

# Nitrate Deposits of the Atacama Desert: A Marker of Long-Term Hyperaridity

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**The nitrate deposits of the Atacama Desert are unique when one considers that in most surface environments nitrate is produced or consumed by biological processes and is easily washed away by rain. Nitrate deposits have puzzled geologists since Charles Darwin's visit to the Atacama in 1835 and several hypotheses have been proposed to explain their origin. Here, we review our current understanding of the nitrate deposits in the Atacama Desert and show that nitrate's primary origin is predominantly atmospheric. However, its massive accumulation and preservation specifically in Atacama is due to the serendipitous convergence of climatic, tectonic and hydrologic conditions that are unique to the Central Andes.**

**KEYWORDS:** Atacama Desert, salts, nitrate deposits, hyperaridity, atmospheric deposition

## INTRODUCTION

The geographic locations on Earth that today experience extreme dryness or hyperaridity all tend to have high rates of evaporation, high ultraviolet radiation, and extremely low annual precipitation. A prime example is the Atacama Desert of northern Chile, which makes up much of the dry margin of western South America (Fig. 1A). The Atacama Desert is located between the Central Andes and the Pacific Ocean and generally comprises three morphotectonic zones (Fig. 1A): the Coastal Cordillera, the Central Depression (or Central Valley), and the Western Cordillera. Of these, the Central Depression is the driest.

The hyperarid core of the Atacama Desert experiences negligible precipitation (<2 mm per year) (Fig. 1A, 1B); scattered rainfall events may occur only once per decade (Houston and Hartley 2003). This unique climate is the result of the confluence of the subtropical high-pressure zone, the cold Humboldt coastal ocean current, offshore winds, and the "rain shadow effect" of the Andes range to the east (Houston and Hartley 2003). Precipitation along the eastern margin of the Atacama Desert is associated with the South American summer monsoon, where air masses spill over the Central Andes and generate precipitation at elevations above 2,800 m but do not cause rainfall in the central Atacama Desert (Fig. 1A).

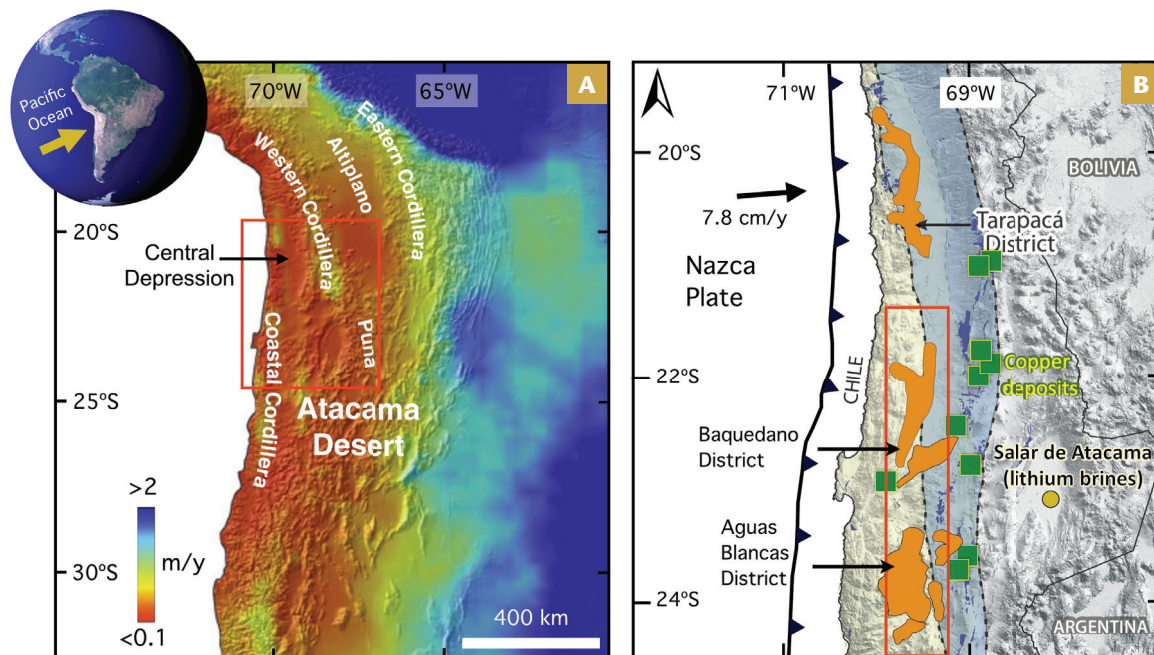
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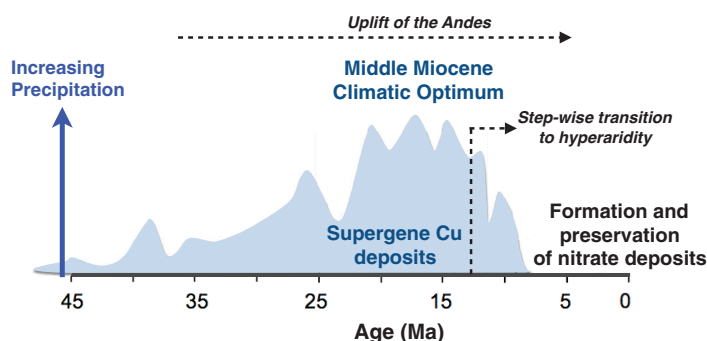
Although the almost total lack of precipitation is the most striking characteristic of the Atacama Desert, previous studies have revealed a wetter past (Oerter et al. 2016 and references therein). The estimated ages for the onset of hyperaridity range from the Late Paleogene through the Pleistocene, although the exact timing is still debated. Geochronological, sedimentological, and geomorphological evidence point to a long history of semi-arid climate from ~45 Ma (Middle Eocene) to 15 Ma (Middle Miocene), followed by a stepwise aridification (Reich et al. 2009) (Fig. 2). Several

