Oxygen-17 anomaly in soil nitrate: A new precipitation proxy for desert landscapes

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A B S T R A C T 

The nitrogen cycle in desert soil ecosystems is particularly sensitive to changes in precipitation, even of relatively small magnitude and short duration, because it is already under water stress. This suggests that desert soils may have preserved past evidence of small variations in continental precipitation. We have measured nitrate (NO$_3^-$) concentrations in soils from the Atacama (Chile), Kumtag (China), Mojave (US), and Thar (India) deserts, and stable nitrogen and oxygen isotope ($^{15}$N, $^{17}$O, and $^{18}$O) abundances of the soil NO$_3^-$ $^{17}$O anomalies ($\Delta^{17}$O), the deviations from the mass-independent isotopic fractionation, were detected in soil NO$_3^-$ from almost all sites of these four deserts. There was a strong negative correlation between the mean annual precipitation (MAP) and soil NO$_3^-$ $\Delta^{17}$O values ($\Delta^{17}$ONO$_3$soil). This MAP-$\Delta^{17}$ONO$_3$soil correlation advocated $\Delta^{17}$ONO$_3$soil as a new precipitation proxy and was then used to assess precipitation changes in southwestern US at the Pliocene–Pleistocene boundary, in South America during the Miocene, and in the Sahara Desert for the past 10 kyr using NO$_3^-$ $\Delta^{17}$O in paleosols or ancient aquifers. Global and the US maps of surface $\Delta^{17}$ONO$_3$soil were also projected with available MAP datasets based on the MAP-$\Delta^{17}$ONO$_3$soil model. 

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1. Introduction 

Nitrate (NO$_3^-$) is often the dominant form of fixed nitrogen in desert soils (Erickson, 1981; Walvoord et al., 2003; Graham et al., 2008), but the mechanisms leading to its accumulation remain uncertain. NO$_3^-$ accrues naturally via atmospheric deposition and in situ biological nitrification (Boring et al., 1988). Atmospheric deposition of NO$_3^-$ occurs through both wet deposition of dissolved NO$_3^-$ in rain, snow, and fog, and dry deposition of aerosol NO$_3^-$ and gaseous nitric acid (Seinfeld and Pandis, 2006). In water-limited desert regions, the wet deposition rate can be proportional to local mean annual precipitation (MAP), while the dry deposition may also be a function of MAP (Seinfeld and Pandis, 2006). Nitrification, the oxidation of ammonia/ammonium into NO$_3^-$ by microbes, is often the main source of NO$_3^-$ in soils on Earth (Boring et al., 1988). The nitrification rates in desert soils are also, in part, controlled by MAP since low soil water contents can inhibit microbial activities by lowering intracellular water (Gleeson et al., 2008). The relative importance of these two sources in desert soils, deposition versus nitrification, and their dependences on MAP, however, are poorly constrained over space and time (Boring et al., 1988; Walvoord et al., 2003).

Oxygen isotope abundances have recently proven useful for distinguishing these two NO$_3^-$ sources (Michalski et al., 2004). Oxygen consists of three stable isotopes: $^{16}$O, $^{17}$O and $^{18}$O. For the majority of material and processes on Earth, there exist isotopic fractionations that are proportional to the relative differences in isotope masses and these are referred as mass-dependent isotopic fractionations (see review in Thiemens, 2006). During nitrification, oxygen atoms of water and air that both comply with the mass-dependent law are proportionally transferred to NO$_3^-$, which itself is a mass-dependent process, leading to $\delta^{17}$O = $0.52 \cdot \delta^{18}$O in biotic NO$_3^-$ (Miller, 2002). Atmospheric NO$_3^-$, on the other hand, contains an “anomalous” $^{17}$O excess over what is expected based on $^{18}$O abundances (Michalski et al., 2003). The deviation from mass-dependent fractionation is called “mass-independent isotopic fractionation” and quantified by $\Delta^{17}$O = $\delta^{17}$O − $0.52 \cdot \delta^{18}$O (Miller, 2002; Thiemens, 2006). The $\Delta^{17}$O values of atmospheric NO$_3^-$ ($\Delta^{17}$ONO$_3$atm) have been observed to range from 20–35‰ (Michalski et al., 2003; Alexander et al., 2009; Morin et al., 2009).
which arises during NO₃ oxidation by tropospheric ozone that has Δ¹⁷O values of 25–35‰ (Michalski and Bhattacharyya, 2009; Vicars and Savarino, 2014). Soil NO₃ Δ¹⁷O (Δ¹⁷O_NO₃soil) values can then be used to apportion the two NO₃ sources by applying a two-component Δ¹⁷O mixing model:

Δ¹⁷O_NO₃soil = f atm • Δ¹⁷O_NO₃atm + f nitr • Δ¹⁷O_NO₃nitr (1)

where Δ¹⁷O_NO₃nitr is the Δ¹⁷O value of soil NO₃ produced from nitrification that is approximately zero, and f atm and f nitr are the mole fractions of atmospheric deposition and nitrification contributing to the soil NO₃ pool, respectively (f atm + f nitr = 1) (Michalski et al., 2004; Dejwakh et al., 2012). Since atmospheric NO₃ deposition and nitrification rates are both sensitive to precipitation changes in desert regions, we hypothesize that MAP variations can alter f atm and f nitr in different proportions and become manifested in Δ¹⁷O_NO₃soil. Thus Δ¹⁷O_NO₃soil can serve as a MAP proxy in desert regions, where nitrification is sufficiently slow that it cannot completely override the NO₃ accumulated by atmospheric NO₃ deposition.

The connection between desert MAP and Δ¹⁷O NO₃soil has previously been noted. Rech et al. (2006) compared the Δ¹⁷O NO₃soil values in a 9 Ma palaeosol stratum along the eastern margin of the Atacama Desert (Chile) with those in the Atacama’s hyperarid core to estimate MAP during the late Miocene. Ewing et al. (2007) demonstrated an increase in Δ¹⁷O NO₃soil along a relatively narrow precipitation transect (MAP: 21 mm to 2 mm) in the Atacama. However, there has been no detailed study evaluating how Δ¹⁷O NO₃soil varies with precipitation in deserts except the Atacama. Here we present the Δ¹⁷O NO₃soil data of four globally distributed deserts and a calibration of Δ¹⁷O NO₃soil versus MAP relationship, then highlight the use of Δ¹⁷O NO₃soil as a precipitation proxy for inferring MAP in past climate states, and ultimately project the global and US overviews of Δ¹⁷O NO₃soil based on available MAP datasets.

