correspondence between NGTs and groundwater age can be established. Correspondence between NGTs and groundwater age has been typically done using ^{14}C groundwater ages. However, accurate groundwater age estimation through ^{14}C remains problematic, particularly due to losses or additions of ^{14}C through dispersion and diffusion [*Phillips and Castro*, 2003]. In addition, because ^{14}C ages are inherently limited to the past 30–40 Kyrs, alternative methods for groundwater age estimation are desirable.

[4] The concept of groundwater age has been recently reexamined by hydrogeologists in order to derive model ages that can be compared to real measurements [*Goode*, 1996; *Phillips and Castro*, 2003]. Groundwater ages are typically estimated taking into account only advection. However, the movement of water in porous media is, like any other tracer, also affected by kinematic dispersion and molecular diffusion, which leads to mixing of water molecules with different ages. More accurate groundwater ages should be obtained by considering transport by advection, dispersion, and diffusion.

[5] We have therefore undertaken the formulation of hydrologic models that yield significantly better constraints on groundwater ages in the Carrizo aquifer of south Texas, where noble gas temperatures have already been determined [*Stute et al.*, 1992; *Castro et al.*, 2000]. The combination of these new water ages and reported NGTs reveal new aspects of mid to late Holocene climate change in southwestern Texas.

2. Regional Setting

[6] The Eocene Carrizo aquifer is a major groundwater flow system exposed on the northwestern margin of the Gulf Coast Basin, in South Texas (Figure 1a). In Atascosa, McMullen and portions of surrounding Counties (Figure 1b), the Carrizo aquifer lies unconformably on the Lower-Wilcox Formation, a confining layer composed of mudstones and clay [*Hamlin*, 1988; Figure 1c]. The confining Recklaw Formation, conformably overlies the Carrizo aquifer and is in turn overlain by the Queen City aquifer. These formations outcrop subparallel to the present-day coastline at an average altitude of ~200 m, and follow a southwest-northeast wide band across Texas, dipping to the southeast (Figures 1a and 1c). The Carrizo aquifer terminates at a major growth-fault system, the Wilcox Geothermal Corridor (Figures 1a and 1b). Groundwater flows gravitationally toward the southeast and discharge occurs by cross-formational upward leakage along the entire formation.

3. Simulation of Groundwater Age

[7] In order to simulate groundwater ages we used a finite element flow model (Figure 1c) in the Carrizo aquifer and surrounding formations that has been validated by ^{4}He [*Castro and Goblet*, 2003] and ^{3}He. Dispersion and diffu-

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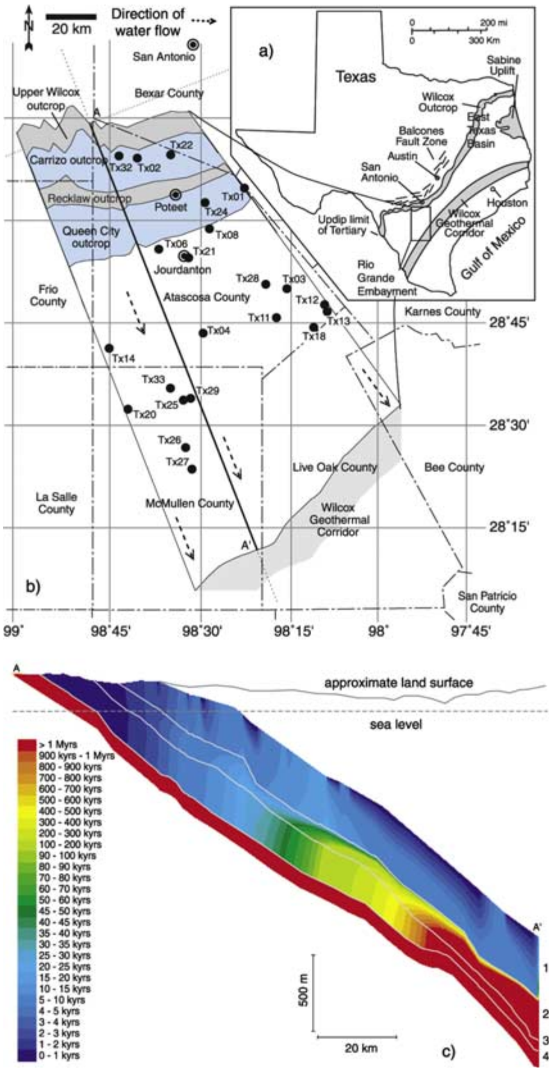

Figure 1. Study area and outcrops in southwestern Texas. (a) Geographical and tectonic setting [after *Hamlin*, 1988]. (b) Detailed setting of the area with location of cross-section A–A′ along which hydrologic simulations of groundwater age were carried out; sample locations for NGTs as closed circles. (c) Distribution of groundwater ages in the Carrizo aquifer and surrounding formations. Water ages in the Carrizo and Recklaw formations are clearly influenced by down dip change in lithology, which leads to a large decrease in water velocity. (1) Queen City aquifer; (2) Recklaw formation; (3) Carrizo aquifer; (4) undifferentiated lower part of the Upper-Wilcox and Lower-Wilcox formations.

sion (cf. Table 1) between the Carrizo and neighboring formations were also taken into account.