authors have proposed predominantly hyperarid conditions since ~12 Ma (Late Miocene), most likely reflecting the growth of the Andes Mountains above a climate threshold (e.g. Rech et al. 2006; Jordan et al. 2014). This view is confirmed by Sun et al. (2018) who focused on the Atacama Gravels, a Miocene-age thick alluvial sedimentary sequence containing a continuous (but often overlooked) geochemical "archive" that records critical climatic transitions. Argon-argon dating of volcanic ash layers within the Atacama Gravels, combined with  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ , and  $\delta^{34}\text{S}$  analyses of soluble salts, show that hyperarid conditions in the Atacama Desert prevailed at least since 9.5 Ma (Late Miocene), and possibly as far back as the Middle Miocene. This evolution, as illustrated in Figure 2, shows a strong feedback between climate and tectonics that is specific to the way that the rapidly uplifting Central Andean convergent margin (Schildgen and Hoke 2018 this issue) experienced pronounced desiccation between ~20 Ma and 10 Ma (i.e. a decrease in precipitation from >200 mm/y down to <20 mm/y). This led to the development of an exclusively endorheic drainage system [an enclosed basin system that receives water but does not have any way for that water to flow out to other bodies of water] that is recharged in the High Andes, where increased elevation creates favorable conditions for increased groundwater flow and mineral precipitation towards the Central Valley (Pérez-Fodich et al. 2014). The sum of these tectonic, climatic, and hydrologic characteristics has shaped, in a singular manner, the supergene metallogenesis of the Atacama Desert. The preservation of these specific supergene deposits is due to the hyperaridity that is the principal factor in this region becoming the world's greatest producer of commodities such as nitrate, iodine, copper, and lithium (Reich et al. 2015) (Fig. 1B).



**FIGURE 1** Maps of the Central Andes of South America, focusing on the Atacama Desert. (A) Digital elevation map with principal morphotectonic provinces of the southern Central Andes labelled. The present-day rainfall patterns are shown with color-coded shading (precipitation in meters per year, m/y). The red rectangle shows the area depicted in FIGURE 1B. MODIFIED FROM MULCH ET AL. (2010). (B) Map of the nitrate deposits of the Atacama Desert displayed on a digital elevation model of northern Chile. The hyper-arid core of the Atacama Desert is shown in light yellow; the

elongate red rectangle shows area of extreme hyperaridity (rainfall  $<3$  mm/y). Three main nitrate districts are shown in orange: Tarapacá, Baquedano, and Aguas Blancas. The location of ten major porphyry copper deposits (green squares) and of lithium-brine resources (yellow circle) in the Salar de Atacama are also indicated. The paleogeographic reconstruction of the Andean Basin during the Jurassic is shown in light blue (zone between the dark dashed lines); the distribution of Late Jurassic marine sedimentary outcrops is indicated in dark blue. MODIFIED FROM PÉREZ-FODICH ET AL. (2014).



**FIGURE 2** Chronology of the precipitation history of the Atacama region during the last ~45 million years, and its relation to the development of supergene oxidation of copper deposits and the formation of nitrate deposits. Radiometric Ar–Ar data for supergene copper minerals define an extended period between ~45 Ma to 9 Ma, with a peak at ~21–14 Ma that is dominated by downward circulation of meteoric water under semi-arid to arid climate conditions (precipitation rate  $>100$  mm/y). A decrease in precipitation at ~12–9 Ma marks the onset of hyper-arid climate conditions (precipitation rate  $<1$ –4 mm/y). SHADED SPECTRUM TAKEN FROM REICH ET AL. (2009) AND REFERENCES THEREIN.

