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Long term atmospheric deposition as the source of nitrate and other salts in the Atacama Desert, Chile: New evidence from mass-independent oxygen isotopic compositions

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Abstract—Isotopic analysis of nitrate and sulfate minerals from the nitrate ore fields of the Atacama Desert in northern Chile has shown anomalous ¹⁷O enrichments in both minerals. $\Delta^{17}\text{O}$ values of 14–21 ‰ in nitrate and 0.4 to 4 ‰ in sulfate are the most positive found in terrestrial minerals to date. Modeling of atmospheric processes indicates that the $\Delta^{17}\text{O}$ signatures are the result of photochemical reactions in the troposphere and stratosphere. We conclude that the bulk of the nitrate, sulfate and other soluble salts in some parts of the Atacama Desert must be the result of atmospheric deposition of particles produced by gas to particle conversion, with minor but varying amounts from sea spray and local terrestrial sources. Flux calculations indicate that the major salt deposits could have accumulated from atmospheric deposition in a period of 200,000 to 2.0 M years during hyper-arid conditions similar to those currently found in the Atacama Desert. Correlations between $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in nitrate salts from the Atacama Desert and Mojave Desert, California, indicate varying fractions of microbial and photochemical end-member sources. The photochemical nitrate isotope signature is well preserved in the driest surficial environments that are almost lifeless, whereas the microbial nitrate isotope signature becomes dominant rapidly with increasing moisture, biologic activity, and nitrogen cycling. These isotopic signatures have important implications for paleoclimate, astrobiology, and N cycling studies. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

The Atacama Desert of northern Chile is one of the driest environments on Earth, with annual rainfall averaging less than 1–2 mm, and it is the premier source of natural nitrate minerals. Although minor amounts of nitrate are present in other desert environments, the nitrate ore deposits of the Atacama Desert are unique because of their high nitrate concentrations, and they have been mined for export as natural fertilizer since ~1830 (Ericksen 1983). Theories on the origin of the Atacama Desert nitrate deposits date to Darwin, who suggested that they formed at the inland margin of an oceanic extension (Darwin 1871). Subsequent studies have suggested a wide variety of sources including nitrification of ammonia derived from seaweed, vegetation in saline lakes, or bird guano (see Ericksen and references therein) (Ericksen 1983). The nitrate also has been attributed to nitrogen fixation and nitrification by microorganisms in the desert soils or in distant Andean salars (dry lakes), from which it may be transported by wind or groundwater to the Atacama basin (Ericksen 1983). This hypothesis is supported by the occurrence of nitrogen fixing bacteria associated with high concentrations of nitrate in playa sediments in the Mojave Desert and great basin region of the southwestern United States (Leatham et al. 1983). Others have argued that the nitrate is the result of magmatic processes that generate nitrate through unidentified catalytic reaction (s) involving water and magmatic nitrogen gases (Chong 1994). Subsequent erosion of the igneous rock by hydrothermal activity and transport of the soluble ions is invoked to explain the regional placement of the nitrate. Several authors postulated that atmo-

spheric deposition was a significant source of nitrate in the Atacama Desert, with potential inputs including sea spray, ammonia deposition and nitric acid deposition (Claridge and Campbell 1968) (Ericksen 1979) (Ericksen 1981). The atmospheric deposition source is strongly supported by isotopic measurements indicating that the Atacama Desert nitrate has $\delta^{18}\text{O}$ values higher than that of atmospheric O_2 (Böhlke et al. 1997), similar to modern rainwater nitrate (Kendall 1998). However, quantifying the influence of atmospheric deposition from these measurements is difficult because of uncertainties regarding how nitrate $\delta^{18}\text{O}$ values are affected by nitrification or denitrification in hyper-arid environments and how modern atmospheric nitrate isotopes are affected by anthropogenic NO_x emissions. Most authors agree that the nitrate and other soluble salts are most likely the result of multiple sources, but the relative magnitudes of the different sources remain uncertain more than one hundred years after Darwin's publication.

In addition to nitrate, the nitrate ore deposits of the Atacama Desert also contain substantial amounts of chloride and sulfate (Ericksen 1981). Composite analyses of ore material indicate that these major anions were present in subequal molar amounts, but sulfate and chloride also are more widespread in the region, and there is considerable heterogeneity within the ore deposits because of selective remobilization and re-crystallization. For example, calcium sulfate minerals typically are more abundant near the land surface because of their relatively low solubility in comparison to nitrate and chloride minerals, which are found at greater depths (Ericksen 1983; Chong 1994; Rech et al. 2003). The origin of the sulfate minerals has been attributed to multiple sulfate sources including sea salt deposition near the coast and rock weathering in regions further inland (Rech et al. 2003). Volcanism has also been suggested as

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a major constituent of the sulfate budget in the region (Ericksen 1981).

The Atacama Desert is located in northern Chile (between 20°S and 26° S) in the rain shadows of the Andes Mountains to the east and the Coastal Cordillera (1000–3000m) to the west (Fig. 1). The local distributions of the salt deposits are believed to be largely a function of remobilization of existing salts by occasional rainfall, eolian transport (Berger and Cooke 1997), capillary action (Mueller 1968), groundwater discharge, possibly hydrothermal reworking (Pueyo et al. 1998), and sedimentation. The spatial distribution, mineralogy, and petrology of the salt deposits in the region have been described previously in relation to these transport mechanisms (Ericksen 1981; Searl and Rankin 1993; Pueyo et al. 1998).

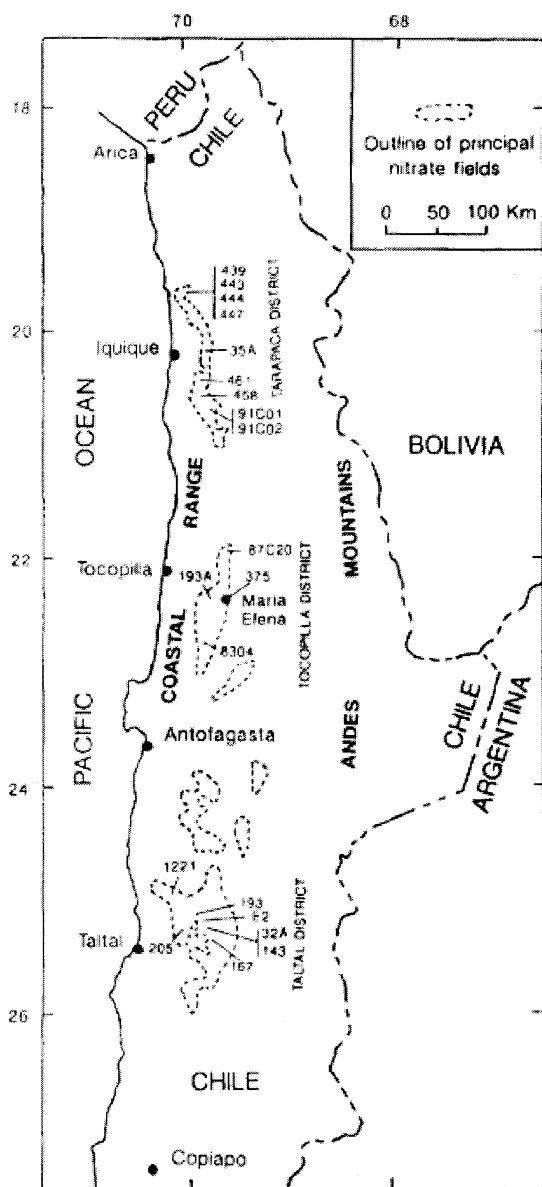


Fig. 1. Map of the major nitrate ore fields of the Atacama Desert in northern Chile with isotope sample localities (modified from Ericksen; 1981).

The current paper reports the use of oxygen isotope measurements, specifically $\Delta^{17}\text{O}$ values, as a tool to probe the influence of atmospheric deposition (wet and dry) as a source of salts in the Atacama Desert region. In addition, it provides quantitative analyses of the atmospheric chemistry and deposition dynamics involved in nitrate and sulfate accumulation. The current focus is on the use of stable isotopes ^{16}O , ^{17}O and ^{18}O to determine the origin of the oxyanions themselves, rather than their subsequent redistribution and mineralogy.

