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A late Pleistocene–Mid-Holocene noble gas and stable isotope climate and subglacial record in southern Michigan

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[1] Stable isotopes (δD, δ^{18}O) and ^{14}C derived ages in the Saginaw aquifer in southern Michigan suggest subglacial meltwater contributions from the Laurentide Ice Sheet of up to 36% in the late Pleistocene, following the Last Glacial Maximum. Contributions of up to 74% from previous glaciation periods are observed. Together with the Marshall record [*Ma et al.*, 2004], noble gas temperatures (NGTs) and excess air (EA) from the Saginaw aquifer capture, for the first time, the onset of the Younger Dryas ($\sim$12.9 kyr BP) with a $\sim$3.3°C cooling accompanied by drier conditions. Mid-Holocene (MH) climatic shifts are also identified, with warming ($\sim$2.9°C), increased aridity starting at $\sim$5.4 kyr BP followed by reversal to cooler, humid conditions at $\sim$4.1 kyr BP. Except for the last MH reversal, the stable isotope record mimics the NGT and EA records. Contrasting trends displayed by δ^{18}O and deuterium-excess in the last MH reversal suggests enhanced vapor transport from the Gulf of Mexico. **Citation:** Castro, M. C., R. B. Warrier, C. M. Hall, and K. C. Lohmann (2012), A late Pleistocene–Mid-Holocene noble gas and stable isotope climate and subglacial record in southern Michigan, *Geophys. Res. Lett.*, *39*, L19709, doi:10.1029/2012GL053098.

1. Introduction

[2] The noble gas temperature (NGT) proxy is regarded as a robust indicator of past climate [*Kipfer et al.*, 2002; *Sun et al.*, 2010]. Unlike other continental proxies, it provides a direct measure of the ground air temperature at the water table [*Mazor*, 1972]. This is because the solubility of atmospheric noble gases (Ne, Ar, Kr, Xe) in groundwater is dependent on the ground air temperature, the mean local atmospheric pressure (altitude of the recharge area) and excess air (EA). The latter is incorporated in groundwater through dissolution of air bubbles due to water table fluctuations [*Heaton and Vogel*, 1981]. High EA values have been linked to significant fluctuations in water table levels due to discrete episodes of intense rainfall typical of arid climates while low EA values have been linked to humid climatic regimes (warm or cool) with shallow water table levels and continuous recharge [*Castro et al.*, 2007; *Hall et al.*, 2012; see also *Aeschbach-Hertig et al.*, 2002]. Similarly, δ^{18}O is expected to reflect the mean annual air temperature (MAAT) in mid-latitude regions, while the deuterium-excess (d-excess) parameter is indicative of non-equilibrium processes [*Dansgaard*, 1964]. In particular, the high relative humidity of air masses overlying oceans [*Merlivat and Jouzel*, 1979] and high evaporation during precipitation typical of drier conditions [*Dansgaard*, 1964] lead to lower d-excess values. Temperature and humid versus arid climatic regimes derived from NGTs and EA can thus be independently compared with corresponding δ^{18}O and d-excess trends, respectively, to achieve an in-depth understanding of abrupt climatic events.

[3] NGTs have been commonly used to identify major contrasting trends between Pleistocene and present time, and the Last Glacial Maximum (LGM) in particular [*Kipfer et al.*, 2002]. Their use to identify abrupt climate shifts, however, remains rare [*Ma et al.*, 2004; *Castro et al.*, 2007]. These are critical to understand current climate patterns, and to provide additional constraints to general circulation models. The NGT study by *Ma et al.* [2004] carried out in the Marshall aquifer in southern Michigan, a region covered by the Laurentide Ice Sheet (LIS) during the LGM and early deglaciation periods, first identified the Bølling-Allerød (BOA) warming event through NGTs.

