SOLVING THE MYSTERY OF THE ATACAMA NITRATE DEPOSITS

Student Author

Ji-Hye Seo is a junior in the Department of Chemistry at Purdue University. She is fascinated by the unique occurrence of massive nitrate deposits in the Atacama Desert, Chile. This fascination initiated her exploration into the origin of these deposits using geochemical and isotopic analysis with Dr. Greg Michalski and his Ph.D. student, Fan Wang, in 2010. To further her research, Seo is currently developing mineralogical methods to investigate the evolution history of nitrate minerals in the Atacama. Since the Atacama is an excellent Martian analog, she is also looking forward to the future implications of her research into Mars.

Faculty Mentor

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Abstract

The Atacama Desert, Chile, one of the oldest and driest deserts on Earth, is unique because it contains the largest known nitrate deposits in the world. The origin of these nitrate deposits has been a mystery since their discovery in the 1800s. There are two possible sources of natural nitrate: microbiological processes and photochemical reactions. The majority of material on Earth follows mass-dependent fractionation between stable oxygen isotopes with the abundance of ^{17}O (denoted by δ) as half that of ^{18}O . This relationship is quantified by $\Delta^{17}\text{O} = \delta^{17}\text{O} - \frac{1}{2} \delta^{18}\text{O}$, where $\Delta^{17}\text{O} = 0$ for most terrestrial material, including microbial nitrate. Photochemically produced atmospheric nitrate, however, has a large mass-independent ^{17}O anomaly with $\Delta^{17}\text{O}$ values of $\sim 23\text{‰}$. Therefore, a novel stable oxygen isotope analysis of nitrate was performed on soils collected from two Atacama sites to delineate between the two main possible sources of nitrate. The observed $\Delta^{17}\text{O}$ values of 17.1–20.4‰ at both sites indicate the Atacama nitrate is mainly from the atmosphere, suggesting that microorganisms are severely limited by hyperaridity. However, small nitrate $\Delta^{17}\text{O}$ variations with depth suggest the relative importance of nitrification may have varied in the past, which is probably related to climate-controlled water availability. Both isotopic and geochemical data suggest that the hydrological history differed at the two sampling sites, resulting in different depth profiles of soluble ions and isotopic signals. Overall, atmospheric inputs and water activities play pivotal roles in the Atacama nitrate deposit formation, providing an important basic insight into the nitrogen cycle in the hyperarid regions.

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Keywords

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SOLVING THE MYSTERY OF THE ATACAMA NITRATE DEPOSITS:

The Use of Stable Oxygen Isotope Analysis and Geochemistry

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INTRODUCTION

History of Atacama nitrate deposits

The Atacama Desert in northern Chile is known to contain the largest nitrate deposits in the world. The nitrates were extensively mined in the early 1800s, and nitrate ore was exported to Europe and the U.S. as agricultural fertilizer and to make gunpowder and explosives. Just like oil reserves in the modern era, the high demand for nitrate and the Atacama's nitrate monopoly fueled the region's economic and geopolitical development during the 1800s (McConnell, 1935). Bolivia, Peru, and Chile all once owned parts of the most valuable nitrate deposits, but disputes over their ownership led to hostilities and resulted in the War of the Pacific in late 1800s. The war lasted five years and ended with a decisive victory for Chile. Peace treaties were made between the three countries; however, there were still boundary disputes over the nitrate deposits after fighting ceased. Later, the Treaty of Peace and Friendship of 1904 between Peru and Chile was established and gave Chile control of the entire Atacama Desert (Bonilla, 1978). With the increasing global demand for nitrate, the Chilean nitrate mining industry flourished and was extremely profitable for many decades. During this period, most Chilean income came from the nitrate mining industry, making it the pillar of the Chilean economy.

Chile's nitrate mining boom came to an abrupt halt in the early 1900s (McConnell, 1935). Blockades prevented Germany from importing the Chilean nitrate needed for

Figure 1. Field photos of typical rugged surface in the Atacama (A) and ruins of old nitrate mining industries (B).

Figure 2. Location map of the Chilean Atacama Desert (modified from Rech, Quade, & Hart, 2003).

gunpowder production during World War I, leading to the invention of a synthetic nitrate process (Haber-Bosch) by German scientists. The Haber-Bosch process converts nitrogen and hydrogen gases into ammonia and was an important breakthrough in chemical synthesis (Erisman, Sutton, Galloway, Klimont, & Winiwarter, 2008). The resulting ammonia was then oxidized to make nitrate, enabling nitrate-importing countries to produce nitrate from the atmosphere. Consequently, the sharp decrease in natural nitrate demand led to a massive economic breakdown in Chile that was known as the Nitrate Crisis, and the nitrate mining industry eventually collapsed in the 1930s (McConnell, 1935). Now the Atacama Desert has only a few operational nitrate mines and is littered with the ruins of the old nitrate works (see Figure 1).