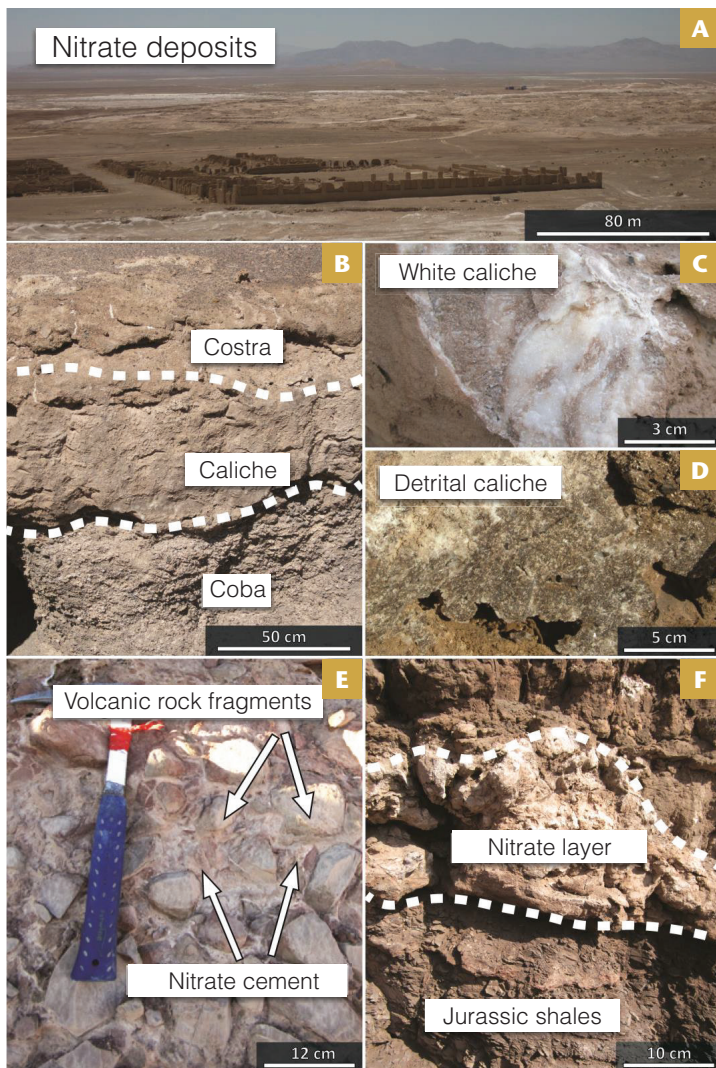
## GEOLOGICAL AND ECONOMIC SIGNIFICANCE OF NITRATE DEPOSITS

The extreme aridity of the Atacama Desert has resulted in some unusual characteristics. Geochemical analyses of soils indicate high abundances of salt minerals such as sulfates, chlorides and carbonates, with extremely low moisture and organic carbon content, which are considered to be at the dry limit for life. However, it is the accumulation and preservation of a massive amount of soluble salts of nitrate in soils that makes the Atacama Desert a unique

place. The nitrate (or, more loosely, “caliche”) deposits of the Atacama are by far the largest nitrate accumulations in the world and make up an almost continuous ~700 km long by ~20 km wide belt on the eastern side of the Coastal Cordillera (FIG. 1B). They are also unusual in containing abundant halogen and transition-metal oxyanions such as iodates ( $\text{IO}_3^-$ ), perchlorates ( $\text{ClO}_4^-$ ), and chromates ( $\text{CrO}_4^{2-}$ ), hosted by a complex mineral layer of ~0.2–3 m thick composed of nitrates, sulfates, and chlorides (FIG. 3). These unique features have puzzled geologists ever since Charles Darwin’s visit to the Atacama in 1835; several hypotheses have been proposed to explain their origin, including atmospheric, terrestrial, and marine sources (Claridge and Campbell 1968; Ericksen 1981; Böhlke et al. 1997; Oyarzun and Oyarzun 2007). Most recent models allude to Ericksen’s seminal work, proposing a multisource genetic model that involves a combination of atmospheric deposition, eolian contribution, and near-surface mineral precipitation driven by groundwater (Pérez-Fodich et al. 2014; Álvarez et al. 2015).

Sodium nitrate, commercially known as Chile or Peru saltpeter or “salitre” [the mineral nitratine,  $\text{Na}(\text{NO}_3)$ ], was central to the manufacture of gunpowder and fertilizers during the 1800s and early 1900s. To paraphrase Wisniak and Garcés (2001), the history of the nitrate industry in Chile is a fascinating example of human effort and the never-ending saga of one technology replacing another. The exploitation of the “salitre” started in 1810, and between 1830 and 1930 the Chilean deposits were the world’s prime source of nitrogen for explosives, fertilizers, and a variety of chemicals (Wisniak and Garcés 2001). The commercial importance of Chilean saltpeter decreased steadily after 1913 due to the development of the Haber–Bosch process, a German-invented process to commercially produce ammonia which really took off in the 1920s and 1930s. After 1930, Chilean production of the nitrates declined