[4] Here, we present a new $\sim$13.1 kyr paleoclimatic reconstruction based on the NGT, EA and stable isotope record derived from the overlying Saginaw aquifer in southern Michigan. Together with the original *Ma et al.* [2004] Marshall aquifer record, new aspects of late Pleistocene and Mid-Holocene climate shifts in southern Michigan are revealed. Based on groundwater ages and the entire stable isotope Saginaw record, which goes beyond the LGM, new constraints on the timing and sources of subglacial meltwater contributions to this system are also provided.

2. Regional Setting

[5] The Saginaw aquifer, a major groundwater flow system composed mostly of sandstones, is located in the central portion of the Michigan Basin, in the Lower Peninsula of Michigan (Figure 1). It is underlain by the Bayport-Michigan confining units, which, in turn, overlies the Marshall aquifer [*Mandle and Westjohn*, 1989]. These formations subcrop at an altitude of $\sim$275–300 m and are overlain by the unconfined Glacial Drift aquifer. In the Saginaw aquifer, groundwater flows gravitationally from the south and north to the NE and SE, respectively, into the Saginaw lowlands (SL) region and Lake Huron, where it discharges (Figure 1). In the Marshall aquifer in southern Michigan, groundwater flows gravitationally to the NW and NE, and discharges into Lake Michigan and Lake Huron (SL area), respectively.

3. Sample Collection and Measurements

[6] Groundwater samples were collected from 16 wells in the Saginaw aquifer along a main groundwater flow path,

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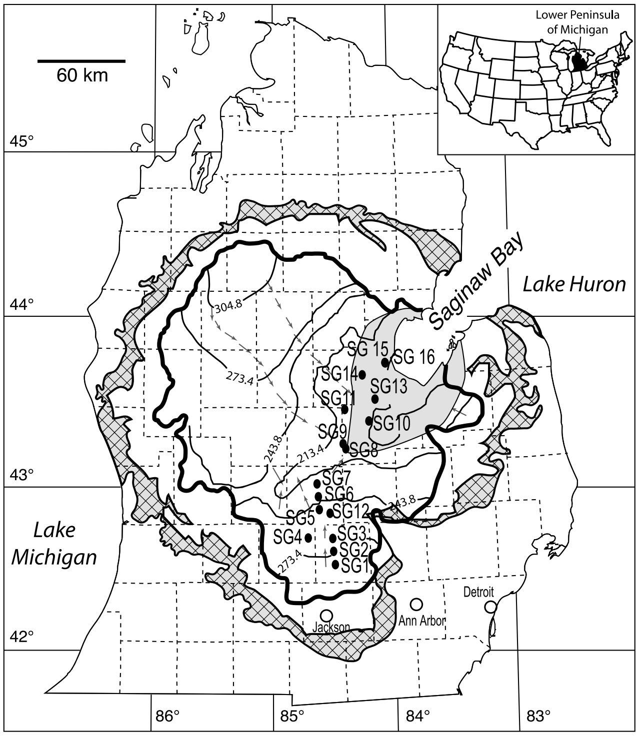

Figure 1. Detailed study area and location of Saginaw aquifer samples in southern Michigan [adapted from *Mandle and Westjohn*, 1989]. Bold contour represents the Saginaw subcrop, gray contour with grid represents the Marshall subcrop. Equipotential line (contour lines) values are shown in meters together with main groundwater flow directions (arrows). Gray area corresponds to the Saginaw lowlands.

from the recharge area in southern Michigan, toward the Saginaw Bay area, in Lake Huron (Figure 1). Samples were analyzed for noble gases (Ne, Ar, Kr and Xe), stable (δD, δ^{18}O) and carbon (δ^{13}C and ^{14}C activity) isotopes as well as major elements (Tables S1–S3 in the auxiliary material).[1] Noble gas concentrations, stable isotope ratios and major elements were measured at the University of Michigan following analytical procedures described in *Hall et al.* [2012]. NGTs and EA were calculated from measured noble gas concentrations using the unfractionated air (UA) model [*Kipfer et al.*, 2002] (Text S1 and Table S4).