[8] To account for groundwater mixing we treat water age as one would treat a solute concentration; water age (in seconds) is simulated by considering the product of water mass (ρV) and age (τ) [cf. *Goode*, 1996], where ρ is the water density (Kg m^{-3}) and V is the water volume (m^3). This quantity, referred to as "age mass" (Kg s) is conserved and is equivalent to moles of a solute tracer. Groundwater age simulations were carried out in steady-state. Boundary conditions included zero-age mass flux across all no flow and inflow boundaries of the domain (A–A′; Figures 1b and 1c) and no age-mass dispersive flux across outflow boundaries. Water ages for all samples with available NGTs were calculated considering their exact distance from the beginning of the recharge area along the direction of water flow (Figure 1b), their depth, and the regional distribution of water ages (Figure 1c).

[9] This newly calculated ages allow for a more accurate paleoclimatic reconstruction in south Texas as they incorporate not only hydrodynamic characteristics that reflect heterogeneities of the media [cf., *Castro and Goblet*, 2003], but also mixing processes of the water molecule [e.g., *Goode*, 1996]. In addition to diffusion processes, mixing with older groundwater also contributes to artificially old ^{14}C estimated groundwater ages. When mixing with older groundwater occurs, i.e., when model groundwater ages are older than advective ages [cf., *Castro and Goblet*, 2003], ^{14}C ages become older by up to many thousand of years. Because of such processes, mid to late Holocene Carrizo waters have been interpreted by *Stute et al.* [1992], and *Castro et al.* [2000] as having Pleistocene ages, and late Wisconsian waters (TX28, TX03) were thought to be much older due to ^{14}C levels below detection limits.

4. Results and Discussion

[10] Carrizo and Recklaw Formation groundwater ages increase exponentially with distance from the recharge area (Figure 1c), a change that reflects exponential decrease of groundwater velocity due to a downdip facies change. Dispersion and diffusion leading to groundwater mixing become more important with increasing flow distance and decreasing hydraulic conductivity. In the Carrizo aquifer, groundwater ages vary from modern (dark blue) to ~8 Myrs (red) in the discharge area.

[11] Simulation of groundwater age indicates that NGT samples (Figure 1b) range in age from modern to ~1,200 Kyrs BP, with a concentration of late Pleistocene ages between ~22 and ~55 Kyrs BP (Figure 2). Samples with modern ages are located in the recharge area and yield an average NGT of 20.3°C. Analytical uncertainty for all NGTs is ±0.5°C (1σ error). Their ages are 8 (TX02), 7 (TX22) and 6 yrs BP (TX32), which translates approximately the average annual temperature of rainfall for the years 1984 to 1986 taking into account the year of sample collection, 1992. Average annual temperatures between 1980 and 1985 for San Antonio, ~15 Km away from the recharge area, is 20.3°C, which is in agreement with our findings. Average annual temperature for the 80s and 90s in San Antonio was 20.6°C and 21°C, respectively. The latter is our reference to modern temperature.

Table 1. Diffusion and Dispersivity Parameters Used in Groundwater Age Calculations

Parameter	Value
Diffusion coefficient for $H^1H^3O^{16}$ at 45°C[a]	$3.83*10^{-9}$ m^2s^{-1}
Tortuosity coefficient	
Carrizo and Queen City aquifers	0.1
Recklaw Formation	0.05
Dispersivity coefficients	
Longitudinal	125 m
Transversal	12.5 m

[a] [*Wang et al.*, 1953].