1.2. Theory of Isotope Distribution and Mass Independent Fractionations

Stable isotope theory has been used successfully in geochemistry for nearly 50 yr, but it is only in the last few years that the use of mass-independent isotopic compositions has yielded new information about terrestrial systems that was unattainable using traditional isotopic methods (Thiemens 1999). In most geochemical transformations, elements partition their isotopes into different phases during kinetic and equilibrium reactions with this partitioning (fractionation) being dependent on temperature and the relative mass differences of the isotopes. These fractionations are quantified by measuring the isotopic ratios of the sample relative to an accepted standard and are reported in delta notation (in units of per mil):

$$\delta\% = \left(\frac{R_{\text{Sample}}}{R_{\text{Std}}} - 1 \right) \times 1000 \quad (1)$$

where R is the ratio of the minor to major isotopes (e.g., $^{18}\text{O}/^{16}\text{O}$ or $^{17}\text{O}/^{16}\text{O}$). For elements that have three stable isotopes, the mass dependence is extended to both minor isotopes and is determined by relative mass differences of the two minor isotopes relative to the third (major) isotope, which for O is $\sim 1/2$. This relationship is quantified by $\alpha_{17/16} = (\alpha_{18/16})^{0.52}$, where α is the fractionation factor for a given reaction (Matsuhisa et al. 1978; Young et al. 2002) and can be converted to delta notation as approximately $\delta^{17}\text{O} \approx 0.52 \times \delta^{18}\text{O}$ (Thiemens 1999; Miller, 2002). Deviations from this rule are quantified by capital delta notation

$$\Delta^{17}\text{O} \approx \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O} \quad (2)$$

Most terrestrial materials have $\Delta^{17}\text{O} \approx 0$, including oceanic and meteoric waters, air O_2 (within tenths of a per mil) and most solids (Miller 2002). The discovery of approximately equal enrichment of both minor isotopes ($\delta^{17}\text{O} \approx \delta^{18}\text{O}$) in the formation of ozone (O_3 , $\Delta^{17}\text{O} \approx 20\text{--}50\text{‰}$) demonstrated the exception to this rule (Thiemens and Heidenreich 1983). Initially of interest primarily to atmospheric chemists, photochemically induced mass-independent fractionations have been found recently in desert varnish (Bao, Michalski, and Thiemens, 2001), sulfate deposits (Bao et al. 2000a), sulfate contained in Antarctica ice cores (Alexander et al. 2002) and Achaean sulfate and sulfide rocks (Farquhar et al. 2000). Minerals containing NO_3^- and SO_4^{2-} are of particular interest because they are stable compounds that do not undergo isotopic exchange with water (Spindel 1969), which allows the preservation of their isotopic signatures in ice, water, soils, and the geologic record. The $\Delta^{17}\text{O}$ (and $\Delta^{33}\text{S}$) signatures in these substances provide a conservative tracer to past photochemical

processes and a measure of the magnitude of atmospheric inputs to various geologic and hydrologic environments.

1.2.1. Origin of $\Delta^{17}\text{O}$ values in photochemically produced NO_3^- and SO_4^{2-}

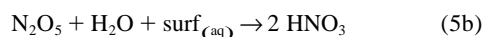
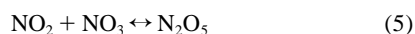
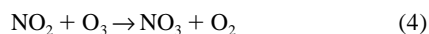
Several accounts on the origin of the salts in the Atacama Desert have invoked “atmospheric or electrochemical N_2 fixation” but provided few details on the atmospheric chemistry or deposition dynamics. It is therefore important to examine the photochemical mechanisms that produce NO_3^- and SO_4^{2-} and how different reaction pathways can mediate the O isotopic composition of these substances.

One of the most important atmospheric oxidants and a key reactant in the formation of NO_3^- and SO_4^{2-} in the atmosphere is O_3 (Seinfeld and Pandis 1998). Numerous experimental, theoretical and in situ measurement efforts (Thiemens 2001) have demonstrated that O_3 can have $\Delta^{17}\text{O}$ values from 20 to 50‰. It is believed the origin of these $\Delta^{17}\text{O}$ enrichments is the result of differential lifetimes of excited O_3 molecules depending on whether the symmetries of the molecules have been altered by isotopic substitution (Hathorn and Marcus 1999; Gao and Marcus 2001). The $\Delta^{17}\text{O}$ values generated during O_3 formation are well constrained for various temperature and pressure regimes (Morton et al. 1990). $\Delta^{17}\text{O}$ enrichments have also been detected recently in aerosol and rainwater NO_3^- (20–30‰) (Michalski et al. 2003) and SO_4^{2-} (0.2–2‰) (Lee 2000). Currently, the accepted mechanism for producing $\Delta^{17}\text{O}$ in both NO_3^- and SO_4^{2-} is through mass transfer of O atoms during gas- and aqueous-phase oxidation reactions involving O_3 . Laboratory experiments (Savarino et al. 2000) have documented this mass transfer scheme in aqueous phase oxidation of SO_2 , and the $\Delta^{17}\text{O}$ values measured in atmospheric NO_3^- samples have been simulated using an isotopic-photochemical box model (Michalski et al. 2003).

1.2.2. Photochemical model for $\Delta^{17}\text{O}$ in $\text{NO}_3^-_{\text{atm}}$

Atmospheric nitrate ($\text{NO}_3^-_{\text{atm}} = \text{HNO}_3(\text{gas}) + \text{NO}_3^- \text{ salts}$) is produced by photochemical reactions involving NO_x that generate gas phase nitric acid. Nitric acid (HNO_3) can then react with sea salt or crustal aerosols in neutralization reactions that generate particulate NO_3 . Gas phase HNO_3 is also highly reactive on land surfaces (dry deposition), and both HNO_3 and NO_3^- aerosols are highly soluble (wet deposition), so that wet and dry deposition are the primary mechanisms for removal of $\text{NO}_3^-_{\text{atm}}$ from the atmosphere.

There are three major reaction pathways involving NO_2 , O_3 , OH and H_2O that produce HNO_3 with varying $\Delta^{17}\text{O}$ values (Michalski et al. 2003):

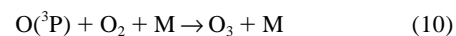
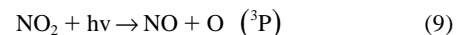
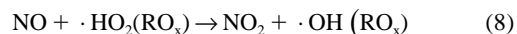
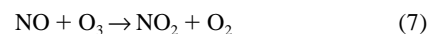


The NO_3 radical reactions involving hydrocarbons (HC) are

important in urban regions and those involving dimethylsulfide (DMS) are more important in the marine boundary layer (Yvon et al. 1996). Since O atoms are conserved in each HNO_3 reaction pathway the $\Delta^{17}\text{O}$ of HNO_3 can be determined by the mass balance equation:

$$\Delta^{17}\text{O}(\text{HNO}_3) = \eta(\Delta^{17}\text{O}(3)) + \beta(\Delta^{17}\text{O}(4)) + \chi(\Delta^{17}\text{O}(5)) \quad (6)$$

Where η , β , and χ are the fractions of HNO_3 produced by reaction pathways 3, 4 and 5 and ($\Delta^{17}\text{O}(3,4,5)$) is the $\Delta^{17}\text{O}$ value of HNO_3 generated by each formation pathway. To evaluate ($\Delta^{17}\text{O}(3,4,5)$) one needs measured or calculated $\Delta^{17}\text{O}$ values for the reactants (O_3 , NO_2 , OH and H_2O). The $\Delta^{17}\text{O}$ values for H_2O have been measured and found to equal zero for all natural terrestrial waters (Meijer and Li 1998). In addition, the rapid isotopic exchange between $\text{H}_2\text{O}_{(\text{g})}$ and OH relative to the sink reaction (3) (Dubey et al. 1997) dictates that $\Delta^{17}\text{O} \sim 0$ for OH in the troposphere (Lyons 2001). Experimental pressure- and temperature-dependent rate data were used to determine O_3 $\Delta^{17}\text{O}$ values, which are $\sim 35\%$ for tropospheric O_3 at mid latitudes (appendix I). Experimental data were used for this estimate because possible sampling artifacts have cast doubt on the accuracy of published tropospheric O_3 $\Delta^{17}\text{O}$ in situ measurements (Krankowsky et al. 1995; Johnston and Thiemens 1997). The $\Delta^{17}\text{O}$ value of tropospheric NO_2 is not known but can be estimated based on its formation mechanism. NO_2 is generated by the oxidation of NO by either O_3 , HO_2 or peroxy radicals (RO_x). NO_2 is also readily photolyzed in visible/uv light to give back NO and O_3 in the classic NO_x cycle:



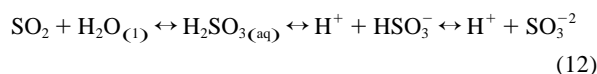
Because the NO_x photo-stationary state (7–10) achieves steady state 3 orders of magnitude faster than the sink reactions (3–5) (Seinfeld and Pandis 1998) the O atoms in NO_2 achieve isotopic equilibrium with O_3 and HO_2 (RO_x). The $\Delta^{17}\text{O}$ value of HO_2 is assumed to be zero, which simplifies the problem and is justified because measured values of $\Delta^{17}\text{O}$ in H_2O_2 (the main product of HO_2 self reaction) are $\sim 1.4\%$ (Savarino and Thiemens 1999). Because the fraction of NO_2 oxidized by peroxy radicals on a global average is only approximately 10%, this assumption only introduces errors at the 0.1‰ level. The resulting NO_2 $\Delta^{17}\text{O}$ values are approximately 31.5‰. Using Eqn. 3–6 with O_3 $\Delta^{17}\text{O} = 35\%$ and both H_2O and OH $\Delta^{17}\text{O} = 0$, we obtain:

$$\Delta^{17}\text{O}(\text{HNO}_3) = \eta(21\text{‰}) + \beta(33\text{‰}) + \chi(27\text{‰}) \quad (11)$$

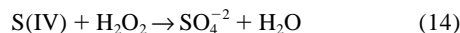
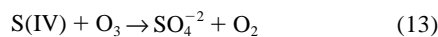
The branching ratios (η , β , χ) are determined using either simple photochemical box models or more complex global climate models with detailed atmospheric chemistry subroutines (see below).

1.2.3. Photochemical model for $\Delta^{17}\text{O}$ in nss- SO_4^{-2}

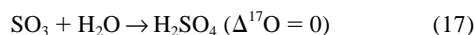
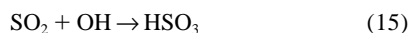
Sulfate aerosols in the atmosphere have two main sources, sea spray and gas-to-particle conversion of SO_2 , which is referred to as non-sea-salt SO_4^{-2} (nss- SO_4^{-2}). The nss- SO_4^{-2} is produced by both gas phase (homogenous) and aqueous phase (heterogeneous/cloud processing) SO_2 oxidation (Seinfeld and Pandis 1998). Sulfate $\Delta^{17}\text{O}$ values are generated during the aqueous phase oxidation of SO_2 to SO_4^{-2} (Savarino et al. 2000), which is initiated by equilibrium between gas phase SO_2 and liquid water droplets:



All S species in (12) have the same oxidation state and are collectively termed S(IV). Isotopic exchange between O in the S(IV) species and H_2O is very fast and rapidly achieves isotopic equilibrium with tropospheric H_2O (Newman, Krouse and Grinenko 1991), for which $\Delta^{17}\text{O} = 0$. Because the oxidation of reduced S species such as H_2S and DMS proceeds through S(IV), isotope effects during the initial oxidation of reduced S do not affect the final $\Delta^{17}\text{O}$ value of nss- SO_4^{-2} and are not explicitly included in the model. The aqueous-phase oxidation of S(IV) to SO_4^{-2} is carried out primarily by O_3 and H_2O_2 , with the branching ratio depending on the localized concentration of each reactant and the pH of the water droplet (Lin and Chameides 1991):



The nss- SO_4^{-2} $\Delta^{17}\text{O}$ values depend on the branching ratio of reactions 13 and 14 and on the $\Delta^{17}\text{O}$ values of O_3 (35‰) and H_2O_2 (~1.4‰) (Savarino and Thiemens 1999). Experimental studies have shown that one O atom is transferred to S(IV) during oxidation by O_3 (yielding SO_4^{-2} $\Delta^{17}\text{O} \sim 9\%$), that two O atoms are transferred during H_2O_2 oxidation (yielding SO_4^{-2} $\Delta^{17}\text{O} \sim 0.7\%$) and that the reaction dynamics generate no mass-independent isotope effects (Savarino et al. 2000). No $\Delta^{17}\text{O}$ signal arises from gas phase SO_2 oxidation because all three sources of O atoms in the gas phase oxidation scheme (OH , O_2 , H_2O , and SO_2) have $\Delta^{17}\text{O} \sim 0$ and the reaction itself has been shown to proceed via a conventional mass-dependent fractionation pathway (Savarino et al. 2000):



Gas phase H_2SO_4 is highly hygroscopic and quickly nucleates with H_2O to form nanometer-size droplets of sulfuric acid (H_2SO_4). The $\Delta^{17}\text{O}$ of nss- SO_4^{-2} is thus given by:

$$\Delta^{17}\text{O}_{\text{nss-}\text{SO}_4^{-2}} = \varepsilon[(\phi \times 9\%) + (\gamma \times 0.7\%)] \quad (18)$$

where ϕ and γ are the oxidation branching ratios for H_2O_2 and O_3 respectively ($\phi + \gamma = 1$) and ε is the fraction of SO_2 oxidized in the aqueous phase. Computer modeling is required to evaluate these parameters. In fact, SO_4^{-2} $\Delta^{17}\text{O}$ measure-

ments can be used to test whether computer models are correctly partitioning the relative importance of homogenous versus heterogeneous SO_2 oxidation (see below).

Aerosols originating from dried seawater droplets generated by bursting air bubbles on the sea surface contain ions in approximately the same ratios as seawater ions (molar $\text{Na}^+/\text{Cl}^- = 0.86$; $\text{SO}_4^{-2}/\text{Cl}^- = 0.052$). This is a significant source of SO_4^{-2} aerosols, as the global atmospheric flux of sea salt is estimated to be $1.17 \times 10^{16} \text{ g yr}^{-1}$. (Gong et al. 1997). The O isotope ratios of oceanic SO_4^{-2} have been measured and have $\Delta^{17}\text{O} = 0$ (Lee and Thiemens 2001), as expected since oceanic SO_4^{-2} is derived mainly from mass-dependent kinetic oxidation of organic and sulfide S phases. The $\Delta^{17}\text{O}$ in aerosol SO_4^{-2} is therefore a function of the relative contribution of sea salt versus nss- SO_4^{-2} production, of the amount of homogenous versus heterogeneous gas phase SO_2 reactions, and of the relative importance of O_3 versus H_2O_2 in aqueous phase oxidation. If $R_{\text{nss/ss}}$ is the ratio of nss- SO_4^{-2} to sea salt SO_4^{-2} , then

$$\Delta^{17}\text{O}_{\text{SO}_4^{-2}} = R_{\text{nss/ss}} \times \Delta^{17}\text{O}_{\text{nss-}\text{SO}_4^{-2}} = R_{\text{nss/ss}} \times \varepsilon[(\phi \times 9\%) + (\gamma \times 0.7\%)] \quad (19)$$

2. METHODS

We have performed isotopic measurements to detect $\Delta^{17}\text{O}$ anomalies in NO_3^- and SO_4^{-2} salts from the Atacama Desert and Mojave Desert that were described previously by Böhlke et al. (1997). More complete descriptions of the mineralogy and locations of the individual samples can be found in Ericksen (1981), Ericksen et al. (1988), and Böhlke et al. (1997), with summary descriptions provided in Table 1. The Atacama Desert samples are all from the nitrate ore fields and are referred to as caliche-type deposits (Ericksen, 1981). Most of the samples are salt crystals or mixed salt cements in soil samples collected from open pits in the nitrate mines. Two of the samples (375 and USGS35) were commercial nitrate salts that were purified by fractional crystallization. The Mojave Desert salt samples are from caliche-type deposits in the clay-hills region near Death Valley, California (Ericksen et al., 1988). Additional NO_3^- samples were extracted from ground water pumped from the Irwin basin in the Mojave Desert of California. Ground-water NO_3^- in the Irwin basin is believed to be derived largely from leaching and recharge of NO_3^- formed naturally within the unsaturated zone, with some localized occurrences of anthropogenic NO_3^- resulting from wastewater disposal (Densmore and Böhlke, 2000).