[7] Groundwater ages for all samples are calculated from ^{14}C activities measured at the AMS facility at Woods Hole Oceanographic Institution. Model corrected ^{14}C ages for all Saginaw (this study) and Marshall [*Ma et al.*, 2004] samples were subsequently converted into calibrated calendar ages (Text S2 and Table S2). Calibrated calendar ages are referred to hereafter simply as ages.

4. Groundwater Ages and Stable Isotope Record: Timing and Source of Subglacial Meltwater Contributions

[8] Saginaw groundwater samples range in age from modern to >50 kyr BP and yield a large range of δD and δ^{18}O values varying between -124.03‰ and -59.17‰, and -17.48‰ and -8.49‰, respectively (Figure 2 and Table S2). It is apparent that δD and δ^{18}O from the Saginaw (this study), the Marshall [*Ma et al.*, 2004] and the Glacial Drift [*Hall et al.*, 2012] aquifers fall close to the Global Meteoric Water Line [*Craig*, 1961] as well as the local meteoric water line in Simcoe, Ontario, Canada (Figure 2), suggesting that δD and δ^{18}O were not significantly modified by water-rock interactions within these aquifers. Samples from all three aquifers fall between mean values for modern rainwater (δD = -26.48‰, δ^{18}O = -4.81‰) and snow (δD = -157.61‰, δ^{18}O = -21.31‰) in southern Michigan (Figure 2). In particular, all Glacial Drift, Marshall and Saginaw samples that range in age from modern to younger than the LGM (∼0–∼18 kyr B.P) display δD and δ^{18}O values closer to values for modern rain (Figure 2). By contrast, with the exception of sample sg13, all Saginaw samples located in the SL region (Figure 1) display ages beyond the LGM and yield extremely depleted δD (<-89.86‰) and δ^{18}O (<-12.83‰) values, similar to values for modern groundwater resulting directly from snowmelt and closer to snow values (Figure 2). The percentage contribution of modern snow to total recharge for all Saginaw samples was calculated assuming that groundwater recharge is simply a binary mixture between mean modern rain and snow (Figure 2 and Table S5). Because the stable isotopic

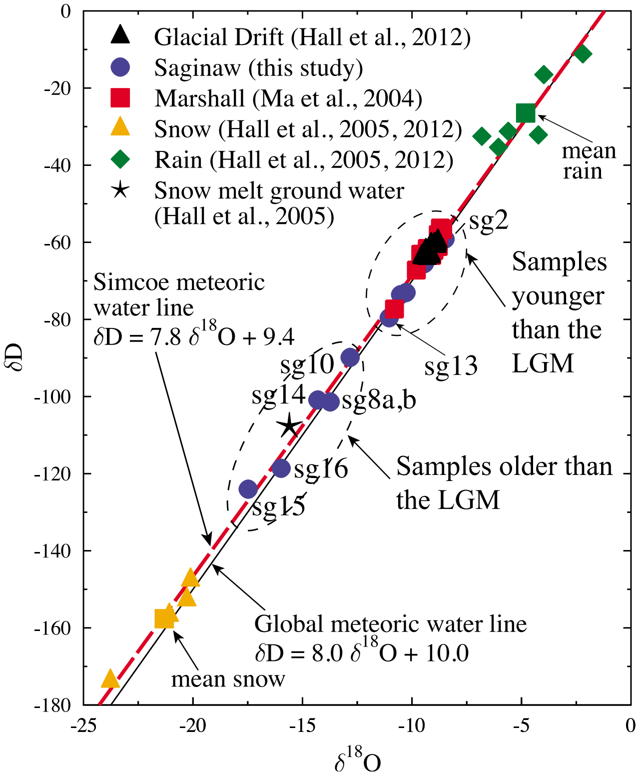

Figure 2. Plot of δD vs. δ^{18}O for all Saginaw (blue circles), Marshall (red squares) and Glacial Drift (black triangles) aquifer samples. Also shown are stable isotope ratios for modern rainfall (green diamonds), snow (yellow triangles) and groundwater from snow meltwater (black star) in southern Michigan. The Global Meteoric Water line as well as the local Simcoe meteoric water line (http://isohis.iaea.org) are also shown.