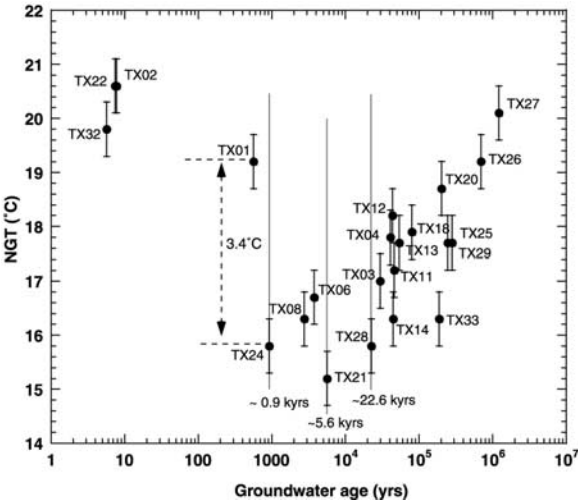

Figure 2. Noble gas temperatures in the Carrizo aquifer versus water age (logarithmic scale). Analytical uncertainty of NGTs is ±0.5°C (1σ error).

[12] Two Holocene periods, at 0.9 Kyrs BP (TX24), and 5.6 Kyrs BP (TX21) are identified when atmospheric temperature was $\geq$5°C cooler than at present (Figure 2). Temperature at ~0.9 Kyrs BP (TX24) was ~3.4°C cooler than that at 0.6 Kyrs BP (TX01; 19.2°C) which approaches mean modern temperature.

[13] More important than individual paleoclimate episodes is the general slow cooling trend between ~1,200 Kyrs (TX27) and ~200 Kyrs BP (TX25), a cooling that accelerates during the late Pleistocene and early Holocene. This cooling trend then changes to an extremely rapid increase in temperature in the late Holocene, at around 0.9 Kyrs BP (Figure 3). Such abrupt warming seems to continue at present. This temperature increase is the most striking feature arising from this new paleoclimatic reconstruction.

[14] Diverse paleoclimatic records show evidence that Holocene climate in southwestern United States has undergone a series of abrupt climate shifts between dry and warm intervals and wet and cool, periglacial intervals. The first perigacial event here dated at 5.6 Kyrs BP follows an earlier Holocene characterized by extreme aridity and megadroughts [*Forman et al.*, 2001]. The age of this cool, wet period is consistent with data from Lubbock Lake in Texas, where wet conditions and landscape stability prevailed between two episodes of eolian sedimentation, the first from 7 to >5 Kyrs BP, and the second, from 5.5 to 4.5 Kyrs [*Forman et al.*, 2001]. This cold period is also consistent with a neoglacial event recorded in the Southern Great Plains of New Mexico during the same period [*Armour et al.*, 2002].

[15] These new water ages also indicate a general cooling trend from 3.7 Kyrs BP (TX06; 16.7°C) to 0.9 Kyrs BP (15.8°C) as previously indicated. Recent studies of mites preserved in stalagmites in southern New Mexico by *Polyak et al.* [2001] also indicate a wet and cool climate that started at least 3171 ± 48 years ago and ceased by 819 ± 82 yr ago. The presence of subgenus Epidamaeus in these stalagmites, typical of Alaskan and Canadian artic, is further evidence for the presence of cold climate during the late Holocene. Periglacial moraine advances also occurred during this same period in northern New Mexico [*Armour et al.*, 2002]. Records from multiple rivers in the southwestern United States and particularly in Texas [*Blum and Valastro*, 1989; *Ely et al.*, 1993] further indicate wet climates and frequent large floods prior to 1 Kyrs BP.

[16] An abrupt transition to a late Holocene dry and warm climate at ~1 Kyrs BP is well document by channel incision and flood plain abandonment of rivers in Texas and Oklahoma [*Hall*, 1990] as well as along the Pedernales river [*Blum and Valastro*, 1989], ~150 Km north of San Antonio. Pollen and plant macrofossil data from the Edwards Plateau, Texas [*Toomey et al.*, 1993] also indicate a dominance of a drought-prone climate over the past 1000 years. Evidence for dune field reactivation in the area in the last millennium is clear. In Lubbock Lake, Texas, two megadroughts have been recorded in the last 1,000 yrs, the latest potentially after 0.6 Kyrs BP [*Forman et al.*, 2001]. These findings are consistent with an abrupt increase in temperature of 3.4°C observed between ~0.9 and 0.6 Kyrs BP, a temperature increase that seems to continue at present.

[17] The alternation of wet/cool and dry/warm intervals during the Holocene in the southwestern United States has been attributed to ENSO oscillations [*Ely et al.*, 1993; *Forman et al.*, 2001]. Specifically, dry conditions and winter warmer temperatures in the area are linked to cooler Pacific sea-surface temperatures [*Cayan and Webb*, 1992]. La Nina conditions would weaken the low level jet, a critical circulation element that funnels surface moisture northward from the Gulf of Mexico. Evidence for multidecade dominance of La Nina conditions between 10 and 6 Kyrs BP in Peru has been presented [*Foutugne et al.*, 1999], which further supports this idea.