For $\Delta^{17}\text{O}$ analysis, archived NO_3^- salts (as KNO_3) were converted to AgNO_3 using a cation exchange membrane (Dionex AMMS-4ml suppression column) utilizing 0.002M Ag_2SO_4 as the regenerant. The AgNO_3 solutions were then freeze-dried in silver capsules (99.9% pure) and thermally decomposed into O_2 and NO_2 by heating in vacuo at 520°C . The NO_2 gas was cryogenically removed using a series of liquid nitrogen traps and the O_2 was collected for isotopic analysis. A Finnigan-MAT 251 isotope ratio mass spectrometer was used to determine $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ isotope ratios in the O_2 , from which $\Delta^{17}\text{O}$ values were determined with a precision of $\pm 0.2\%$. Complete details of the experimental method may be found in Michalski et al. (2002). In addition to

Table 1. Isotopic and chemical data for nitrate and sulfate from the Atacama Desert and Mojave Desert.

Sample	$\Delta^{17}\text{O}$ NO_3^-	$\delta^{18}\text{O}$ NO_3^-	$\Delta^{17}\text{O}$ SO_4^{-2}	$\delta^{18}\text{O}$ SO_4^{-2}	$\delta^{15}\text{N}$ NO_3^-	$\delta^{34}\text{S}$ SO_4^{-2}	Cl/N mol.	S/N mol.	Long.	Lat.	Description
Atacama											
Desert Salts	a	a	a	a	b	b	b	b	b	b	b
439	18.0	55.1	na	na	-1.0	na	0.73	0.001	69° 55' W	19° 40' S	Of. Dolores; blocky NaNO_3 crystals
443	15.2	50.1	na	na	-1.0	na	0.001	0.000	69° 59' W	19° 39' S	Of. San Antonio; blocky NaNO_3 crystals
444	17.2	44.8	0.9	2.9	-4.9	-2.8	0.31	0.026	69° 59' W	19° 39' S	Of. San Antonio; blue granular mixed salts
447	15.6	45.8	na	na	-2.2	na	1.11	0.000	69° 59' W	19°39' S	Of. San Antonio; acicular NaNO_3 crystals
461	19.6	60.2	na	na	-1.0	na	0.95	0.012	69° 42' W	20° 24' S	Of. San Pablo; acicular NaNO_3 crystals
458	16.2	49.1	0.7	2.7	0.6	-0.2	0.56	0.033	69° 46' W	20° 32' S	Pintados; granular mixed salts
91c-01	16.6	52.8	0.4	5.4	-0.8	na	na	na	69° 43' W	20° 41' S	Of. Victoria; darapskite crystals
91c-02	16.4	51.9	na	na	-1.6	na	na	na	69° 43' W	20° 41' S	Of. Victoria; granular mixed salts
87c-20	13.7	44.4	2.4	5.3	-0.8	2.0	0.74	0.047	69° 34' W	21° 51' S	Of. Santa Fe; granular mixed salts
375	19.2	52.9	na	na	-0.4	na	0.014	0.002	69° 37' W	22° 20' S	Of. Maria Elena; fertilizer product, NaNO_3 pellets
8304	18.7	52.1	na	na	-2.6	na	na	na	69° 47' W	22° 45' S	Of. Pedro de Valdivia; granular mixed salts
1221a	19.9	48.9	4.0	5.5	1.5	5.4	0.003	0.039	70° 10' W	24° 55' S	Pampa Yumbas; salt cemented soil
193	19.4	50.8	1.5	7.3	0.9	4.5	0.013	2.3	69° 55' W	25° 07' S	Of. Alemania; humberstonite-rich salt
143	17.6	52.8	na	na	3.0	na	0.017	0.002	69° 49' W	25° 13' S	Of. Lautaro; blocky NaNO_3 crystals
32a	16.8	52.4	na	na	4.1	na	0.000	0.001	69° 49' W	25° 13' S	Of. Lautaro; acicular NaNO_3 crystals
205	18.0	52.4	na	4.7	2.9	0.4	0.40	0.017	70° 08' W	25° 14' S	Of. Santa Luisa; mixed salts
USGS35	21.6	57.5	na	na	2.7	na	0.010	0.002			fertilizer product, granular NaNO_3
Mojave Desert											
Salts											
8401	7.2	21.3	0.6	3.2	4.8	-19.4	6.9	0.93	116° 12' W	35° 42' N	Bully Hill, Upper Canyon area; salts leached from soil
8405c	13.1	35.9	2.0	5.3	0.1	9.9	1.7	0.10	116° 36' W	35° 50' N	Confidence Hills; salts leached from soil
8414	12.4	34.5	1.9	5.4	0.0	9.7	1.6	0.080	116° 36' W	35° 50' N	Confidence Hills; salts leached from soil
8419	12.6	36.0	0.7	1.8	0.9	5.4	13.6	1.49	116° 28' W	35° 39' N	Saratoga hills; salts leached from soil
Mojave Desert											
Ground Water											
WC1-150	0.4	2.8	na	na	11.4	na	8.9	3.9	116° 40' W	35° 15' N	Irwin Basin; pumped well
NH1-300	0.9	2.9	na	na	7.5	na	9.4	8.4	116° 41' W	35° 16' N	Irwin Basin; pumped well
BC1-185	0.4	1.4	na	na	6.7	na	2.6	2.3	116° 40' W	35° 16' N	Irwin Basin; pumped well

a = this study b = Böhlke et. al. (1997); Densmore and Böhlke (2000); Böhlke et al. (2003)

the thermal decomposition measurements, we also re-determined the $\delta^{18}\text{O}$ values of the KNO_3 samples by continuous-flow mass spectrometry on CO produced by high-temperature reaction with carbon (CO-CFIRMS) (Kornexl et al. 1999; Böhlke et al., 2003). These analyses were calibrated by analyses of reference materials IAEA-NO-3 and USGS35, which were assumed to have $\delta^{18}\text{O}$ values of +25.6 and +57.5 ‰, respectively (Böhlke et al., 2003). A subset of the original salt samples consisting of relatively pure NaNO_3 crystals was also analyzed by the CO-CFIRMS method and by the bacterial N_2O method of Casciotti et al. (2002), which yielded similar results. The new NO_3^- $\delta^{18}\text{O}$ values determined by CO-CFIRMS and the bacterial method are systematically higher than the values determined previously by an off-line preparation technique (Böhlke et al. 1997; Revesz et al. 1997). The systematic difference between these two sets of results is consistent with reported $\delta^{18}\text{O}$ scale contraction in samples prepared by off-line

combustion in sealed glass tubes (Revesz and Böhlke 2002). The NO_3^- $\delta^{18}\text{O}$ values reported in this paper are averages of all available normalized data produced by the CO-CFIRMS and bacterial methods, which are believed to be more reliable than the previously published off-line values and have a reproducibility of approximately ± 0.3 to 1.0 ‰ ($1-\sigma$).

Sulfate samples for $\Delta^{17}\text{O}$ analysis were obtained by hydrating bulk salt samples with Millipore water, heating the solution to 80°C and slightly acidifying the solution using HCl. Sulfate was then precipitated from solution by adding excess BaCl_2 . The resulting BaSO_4 solid was concentrated by centrifugation (10 min) followed by decantation of the supernatant. The BaSO_4 pellets were rinsed in 10 mL of Millipore water, re-centrifuged and decanted, and dried at 100°C overnight. O_2 was generated by fluorination of BaSO_4 (~8mg) using BrF_5 gas and a CO_2 IR laser as described by Bao and Thiemens (2000b). The $\delta^{18}\text{O}$ values were determined by the CO-CFIRMS method in

BaSO₄ precipitates prepared previously and calibrated against analyses of NBS-127 BaSO₄, for which a value of +8.6 ‰ was assumed (Kornexl et al., 1999; Böhlke et al., 2003). Experimental precision for sulfate was ±0.2 ‰ for Δ¹⁷O and ±0.5 ‰ for δ¹⁸O, based on replicate samples. The δ¹⁸O data (NO₃⁻ and SO₄⁻²) presented here are from the CO-CFIRMS and bacterial methods because the thermal decomposition and laser fluorination techniques used for Δ¹⁷O measurements can have mass-dependent fractionation variations of 1–4‰.