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[1] Auxiliary materials are available in the HTML. doi:10.1029/2012GL053098.

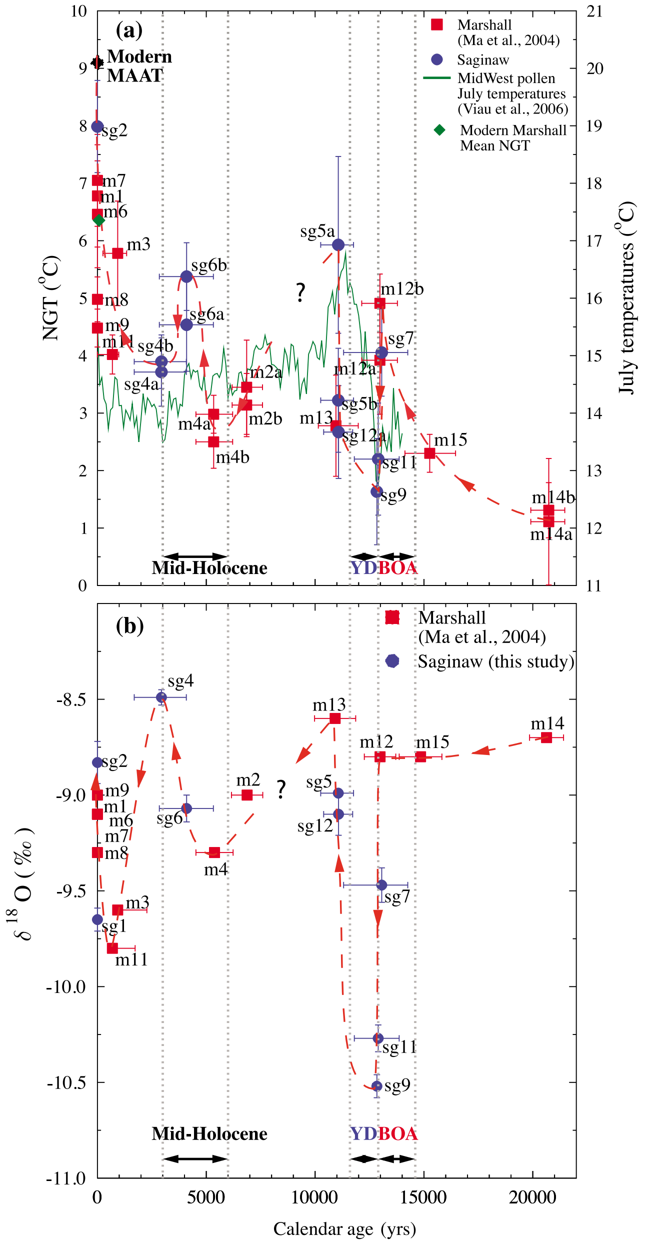

Figure 3. Comparison of (a) NGTs and (b) δ^{18}O as a function of groundwater ages for the Saginaw and Marshall aquifers. July high-resolution temperature reconstruction (Y right axis) from pollen in the Midwest [*Viau et al.*, 2006; World Data Center for Paleoclimatology, http://www.ncdc.noaa.gov/paleo/recons.html] is also shown. We are only able to compare temperature differences for both the pollen and NGT records rather than absolute temperatures. The temperature differences recorded by both methods are comparable for both the YD and MH climate variations. MAAT is also indicated together with time periods corresponding to the BOA, YD and MH climatic events. Also shown is a schematic line (red dashed line), similar to the moving average, for visualization of climatic trends.