**FIGURE 3** Occurrence and types of nitrate deposits in Chile. (A) Abandoned nitrate mine in the Aguas Blancas district south of the city of Antofagasta. Nitrate fields are visible as white-colored soil material. (B) Representative nitrate-rich soil profile. **TOP:** “Costra”, thick horizon (~50 cm to 2 m), composed of cemented gypsum and anhydrite. **CENTER:** “Caliche”, firmly cemented horizon below the costra that varies from 1 m to 5 m in thickness and contains nitrate and other soluble salts. **BOTTOM:** “Coba”, loose, unconsolidated soil. (C) White nitrate “caliche”, which includes pure soluble salts. (D) Detrital nitrate “caliche”, exemplified by salts plus lithic fragments. (E) Nitrate cement, in the form of salt impregnations in porous rocks, associated with volcanic rock fragments. (F) Nitrate as layers (sometimes as veins) above Jurassic shale bedrock. PHOTOS: FERNANDA ÁLVAREZ AND MARTIN REICH.

to the extent that by 1960 most of the mining complexes became abandoned ghost towns (FIG. 3A). However, since about 2010, the nitrate deposits of the Atacama have seen a resurgence of interest due to their iodine content, iodine now being a commodity that has increased in price due to new technological and medical developments. Currently, the nitrate deposits of the Atacama dominate the global iodine market.

### ACCUMULATION OF NITRATE IN DESERTS

Nitrate ( $\text{NO}_3^-$ ) can be produced naturally via microbial nitrification (ammonia oxidation) and by atmospheric chemistry, i.e. the oxidation of nitrogen oxides or  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ). Nitrate salts are all highly soluble, rendering massive deposits rare at Earth's surface. In places of low total annual precipitation, atmospheric wet and dry deposi-

tions of nitrate can accumulate at the surface. If the surface is old enough, a significant quantity of nitrate can form. Because nitrate salts are more soluble than sulfate salts, peak nitrate concentration is usually found below the peak sulfate concentration on a surface soil profile at a hyperarid site where downward leaching by occasional wet events is the only significant hydrological process. Such “top down” profiles are common in soils of the Atacama Desert and of the McMurdo Dry Valleys in Antarctica (Lybrand et al. 2016). Conversely, in a generally arid setting that is occasionally supplied by ample groundwater or floodwater, such as arid valley floors surrounded by high-elevation mountains, strong evaporation and capillary force can result in the accumulation of more soluble salts, such as nitrate, on the upper part, while the less soluble sulfate tends to concentrate in the lower part of a soil profile. Such “bottom up” profiles are common in continental interior valleys or basins such as Death Valley in California (USA) or the Turpan–Hami Basin in the Gobi Desert (China) (Qin et al. 2012; Lybrand et al. 2016).

However, “bottom up” profiles locally occur in the Atacama Desert because of an intermittent wet climate in the past and because deep groundwater can make its way to the surface, as evidenced by studies of the iodine and chromium components in nitrate deposits (Pérez-Fodich et al. 2014; Álvarez et al. 2015). Cosmogenic iodine ( $^{129}\text{I}$ ) and stable chromium isotope ( $\delta^{53/52}\text{Cr}$ ) data of nitrates point toward an important role played by groundwater during leaching and transport of the exotic I and Cr chemical components of the Atacama nitrates. The isotopic signature of I in the nitrates ( $^{129}\text{I}/\text{I} \sim 150\text{--}600 \times 10^{-15}$ ) shares similarities with deep sedimentary (marine) pore waters and shales, deviating significantly from atmospheric iodine ( $^{129}\text{I}/\text{I} \sim 1,500 \times 10^{-15}$ ). Furthermore, the positive and highly fractionated  $\delta^{53/52}\text{Cr}$  values (+0.7‰ to +3‰) are indicative of intense Cr redox cycling via groundwater transport. The cited studies point, respectively, to leaching of I and oxidized Cr from sedimentary sequences and volcanic rocks in the High Andes that were then transported westwards along with other soluble chemical species to the Central Valley by groundwater. The precipitation of iodates and chromates was favored downstream in the Central Basin by an “impermeable” barrier effect of the eastern slope of the Coastal Range that allowed saline and reduced groundwater to rise, evaporate, and oxidize in the presence of a continuous, dry-deposition flux of atmospheric nitrate (Pérez-Fodich et al. 2014).

### SOURCES OF NITROGEN AND OXYGEN IN NITRATE

After decades of studies, it has become clear that on arid and hyperarid surfaces  $\text{NO}_3^-$  ultimately derives exclusively from atmospheric chemistry. Atmospheric  $\text{NO}_3^-$  accumulates on the surface via wet and dry atmospheric deposition and can be altered and transported by wind, ephemeral lake water, groundwater, floodwater, or capillary forces during evaporation. The only significant alteration process is microbial utilization of nitrate as an electron acceptor in some oxygen-poor solutions, or as a source of metabolic N. Some degree of nitrification is expected when reduced nitrogen species, such as nitrite ( $\text{NO}_2^-$ ), are reoxidized back to  $\text{NO}_3^-$ . These processes result in changes to both concentration and isotope composition of the original atmospheric nitrate to form what is termed “biologically altered nitrate”. Because biological nitrate alteration requires certain levels of moisture or water content to permit microbial activity, the relative content of biologically altered nitrate is often a good indicator of present or past climate conditions in an arid region. Chemically, atmospheric nitrate and biologically altered nitrate are indistinguishable. Isotopically,