3. RESULTS OF ANALYSES

The Δ¹⁷O and δ¹⁸O values for both NO₃⁻ and SO₄⁻² minerals are given in Table 1, along with the δ¹⁵N and δ³⁴S values given by Böhlke et al. (1997). The data are also shown in three-isotope plots in Figures 2 and 3. The NO₃⁻ samples from the Atacama Desert have large Δ¹⁷O values (14–21‰), which are a factor of 5 larger than those of any other terrestrial minerals reported to date (Thiemens et al. 2001). The highest Δ¹⁷O value (21.5‰) is at the lower end of Δ¹⁷O values measured in aerosol and precipitation NO₃⁻ in a variety of environments (21–31‰) (Michalski et al. 2003 Michalski unpublished data). Smaller though significant Δ¹⁷O values are also observed in SO₄⁻² that is associated with the Atacama Desert nitrate ore deposits (0.4–4 ‰). These values fall within the high end of the range of Δ¹⁷O values measured in aerosol SO₄⁻² in the northern hemisphere (Lee 2001; Bao, Michalski, and Thiemens 2001) and in some SO₄⁻² deposits associated with ancient volcanic eruptions (Bao et al. 2000a). Since the only processes known to cause Δ¹⁷O values of these magnitudes on Earth are photochemical reactions in the troposphere and stratosphere, the new data provide strong evidence that photochemical production and subsequent deposition is responsible for a substantial portion of both the NO₃⁻ and SO₄⁻² in minerals found in the nitrate ore deposits of the Atacama Desert.

Among the NO₃⁻ samples, there is a positive correlation between Δ¹⁷O and δ¹⁸O (Fig. 2b), but no apparent correlation between Δ¹⁷O and either mineral type or δ¹⁵N (Table 1). The Δ¹⁷O and δ¹⁸O values are highest in NO₃⁻ from the Atacama Desert nitrate ore deposits and somewhat lower in surficial nitrate mineral samples from the Death Valley region of the Mojave Desert, California. Samples of NO₃⁻ in ground water from the Mojave Desert have Δ¹⁷O and δ¹⁸O values near 0, as expected for NO₃⁻ formed by biologic processes in moist environments. Similarly, among the SO₄⁻² samples, there appears to be a positive correlation between Δ¹⁷O and δ¹⁸O, with values slightly higher on average in the Atacama Desert samples. The lowest SO₄⁻² Δ¹⁷O values are near 0, as expected for either sea-salt SO₄⁻² or SO₄⁻² formed by chemical or microbial S oxidation in soils and most other terrestrial aqueous environments.

It is important to recognize that the correlations observed in the three oxygen isotope plots can have a variety of meanings. For example, plots of δ¹⁷O/δ¹⁸O of O₃ formed in laboratory experiments that remove O₃ immediately after formation follow a slope of ~1 (Thiemens and Heidenreich 1983), yet stratospheric O₃ samples follow a slope of ~0.62 (Lammerzahl et al. 2002). This can be explained by mass-dependent fractionations, such as photolysis and catalytic destruction that

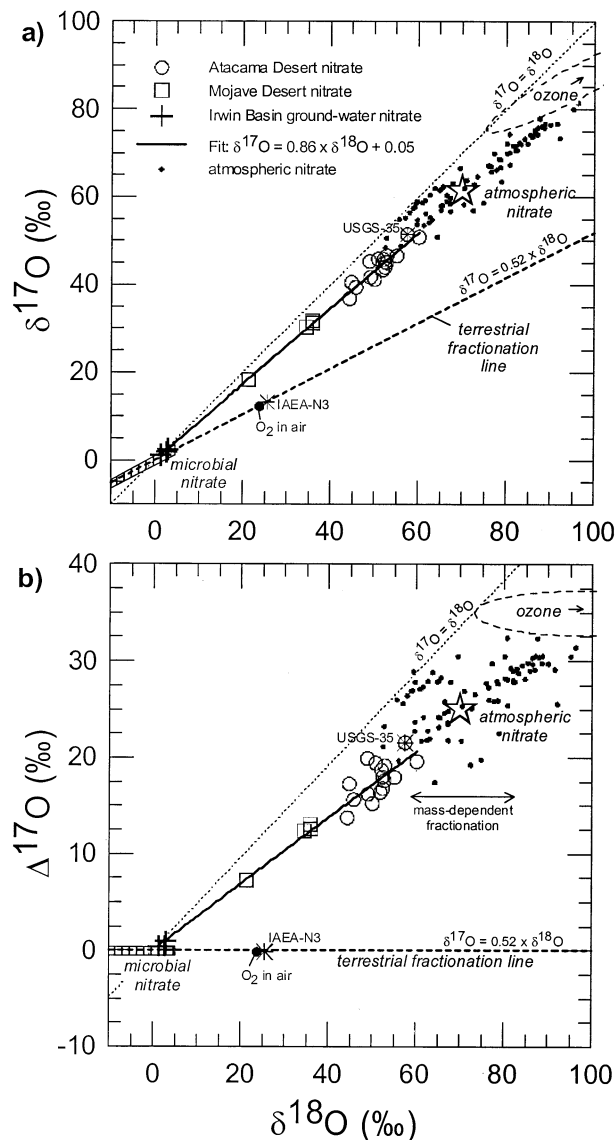


Fig. 2. Nitrate O isotopic variations in samples of Atacama Desert caliche-type salts, Mojave Desert caliche-type salts, and Mojave Desert (Irwin Basin) groundwater nitrate: **a)** Δ¹⁷O versus δ¹⁸O; **b)** Δ¹⁷O versus δ¹⁸O. Data shown for comparison include atmospheric nitrate in rain and aerosols from California and Antarctica (Michalski et al., 2003 unpublished data) and nitrate isotopic reference materials IAEA-N3 and USGS35 (Michalski et al., 2002; Böhlke et al., 2003). The terrestrial fractionation line indicates the trajectory followed by mass-dependent isotopic variations. The ozone field is centered on the modeled value of Δ¹⁷O, with varying mass-dependent fractionation, as explained in the text. Correlated variations in the NO₃⁻_{atm} data are interpreted to reflect the proportion of O atoms that are derived from O₃ or tropospheric H₂O, which depends on the photo-oxidation pathway. The fit to the desert nitrate data is interpreted to indicate varying mixtures of atmospheric photochemical nitrate (star = model) and terrestrial microbial nitrate (shaded rectangle at Δ¹⁷O = 0). The Δ¹⁷O versus δ¹⁸O plot (b) emphasizes the effects of mass-dependent fractionations (horizontal vectors) that are less obvious in the δ¹⁷O/δ¹⁸O plot.