2. Soil sampling and analysis

Undisturbed soils were collected from 22 sites in four hot deserts (Atacama, Chile; Kumtag, China; Mojave, United States; and Thar, India) (Fig. 1, Table 1). The Atacama Desert, located between the Coastal Range to the west and the Andes to the east in northern Chile, is one of the driest places on Earth with modern-time MAP <2 mm in its hyper-arid core (Houston, 2006b). It is well known to contain massive NO₃ deposits in the world that have been extensively mined since early 1800s (Ericksen, 1981). The Kumtag Desert is located in the Turpan–Hami Basin in western China, which is the second driest and the only inland desert among these four deserts with typical MAP of 30–50 mm in most areas (Li et al., 2011). 2.5 billion ton NO₃ deposits, rivaling those in the Atacama, have recently been identified in the Kumtag (Qin et al., 2012). The Mojave Desert is situated in southwestern US between the Great Basin Desert to the north and the Sonoran Desert to the south with typical MAP of 30–300 mm (Hereford et al., 2006). Sporadic subsurface (~2 m) NO₃ deposits have been found in the Mojave (Walvoord et al., 2003; Graham et al., 2008). The Thar Desert, located in northwestern India forming a natural boundary along the border between India and Pakistan, is wettest among the four deserts with typical MAP of 100–500 mm (Pramanik, 1952). NO₃ deposits in the Thar have not been documented, but sufficient NO₃ was found in soils analyzed in this study for oxygen isotope analysis.

Sampling sites on stable and ancient landforms with typical desert surfaces were selected also based on the distinction from mining excavations and roads as well as the availability of MAP data in order to span a wide range of MAP rates. Decadal MAP data of nearby meteorological stations were obtained for the Atacama sites from Houston (2006b), Kumtag sites from Li et al. (2011), and Thar sites from Indian National Data Center, while MAP data for the Mojave sites were interpolated using the PRISM model (http://oldprism.nacse.org). At most of these sites, the soil was mantled by desert pavement, a common land-surface feature in desert regions. Patchy bushes were found at some sites (see detailed site descriptions in SI Table S1), and only the open space between bushes was sampled. All soil profiles were hand sampled from the surface to a depth of 20–50 cm. Samples were stored in air-tight plastic bags at 20°C until analysis.

Bulk soils were first sieved using 2 mm sieves. 1–20 g of the sieved soil was added to 30–40 ml of Millipore water and the soil–water mixture was vortexed to extract water soluble salts. NO₃ concentrations ([NO₃⁻]) were measured by Dionex DX-500 ion chromatography. The sieved Kumtag soils were weighed of ~2 mg into tin capsules that are loaded to the Sercon (Crewe, UK) GLS elemental analyzer-Hydra 20/22 isotope ratio mass spectrometer (EA-IRMS) system for δ¹⁵N analysis. The measurement of our laboratory working references NC12 yielded δ¹⁵N of 15.3 ± 0.3‰. The NC32 was mixed by the potassium nitrate (KNO₃) obtained from North Carolina State University (NCSU, prepared by equilibrating water and reagent grade HNO₃ per Böhleke et al., 2003) and USGS32 (δ¹⁵N = 180‰) in the ratio of 93:7. The sample run was also calibrated by international references of NIST 1547 peach leave (δ¹⁵N = 1.5‰), USGS34 (δ¹⁵N = −1.8‰) and USGS35 (δ¹⁵N = 2.7‰). Meanwhile, the sieved soils from the Kumtag and Thar were extracted of NO₃ that was then purified by removing sulfate salts, converted into AgNO₃, and thermally decomposed with the resulting O2 analyzed by Delta (Thermo Fisher, US) V Plus IRMS (Michalski et al., 2004). The δ¹⁸O and Δ¹⁷O precision were both ±0.2‰ obtained by replicate analysis of our Δ¹⁷O = 19.8‰ laboratory working reference (20H) that was the purified Hoffman nitrate fertilizer (Hi-Yield Nitrate of Soda) mined from ore deposits in the Atacama. Instead, samples from the Atacama and Mojave were analyzed of δ¹⁸O, δ¹⁸O and Δ¹⁷O simultaneously using a recent bacterial reduction and gold redox method (Kaiser et al., 2007). Six laboratory NO₃ working references with Δ¹⁷O = 0, 1‰, 2‰, 5‰, 10‰ and 19‰ were run to generate duplicate calibration curves and for quality control, showing precision for δ¹⁸O, δ¹⁸O and Δ¹⁷O of ±0.4‰, ±1‰ and ±0.5‰, respectively (Riba, 2013). The Δ¹⁷O = 0 working reference NC12 and Δ¹⁷O = 19.8‰ working reference 20H were described above, and four other working references were made by appropriately mixing NC12 and 20H (Riba, 2013). All working references were previously calibrated using international NO₃ isotope references, i.e. USGS32 (δ¹⁸O = 25.7‰), USGS34 (δ¹⁸O = −14.8‰, Δ¹⁷O = 0) and USGS35 (δ¹⁸O = 51.5‰, Δ¹⁷O = 21.1‰). All δ¹⁸O values were reported versus air N₂ and oxygen values (δ¹⁸O, Δ¹⁷O) were reported with respect to VSMOW. All analyses were performed at the Purdue Stable Isotope Facility.

3. Results and discussion

3.1. NO₃ concentrations and isotopic signatures

[NO₃⁻] were highest in Kumtag soils ranging from 3.8–94.0 μmol/g soil), typically one order of magnitude higher than those from the Atacama (0.2–8.5 μmol/g soil) or the Mojave (0.2–3.3 μmol/g soil) (Table 1). This is because all the Kumtag sites were located in major mining areas where nitrate deposits of high ore grades were reported to have mainly accumulated in the surface or subsurface (15–70 cm) (Qin et al., 2012), while the sites in other deserts were in non-mining or mine tailing areas. Further data analysis indicated that the Atacama soil [NO₃⁻] were a power
Fig. 1. Bottom: the predicted global distribution of surface $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ between 50°N and 50°S based on the MAP-$\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ model (inverted Eq. (2)): $\Delta^{17}$O$_{\text{NO}_3,\text{soil}} = -8.28 \ln(\text{MAP}) + 45.8$ with global MAP data from http://www.worldclim.org; upper (A): the predicted surface $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ around the USA with MAP data of higher-resolution from http://www.prism.oregonstate.edu; upper (B) and (C): the zoom-in pictures of the $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ distribution in South America and Asia continents, respectively.
Table 1
Precipitation gradient site information and the concentration and isotopic data.

