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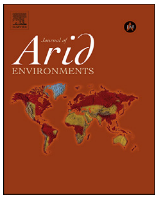

Isotope stratigraphy: Insights on paleoclimate and formation of nitrate deposits in the Atacama Desert, Chile

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ABSTRACT

Arid environment nitrate deposits are economically important and analogous to Martian environments, but their formation is poorly understood. Detailed N, O, and C isotope stratigraphy suggests Atacama Desert nitrate deposits form abiologically by differential leaching during hyperaridity (precipitation <2 mm/year). Nitrate deposit chemo-stratigraphy (top - bottom) shows sulfate depletion from 25.5 wt.% to 1.5 wt.%, and nitrate enrichment similar to ore deposit leaching models from 0.7 wt.% to 6.5 wt.%. The inverse relationship with depth of nitrogen ($\delta^{15}N_{(AIR)}$ 5.6 to −2.8‰) and oxygen ($\delta^{18}O_{(VSMOW)}$ 44.1 −51.8‰) isotope values for these sediments suggests this was an abiological process, produced by nitrogen deposition during extreme hyperaridity, and overprinted by subsurface nitrate enrichment through mobilization by slightly higher and variable precipitation events. Carbon isotope values in the topmost and bottommost units ($\delta^{13}C_{(PBD)}$ −25.1, −22.2, and −22.9‰) suggest this occurred when soil microbial life was active, though not abundant. The overprint of nitrate enrichment/leaching by precipitation produced carbon isotope values in the middle unit ($\delta^{13}C_{(PBD)}$ −2.1‰) consistent with incipient freshwater carbonate. While biological processes are called upon to explain leaching and enrichment in metallic ore deposits, nitrate deposits appear to have secondary enrichment which is predominantly abiological.

1. Introduction

This study presents nitrogen, oxygen, and carbon isotope data for samples from different depths within shallow and surficial nitrate deposits of the Atacama Desert of Chile. Understanding this isotope stratigraphy will lend insights into the paleoenvironmental conditions which govern their formation and modification, and will have application to soil scientists, mineralogists, biogeochemists, and astrobiologists wishing to differentiate biological vs. abiological nitrogen sources in paleoenvironments. This is particularly timely, given the recent findings of nitrate on Mars (e.g., Archer et al., 2014).

Samples for this study were collected from the southern portion of the Tocopilla District, the Baquedano District, and the northern portion of the Aguas Blancas District. These districts form a belt within the Atacama Desert, in an arc approximately 125 km southeast to northeast of Antofagasta, Chile (Fig. 1). These nitrate deposits occur within a hyper-arid region of the Atacama Desert. This region receives as little as 1 mm of precipitation per year, and some workers suggest that specific areas within this portion of the Atacama may not have had any significant rainfall from 1570 to 1971 (Ericksen, 1983).

This hyper-arid desert is home to one of the largest accumulations of fixed mineral nitrogen in the World. These vast "caliche" nitrate deposits have been mined commercially for fertilizer and explosives since the 1830s (e.g. Ericksen, 1983), and debate over the origin of these unusual deposits began with their scientific description by Charles Darwin (1871). It is no understatement that the Chilean nitrate deposits "… are so extraordinary that, were it not for their existence, geologists could easily conclude that such deposits could not form in nature" (Ericksen, 1983). Workers have attributed the formation of these deposits to nitrogen fixation and nitrification by microorganisms (e.g., Ericksen, 1979, 1983) and

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Fig. 1. Index map of nitrate deposit sample localities from Table 1.

magmatic processes (e.g., Chong, 1994). However, much recent work has focused on nitrate accumulation through atmospheric deposition by various mechanisms (e.g., Michalski et al., 2004), and by deep groundwater sources (e.g., Álvarez et al., 2015, 2016; Pérez-Fodich et al., 2014).