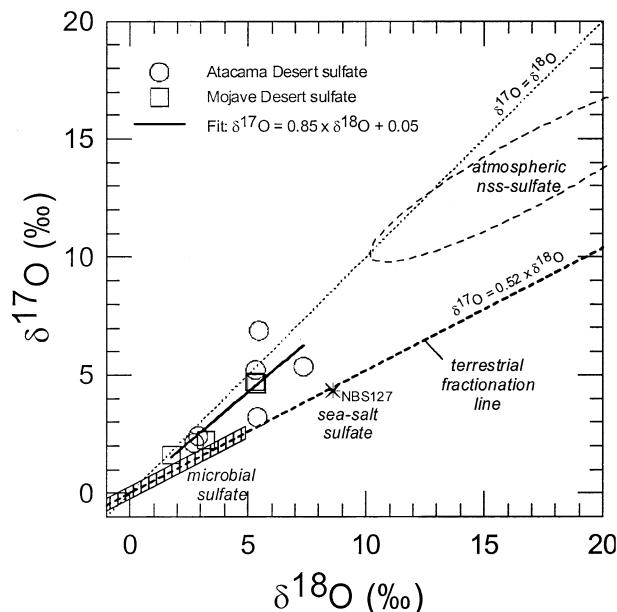


Fig. 3. Sulfate O isotopic variations in samples of nitrate-rich caliche-type salts from the Atacama Desert and Mojave Desert. The terrestrial fractionation line indicates the trajectory followed by mass-dependent variations. The nss-sulfate field is centered around the modeled value of $\Delta^{17}\text{O}$, with varying mass-dependent fractionation, as explained in the text. The sulfate isotopic reference material (NBS-127) is similar isotopically to seawater sulfate. The poorly correlated isotopic variations among the salt samples are consistent with varying mixtures of atmospheric nss-sulfate, sea-salt sulfate, and terrestrial microbial sulfate (e.g., from sulfide oxidation; Van Stempvoort and Krouse, 1994).

follow of slope 0.52, superimposed on the formation line with slope 1.0. In contrast, the slope of 0.8 observed in NO_3^- is considered to be primarily a mixing line between the two main isotopic reservoirs contributing to NO_3^- formation (O_3 and H_2O) in the relative absence of fractionation effects (Michalski et al., 2003). Below it is proposed that the correlations observed among the desert NO_3^- samples also represent mixing lines, but with different end members (NO_3^- and microbial nitrification NO_3^-).

4. SOURCES OF NITRATE AND SULFATE IN THE ATACAMA DESERT

4.1. Isotopic Constraints on NO_3^- Sources

To evaluate the proportion of Atacama Desert NO_3^- attributable to atmospheric photochemistry and deposition we employed the isotope/photochemical box model for NO_3^- $\Delta^{17}\text{O}$ production presented by Michalski et al. (2003). This model uses the mass transfer mechanism discussed in the introduction in conjunction with a photochemical box model from Yvon et al. (1996) to evaluate η , β and χ and the importance of reactions 7 and 8. The input parameters were representative estimates for trace gas concentrations and emissions in the preindustrial atmosphere in the southern hemisphere given by Holland et al. (1999) and Logan et al. (1981). Trace gas concentrations were assumed constant through time, and the temperature was estimated by a simple seasonal tem-

perature model for 20°S. The model yielded an annual mean NO_3^- $\Delta^{17}\text{O}$ value of 24‰, slightly less than modern urban averages (26‰) because of the much smaller concentrations of NO_x and the associated reduced importance of the N_2O_5 production pathway (5) in comparison to modern polluted regions. These results are in general agreement with results from global climate models (GCM) that estimated the proportion of NO_3^- produced by each formation pathway and the corresponding deposition rates (Dentener and Crutzen 1993; Derwent et al. 2003). The GCM of Derwent et al. (2003) yielded $\eta = 0.91$, $\beta = 0$, and $\chi = 0.09$, giving a global average HNO_3 $\Delta^{17}\text{O} \sim 24.7\%$. Using this basis, the sample-to-sample contribution of NO_3^- to the nitrate minerals ranges from 55 to 88%. If each of the samples is assumed to represent an equal proportion of the total NO_3^- in the region, the average $\Delta^{17}\text{O}$ value (17.8‰) indicates at least 74% of the NO_3^- in the Atacama Desert nitrate ore deposits is the direct result of atmospheric deposition of photochemically produced NO_3^- .

There appears to be significant local variation in the $\Delta^{17}\text{O}$ values but no systematic trends with longitude or latitude were observed. The local variation may have at least two interpretations. The first is that all sources of NO_3^- have constant fluxes and the $\Delta^{17}\text{O}$ variation reflects fluctuations in the $\Delta^{17}\text{O}$ values of NO_3^- . The observed seasonal variation in $\Delta^{17}\text{O}$ values of modern NO_3^- ($\pm 5\%$) (Michalski et al. 2003) reflects changing oxidation pathways that alter as a function of solar intensity, NO_x concentrations, and temperature. However, these $\Delta^{17}\text{O}$ values should converge on a constant value when averaged over one or multiple years of collection. Variations in NO_3^- average $\Delta^{17}\text{O}$ values over longer time scales are expected to be small. Only a few per mil difference is observed (calculated) between ancient and modern NO_3^- $\Delta^{17}\text{O}$ values and the modern atmosphere has been perturbed by anthropogenic NO_x to a much greater degree than in long term climatic events. The possibility that tropospheric chemistry varied spatially and this was reflected in the isotopic composition in the individual deposits is considered unlikely. More plausible is that NO_3^- from long-term deposition, with little integrated $\Delta^{17}\text{O}$ variability, is mixed with NO_3^- derived from other mass-dependent sources whose importance varies temporally and spatially. The most likely source of this additional NO_3^- is nitrification of NH_4^+ derived from soil organic N (and possibly marine organic N) that was either co-deposited with NO_3^- or produced locally (e.g., by N_2 -fixing bacteria). Modern $\text{NH}_4^+/\text{NO}_3^-$ ratios in the remote, clean oceanic atmosphere are typically 1:1, but may be as high as 2:1, and organic N can equal NH_4^+ (as N) in coastal regions (Dentener and Crutzen 1994; Peierls and Paerl 1997). Even if some of the deposited NH_4^+ was volatilized as NH_3 , only a fraction of the available N would have to be nitrified to account for the remaining $\sim 25\%$ of the mineral nitrate in the absence of local N_2 fixation.

This two-source hypothesis is supported by analyses of caliche-type nitrate deposits from the milder, wetter Mojave Desert, where nitrification is more likely to be an important source of soil NO_3^- (Leatham et al. 1983). The $\delta^{17}\text{O}$, $\Delta^{17}\text{O}$, and $\delta^{18}\text{O}$ values of the Mojave Desert NO_3^- are presented along with the Atacama Desert NO_3^- values in Figure 2. There is a strong linear correlation between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values in the NO_3^- ($R^2 = 0.96$), which intercepts the terrestrial mass-dependent fractionation line near the zero intercept. A similar

correlation exists between the $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values. Experiments indicate that nitrate formed by microbial nitrification of NH_4^+ obtains two of its O atoms from water and one from air O_2 ($\delta^{18}\text{O} = 23.5\text{‰}$) (Andersson and Hooper 1983; Hollocher 1984). If this occurs with no associated isotopic fractionation, then microbial nitrification in the presence of water with an average $\delta^{18}\text{O}$ value of about -6‰ or lower, similar to meteoric water values in both regions (Williams and Rodoni 1997; Aravena et al. 1999), would yield $\delta^{18}\text{O}$ values of $\sim 4\text{‰}$ or lower. Several samples of NO_3^- from ground water in the Mojave Desert had $\delta^{18}\text{O}$ values of around $+1$ to $+3\text{‰}$ and $\Delta^{17}\text{O}$ values of around $+0.4$ to $+0.9\text{‰}$. The NO_3^- in those samples has relatively high $\delta^{15}\text{N}$ ($+7$ to 11‰) and is believed to have formed biologically by nitrification of both natural and anthropogenic reduced N (Densmore and Böhlke 2000). Therefore, the linear correlations among $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\Delta^{17}\text{O}$ are interpreted as mixing lines with end members representing $\text{NO}_3^-_{\text{atm}}$ and microbial NO_3^- , where the microbial NO_3^- may be derived from either atmospherically deposited reduced N or terrestrial reduced N. The limited extent of mixing indicated by the Atacama Desert deposits is consistent with as much as 100% of the total N being derived from atmospheric deposition: $\sim 75\%$ from direct deposition of $\text{NO}_3^-_{\text{atm}}$ derived from photochemical NO_x oxidation and $\sim 25\%$ from nitrification of inorganic/organic N that was also deposited from the atmosphere. In contrast, the Mojave Desert caliche NO_3^- samples appear to be partially derived from atmospherically deposited N, but also contain substantial amounts of N from terrestrial N_2 fixation, rock weathering, or plant N recycling.