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Coordinates (elevation, m)</th>
<th>MAP (mm)</th>
<th>Sampling depth (cm)</th>
<th>Average [NO$_3^-$]$^a$ (μmol[g soil]$^{-1}$)</th>
<th>$\delta^{15}$NO$<em>3$$</em>{soil}$ $(%e) \pm 1\sigma$ (n$^b$)</th>
<th>$\delta^{18}$O$<em>{NO_3}$$</em>{soil}$ $(%e) \pm 1\sigma$ (n$^b$)</th>
<th>$\Delta^{17}$O$<em>{NO_3}$$</em>{soil}$ $(%e) \pm 1\sigma$ (n$^b$)</th>
</tr>
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<tbody>
<tr>
<td>Atacama Desert, Chile</td>
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</tr>
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<td>Calama</td>
<td>22.53°S 68.97°W (4374)</td>
<td>4.2</td>
<td>0–20</td>
<td>0.8</td>
<td>$-4.3 \pm 0.7$ (2)$^c$</td>
<td>$44.9 \pm 2.9$ (2)$^c$</td>
<td>$16.0 \pm 1.9$ (2)$^c$</td>
</tr>
<tr>
<td>Chiu Chiu</td>
<td>22.34°S 68.66°W (2555)</td>
<td>4.4</td>
<td>0–25</td>
<td>0.9</td>
<td>$-1.1 \pm 0.4$ (2)$^c$</td>
<td>$38.1 \pm 0.6$ (3)$^c$</td>
<td>$19.1 \pm 0.6$ (3)$^c$</td>
</tr>
<tr>
<td>Copaque</td>
<td>20.94°S 69.07°W (3384)</td>
<td>54.1</td>
<td>0–20</td>
<td>0.6</td>
<td>$5.9$ (1)$^c$</td>
<td>$29.1$ (1)$^c$</td>
<td>$9.6$ (1)$^c$</td>
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<tr>
<td>Coya Sur</td>
<td>22.40°S 69.58°W (1220)</td>
<td>0.4</td>
<td>0–30</td>
<td>6.5</td>
<td>$-1.9 \pm 0.6$ (4)$^c$</td>
<td>$47.2 \pm 3.6$ (4)$^c$</td>
<td>$21.3 \pm 1.4$ (4)$^c$</td>
</tr>
<tr>
<td>El Tatio</td>
<td>22.38°S 68.02°W (4374)</td>
<td>153.9</td>
<td>0–30</td>
<td>0.2</td>
<td>$5.3 \pm 12.3$ (1)$^c$</td>
<td>$38.0 \pm 3.0$ (2)$^c$</td>
<td>$6.1 \pm 8.6$ (2)$^c$</td>
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<tr>
<td>Huatacoondo</td>
<td>20.92°S 69.04°W (2219)</td>
<td>11.5</td>
<td>0–50</td>
<td>1.7</td>
<td>$-10.4 \pm 3.7$ (2)$^c$</td>
<td>$52.8 \pm 1.0$ (2)$^c$</td>
<td>$20.6 \pm 1.5$ (2)$^c$</td>
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<tr>
<td>Ojos</td>
<td>19.96°S 69.54°W (1336)</td>
<td>0.9</td>
<td>0–20</td>
<td>3.0</td>
<td>$7.1$ (1)$^c$</td>
<td>$38.1 \pm 1.3$ (2)$^c$</td>
<td>$16.2 \pm 0.5$ (2)$^c$</td>
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<tr>
<td>Quillagua</td>
<td>21.68°S 69.54°W (906)</td>
<td>0.2</td>
<td>0–10</td>
<td>8.5</td>
<td>$-3.2 \pm 0.4$ (2)$^e$</td>
<td>$46.6 \pm 1.0$ (2)$^c$</td>
<td>$19.7 \pm 0.5$ (2)$^c$</td>
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<td>Toceno</td>
<td>22.26°S 68.19°W (3237)</td>
<td>94.1</td>
<td>0–40</td>
<td>N.A.</td>
<td>$14.4$ (1)$^e$</td>
<td>$22.1$ (1)$^c$</td>
<td>$5.1$ (1)$^c$</td>
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<td>Kumtag Desert, China</td>
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<td>Dananhu</td>
<td>42.37°N 92.82°E (543)</td>
<td>40.5</td>
<td>0–30</td>
<td>20.6</td>
<td>$3.3 \pm 0.6$ (7)$^d$</td>
<td>$47.6 \pm 1.8$ (7)$^d$</td>
<td>$16.5 \pm 0.5$ (7)$^d$</td>
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<tr>
<td>Dawadi</td>
<td>41.45°N 92.65°E (1028)</td>
<td>49.1</td>
<td>0–30</td>
<td>21.9</td>
<td>$6.5$ (1)$^d$</td>
<td>$55.1$ (1)$^c$</td>
<td>$14.4$ (1)$^c$</td>
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<td>Kumtag mine</td>
<td>42.69°N 91.17°E (312)</td>
<td>36.5</td>
<td>0–30</td>
<td>59.2</td>
<td>$6.3$ (1)$^d$</td>
<td>$47.4$ (1)$^c$</td>
<td>$16.3 \pm 0.2$ (2)$^e$</td>
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<td>Kuzishan</td>
<td>41.45°N 92.80°E (1079)</td>
<td>40.1</td>
<td>0–10</td>
<td>94.0</td>
<td>$10.8 \pm 0.8$ (2)$^d$</td>
<td>$44.5 \pm 1.2$ (2)$^c$</td>
<td>$12.3 \pm 0.2$ (2)$^c$</td>
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<tr>
<td>Qietai</td>
<td>42.92°N 90.88°E (408)</td>
<td>36.5</td>
<td>0–20</td>
<td>3.8</td>
<td>$1.5$ (1)$^d$</td>
<td>$44.5$ (1)$^e$</td>
<td>$17.5$ (1)$^c$</td>
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<td>Xiaoaochu</td>
<td>43.10°N 90.30°E (713)</td>
<td>36.5</td>
<td>0–50</td>
<td>5.1</td>
<td>$2.1$ (1)$^d$</td>
<td>$39.8$ (1)$^e$</td>
<td>$17.6$ (1)$^e$</td>
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<td>Xigebi</td>
<td>42.05°N 92.95°E (767)</td>
<td>40.5</td>
<td>0–30</td>
<td>11.6</td>
<td>$5.4 \pm 0.3$ (2)$^d$</td>
<td>$41.5 \pm 2.0$ (2)$^c$</td>
<td>$14.9 \pm 0.5$ (2)$^c$</td>
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<td>Mojave Desert, USA</td>
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<td>Cima</td>
<td>35.20°N 115.87°W (1106)</td>
<td>149.9</td>
<td>0–30</td>
<td>0.2</td>
<td>$0.9 \pm 1.7$ (4)$^c$</td>
<td>$23.7 \pm 1.0$ (4)$^c$</td>
<td>$7.4 \pm 0.5$ (4)$^c$</td>
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<td>Lower canyon</td>
<td>35.71°N 116.23°W (217)</td>
<td>90.7</td>
<td>0–30</td>
<td>N.A.</td>
<td>$15.1$ (1)$^c$</td>
<td>$48.9$ (1)$^c$</td>
<td>$9.3$ (1)$^c$</td>
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<td>Panamint</td>
<td>36.03°N 117.30°W (469)</td>
<td>106.2</td>
<td>0–43</td>
<td>3.3</td>
<td>$9.9 \pm 2.2$ (3)$^c$</td>
<td>$27.6 \pm 2.3$ (3)$^c$</td>
<td>$11.1 \pm 0.6$ (3)$^c$</td>
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<td>Thar Desert, India</td>
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<tr>
<td>Bikaner</td>
<td>28.05°N 73.24°E (215)</td>
<td>305.0</td>
<td>0–50</td>
<td>N.A.</td>
<td>N.A.</td>
<td>$15.2$ (1)$^e$</td>
<td>$0.3$ (1)$^e$</td>
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<tr>
<td>Ganganagar</td>
<td>29.87°N 73.89°E (176)</td>
<td>200.0</td>
<td>0–50</td>
<td>N.A.</td>
<td>N.A.</td>
<td>$12.0$ (1)$^e$</td>
<td>$1.2$ (1)$^e$</td>
</tr>
<tr>
<td>Jasalmer</td>
<td>26.94°N 70.94°E (218)</td>
<td>212.0</td>
<td>0–50</td>
<td>N.A.</td>
<td>N.A.</td>
<td>$11.0 \pm 0.2$ (2)$^f$</td>
<td>$0.4 \pm 0.2$ (2)$^f$</td>
</tr>
</tbody>
</table>