The origin of Atacama nitrate deposits

Why are the only known massive nitrate deposits located in the Atacama? In most regions on Earth, nitrate is scarcely retained in soil because its high solubility causes it to leach into groundwater, rivers, lakes, or the ocean. The Atacama Desert, however, is unique because its hyperarid climate minimizes leaching losses and preserves nitrate (Ericksen, 1983). The hyperarid climate of the desert comes from its geographical location. The desert is located between the Chilean Coast Range and the Andes Mountains (see Figure 2). These two mountain ranges create rain shadows, preventing most of the moisture from the Pacific Ocean and Amazon basin from reaching the desert (Houston & Hartley, 2003). Also, the cold Peru Current causes condensation of low clouds, dew, and fogs in the lower atmosphere, limiting rainfall coming from the Pacific Ocean (Cereceda et al., 2002; Garreaud & Rutllant, 2003). These effects limit annual precipitation in the Atacama to less than 2 millimeters (Ericksen, 1983). This is extremely dry. By comparison, Indiana's annual precipitation averages 1,041 millimeters (Baker, 2011). Remarkably, there are some locations in the Atacama where rainfall has not been recorded for centuries. These conditions have earned the Atacama the title of the "Driest Place on Earth" (History Channel, 2008).

While the hyperaridity stabilizes the nitrate, the origin of the nitrate itself has been a mystery for more than two centuries. Many studies have speculated that the nitrate deposits could be from ancient plant materials, precipitation of groundwater (saline water), or the oxidation of nitrogen gases from buried magma (Ericksen, 1983).

However, the leading theory for decades suggested that nitrate was formed by bacteria through nitrification. Nitrification is the process in which bacteria convert ammonia to nitrate, and it is the main mechanism for the natural production of nitrate in soils throughout the world. The decomposition of seaweed or bird guano (excrement) may have provided the ammonia needed for nitrification (Erickson, 1983). However, this theory has some drawbacks: the sources of ammonia only occur in specific locations, and the extremely dry conditions of the Atacama Desert limit biological activity. A competing theory on the origin of nitrate ore is the deposition of nitrate. Nitrate is produced in the atmosphere when nitrogen oxides, produced by lightning, are oxidized through chemical reactions into nitrate. This nitrate is then deposited to the ground as dust (dry deposition) or rain (wet deposition). In the case of the Atacama, dry deposition dominates because there is little wet deposition in the hyperarid setting.

Stable isotope techniques

Stable isotope analysis has proven to be a powerful technique that can be used to trace sources of compounds such as nitrate (Kendall and McDonnell, 1998). Oxygen has three stable isotopes (^{16}O , ^{17}O , and ^{18}O), and the majority of material on Earth containing oxygen follows the proportionality: $\delta^{17}\text{O} \approx \frac{1}{2} \delta^{18}\text{O}$, known as mass-dependent isotopic fractionation (Young, Galy, & Nagahara, 2002). The δ denotes the difference in the isotope abundance ratio ($^{17}\text{O}/^{16}\text{O}$ or $^{18}\text{O}/^{16}\text{O}$) of a sample relative to an accepted reference material. This difference is reported in parts per thousand or permil (‰). Atmospheric nitrate, produced naturally by lightning and through human activities such as fossil fuel burning, however, has a large mass-independent isotope anomaly. This anomaly is a ^{17}O excess that is quantified by $\Delta^{17}\text{O} = \delta^{17}\text{O} - \frac{1}{2} \delta^{18}\text{O}$ (Miller, 2002), which ranges from 20-30‰ annually averaging ~23‰ for atmospheric nitrate. Conversely, terrestrial nitrate from nitrification obeys the mass-dependent isotope fractionation with $\Delta^{17}\text{O}=0$ (Michalski, Scott, Kabiling, & Thiemens, 2003). Therefore, the isotopic anomaly signature ($\Delta^{17}\text{O}$) of nitrate has the potential to be utilized as a tracer to delineate between atmospheric and nitrification sources of nitrate.

Despite numerous studies, there is still no clear answer to the question: What is the source of the immense nitrate deposits in the Atacama? To address this question, a research hypothesis was formed: the hyperaridity in the

Atacama allows the retention of nitrate from atmospheric deposition across the entire region of Atacama, and the minimal precipitation prohibits biological nitrification. To test this hypothesis, stable oxygen isotopes were used to determine the source of nitrate and unravel the mystery of the Atacama nitrate deposits. In addition to isotopic analysis, geochemical analysis was also performed to assess if local water sources might change the nitrate sources.