however, both nitrogen ( $\delta^{15}\text{N}$ ) and oxygen ( $\delta^{18}\text{O}$ ) isotope compositions carry information on the source and formative reaction paths. Comprehensive reviews on the stable isotope compositions of nitrate and perchlorate in deserts are by Jackson et al. (2015) and Lybrand et al. (2016). Below, we highlight these studies from a different perspective.

### Nitrogen ( $\delta^{15}\text{N}$ ) Isotope Signature

The  $\delta^{15}\text{N}$  of nitrate often reflects its source and the postformational processes of that nitrate. Because atmospheric nitrate is generated by the progressive oxidation of  $\text{NO}_x$  initially derived from air  $\text{N}_2$ , which by definition has a  $\delta^{15}\text{N}$  of 0 per mil (‰), atmospheric nitrate appears to have an initial  $\delta^{15}\text{N}$  very close to zero. If the initial nitrate is deposited in or transported to wet environments and becomes reduced by microbes (i.e. denitrifiers), then the leftover nitrate's  $\delta^{15}\text{N}$  would increase up to  $\sim 28\text{‰}$ , as seen in the Turpan–Hami Basin of northwestern China (Qin et al. 2012). In the Atacama Desert, however, we see the  $\delta^{15}\text{N}$  of nitrate ranging from  $-4.9\text{‰}$  to  $+4.1\text{‰}$  (Böhlke et al. 1997; Michalski et al. 2004; Melchiorre et al. 2018) (FIG. 4A), indicating a minimal, or much reduced, rate of consumption of nitrate by microbes. This difference may suggest that there are settings, such as ephemeral lakes with algal blooms, where the ultimate denitrification product is  $\text{N}_2$  which escapes from the system, as in the case of the Turpan–Hami nitrates.

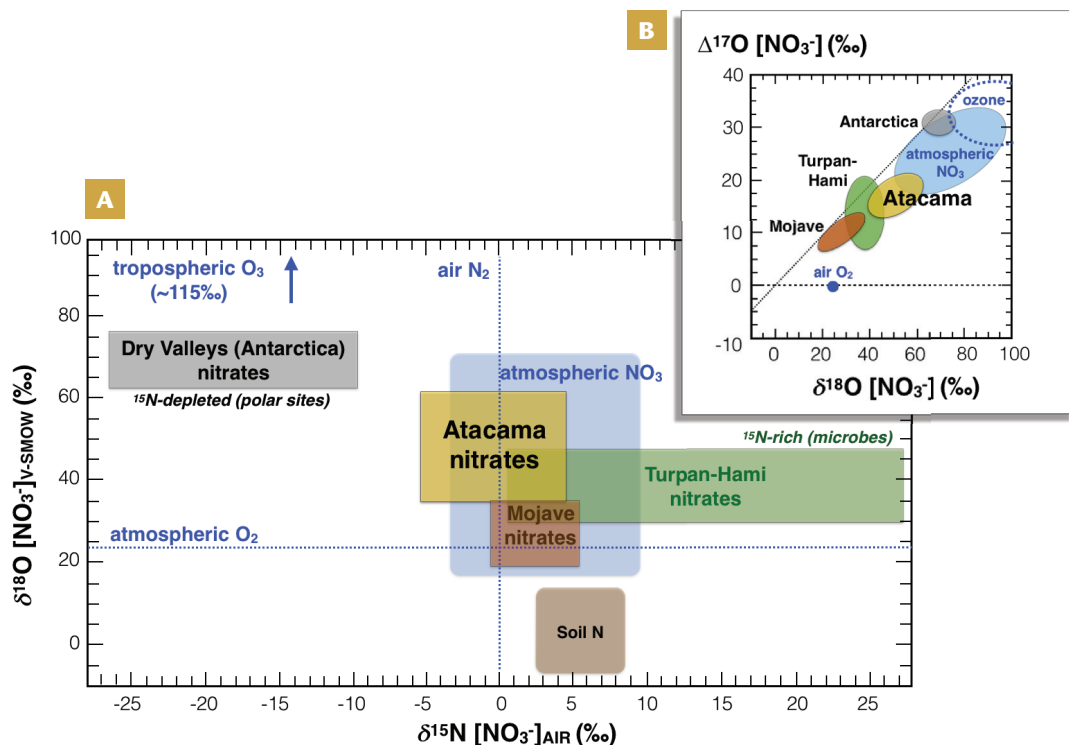
Microbial nitrification processes can also produce nitrate. Its precursor N compounds, such as air  $\text{N}_2$  and organic-bound N, determine the  $\delta^{15}\text{N}$  of this variety of nitrate, usually in the range of  $0\text{‰}$  to  $5\text{‰}$ . However, we expect microbial nitrification from air  $\text{N}_2$  and organic N to be negligible in arid surface soil profiles. Even in shallow groundwater, nitrification is unlikely to be important due to the oxidizing and high  $[\text{NO}_3^-]$  conditions and the lack of organic matter.