N.A.: not applicable because not measured.

a For sites with sub-samples from different depths, the concentrations were depth weighed average concentrations.
b Sample replicates for the same site.
c Measured by bacterial reduction method.
d Measured by the EA-IRMS system.
e Measured by thermal decomposition method.
function of MAP ([NO$_3^-$] = 3.0 • MAP$^{-0.5}$, $r^2 = 0.88$), evidencing that drier climates are more advantageous for nitrate accumulation. However, this [NO$_3^-$]–MAP relationship was not significant for the Mojave or Kumtag soils. This suggested that NO$_3^-$ accumulation varied in different deserts and was also affected by geographic differences. We suspect that the wettest Thar, where the sampled ~10 g soils were only sufficient for $\delta^{18}$O and $\Delta^{17}$O analysis without the [NO$_3^-$] and $\delta^{15}$N data, had the lowest soil [NO$_3^-$] among the four deserts.

The Atacama sites had soil NO$_3^-$ $\delta^{15}$N ($\delta^{15}$N$\text{NO}_3$$_\text{soil}$) and $\delta^{18}$O ($\delta^{18}$O$_\text{NO}_3$$_\text{soil}$) values of $-10.4$–$14.4\%$ and $22.1$–$52.8\%$, respectively (Table 1). These values spanned broader ranges compared to those reported for the Atacama sites by Böhlke et al. (1997) and Michalski et al. (2004), probably owing to that this study covered more climatic zones and non-mining areas. While $\delta^{15}$N$_\text{NO}_3$$_\text{soil}$ does not significantly differ between potential sources and cannot be used to distinguish different sources with certainty, high $\delta^{18}$O$_\text{NO}_3$$_\text{soil}$ values were usually ascribed to atmospheric deposition that usually has NO$_3^-$ $\delta^{18}$O values of 40–70\% (Böhlke et al.; Michalski et al., 2004). In this study, low $\delta^{18}$O$_\text{NO}_3$$_\text{soil}$ values (<40\%) associated with positive $\delta^{15}$N$_\text{NO}_3$$_\text{soil}$ occurred in high-altitude sites with high MAP rates (El Tatio, Tocenac and Cepaquaire), as well as the northermost Ojos site, probably suggesting the terrestrial sources of NO$_3^-$ (nitrification). The negative correlation between $\delta^{15}$N$_\text{NO}_3$$_\text{soil}$ and $\delta^{18}$O$_\text{NO}_3$$_\text{soil}$ for the Atacama ($\delta^{15}$N$_\text{NO}_3$$_\text{soil}$ = $-0.7\delta^{18}$O$_\text{NO}_3$$_\text{soil} + 27.3$, $r^2 = 0.89$) may also suggest the mixing of NO$_3^-$ from atmospheric and terrestrial sources. The high $\delta^{18}$O$_\text{NO}_3$$_\text{soil}$ values (39.8–55.1\%) for the Kumtag sites were also likely related to the atmospheric origin. The Kumtag $\delta^{15}$N$_\text{NO}_3$$_\text{soil}$ values (1.5–10.8\%) were for bulk soils, but consistent with those for NO$_3^-$ reported for the same sites by Qin et al. (2012), suggesting NO$_3^-$ is the major form of nitrogen in Kumtag soils. The highest $\delta^{15}$N$_\text{NO}_3$$_\text{soil}$ values were found in Kuzishan (10.8\%) and Dawadi (6.5\%), two sites with salt lake-type deposits of niter (KNO$_3$), while the other Kumtag sites with caliche-type deposits of sodium niter (NaNO$_3$) had low $\delta^{15}$N values of 1.5–6.3\% (Table 1). This is in agreement with the discovery by Qin et al. (2012) that the isotopic compositions were mineralogically different, but we did not observe lower $\delta^{18}$O$_\text{NO}_3$$_\text{soil}$ values in salt lake-type deposits compared to the caliche-type deposits in our study as suggested by Qin et al. (2012). The $\delta^{15}$N$_\text{NO}_3$$_\text{soil}$ and $\delta^{18}$O$_\text{NO}_3$$_\text{soil}$ were not correlated in the Kumtag. The Cima and Penmann sites had similar $\delta^{15}$N$_\text{NO}_3$$_\text{soil}$ (0–4.8\%) and $\delta^{18}$O$_\text{NO}_3$$_\text{soil}$ (21.3–36.0\%) values to those for the Mojave reported in Böhlke et al. (1997) and Michalski et al. (2004), but the Lower canyon site had significantly higher $\delta^{15}$N$_\text{NO}_3$$_\text{soil}$ (15.1\%) and $\delta^{18}$O$_\text{NO}_3$$_\text{soil}$ (48.9\%) values than previously reported values (Table 1). As far as we know, the $\delta^{15}$N$_\text{NO}_3$$_\text{soil}$ and $\delta^{18}$O$_\text{NO}_3$$_\text{soil}$ of the Thar Desert are hereby reported for the first time.