Microbial N_2 fixation and nitrification of reduced N in the Atacama Desert could occur sporadically after occasional rainfall events or during longer periods of wetter climate. NO_3^- accumulated from nitrification and from $\text{NO}_3^-_{\text{atm}}$ deposition may not have mixed completely and this could account for some of the variability in the measured $\Delta^{17}\text{O}$ values of different samples. For example, long term (>100 yr) deposition of NO_3^- , NH_4^+ and organic N could accumulate these N species on the desert surface. During rare rain infiltration events, the

NO_3^- would be leached rapidly to depth, whereas the soil matrix might retain NH_4^+ and organic N. Subsequent nitrification of the reduced N would produce NO_3^- that would then be mixed with $\text{NO}_3^-_{\text{atm}}$ deposited during the next desiccation/infiltration cycle and the system could become heterogeneously mixed depending on water content, which could vary spatially by topography and soil composition. Partial dissolution and sequential crystallization during such events would result in heterogeneous deposits containing zones and veins of different composition, mineralogy, and O isotopic composition. Numerous cycles of NO_3^- deposition, nitrification, re-solution, and re-crystallization would be consistent with complex mineralogic assemblages and sequences described from detailed petrographic studies of the deposits (Searl and Rankin 1993). In future studies it would be interesting to determine if the nitrate morphology associated with different dissolution/crystallization dynamics have correlated $\Delta^{17}\text{O}$ values.

4.2. Isotopic Constraints on SO_4^{2-} Sources

To evaluate the contribution of nss- SO_4^{2-} to total mineral sulfate we have modeled the possible $\Delta^{17}\text{O}$ values for nss- SO_4^{2-} using various global climate models (GCMs), and the mass balance considerations discussed in the introduction. The GCM modeled $\Delta^{17}\text{O}$ values (0.4 to 1.2‰) are given in Table 2 and are similar to measured values in aerosol and rainwater SO_4^{2-} from La Jolla, California (Lee 2000). However, several of the Atacama Desert SO_4^{2-} $\Delta^{17}\text{O}$ values are higher than those, one by a factor of three. This suggests either that the GCMs are incorrectly partitioning oxidation pathways or that the oxidation pathways that generated SO_4^{2-} aerosols that were deposited in the Atacama Desert were markedly different from those in modern environments. A re-analysis of the GCM predictions indicates that the former explanation may be more likely.

GCM's commonly use simplified aqueous-phase chemistry to reduce model run times. One of these simplifications is the "bulk pH" parameterization, in which all cloud droplets are

Table 2. Global Circulation Model estimates of total SO_2 oxidation (top) and box model heterogeneous oxidation coupled to OH oxidation from the GCMs (bottom). $\Delta^{17}\text{O}$ for nss- SO_4^{2-} are estimated using the mass balance approach with $\Delta^{17}\text{O} (\text{‰}) = (1.4\text{‰}) \times \% \text{H}_2\text{O}_2 + (35\text{‰}) \times \% \text{O}_3 + (0\text{‰}) \times \% \text{OH}$. GCMs are ECHAM (European Centre Hamburg Model), GISS (Goddard Institute for Space Studies), GOCART (Goddard Global Ozone Chemistry Aerosol Radiation Transport) NCAR (National Center for Atmospheric Research), MOGUNTIA (Model of the Global Universal Tracer Transport in the Atmosphere).

Author	GCM Model	% OH	% O_3	% H_2O_2	nss- SO_4 $\Delta^{17}\text{O}$
Feichter (Feichter J. et. al. 1996)	ECHAM	35.9	13.5	50.4	1.1
Rasch (Rasch P. J. et. al. 2000)	ECHAM	18	8	74.0	1.2
Barth (Barth M. C. et al. 2000)	NCAR	17	0	83.0	0.7
Koch (Koch D. et. al. 1999)	GISS	29	0	70.7	0.5
Chin (Chin M. et. al. 2000)	GOCART	36	0	64.0	0.4
Langner (Langner J. and Rodhe H. 1991)	MOGUNTIA	15	na	na	?
Box Model					
O'Dowd (O'Dowd C. D. et al. 2000)		30	42	28.0	2.8
Lin (Lin X. and Chameides W. L. 1991)	Langer	15	33	52.0	3.0
Lin	Langer	15	63	22.0	5.0
Lin	Feichter	35.9	47.5	13.6	2.8
Lin	Rasch	18	60.8	10.2	4.6
Lin	Barth	17	61.5	10.0	4.7
Lin	Koch	29	52.6	12.3	3.4

assumed to have the pH of the total cloud (Lin and Chameides 1991). Since cloud water typically has pH values less than 4, H_2O_2 generally is considered to be the only oxidant because rates of O_3 oxidation of S(IV) decrease by 4 orders of magnitude between pH 5 and pH 4 (Savarino et al. 2000). The GCMs that use this assumption also predict the lowest $\Delta^{17}\text{O}$ values. A more refined analysis of cloud water S chemistry indicates that this simplification is not valid for estimating which oxidant is dominant in S(IV) oxidation (Lin and Chameides 1991; Chameides and Stelson 1992; Liang and Jacobson 1999). Lin and Chameides pointed out that overall cloud pH is actually an ensemble of two droplet populations, one acidic and one basic. The acidic droplets form from H_2SO_4 nuclei generated by OH oxidation of SO_2 , whereas the basic droplets arise from hydration of sea salt whose pH ranges from 6 to 8 in the marine boundary layer (MBL). Modeling the pH of the droplets as binned values, as opposed to bulk values, Lin and Chameides (1991) calculated that 74% of in-cloud oxidation is due to O_3 compared with 39% using the “bulk pH” approximation. Others have reached similar conclusions and have shown that this additional oxidation also increases the overall aqueous-phase oxidation proportion of nss- SO_4^{-2} (Liang and Jacobson 1999). The importance of O_3 oxidation of SO_2 in wet sea-salt droplets has also been inferred from field studies that found a larger fraction of nss- SO_4^{-2} in sea-salt particles than in smaller particles associated with H_2SO_4 nuclei (O’Dowd, Lowe and Smith 1999; Sievering et al. 1999).

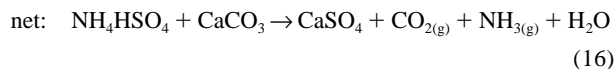
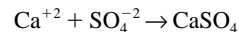
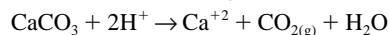
Recalculations of the modeled $\Delta^{17}\text{O}$ values using box models accounting for heterogeneous cloud chemistry and the GCM estimates of OH oxidation are summarized in Table 2. These values are in better agreement with the observed desert SO_4^{-2} values. The largest Atacama sulfate $\Delta^{17}\text{O}$ value (4 ‰) indicates that the Lin box model coupled to either the Langer, Barth or Rasch GCM may provide the best representation of S(IV) oxidation since these are the only combinations that yield $\Delta^{17}\text{O} > 4\text{‰}$. These model results are also in good agreement with SO_4^{-2} $\Delta^{17}\text{O}$ measurements from the Vostok ice core, which indicate nss- SO_4^{-2} $\Delta^{17}\text{O}$ fluctuations ranging from 1.3 to 4.8‰ over the past 140000 yr (Alexander et al. 2002).

Using the modeled 5‰ value as the average nss- SO_4^{-2} $\Delta^{17}\text{O}$ value, we estimate that between 10 and 80% (average = 34 ± 24) of the SO_4^{-2} associated with the nitrate ore deposits in the Atacama Desert is derived from nss- SO_4^{-2} , with the remainder from other sources such as sea salt or rock weathering. Direct comparison with data from the Vostok ice core, where continental aerosols and sea salt are less than 10% of the total SO_4^{-2} , could indicate between 30 and 100% of the Atacama Desert SO_4^{-2} is from atmospheric sources. It is emphasized that the SO_4^{-2} samples analyzed in this study are from the nitrate ores and may not represent all of the SO_4^{-2} in the soil profiles within the ore fields and elsewhere in the region (see section 3.3.1). The Mojave Desert SO_4^{-2} samples appear to have a slightly smaller average nss- SO_4^{-2} component, but the data are too limited to determine if they are systematically different (Table 1).