composition in the past has changed, these values should be taken as a first order indication. Snowmelt contribution for modern Saginaw samples (sg1, sg2) varies between 26% and 29%, a value similar to that of modern Glacial Drift samples (Table S5). This is expected as the Saginaw aquifer is recharged through the Glacial Drift aquifer. As samples get older (≤∼13 kyr BP), the percentage of snowmelt contribution increases up to 36%. Such an increase might be due to: a) a climate cooler than present at that time as also shown by our NGT record (below) where the presence of a thicker and longer winter snow cover was likely in place; or b) contribution of LIS subglacial meltwater as the deglaciation proceeded [see, e.g., *Ma et al.*, 2004] and as also previously suggested [e.g., *Hoaglund et al.*, 2004; *McIntosh et al.*, 2011]. In contrast, except for sample sg13, snow contributions for samples in the SL area (sg8, sg10, sg14, sg15, sg16), all of which display ages beyond the LGM (∼26.6 kyr–>50 kyr), are much greater (48% to 74%) than observed for modern groundwater recharge. Unlike younger samples, however, late Pleistocene (following the LGM) LIS subglacial meltwater contribution to the Saginaw aquifer in the SL area is not supported by our newly estimated groundwater ages, as previously suggested by *Hoaglund et al.* [2004]. Indeed, our ^{14}C measurements and subsequently derived calendar ages point instead to subglacial meltwater contributions from previous glacial ice advances or deglaciation periods. Alternatively, it is also possible that ^{14}C activity has been reduced due to mixing with older groundwaters from the Marshall aquifer or the Bayport-Michigan confining unit [see, e.g., *Ma et al.*, 2005]. Indeed, as shown by *Castro and Goblet* [2005], mixing with older groundwaters can lead to apparently older ^{14}C ages. At present it is not possible to ascertain whether or not ^{14}C ages in this area are providing entirely accurate information. In addition to extremely depleted δD and δ^{18}O values, most of these samples with ages beyond the LGM display also unusually high (∼80%–120%) atmospheric noble gas excesses (Table S1) which result in poor NGT fits using existing NGT models (Text S1). Mechanisms leading to unusually large atmospheric noble gas excesses for these samples are discussed in detail elsewhere (R. B. Warrier et al., Evidence for a thermal event in the Michigan Basin through near-surface atmospheric noble gas signatures in the Saginaw Bay discharge area, submitted to *Earth and Planetary Science Letters*, 2012). While a number of these older samples in the SL area present poor model fits and thus poorly constrained NGT estimates, most Saginaw samples with ages <LGM display robust NGT fits and are thus suited for a paleoclimatic reconstruction (Text S1). These are the results discussed below. The focus is thus on climatic events during the late Pleistocene, Mid-Holocene (MH) and present time.

5. NGTs, Excess Air, δ^{18}O and d-excess: Younger Dryas and Mid-Holocene Climatic Oscillations Record

[9] Saginaw samples younger than the LGM range in age from modern to ∼13.1 kyr and yield NGTs varying between 8.0 ± 0.8°C and 1.6 ± 0.9°C (Figure 3a and Tables S2 and S4). Our modern Saginaw sample (sg2) displays the highest NGT of the entire set of samples (8.0 ± 0.8°C) pointing to an overall warming trend in southern Michigan since the late Pleistocene, and, more broadly, since the LGM (Figure 3a). While our modern Saginaw sample displays a NGT value close to the MAAT of 9.1 ± 0.8°C of southern Michigan (Figure 3a), the mean of modern samples from the Marshall (m1, 6, 7, 8, 9) of 6.3 ± 0.8°C (Figure 3a) [*Ma et al.*, 2004] displays a strong bias to low NGTs. However, as pointed out