[18] By contrast, El Nino conditions lead to increased cool-season precipitation and increased flood frequency in the region due to low pressure activity. Cool-season large floods such as those resulting from winter North Pacific frontal storms are associated with multi-year dominated El Nino conditions [*Cayan and Webb*, 1992; *Ely et al.*, 1993]. Paleoflood analogy from 19 rivers in Arizona and Utah [*Ely et al.*, 1993] further reveal that the largest floods coincide with periods of cool, moist climate and frequent El

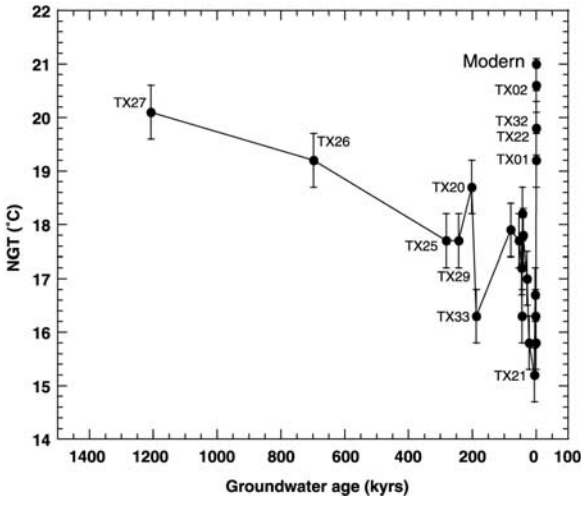

Figure 3. Noble gas temperatures in the Carrizo aquifer versus water age (linear scale). Analytical uncertainty of NGTs is ±0.5°C (1σ error).

Nino events during most of the Holocene. Our new paleoclimatic reconstruction in Texas supports this concept, in particular, for the late Holocene where cold temperatures were in place between ~3.7 and 0.9 Kyrs BP simultaneously to the well documented occurrence of large frequent floods in the area [e.g., *Blum and Valastro*, 1989].

[19] We interpret a third cooler period in Carrizo groundwaters at 22.6 Kyrs BP (TX28) as a signature of the early stages of the Last Glacial Maximum (LGM). Surprisingly, the degree of cooling during this period, ~5.2°C as compared to the present, is of similar magnitude to the other two more recent time intervals. It is possible that the temperature obtained from TX28 is not fully representative of the LGM maximum cooling. Indeed, additional NGTs and groundwater ages that span the interval when land-based ice volume was at its maximum [~19 to 22 Kyrs BP; *Yokoyama et al.*, 2000] will be needed to assess the extent of the cooling during this period.

[20] Before ~22.6 Kyrs the NGT record follows a previously identified "plateau" [*Stute et al.*, 1992] with temperatures intermediate between those of the present time and those of the early LGM, with an average of 17.4°C (samples TX03, TX04, TX11, TX12, TX13, and TX14). The remaining samples are much older as the Carrizo groundwater slows dramatically away from the recharge area, indicating an intermediate temperature of 17.9°C at ~80 Kyrs BP (TX18), slightly warmer conditions (18.7°C) at ~200 Kyrs BP (TX20), slight cooler conditions (17.7°C) at ~244 and ~282 Kyrs BP (TX25, TX29) and significantly warmer conditions (19.2°C) at ~700 Kyrs (TX26). The oldest sample (TX27), with a age of 1,200 Kyrs BP reveals atmospheric conditions very similar to the present ones, with a temperature of 20.1°C.

5. Conclusions

[21] Incorporation of the effects of dispersion and diffusion into the calculation of groundwater ages affords greater confidence in the reconstruction of paleotemperatures through noble gases dissolved in groundwater. The recognition of dispersion and diffusion of the water molecule itself may also place questions on how such mixing processes will affect the estimation of noble gas temperatures. This aspect of paleoclimatologic research will require further analysis in the future. Perhaps of greater importance than estimating absolute noble gas temperatures, is assessing the nature of differences between observed temperatures among different samples. If mixing processes were to significantly affect calculated NGTs, they would likely affect different samples in a similar manner, while having a minimal effect on the magnitudes of differences between different samples.

[22] Although we cannot be fully confident that hydrologic determinations of groundwater ages translate exactly the distribution of groundwater ages across this regional groundwater flow system, the complexities of such aquifer systems that are specifically addressed by this new approach surely results in more realistic paleoclimatic reconstruction in the area.