The soil NO$_3^-$ $\Delta^{17}$O ($\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$) of the 22 sites across four deserts varied from 0.3–21.3\% (Table 1). The largest $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ values were observed in hyper-arid regions (MAP < 50 mm, UNEP, 1997) of the Atacama (16.0–21.3\%) and the Kumtag (12.3–17.6\%), indicating the major origin of soil NO$_3^-$ from atmospheric deposition that is consistent with the inference from the $\delta^{18}$O$_\text{NO}_3$$_\text{soil}$. In the arid regions (50 < MAP < 200 mm, UNEP, 1997) of the Mojave as well as some high-altitude sites in the Atacama, the $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ values were significantly lower (5.1–11.1\%), which suggested the increasing importance of nitrification to the soil NO$_3^-$ pool. The lowest $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ of 0–1\% occurred in the semi-arid Thar (200 < MAP < 500 mm, UNEP, 1997), suggesting the shift in the origin of soil NO$_3^-$ to predominantly nitrification.

3.2. The derivation of $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ as a precipitation proxy

Further, the $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ showed a linear dependence on MAP over the sampling site MAP range of 0.4–305 mm: MAP = −11.3 • $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ + 216.7 ($r^2 = 0.84$) (Fig. 2), suggesting the potential of $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ as a MAP proxy. However, there are upper and lower limits of MAP after which the $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ proxy becomes invalid for precipitation inference. The upper limit of MAP would correspond to the analytical detection limit of $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ of 0.5\%. This upper limit (MAP > 210 mm) is reached in the Jaisalmer area of the Thar where nitrification has outpaced atmospheric NO$_3^-$ deposition, with only ~2% contribution of atmospheric NO$_3^-$ to total soil NO$_3^-$ budget based on Eq. (1) using the modern-time average $\Delta^{17}$O$_{\text{NO}_3}$$_\text{atm}$ value of ~23\% (Michalski et al., 2003). The lower limit of MAP occurs where atmospheric deposition is the only NO$_3^-$ input source in the soil. When MAP = 0, there should be no nitrification contributing to soil NO$_3^-$, and the MAP–$\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ equation indicates $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ $\sim$ 20\%, close to the observed $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ of 20.6 ± 1.5\% at the Huatacondo sites (MAP = 11.5 mm), suggesting a $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ plateau likely occurring when MAP = 11.5 mm. Therefore, approximately 11.5 mm can be the dry end of microbial activities below which nitrification is nearly eliminated, as nitrification (and $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$) can vary strongly with small increases in MAP (Fig. 2). 11.5 mm is then set as the lower limit of MAP that can be determined by the $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ proxy. $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ values from sites with MAP rates between that of Huatacondo and Jaisalmer, i.e. 11.5–212 mm, were then used to recalibrate the MAP–$\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ relationship. After comparison, an exponential function (Fig. 2) was adopted:

MAP = 253.8 exp(−0.12 $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$) ($r^2 = 0.87$) (2)

This significant correlation between MAP and $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ advocates that $\Delta^{15}$N$_{\text{NO}_3}$$_\text{soil}$ can work as a MAP proxy for ancient nitrate deposits with the applicable range of 11.5–212 mm.

Beyond these application limits, we acknowledge that there are also some uncertainties inherent in the $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ proxy. The first uncertainty in the MAP–$\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$ relationship arises from using the modern-time precipitation data to represent the precipitation information over the timescales of soil NO$_3^-$ accumulation that may span geological periods. However, precipitation records before 1900 A.D., especially in desert regions, are rarely available. Therefore, the existing decade-scale precipitation data (Table 1) were used to constrain the relationship between MAP and $\Delta^{17}$O$_{\text{NO}_3}$$_\text{soil}$, but the uncertainty was minimized by only using surface or near-surface (<50 cm) soils that would represent NO$_3^-$ that has recently accumulated.
The second uncertainty in the MAP-$\Delta^{17}$O$_{\text{NO}_3}$ model is that $\Delta^{17}$O$_{\text{NO}_3,\text{atm}}$ was assumed constant but indeed may have varied between different sites or over time at the same site (Eq. (1)), complicating the direct derivation of the MAP-$\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ relationship. Observations (Michalski et al. 2003) and isotope models (Alexander et al. 2009) have shown that $\Delta^{17}$O$_{\text{NO}_3,\text{atm}}$ values are determined mainly by the oxidation capacity (the interaction of three principal oxidants in the lower atmosphere: O$_3$, •OH and H$_2$O). All the four studied deserts are geographically similar (mid-latitude, bounded by mountain ranges, high temperatures, high actinic flux, low biogenic emissions) and their spatial extents are relatively small. Therefore, the oxidation capacity in each desert that controls $\Delta^{17}$O$_{\text{NO}_3,\text{atm}}$ values is not likely to be significantly different. Temporal variations of $\Delta^{17}$O$_{\text{NO}_3,\text{atm}}$ also cannot be significant for using the MAP-$\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ proxy because these variations would average out over the NO$_3^-$ accumulation timescales (100–1000 yrs) (Walvoord et al., 2003, Michalski et al., 2004). The modulation of annual $\Delta^{17}$O$_{\text{NO}_3,\text{atm}}$ values by long-term accumulation is exemplified in recent analysis of dust collected for 2.5 years along an east-west transect in the Atacama (Wang et al., 2014). The $\Delta^{17}$O values of NO$_3^-$ extracted from the seven dust collectors located in the hyper-arid core (∼160 km wide) were relatively consistent of 25.8 ± 0.5‰ (Wang et al., 2014), in contrast to the annual $\Delta^{17}$O$_{\text{NO}_3,\text{atm}}$ variations of ∼10‰ for an Andean ice core (Buffen et al., 2014). For its secular variations, the 30-year running average of the $\Delta^{17}$O$_{\text{NO}_3,\text{atm}}$ values for the Site A, Greenland ice core during 1680–1830 only showed a 2.5‰ variation, with the high values mainly owing to an elevation of O$_3$ and decrease of •OH in the atmosphere induced by the intense biomass burning recorded in North America (Alexander et al., 2004). Over the longer NO$_3^-$ accumulation timescales (100–1000 yr), the $\Delta^{17}$O$_{\text{NO}_3,\text{atm}}$ variations should be even smaller, especially considering additional processes such as physical mixing at the soil surface might further homogenize the temporal and spatial differences in the $\Delta^{17}$O$_{\text{NO}_3,\text{atm}}$. Besides, the $\Delta^{17}$O$_{\text{atm}}$ variations in mid-latitude deserts are still difficult to resolve because of the great challenges in reconstructing oxidation chemistry, especially for ancient times. Therefore, no correction for the $\Delta^{17}$O$_{\text{NO}_3,\text{atm}}$ effects was made during the derivation of the MAP-$\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ relationship.