### Oxygen Isotope ( $\delta^{18}\text{O}$ ) Signature

Oxygen in atmospheric nitrate comes mostly from ozone ( $\text{O}_3$ ), with a small fraction derived from atmospheric water (Michalski et al. 2003, 2014). Tropospheric bulk ozone has

a  $\delta^{18}\text{O}$  value of  $\sim 115\text{‰}$  (Vicars and Savarino 2014), hence, atmospheric nitrate tends to have very positive  $\delta^{18}\text{O}$  values. These values can be up to  $61\text{‰}$  in the Atacama Desert,  $47\text{‰}$  in the Turpan–Hami Basin, and  $76\text{‰}$  in the Dry Valleys of Antarctica (Michalski et al. 2004, 2005; Qin et al. 2012) (FIG. 4A). Even though the relative contribution of  $\text{O}_3$  and  $\text{H}_2\text{O}$  signatures to atmospheric nitrate  $\delta^{18}\text{O}$  varies with meteorological conditions or season, this variability or cyclicity occurs frequently over short timescales in nature, rendering the geological record of atmospheric nitrate uniform in both  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ . Like  $\delta^{15}\text{N}$ , the measured  $\delta^{18}\text{O}$  value of desert nitrate can be changed from that of the initial atmospheric nitrate. Microbial denitrification processes can also alter the  $\delta^{18}\text{O}$  of the leftover nitrate. However, there is a distinction here. The  $\delta^{15}\text{N}$  of the leftover nitrate can only increase due to the preferential reduction of  $^{14}\text{N}$ -nitrate over  $^{15}\text{N}$ -nitrate, and, most importantly, due to the lack of other exchangeable N-bearing species in the solution. Conversely, for the  $\delta^{18}\text{O}$  there is an overwhelming exchangeable O-bearing species in solution, namely  $\text{H}_2\text{O}$ . Oxygen isotope exchange between intermediate N-species, such as  $\text{NO}_2^-$ , and water may overwrite all other isotope signals during microbial denitrification (Casciotti et al. 2009). Thus, the leftover nitrate's  $\delta^{18}\text{O}$  value approaches an equilibrium value set by that of local meteoric water. The consequence of microbial denitrification and nitrification cycling of atmospheric nitrate is, therefore, a decrease of the leftover nitrate's  $\delta^{18}\text{O}$  because the  $\delta^{18}\text{O}$  of local water (mostly snowmelt) in the Atacama region is rather negative. The overall trajectory in  $\delta^{18}\text{O}$ – $\delta^{15}\text{N}$  space for nitrate experiencing variable degrees of biological alteration depends on linked isotopic effects of both nitrogen and oxygen. Currently, a well-controlled laboratory or field-sampling study targeting biological nitrate alteration in hyperarid desert conditions is lacking. The molecular-level mechanism of N and O isotope behaviors during biological nitrate alteration are less well-known than for the parallel case of microbial sulfate alteration (Antler et al. 2017).

**FIGURE 4** Oxygen and nitrogen stable isotope signatures of desert nitrates worldwide. **(A)** Variations in  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  from different nitrate sources. These include “caliche-type” desert nitrate from the Atacama Desert (Chile) (yellow), the Mojave Desert (USA) (red), the Turpan–Hami Basin (China) (green), the Antarctica Dry Valleys (grey); also shown are soil nitrate (brown) and atmospheric nitrate (blue). **(B)** The  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  isotopic variations of nitrate in samples from the same materials as in FIGURE 4A, including ozone. The desert nitrate data show  $^{17}\text{O}$  anomalies, which are interpreted to indicate varying degrees of alteration of atmospheric nitrate by microbial activities and varying mixtures of atmospheric nitrate and terrestrial nitrate produced by microbial nitrification. Abbreviation VSMOW = Vienna Standard Mean Ocean Water. DATA FROM BÖHLKE ET AL. (1997), MICHALSKI ET AL. (2004, 2005), QIN ET AL. (2012), VICARS AND SAVARINO (2014), AND MELCHIORRE ET AL. (2018).