It has been shown that nitrogen deposition from the atmosphere, in the absence of significant precipitation, is sufficient to account for the nitrogen contained within nitrate deposits of the Atacama Desert (Ericksen, 1981), Mojave Desert (Ericksen et al., 1988), and the Negev Desert of Israel (Offer et al., 1992). An atmospheric source is supported by oxygen isotope work which indicates that atmospheric O_2 (Böhlke et al., 1997) is similar to modern rainwater nitrate with respect to $\delta^{18}O$ (Kendall, 1998). Copper nitrate minerals associated with copper deposits of the Atacama Desert have nitrogen isotope values consistent with nitrogen from an atmospheric source, or nitrogen associated with natural gas like that measured from Kazakhstan (Melchiorre and Talyn, 2014).

Other studies explored the role of groundwater on the formation of the nitrate and supergene copper deposits of the Atacama (e.g., Reich et al., 2013). These important studies provide evidence beyond that which is stored in the useful C, N, and O isotope values in the deposits, focusing on the rarer and less studied components of the deposits such as iodine and chromium (e.g., Pérez-Fodich et al., 2014). In particular, the cosmogenic iodine ($^{129}I/I$) and stable chromium ($\delta^{53/52}Cr$) isotope data of the Chilean nitrates show that groundwater may have played a key role in the formation of these deposits. The cosmogenic iodine tracer data of the Atacama nitrates from Álvarez et al. (2015) show similarities with deep marine sedimentary pore waters and associated shale ($^{129}I/I$ ~150–600 × 10^{-15}), an order of magnitude less than that of atmospheric iodine ($^{129}I/I$ ~1500 × 10^{-15}). A role for groundwater is also suggested by positive $\delta^{53/52}Cr$ values (+0.7‰ to +3‰), which are typically indicative of intense Cr redox cycling due to groundwater transport (Pérez-Fodich et al., 2014).

A third source for the minerals of the Atacama nitrate deposits is oceanic aerosols. Strontium and sulfur stable isotope evidence suggests that at least some of the Ca and S in these deposits is derived from a marine source, though the exact amount is highly variable and contingent upon complex geographic and climactic conditions (Rech et al., 2003).

However, there has long been general agreement among authors that the nitrate in the Atacama deposits is probably the result of nitrogen input from multiple sources. Thus it is likely that the origin of these deposits cannot be fully addressed as a single simple mechanism (e.g., Chong, 1994). The evidence presented above supports a multi-source genetic model for the Chilean nitrate deposits. In this model (e.g., Pérez-Fodich et al., 2014), a period of increasing aridity and tectonic uplift prompts long-lived, near-surface mineral precipitation driven by groundwater (chromates, iodates) coupled with dry atmospheric deposition (nitrates, perchlorates) and sea spray inputs (sulfates, chlorides). The quantified contributions of the different sources remain uncertain, and it is beyond the scope of this paper to address this issue specifically.

Resolution of this issue has been complicated through confusion as to what has been measured during studies of “Chilean Nitrates.” Any discussion of the genesis or implications of these deposits must examine the formation of different types of caliche, provide stratigraphic context, and explain the full suite of associated elements and minerals. In this study, we examined the stratigraphic context of caliche formation, which allows us to better constrain the genesis of these deposits.

1.1. Nitrate deposit stratigraphy

Details of nitrate deposit stratigraphy can be found in several sources (e.g., Whitbeck, 1931; Ericksen, 1983). The main stratigraphic units we sampled, from top to bottom (youngest to oldest), were the Chuca, Costra, Caliche, and Conjelo/Coba (Fig. 2). Crosscutting veins of high-grade “Caliche Blanco” nitrate, and nitrate deposits occurring within bedrock fracture systems were not examined in this present study.

The youngest deposit, the Chuca, is generally a 10–50 cm thick unit consisting of surface soils, and poorly-cemented silt, sand, and rock clasts. In some localities it may be up to 200 cm thick, and crop out extensively where relief is low. Gypsum and other lower-

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