Thirdly, sampling issues may also account for some small uncertainties when applying the MAP-$\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ proxy. To reduce sampling biases, replicates were collected from different depths (but <50 cm as discussed above) or locations at some sites and these typically showed only small differences in $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ (<1‰). However, two sites showed significant $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ variations with location or depth. The El Tatio site is hilly (elevation > 4000 m, SI Table S1), and the $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ value of 12.1‰ for the sample from the hilltop is significantly larger than the $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ of zero for the sample from the hill slope (0–20 cm integrated sample). This is probably because water was unevenly distributed over the hill with the hill slope receiving and holding a significant amount of water drained from the hilltop, which was evident from the shrub coverage on the hill slope and barren surface with desert pavements on the hilltop (SI Table S1). Therefore, the average $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ of 6.1‰ for the two locations was used to calibrate the MAP-$\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ relationship. The Copaquire site is a valley surrounded by mountains, and its $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ values are 9.6‰ at 0–3 cm and 3.3‰ at 10–20 cm. The significant disparity between these two different depths may indicate a wetter climate in ancient times when possible surface runoff brought in NO$_3^-$ from other sources featured by lower $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ values or ancient water availability could sustain more in situ nitration. To correspond to the modern-time precipitation data, the surface 0–3 cm $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ was adopted. However, the $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ of 9.6‰ is still low compared to the $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ at other sites with similar MAP (Fig. 2), probably due to that the Copaquire site that is subject to drain water from the surrounding mountains, different from most of other sites where precipitation is the major water source. The Tocene site, located in a mountain basin with 40% bush coverage (SI Table S1), also had a lower $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ (5.1‰) than expected, suggesting the possibly similar existence of drain water from mountains.

Fourthly, the model-data deviations might also arise if there were variations in evaporation between sites that might have influenced the $\Delta^{15}$NO$_{\text{atm}}$ by varying the extents of microbial nitritification. Pan evaporation rates generally far exceed the actual evaporation because of the water limits in desert regions. For example, the recorded annual pan evaporation for our sites in the Atacama were 1984–3631 mm (Houston, 2006a), ~3000 mm in the Kumtag (Qin et al., 2012), and ~2000 mm in the Mojave (Blaney, 1957), which were similar in values between deserts but typically one or two orders of magnitude higher than their local MAP. Obviously, these desert evaporation potentials could not be fulfilled, and the local actual evaporation should approximate to local precipitation. Therefore, evaporation was not treated as an independent factor and thus not corrected for variations when deriving the MAP-$\Delta^{15}$NO$_{\text{atm}}$ relationship. However, the typical vertical distribution of nitrate, chloride, and sulfate with increasing depths in the Kumtag suggested that soluble salts were up-drawn by capillary force and evaporation to precipitate in the sequence of solubility from salt-enriched ground water in the Kumtag, though the nitrate all mainly originated from atmospheric deposition (Qin et al., 2012). This “bottom-up” mechanism of shallow nitrate deposition is clearly different from the “top-down” infiltration mechanism occurring in the Atacama that induced the concentration of nitrate at depth and below sulfate (Erickson, 1981). Nevertheless, we did not think that the difference in re-concentration mechanism could ruin the MAP-$\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ relationship, though the $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ in the Kumtag might reflect the isotopic signatures of NO$_3^-$ and precipitation information averaged over a larger groundwater-influenced area.

3.3. Evaluating the MAP-$\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ calibration

The MAP-$\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ calibration was evaluated by comparing our estimates with other published $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ values and regional precipitation records. Qin et al. (2012) measured the $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ of several NO$_3^-$ deposits ranging from 5.9‰ to 20.7‰ in the Turpan–Hami basin in northwestern China (see sites in Fig. 1). Their wider $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ range than our measurements is mainly owing to those sites that did not overlap with our sites. The highest $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ of 20.7‰ yields an estimate of the MAP of 21.2 mm, which is similar to their reported average MAP of 15 mm for the Turpan–Hami basin and that of 17.3 mm for its nearby Turpan weather station (Li et al., 2011). The lowest value of 5.9‰ suggests a MAP of 125.0 mm, typical of precipitation in the local mountain range (Li et al., 2011). This supports the authors’ proposed mechanism that the deposits are a mixture of local (hyper-arid) and remote (semi-arid) NO$_3^-$ sources that are connected through a groundwater system.