## THE $^{17}\text{O}$ ANOMALY: A FINGERPRINT OF ATMOSPHERIC NITRATE

Although the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of the Atacama Desert nitrates can provide insights into their origin, mixing, and subsequent alteration processes, there are still many uncertainties that are unresolvable by two isotope parameters alone. For example, high  $\delta^{18}\text{O}$  values ( $>30\text{‰}$ – $40\text{‰}$ ) are a characteristic of atmospheric nitrate (Fig. 4A), yet moderately high  $\delta^{18}\text{O}$  ( $\sim 20\text{‰}$ – $30\text{‰}$ ) can be achieved by biological alteration or by mixing biologically altered nitrate with atmospheric nitrate. Once  $\delta^{18}\text{O}$  is measured, the corresponding  $\delta^{17}\text{O}$  value of most oxygen-bearing compounds on Earth is rarely measured because the  $\delta^{17}\text{O}$  can be calculated assuming a mass-dependent fractionation. However, atmospheric ozone, both in the troposphere and the stratosphere, is an exception to this rule. Ozone carries a large, non-mass-dependent  $^{17}\text{O}$  enrichment. In this case, the  $^{17}\text{O}$  anomaly allows us to examine, independently, the source of nitrate and to quantify the role of biological alteration. The  $^{17}\text{O}$  anomaly is recorded in terms of  $\Delta^{17}\text{O}$ , defined as  $\Delta^{17}\text{O} = \delta^{17}\text{O} - C \times \delta^{18}\text{O}$ , where  $C$  is a reference slope with a value of 0.5305 or 0.52, or other choices (Fig. 4B). The tropospheric bulk  $\text{O}_3$  and  $\text{O}_3$ 's transferrable O have  $\Delta^{17}\text{O}$  values of  $\sim 26\text{‰}$  and  $\sim 39\text{‰}$ , respectively (Vicars and Savarino 2014). Atmospheric nitrate formation chemistry itself may not be non-mass-dependent (Michalski 2003). However, nitrate oxygen derives mostly from ozone, which results in atmospheric nitrate being highly enriched in  $^{17}\text{O}$ , as high as that of the transferrable ozone oxygen. Atacama nitrate has a highly positive  $\Delta^{17}\text{O}$  value, ranging from  $14\text{‰}$  to  $21\text{‰}$  (Michalski et al. 2004) (Fig. 4B). These large and positive  $\Delta^{17}\text{O}$  values eliminate any doubt as to the atmospheric origin of this oxygen, especially when considering that nitrate generated by microbial nitrification has a  $\Delta^{17}\text{O}$  close to zero when the source of the nitrogen is air  $\text{N}_2$  or organic N.

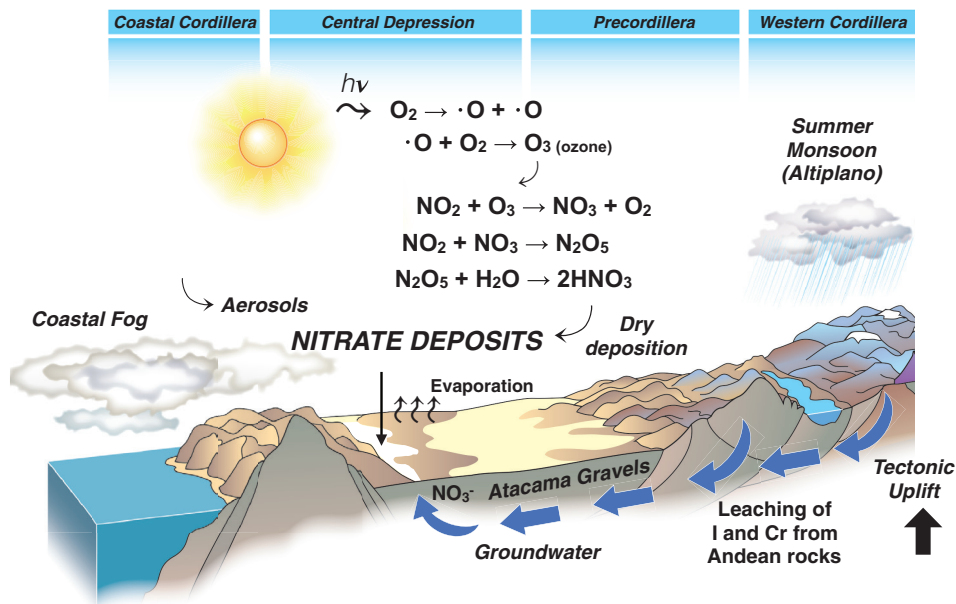
The only processes that can potentially remove the  $^{17}\text{O}$  anomaly or reduce nitrate's  $\Delta^{17}\text{O}$  value is oxygen isotope exchange associated with denitrification of the atmospheric nitrate in solution. During microbial denitrification, the oxygen in the leftover nitrate will experience variable degrees of exchange with the  $\text{H}_2\text{O}$  oxygen in solution, a process most likely catalyzed by enzymes. Therefore, in environments where lake water, groundwater, or floodwater is present, microbial denitrification can reset atmospheric nitrate's highly positive  $\Delta^{17}\text{O}$  value to zero. The terms "biological nitrate" or "biogenic  $\text{NO}_3^-$ " are often used to refer to nitrate that has a  $\Delta^{17}\text{O} \approx 0$ . This is inaccurate and potentially misleading. Atmospheric nitrate with a positive  $\Delta^{17}\text{O}$  can be reduced by microbial activities, and the leftover nitrate can have a lower value than the initial  $\Delta^{17}\text{O}$  value due to variable degrees of nitrite–water oxygen exchange. Thus, biologically altered nitrate need not have a zero value of  $\Delta^{17}\text{O}$ .