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References

Armour, J., P. J. Fawcett, and J. W. Geissman, 15 k. y. paleoclimatic and glacial record from northern New Mexico, *Geolog. Soc. of Am.*, *30*(8), 723–726, 2002.

Blum, M. D., and S. Valastro Jr., Response of the Pedernales River of central Texas to Late Holocene climatic change, *Annals of the Assoc. of Am. Geographers*, *79*(3), 435–456, 1989.

Castro, M. C., M. Stute, and P. Schlosser, Comparison of ^{4}He and ^{14}C ages in simple aquifer systems: Implications for groundwater flow and chronologies, *Appl. Geochem.*, *15*, 1137–1167, 2000.

Castro, M. C., and P. Goblet, Calibration of regional groundwater flow models—working toward a better understanding of site-specific systems, *Water Resour. Res.*, *39*(6), 1172, doi:10.1029/2002WR001653, 2003.

Cayan, D. R., and R. Webb, El Nino/Southern Oscillation and streamflow in the western United States, in El Nino, Historical and Paleoclimatic aspects of the Southern Oscillation, edited by H. F. Diaz and V. Markgraf, 20–68, 1992.

Ely, L. L., Y. Enzel, V. R. Baker, and D. R. Cayan, A 5,000-Year record of extreme floods and climate change in the Southwestern United States, *Science*, *262*, 410–412, 1993.

Forman, S. L., R. Oglesby, and R. S. Webb, Temporal and spatial patterns of Holocene dune activity on the Great Plains of North America: Megadroughts and climate links, *Global and Planetary Change*, *20*, 1–29, 2001.

Foutugne, M., P. Usselmann, D. Lavallee, M. Julien, and C. Hatte, El Nino variability in the coastal desert of southern Peru during the mid-Holocene, *Quaternary Research*, *52*, 171–179, 1999.

Goode, D. J., Direct simulation of groundwater age, *Water Resour. Res.*, *32*(2), 289–296, 1996.

Hall, S. A., Channel trenching and climatic-change in the southern United States Great Plains, *Geology*, *18*(4), 342–345, 1990.

Hamlin, H. S., Depositional and groundwater flow systems of the Carrizo-Upper Wilcox, South Texas, Bureau of Economic Geology, Report of Investigations, *175*, 61 pp, 1988.

Phillips, F. M., and M. C. Castro, Ground Water Dating and Residence Time Measurements, pp. 451–497, in *Surface and Groundwater, Weathering, and Soils*, edited by J. I. Drever, Vol. 5, *Treatise on Geochemistry*, edited by H. D. Holland and K. K. Turekian, Elsevier, Oxford, 2003.

Polyak, V. J., J. C. Cokendolpher, R. A. Norton, and Y. Asmeron, Wetter and cooler late Holocene climate in the southwestern United States from mites preserved in stalagmites, *Geolog. Soc. of Am.*, *29*(7), 643–646, 2001.

Porcelli, D., C. J. Ballentine, and R. Wieler, An overview of noble gas - Geochemistry and cosmochemistry, in "*Noble Gases in Geochemistry and Cosmochemistry, Reviews in Mineralogy and Geochemistry*", *47*, 1–19, 2002.

Stute, M., and P. Schlosser, Principles and Applications of the Noble Gas Paleothermometer, AGU Monograph on "Climate Change in Continental Isotopic Records", *Geophys. Monograph*, *78*, 89–100, 1993.

Stute, M., P. Schlosser, J. F. Clark, and W. S. Broecker, Paleotemperatures in the southwestern United States derived from noble gas measurements in groundwater, *Science*, *256*, 1000–1003, 1992.

Toomey, R. S., III, M. D. Blum, and S. Valastro Jr., Late Quaternary climates and environments of the Edwards Plateau, Texas, *Global and Planetary Change*, *7*(4), 299–320, 1993.

Yokoyama, Y., K. Lambeck, P. Deckker, P. Johnston, and L. K. Fifields, Time of the Last Glacial Maximum from Observed Sea-Level minima, *Nature*, *406*, doi:10.1038/35021035, 2000.

Wang, J. H., C. V. Robinson, and I. S. Edelman, Self-Diffusion and structure of Liquid water. III. Measurement of self-diffusion of Liquid water with H^2, H^3 and O^{18} as Tracers, *J. Am. Soc.*, *75*, 466–470, 1953.

Weyhenmeyer, C. E., S. J. Burns, H. N. Waber, W. Aeschbach-Hertig, R. Kipfer, H. H. Loosli, and A. Matter, Cool glacial temperatures and changes in moisture source recorded in Oman groundwaters, *Science*, *287*, 5454, 842–845, 2000.

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