Ewing et al. (2007) reported average $\Delta^{17}$O$_{\text{NO}_3,\text{soil}}$ values of 17.1‰, 13.8‰, and 9.3‰ for three sites on Pliocene landforms along a south–north MAP transect in the Atacama (see sites in Fig. 1). Though Ewing et al. were among the first who recognized the control of $\Delta^{15}$NO$_{\text{atm}}$ by MAP, they mainly focused on the transformation of soil nitrogen cycle from the nitrogen input and loss balance with mainly organic nitrogen in arid regions to inorganic nitrogen (mostly NO$_3^-$) accumulation and storage in hyper-arid regions as reflected by nitrogen species concentrations and NO$_3^-$ isotope data along the MAP transect. Their data over a narrow precipitation transect were also insufficient to
develop a robust MAP-$\Delta^{17}$NO$_3$soil relationship that can be used for paleoprecipitation estimation, but should be ideal for testing our MAP-$\Delta^{17}$NO$_3$soil model. The $\Delta^{17}$NO$_3$soil values by Ewing et al. (2007) would correspond to MAP of 32.6, 48.4 and 83.1 mm based on Eq. (2), which are significantly higher than the observed modern-time MAP of <2, 10, and 21 mm. There are two possible explanations for these discrepancies. First, most of these were subsurface NO$_3^-$ (>50 cm deep) including older NO$_3^-$ that was possibly formed under a wetter climate than the modern-time rainfall regime. A better comparison would be to only consider the surface NO$_3^-$ . The $\Delta^{17}$NO$_3$soil values of 19.4 ± 0.1% in the surface 1-3 cm layer at the MAP < 2 mm site (Yungay) by Ewing et al. (2007) is near the lower MAP limit of the $\Delta^{17}$NO$_3$soil proxy, suggesting the MAP < 11.5 mm for the driest site, close to the observed <2 mm. There were no surface $\Delta^{17}$NO$_3$soil data for the MAP = 10 mm and MAP = 21 mm sites but these can be inferred using the observed correlation of $\Delta^{17}$NO$_3$soil = −3.4 + 0.43 $\times$ $\delta^{18}$O_NO$_3$soil ($R^2$ = 0.92, Fig. 5 of Ewing et al. 2007). The surface 2 cm $\delta^{18}$O_NO$_3$soil values were 49.9% at the MAP = 10 mm site and 43.8% for the MAP = 21 mm site, suggesting the surface $\Delta^{17}$NO$_3$soil of 18.0% and 15.4% at the two sites, respectively. These values can yield MAP of 29.1 mm and 39.8 mm, closer to their MAP of 10 mm and 21 mm, respectively. The remaining discrepancies may then be due to the second possibility that fog plays a role in supplying water to nitrifying microbes. Intrusion of thick fogs through the Coastal Range into the inland sites in the Atacama iscommon (Cereceda and Schenmuer, 1991), and the deposited fog water may support sparse plant life and promote microbial activity (Warren-Rhodes et al., 2006). Thus, slightly higher predictions of MAP by our MAP-$\Delta^{17}$NO$_3$soil proxy calibration compared to local precipitation data in coastal deserts could be due to fog precipitation being neglected from the local precipitation data.

### 3.4. Re-interpreting previous paleoclimate studies

The $\Delta^{17}$NO$_3$soil proxy can be used to re-evaluate previously published paleoclimate interpretations for paleosols. However, NO$_3^-$ salts are soluble, and can be mobilized within the soil profile or leached into the groundwater in the presence of small amounts of water. Large aqueous activities likely further mix and even homogenize NO$_3^-$ from different sources or different depths, while wet periods may facilitate nitrification significantly to erase positive $\Delta^{17}$NO$_3$soil legacies from previous dry periods. Therefore, caution should be borne in mind when using the $\Delta^{17}$NO$_3$soil proxy, and supplementary information (the site geological context and paleohydrology history evidences etc.), and additional analyses, such as the distribution of soluble salts that are indicative of dissolution and transport processes, are desired to help eventually decipher the climate information. Nevertheless, the robust MAP-$\Delta^{17}$NO$_3$soil relationship for surface NO$_3^-$ in desert regions suggested that aqueous activities or wet periods are not frequent to disturb the surface or subsurface NO$_3^-$ preservation in some parts of desert regions. Hyper-aridity can further minimize the influences of aqueous events and help preserve NO$_3^-$ at depth from mixing and leaching, which is exemplified by our previous research that heterogeneous $\Delta^{17}$NO$_3$soil reflecting climate states in different periods were preserved in a ~2 m deep soil profile from the hyper-arid core of the Atacama (Wang, 2013). Therefore, at sites absent of large-scale hydrological impacts, coupling the $\Delta^{17}$NO$_3$soil evidences with the interpretation of other geological and geochemical information can help guarantee the feasibility of the $\Delta^{17}$NO$_3$soil proxy for paleoprecipitation inference. In addition, groundwater in deserts is widely known to have high concentrations of NO$_3^-$ that is mainly from surface NO$_3^-$ deposits (Dietzel et al., 2014). Since the recharge of desert groundwater is typically slow and not appreciable, ancient groundwater may also preserve paleoprecipitation information like paleosol, and the groundwater NO$_3^-$ $\Delta^{17}$O may then help constrain the paleoprecipitation.

Lybrand et al. (2013) measured $\Delta^{17}$NO$_3$soil values of 7.0–13.2% of several clay hills in the southernmost region of Death Valley of the Mojave (see sites in Fig. 1). Those clay hills were covered with thin and blistered surface crusts and nearly absent of vegetation, but high contents of NO$_3^-$ salts accumulate in “caliche” layers above the clay beds that were proposed to have been moved in a “bottom-up” manner by capillary rise. It was postulated that these field sites were once playa or evaporating lakes that became desiccated after the Pleistocene and further buried and deformed by tectonic activities. After desiccation, biological soil crusts might be established with nitrate produced, while biotic and atmospheric nitrate from the surrounding areas could also be leached to the newly-exposed lake sediments. The $\Delta^{17}$NO$_3$soil at the Sperry and Bully Hill sites were similar of 8.6 ± 0.2% and 7.3 ± 0.2%, respectively, while the Confidence Hills site averaged 11.8 ± 2.0%. These average $\Delta^{17}$NO$_3$soil values yield a MAP of 61.6 mm for Confidence Hills, 90.4 mm for Sperry, and 105.7 mm for Bully Hill. Magneto stratigraphy suggested that the Confidence Hills formation was dated at late Pliocene, 214–215 Ma (Pluhar et al., 1991), and continued into the early Pleistocene (1.8 Ma) while Sperry and Bully Hill were younger than 1.8 Ma (Wright, 1974). This indicates that the Mojave was dry at 2.15 Ma (MAP ~50 mm), before transitioning to a wetter climate around 1.8 Ma. This is consistent with the relatively drier late Pliocene and Early Pleistocene inferred from compilation of proxy-based reconstructions in southwestern US (Thompson, 1991; Winnick et al., 2012) and then increased desiccation in the Holocene from an intermediate wet period (Walvoord et al., 2003). The advantage of our $\Delta^{17}$NO$_3$soil proxy is its ability to quantify MAP during this dry-to-wet transition. The future improved positional age constraints on the Death Valley region may be used for higher resolution detection of MAP changes in southwestern US at the Pliocene–Pleistocene boundary.