METHODOLOGY

Atacama study sites

Soil samples were collected at two study sites in the Atacama by Dr. Michalski's research group in the Department of Earth and Atmospheric Sciences at Purdue University. The first sampling site (S22°02'42.3", W69°07'39.2") is a four-meter high incised paleosol ("old soil") profile near the Cerro Unita geoglyph, while the second site (S22°52'55.1", W69°38'13.1") is a two-meter deep pipeline trench located in Baquedano region (see Figure 3, E). The Chug-Chug paleosol (CCP) and Baquedano Long Trench (LT) sites are both located in the hyperarid region in the central Atacama but are locally unique. The CCP profile is located in an ancient riverbed with sediment channels preserved in the upper stratum and a spring with sparse vegetation located nearby (see Figure 3, D), suggesting the presence of seasonal water flow in the past. All horizons of the profile consisted of well-cemented rocks, requiring electric saws for sampling. The age of this profile is estimated to be approximately one million years old based on ^{36}Cl radiometric dating technique (preliminary data). The LT site is located in the Baquedano basin and has a flat, rugged, and barren surface (see Figure 3, F), receiving less than 0.4 millimeters of precipitation annually (Houston, 2006). Unlike the CCP soils, LT exhibited no evidence of flowing water, and the soils were loosely cemented and could be sampled with hand shovels. Sixteen soil samples from CCP and 12 from LT were collected from the bottom of the paleosol profile/trench up to the surface.

Isotopic and geochemical analysis

Each soil sample was homogenized and ground by ball mill or hand. Soluble salts were then extracted in distilled water. Isotopic and geochemical analyses were performed on the soil extracts. Cation (Ca^{2+} and Na^{+}) concentrations were determined using inductively coupled plasma-optical emission spectroscopy (Thermo Scientific iCAP 6500) at the Purdue Rare Isotope Measurement (PRIME)

Figure 3. The four-meter high incised Chug-Chug paleosol (CCP) profile (A) is located near the Cerro Unita geoglyph, a prehistoric drawing etched into the landscape by scratching and arranging stones to depict a ~100-meter tall human figure, “The Lord of the Atacama” (B). The wide riverbed (C) at the CCP site is evidence of a past seasonal river. A spring with sparse vegetation (D) nearby also indicates traces of water might have influenced the CCP site. The two-meter deep long trench (LT) profile (E) is located in the Baquedano basin and has a flat, rugged, and barren surface (F).

laboratory (<http://www.physics.purdue.edu/primelab/>). Ion Chromatography (IC) with suppressed conductivity detector (Alltech 626 model) was used for anion analysis (NO_3^- , SO_4^{2-} , Cl^-). Soil nitrate was converted to AgNO_3 by cation exchange and reaction with Ag_2O (Silva et al., 2000), and stable oxygen isotope analysis was performed using the silver salt thermal decomposition method (Michalski, Savarino, Böhlke, & Thiemens, 2002) with Thermo Electron DeltaV isotope ratio mass spectrometry at Purdue Stable Isotope (PSI) Facility (<http://www.purdue.edu/eas/psi/>).

RESULTS AND DISCUSSION

Isotopic data

The observed nitrate $\Delta^{17}\text{O}$ values from both field sites are shown in Figure 4. The CCP site has fairly consistent $\Delta^{17}\text{O}$ values with depth that range from 18.1–19.2‰. In contrast, the LT $\Delta^{17}\text{O}$ values vary significantly with depth over the range of 17.1–20.4‰ (see Figure 4). Because of the difference in $\Delta^{17}\text{O}$ values between atmospheric nitrate ($\Delta^{17}\text{O} = \sim 23\text{‰}$) and microbial nitrate ($\Delta^{17}\text{O} = 0$) (Michalski et al., 2003), the values of $\Delta^{17}\text{O}$ of both sites indicated that the nitrate was mostly originated from atmospheric deposition, while a small percentage of the nitrate was from nitrification.

Compared to CCP, there is a high variation of $\Delta^{17}\text{O}$ values in LT. These differences may be due to different geological settings in the two sampling sites. The deserted river channels indicate seasonal rivers existed in the past at the CCP site and probably resulted in dissolution and mixing of nitrates, which homogenized the $\Delta^{17}\text{O}$ signals in the profile. On the other hand, frequent fog events but little evidence of significant rainfall in the Baquedano region suggests that water might not be enough to homogenize the entire nitrate in different layers. Therefore, the significant variation of $\Delta^{17}\text{O}$ values with depth at the LT site indicates that the amount of nitrification may have varied in different periods, probably in response to the change in water availability that controls the microbial activities. El Niño, a Pacific Ocean weather pattern characterized by warming of the surface ocean water, has been recognized as being important for modulating the precipitation regime in the Atacama (Houston, 2006). Therefore, the low $\Delta^{17}\text{O}$ values with depth, suggesting more nitrification (water), may record the transition to wetter periods, indicating an increase in the number of El Niño events in the past.