## NITRATE DEPOSITS: THE UNIQUENESS OF THE ATACAMA DESERT

Over the years, proposed origins for the Atacama Desert nitrate deposits have ranged from sea-spray, fog, and/or nitrogen fixation by volcanic lightning. These are all valid sources of precursor  $\text{NO}_x$  for the subsequent atmospheric oxidation to nitrate by  $\text{O}_3$ . Highly positive  $\Delta^{17}\text{O}$  values

alone require that the chemical origin must involve atmospheric  $\text{O}_3$  (Fig. 4B). However, sea-spray, fog, or volcanism cannot produce nitrate with anomalous  $^{17}\text{O}$ . Recently, Campisi (2016) raised the possibility that the observed  $^{17}\text{O}$  anomalies in Atacama nitrate can be partially or entirely produced by diffusional processes during nitrate mineral growth and reprecipitation (Ostwald ripening). The lack of such anomalies in most other oxygen-bearing minerals, such as carbonates and silicates in the Atacama Desert or nitrate in wetter places on Earth, dismisses this possibility.

The initial atmospheric origin of the nitrate, the occurrence of massive nitrate deposits, and the absence of such deposits in most other deserts, attests to the Atacama Desert being arid or hyperarid for at least the last 10 million years (Sun et al. 2018). Thus, we have come a full circle back to the original hypothesis of Claridge and Campbell (1968), and later also by Ericksen (1981): namely, that anywhere on Earth experiencing similar long-term arid conditions would be expected to have similarly massive nitrate deposits (Fig. 5). However, as no two deserts are alike, the quantity and the physical, chemical, and stable isotopic characteristics of any highly soluble salt deposits will vary. The Atacama Desert nitrate  $\delta^{15}\text{N}$  is close to  $0\text{‰}$ , while the equivalent Antarctic Dry Valleys' nitrate has an extremely negative  $\delta^{15}\text{N}$  value down to  $\sim -26\text{‰}$  (Michalski et al. 2005). This difference may be due to secondary processes, including photolytic nitrate loss, local oxidation of  $\text{NO}_x$ , and nitrate redeposition in snowpack, as well as nitrate sedimentation from polar stratospheric clouds above Antarctica (Erbland et al. 2015). However, a direct link has not been fully established. Another unexplained



**FIGURE 5** Conceptual model for nitrate deposition in the Atacama Desert of northern Chile. This west–east section shows the main morphotectonic units and the processes involved in forming nitrate deposits. Atmospheric nitrate ( $\text{NO}_3^-$ ) is produced by photochemical reactions involving  $\text{NO}_x$  compounds (e.g.  $\text{NO}_2$ ) and ozone ( $\text{O}_3$ ) that generate gas-phase nitric acid ( $\text{HNO}_3$ ). The  $\text{HNO}_3$  then reacts on aerosol surfaces to form particulate nitrate, which accumulates on the ground surface and mixes with microbial  $\text{NO}_3^-$  carried by groundwater. The trigger for the formation of the Atacama's extensive nitrate deposits was the concomitant increase in tectonic uplift and in desiccation, which allowed not only the long-term accumulation and preservation of atmospheric nitrate but also the precipitation of transported species (iodine, chromium) from ascending groundwater in the Central Depression due to evaporation. MODIFIED FROM PÉREZ-FODICH ET AL. (2014).

peculiarity is that the Atacama Desert and the McMurdo Dry Valleys have similar nitrate concentrations, whereas perchlorate content is, on average, one order of magnitude higher in the Atacama Desert (Jackson et al. 2015). These and other differences, including the anomalous iodine and chromium enrichment of the nitrates (Pérez-Fodich et al. 2014; Álvarez et al. 2015), point to factors other than the presence and longevity of aridity that are making important contributions to salt composition and quantity (Fig. 5). These other factors might include the source rocks in the High Andes and groundwater geochemistry, highlighting the need for future research in these areas.

The extreme climate of the Atacama Desert has contributed to several unique features, including the formation and preservation of massive nitrate deposits. The timing, history, and cause(s) of the climatic transition from semi-aridity to aridity, and finally to current hyperaridity, are still a matter of debate among geoscientists. However, there is agreement that the massive accumulation of nitrate in the Atacama Desert represents an unusual convergence of common physical and chemical processes with a geologic,

tectonic, hydrologic, and climatic setting that is specific to this region (Fig. 5). And because these nitrate deposits formed during a protracted period spanning ~10 million years, they preserve valuable information not only about the climatic history of the region but also to the geological evolution of the Central Andes themselves.

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