$\Delta^{17}$NO$_3$soil of 4.6–14.4% (mean 9.9%) were determined by Rech et al. (2006) for the Barros Arana paleosol that was developed on basement rock or alluvial fan at elevations between 2200–3500 m along the southeastern margin of the Calama Basin of the Atacama (see sites in Fig. 1). The paleosol was estimated to have a minimum age of 9.4 Ma from ignimbrite dating. High concentrations of near-surface sulfates and chlorides and nitrates at depth as well as large vertical salt fractures were identified, which were not likely formed by capillary migration but the downward translocation of salt enriched dust into the profile during rare precipitation events (known as the “top–down” formation mechanism). Rech et al. inferred a MAP of 5–10 mm by comparing their $\Delta^{17}$NO$_3$soil values to a limited amount of pre-existing $\Delta^{17}$NO$_3$soil data. Our new MAP-$\Delta^{17}$NO$_3$soil proxy calibration, however, suggests that the largest $\Delta^{17}$NO$_3$soil value of 14.4% arose when the MAP was significantly higher, ~45 mm, not 5–10 mm. The lower $\Delta^{17}$NO$_3$soil values in Rech et al. (2006) were for deep NO$_3^-$, which might have been formed under even wetter climatic conditions. This reinterpretation is important because the onset of hyper-aridity in the Atacama was suggested to occur in middle Miocene or even later and should have been linked to the uplift of the Andean Cordillera (Hartley et al., 2005; Bussig and Riquelme, 2010). This reinterpretation points to a stepwise aridification rather than a single major climate shift (Reich et al., 2005).

NO$_3^-$ found in the Cambro-Ordovician Nubian sandstone aquifer system in the Hasouna area (Libya) had $\Delta^{17}$O values between 0.4 and 5% (Dietzel et al., 2014). The Nubian sandstone aquifer, one of the world’s largest paleo-groundwater aquifers (~2,000,000 km$^3$), is situated in the Eastern end of the Sahara Desert and consists of fractured quartzitic sandstone that spans 500–1500 m in thickness (see sites in Fig. 1). High contents of NO$_3^-$ (0.47–1.87 mM)
have been found in the Hasoua groundwater for decades, and stable isotope evidence suggested that this groundwater NO$_3^-$ was mainly solid NO$_3^-$ that were flushed from surface soil and not influenced by subsequent denitrification or mixing of in situ biotic NO$_3^-$ from nitrification in the aquifer owing to the limited organic matter and dissolved oxygen, respectively (Dietzel et al., 2014). $^{14}$C dating indicates this paleo-aquifer was recently recharged at 10 ± 3 ka, after which the recharge is slow under the present arid conditions (Edmunds and Wright, 1979). By using the MAP-$\Delta ^{17}$ONO$_3$soil model, the ground water $\Delta ^{17}$O values of 0.4–5.5‰ suggest that this soil-derived NO$_3^-$ originated when MAP was 139.3–200 mm, significantly higher than modern-time MAP in central Libya of ~10 mm (Mamtimim et al., 2011). This higher MAP rate before 10 ± 3 ka agrees with aquifer water isotopes that suggested the Hasoua Nubian Sandstone aquifer recharged during a cooler and more humid climate compared to the current conditions (Sonntag et al., 1978) but failed to infer the magnitude of change in regional MAP.

3.5. Predicting $\Delta ^{17}$ONO$_3$soil Values in other deserts across the globe and the US

The MAP-$\Delta ^{17}$ONO$_3$soil proxy calibration can also be used to predict $\Delta ^{17}$ONO$_3$soil values in mid-latitude deserts, by inverting the Eq. (2) to give $\Delta ^{17}$ONO$_3$soil = −8.28 ln(MAP) + 45.8. Global MAP data from http://www.worldclim.org (Hijmans et al., 2005) and high-resolution MAP in the US based on the PRISM model (http://www.prism.oregonstate.edu/) were used in geographic information system (GIS) to generate global middle-latitude and detailed southwestern US $\Delta ^{17}$ONO$_3$soil isoscapes (Fig. 1). The model predicts that near surface NO$_3^-$ deposits recently found in the Northwestern Badi region of Jordan (Al-Taami and Al-Qudah, 2013), where MAP is between 46 and 96 mm (Al-Ansari and Baban, 2005), would have $\Delta ^{17}$ONO$_3$soil between 8.0 and 14.1‰. Deposits of NO$_3^-$ found in Israel’s southern Negev Desert, which has MAP of ~65 ± 14 mm (Rosenthal, 1987), should have $\Delta ^{17}$ONO$_3$soil values in the range of 9.6–13.2‰. In many deserts, there are scant soil NO$_3^-$ concentration data and even less isotopic data. However, these regions (Australia, North Africa, and others) are likely to have shallow surface NO$_3^-$ deposits with $\Delta ^{17}$ONO$_3$soil values reflecting local MAP as predicted by the GIS model. Modern-time surface NO$_3^-$ analysis in these regions could be used to further refine the MAP-$\Delta ^{17}$ONO$_3$soil proxy calibration and test its theoretical underpinnings.

4. Conclusions

It has been demonstrated that there is a strong negative correlation between MAP and $\Delta ^{17}$ONO$_3$soil, and within the MAP range of 11.5–212 mm, $\Delta ^{17}$ONO$_3$soil can serve as an excellent MAP proxy with MAP = 233.8 • exp(−0.12 • $\Delta ^{17}$ONO$_3$soil) ($r^2$ = 0.87). The cause of this correlation is the differences in the relative importance of NO$_3^-$ deposited from the atmosphere and that produced in situ by microbial nitrification as precipitation varies. Nitrification becomes dominant when MAP exceeds 210 mm, but scarce when MAP < 11.5 mm. In paleosols and ancient groundwater that were not greatly influenced by aqueous activities and can be accurately dated using radioisotope or other chronologic proxies, the preserved NO$_3^-$ $\Delta ^{17}$O can be used as a paleoprecipitation proxy. The challenge then is finding where such deposits occur in geologic records. We also note that in modern-time soils, spatial and temporal changes in NO$_3^-$ $\Delta ^{17}$O values can be a tracer of biologic nitrogen turnover rates and used to assess nitrogen cycling dynamics.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2016.01.002.

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