Geochemical data

Geochemical data were collected to provide the general information of the chemical composition of the soils. The cation and anion analysis showed that both of the soil profiles at CCP and LT are rich in chloride, nitrate, and sulfate anions that are coupled with sodium and calcium cations. At both of the sites, the ratios of $\text{Ca}^{2+}/\text{SO}_4^{2-}$ and $\text{Na}^+(\text{Cl}^- + \text{NO}_3^-)$ are approximate to 1 (see Figure 5), indicating there were presences of CaSO_4 , NaNO_3 , and NaCl . This is consistent with reports that common minerals in the Atacama are soda niter (NaNO_3), halite (NaCl), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and anhydrite (CaSO_4) (Ericksen, 1983).

At the CCP site, pronounced concentration peaks of the main soluble ions are observed (see Figure 5), for example, at the depth of 167 cm for Na^+ , NO_3^- and Cl^- , suggesting there was significant downward aqueous leaching and mixing of soluble salts occurring in the profile. This is logical, given that the CCP site is in an ancient riverbed and large amounts of water must have been present at some point in the past. However, the concentration peaks could be attributed to a leaching downward of soluble salts during a wet period, or an extremely dry period when the higher concentrations arise because of the accumulation of atmospheric salts

Figure 4. The $\Delta^{17}\text{O}$ values for CCP and LT sites range from 17.1–20.4‰, indicating the Atacama nitrate is mainly from the atmosphere, with a small percentage of the nitrate resulting from nitrification. The $\Delta^{17}\text{O}$ values of CCP are consistent with depth (A), probably due to the past seasonal rivers mixing the profile nitrate and homogenizing the isotopic signals. Significant variations of $\Delta^{17}\text{O}$ values are observed in LT profile (B), suggesting the importance of nitrification may have changed in the past in response to the climate-controlled water availability change.

Figure 5. The molar ion concentration profiles of CCP and LT sites. The pronounced concentration peaks in CCP profile could be attributed to downward aqueous leaching considering the presence of past seasonal rivers (left panel). The variations of both cation and anion concentrations were minor, indicating a minimal mixing of salts that may be related to precipitation variability (right panel).

without leaching. The presences of significant leaching and the resulting salt mixing are also supported by the conservative $\Delta^{17}\text{O}$ values with depth. While flowing water seems to have homogenized the salts, the isotopic evidence indicates the water did not induce excessive nitrification.

At the LT site, both anion and cation concentrations show minor variations as a function of depth. This is consistent with the isotopic data that there is a minimal mixing of salts and that the salt distribution is influenced only by small changes in rainfall over time. However, the inconsistency of the LT nitrate $\Delta^{17}\text{O}$ values indicates that there must have been some precipitation variability at LT site in the past, which may also have accounted for the deviations in the concentration profiles. Therefore, past increases in rainfall at the LT site must have been great enough to enhance nitrification and cause the variations in the salt distribution, but were not enough to dissolve and mix the salts completely.

Conclusion

Large mass-independent isotope anomalies (large $\Delta^{17}\text{O}$ values) were detected in nitrate deposits in the Atacama Desert. The $\Delta^{17}\text{O}$ values were 18.1-19.2‰ in CCP and 17.1-20.4‰ in LT, close to the atmospheric $\Delta^{17}\text{O}$ value of ~23‰. This shows that the nitrate deposits are mainly from atmospheric deposition rather than nitrification, as suggested by other authors. This is remarkably different relative to temperate ecosystems where nitrification is dominant and is likely due to the near absence of water in the Atacama, which precludes most nitrification. There is a significant $\Delta^{17}\text{O}$ variation as a function of depth at the LT site, suggesting that the importance of nitrification may have differed in the past. The change of water availability caused by El Niño events may account for the shift in the contribution of nitrification. In contrast, the $\Delta^{17}\text{O}$ values are more consistent with depth at the CCP site, probably because there were seasonal rivers in the past that mixed the nitrate from different depths and thus homogenized the isotopic signals. Geochemical analysis is evidence of common salts in the profile. It also provides the information of water availability on salts, which is consistent with the isotopic data. The distribution of soluble anion concentrations with depth at the CCP site suggests that there was downward aqueous leaching due to an ancient body of water. The minimal variation of soluble anion concentration in LT indicates small leaching of water due to minute precipitation. Water availability related to location and climate change may have a large

influence on the relative contribution of nitrification. Both geochemical and isotopic data indicate the varying hydrological history and water availability related to nitrate formation in the two sites, which provides opportunity for future research to continue to use the Atacama nitrate deposits to understand climate change in the past.

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