by *Ma et al.* [2004], some of these "modern" samples could possibly be hundreds of years old and representative of a cooler period instead. Other Marshall modern samples are likely recording specific recharge conditions at the time they were sampled rather than true soil temperature. Indeed, field observations and noble gas measurements strongly suggest that at least part of this bias is due to net depletion of O_2 in the soil air due to biological processes without corresponding build-up of CO_2, leading to higher noble gas partial pressures [*Hall et al.*, 2005; *Sun et al.*, 2008]. Our modern Saginaw NGT value shows that soil air noble gases partial pressures are similar to standard air and suggest that recharge conditions for this sample are distinct from those of the Marshall modern samples (Text S1). *Hall et al.* [2012] have shown that large precipitation events such as Hurricane Ike can significantly modify recharge conditions within aquifer systems and bring O_2 depleted soil air back to standard conditions, with simultaneous incorporation of high levels of EA at the water table. Sample sg2's EA value is at a level similar to that measured in the Glacial Drift aquifer following Hurricane Ike suggesting the occurrence of a major storm event prior to recharge. In contrast, modern Marshall samples are compatible with conditions prior to Hurricane Ike [*Hall et al.*, 2012]. It is thus possible that modern NGTs are reflecting mostly recharge conditions rather than the MAAT. The study of *Hall et al.* [2012] suggests, however, that the NGT temperature proxy should be viewed as an average of recharge conditions over several years. It is possible that once averaged over several years, such bias might vanish. However, in the event that such a bias to low NGTs in the Marshall recharge area would apply to all the Marshall NGT record, all the main conclusions of this study (below) would still apply (cf. Text S1).

[10] Particularly relevant aspects of our combined Saginaw and Marshall NGT paleoclimatic reconstruction are the abrupt climatic oscillations recorded both in the late Pleistocene and Mid-Holocene within the overall warming trend observed since the LGM (Figure 3a; cf. Text S3). A dispersion analysis of both events indicates that these climatic records should be well preserved in both the Saginaw and Marshall aquifers (Text S4). Rapid climatic oscillations in northeast US began with warming at the onset of the Bølling/Allerød (BOA) event at ~14.6 kyr BP and were followed by a rapid climatic reversal to cooler conditions during the Younger Dryas (YD) at ~12.9 kyr BP [*Shuman et al.*, 2002]. Although *Ma et al.* [2004] were able to identify overall climatic trends associated with the occurrence of the BOA and YD events, the onset and termination of the YD were almost entirely missed. Our new NGT record in the Saginaw aquifer has now allowed us to close this gap by capturing for the first time both the onset and termination of the YD. Indeed, our combined Saginaw and Marshall NGT record identifies statistically distinct rapid climatic variations (Text S3) both at the onset (m12b, sg7, m12a, sg11, sg9) and termination (sg9, sg12a, m13, sg5b, sg5a) of the YD. More specifically, our NGT record points to a cooling of ~3.3 ± 1°C (m12b-sg9, Figure 3a) at the onset of the YD which is comparable with regional cooling estimates of 3–4°C obtained through pollen temperature proxies (Figure 3a) [*Viau et al.*, 2006], macrofossils and fish remains [*Peteet et al.*, 1993] as well as endogenic lake calcite in northeastern USA [*Zhao et al.*, 2010]. Some proxies in Midwest lakes, however, indicate a greater regional cooling (5–5.6°C [*Hou et al.*, 2007; *Yu*, 2007]). It is possible that our slightly lower (~1°C) NGT estimates may partly be due to increased duration of snow cover during the YD. Snow cover has an insulating effect which might lead to an overestimation of NGTs and thus, an underestimation of the MAAT cooling [*Cey*, 2009]. Transition from warm BOA to cool YD NGTs is also corroborated by a sudden decrease in our δ^{18}O record of 1.7‰ (m12-sg9, Figure 3b). Such depletion is also consistent with a δ^{18}O decrease of 1.5‰ observed in carbonates from a lake in Southern Ontario [*Yu*, 2000]. The onset of the YD recorded by both NGTs and δ^{18}O (Figures 3a and 3b) is also accompanied by a distinct increase in EA (m12b-sg9, 11, Figure 4a) and a simultaneous decrease in d-excess (m12-sg9, 11, Figure 4b) of 3.3‰ indicating a transition from a warm, humid (BOA) environment to a cool, arid one (YD). Transition from a warm, humid climate at the peak of BOA to cold, arid conditions during the YD were also previously recorded through vegetation changes [e.g., *Shuman et al.*, 2002] and low lake levels [e.g., *Webb*, 1990] in the Great Lakes region.

[11] Termination of the YD at ~11.6 kyr BP was marked by rapid (~50 yr) warming in eastern North America [*Peteet et al.*, 1993; *Viau et al.*, 2006]. Our combined NGT record displays a general warming trend (sg9, sg12a, m13, sg5b, sg5a; Text S1) within this time period of 4.3 ± 1.8°C (sg9-sg5a, Figure 3a), a value comparable to regional warming estimates from pollen data (~4°C) [*Viau et al.*, 2006] and lake carbonates (5.4–8°C) [*Hou et al.*, 2007]. Our NGT increase is accompanied by a 1.9‰ δ^{18}O increase (Figure 3b), in excellent agreement with a 2‰ increase recorded by *Yu* [2000] in southern Ontario. Termination of the YD is also accompanied by a strong decrease in EA (Figure 4a) as well as an increase in d-excess of ~3‰ (Figure 4b) suggesting a return to a warmer, humid climate immediately following the YD.

[12] Our Saginaw samples have also recorded, for the first time, the MH climatic oscillations through NGTs. Unlike previous climatic events (e.g., BOA, YD), the timing and magnitude of MH climatic oscillations varied regionally [e.g., *Bartlein et al.*, 2011]. Numerous proxies in the Midwest, including fossil pollen [*Winkler et al.*, 1986; *Viau et al.*, 2006] and speleothems [*Dorale et al.*, 1992] show evidence for a temperature increase of ~0.5–4°C between ~6 kyr and ~3 kyr BP [e.g., *Kirby et al.*, 2002] followed by a rapid cooling of ~4°C up to ~2.5 kyr [e.g., *Dorale et al.*, 1992]. Our combined NGT record points to the MH warming onset at ~5.4 kyr (m4b) peaking at ~4.1 kyr BP with a corresponding NGT increase of 2.9 ± 0.8°C (sg6b; Figure 3a). This warming period is followed by a rapid NGT cooling of 1.7 ± 0.9°C between ~4.1 kyr and ~2.9 kyr BP (sg6b, sg4a; Figure 3a). The timing and magnitude of MH climatic oscillations observed through NGTs generally correlates well with regional proxies. Corresponding EA variations are observed. Specifically, increased EA values between the onset of the MH warming at ~5.4 kyr BP (m4b, Figure 4a) and its peak at ~4.1 kyr (sg6b, Figure 4a), a sign of increasing aridity within a warmer climate, followed by return to low EA values (sg4b, Figure 4a) and thus, a return to greater humidity levels in a cooler environment. This change in arid versus humid climatic regimes is also well documented through a host of regional studies including vegetation changes [*Bartlein et al.*, 2011; *Baker et al.*, 1998] and low lake levels [e.g., *Winkler et al.*, 1986]. As shown by the NGT and EA record, transition from cool, humid conditions

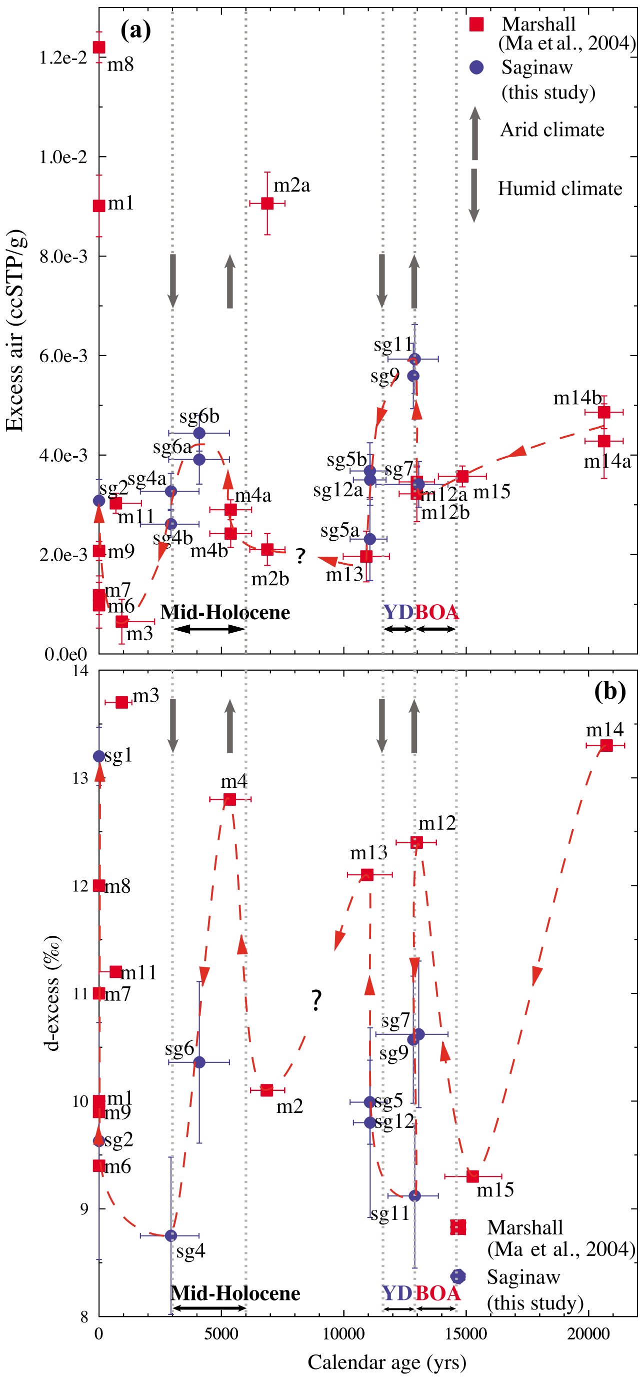

Figure 4. Comparison of (a) EA and (b) d-excess as a function of groundwater ages for the Saginaw and Marshall aquifers. Also shown are the time periods corresponding to the BOA, YD and MH climatic events. A schematic line (red dashed line) similar to the moving average is also indicated for visualization of climatic trends. Upward and downward arrows indicate change into arid and humid regimes, respectively.

to warm, drier conditions at the peak of the MH are also corroborated by enriched δ^{18}O values accompanied by decreasing d-excess values (m4-sg6, Figures 3b and 4b). In contrast, cooling and the return to more humid conditions at the end of the MH climatic event (sg6b-sg4a, Figures 3a and 4a) are not reflected in the δ^{18}O and d-excess record. More specifically, δ^{18}O and d-excess values are more enriched and lower, respectively, at the termination of the MH cooling period at ~2.9 kyr BP (sg4, Figures 3b and 4b). Previous studies have hypothesized a change in air-mass distribution over the Great Lakes region during the MH [*Krishnamurthy et al.*, 1995]. An increase in vapor transport from the Gulf of Mexico would lead to enriched δ^{18}O values [see, e.g., *Ma et al.*, 2004; *Hall et al.*, 2012] as well as lower d-excess values due to expected higher relative humidity at the Gulf of Mexico ocean source as compared to other moisture sources in the Midwest [*Shadbolt et al.*, 2006]. Our δ^{18}O and d-excess results from the late MH are consistent with this hypothesis.

6. Concluding Remarks

[13] NGTs and EA hold great potential in identifying rapid climatic shifts both, in terms of actual temperature changes (NGTs) and humid versus arid climatic regimes (EA). Here, for the first time, the onset and termination of the YD and MH oscillations are identified through NGTs and EA and further strengthened by direct correlation of δ^{18}O and d-excess signatures for most of the record. Together with groundwater age information, the stable isotope record (δD, δ^{18}O) also places new constraints on timing and sources of subglacial meltwater contributions from the LIS both prior and following the LGM.

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