The large spread in SO_4^{-2} $\Delta^{17}\text{O}$ values (Fig. 3) indicates that there are multiple SO_4^{-2} sources and that some process has limited homogenization of these sources in the depositional environment. For SO_4^{-2} , with a dominant atmospheric $\Delta^{17}\text{O}$

value of $\sim 5\text{‰}$, variability among samples may be due to mixing of SO_4^{-2} with $\Delta^{17}\text{O} = 0$ derived from sea salt, mineral weathering, and volcanic sources that vary spatially. In addition, in contrast to NO_3^- $\Delta^{17}\text{O}$, long-term variations in atmospheric SO_4^{-2} $\Delta^{17}\text{O}$ values (Alexander et al. 2002) also may be reflected in the variability of the $\Delta^{17}\text{O}$ found in the sulfate minerals. Another possible explanation for SO_4^{-2} $\Delta^{17}\text{O}$ heterogeneity is selective leaching of the different aerosol types. Bao et al. (2000b) proposed a selective leaching mechanism based on aerosol size to explain SO_4^{-2} $\Delta^{17}\text{O}$ variability with depth in the Dry Valleys region of Antarctica. This mechanism may be viable near the coast but we consider it to be less likely in areas more than 10 km inland, especially in regions isolated by mountains, where size segregation by gravitational settling has already taken place (Wakshal and Nielsen 1982). An alternative selective leaching model that is based on the chemical composition and reactivity of the individual aerosols is now suggested.

Submicron size NH_4HSO_4 aerosols, derived from gas phase SO_2 oxidation and H_2O_2 aqueous phase oxidation, are acidic particles and would have correspondingly low $\Delta^{17}\text{O}$ values. In the Atacama Desert boundary layer, where relative humidity is often less than 20% (Cortes et al. 2000), these particles would be crystalline and would be dry deposited. Submicron sea salt aerosols are also present and are initially alkaline but will be progressively acidified by reactions with HNO_3 and by nss- SO_4^{-2} formation (dominated by O_3 oxidation, with large $\Delta^{17}\text{O}$). Nevertheless, even if the buffering capacity of the sea salt is overwhelmed by acidification, the sea-salt-derived particles will still be neutral upon drying because of expulsion of HCl gas. These two major SO_4^{-2} aerosol types would have not only different $\Delta^{17}\text{O}$ values, but also different deliquescence points and reactivity. During the onset of a wetting event (precipitation or fog), as relative humidity at the surface reaches 40%, the NH_4HSO_4 will reach its deliquescence point and form an acidic liquid droplet (Seinfeld and Pandis 1998). If this droplet is on CaCO_3 then dissolution of the CaCO_3 will occur with liberation of Ca^{2+} and CO_2 . Continued reaction with CaCO_3 eventually could raise the pH and promote volatilization of NH_3 , converting soluble NH_4HSO_4 to relatively insoluble CaSO_4 :



In contrast, the sea salt particles are predominately NaCl, with additional NaNO_3 and NaSO_4 from gas to particle conversion, and sulfate minerals similar to marine evaporates. The deliquescence of these particles occurs at approximately 75% relative humidity (Seinfeld and Pandis 1998), but low $\text{Ca}/\text{SO}_4^{-2}$ ratios and lack of H^+ limit the formation of insoluble CaSO_4 and the more soluble sulfate salts are leached below the surface. These contrasts in the surface behavior of different SO_4^{-2} aerosols can account for several important observations: (i) the paucity of carbonate in the soils of the Atacama Desert in

comparison to other deserts (Berger and Cooke, 1997); (ii) the abundance of CaSO_4 at the surface (Rech et al. 2003); (iii) the prevalence of sodium sulfate minerals in the nitrate ores (Searl and Rankin 1993) and (iv) the increased $\Delta^{17}\text{O}$ values with depth observed in polar deserts (Bao et al. 2000b).

4.3. Oceanic Versus Continental SO_4^{-2} Aerosol Deposition in the Atacama Desert

Given the isotopic evidence for large amounts of NO_3^- and nss-SO_4^{-2} in Atacama Desert salts, along with meteorological evidence showing that air masses arriving in the Atacama Desert can be either marine or continental in origin (Gallardo et al. 2002; Paluch et al. 1999) it is considered likely that there is significant input of both marine and continental SO_4^{-2} aerosols to the desert surface. It is emphasized that marine aerosols are not strictly sea salt particles, e.g., aerosols generated by sea spray, but also include particles generated by atmospheric chemistry in the MBL (nss-SO_4^{-2} , NO_3^- , organics). Sea salt particles that are derived from bursting air bubbles at the sea surface generate jet drops (diameter $>8\ \mu\text{m}$) and film droplets ($>3\ \mu\text{m}$). These are large particles and are rapidly removed by gravitational settling, with the rates being a function of particle size, altitude, and distance from the ocean. Although these large particles make up the majority of sea salt on a mass basis, their removal by dry and wet deposition on the Coastal Cordillera would rapidly deplete their importance in the air mass reaching the Atacama Desert. This phenomenon was clearly shown in the $\delta^{34}\text{S}$ and Sr isotope data of Rech et al. (2003) and has been used to interpret $\delta^{34}\text{S}$ gradients in SO_4^{-2} in other coastal areas (Wakshal and Nielsen 1982).

It is considered likely that the main component of marine aerosols reaching the desert surface are particles roughly $1\ \mu\text{m}$ in diameter or smaller. Submicron particles are readily entrained into the free troposphere, where they can be transported great distances, and can grow during cloud processing to micron size particles (the size fraction most efficient for HNO_3 reactions) that are then removed by deposition. Submicron SO_4^{-2} aerosols obtained in the Atlantic at $23\text{--}27^\circ\text{S}$ that were considered a mixture of DMS oxidation products and submicron sea salt particles have $\delta^{34}\text{S}$ values of 7 to 15‰ (Patris et al. 2000). A similar study in the south Pacific gave $\delta^{34}\text{S}$ values of $\sim 15\%$ for submicron SO_4^{-2} aerosols (Calhoun et al. 1991). The primary sources of preindustrial continental sulfur, volcanic and biogenic emissions, have average $\delta^{34}\text{S} \sim 0\%$ (Newman, Krouse, and Grinenko 1991). Therefore a model in which roughly sub equal amounts of SO_4^{-2} are derived from continental aerosols ($\delta^{34}\text{S} \sim 0\%$) and submicron marine aerosols ($\delta^{34}\text{S} \sim 10\text{--}15\%$) is consistent with the S isotope data from our study and that of Rech et al. (2003), and supports our hypothesis that most of the SO_4^{-2} in the nitrate deposits in the Atacama Desert is the result of atmospheric deposition.

5. SALT ACCUMULATION RATES IN THE ATACAMA DESERT

Given isotopic evidence that the nitrate ores of the Atacama Desert mainly represent long-term accumulation of atmospheric deposition, it is possible to estimate the amount of time required for the deposits to form if estimates of the preindus-

trial atmospheric deposition rates (dry and wet) and the accumulated mass of the deposits are known.

5.1. Accumulation Rate of NO_3^- by Dry Deposition

Nitrate accumulation by dry deposition of gas phase nitrogen oxides and NO_3^- can be estimated based on known or modeled deposition fluxes. Estimates of preindustrial N (and S) concentrations based on the limited number of studies on modern NO_x or NO_3^- aerosol concentrations in the Atacama Desert, which are biased due to current anthropogenic emissions (Saltzman et al. 1986; Prado-Fiedler and Fuenzalida 1996; Gallardo et al. 2002), would have large uncertainties. With the exception of polar regions and some midocean islands, continental air mass NO_3^- concentrations are generally always perturbed by human activity (Prospero and Savoie 1989). An alternative approach is to use global N deposition models, which are influenced by air mass origins, to derive estimates of past NO_3^- deposition rates. The coastal range is dominated by southerly winds driven by the Humboldt Current, however the exact origin of the air masses reaching the interior desert is less clear. Several studies suggest that air masses arriving in the Atacama Desert are a mixture of oceanic and continental (Paluch et al. 1999; Gallardo et al. 2002). We will assume equal proportions of oceanic and continental N deposition and models for each type of air mass will be utilized. The contribution of N by direct deposition of NO_x has been shown to be insignificant in comparison to NO_3^- deposition and will not be considered further (Duce et al. 1991).

The global oceanic deposition model of Duce et al. (1991) yielded deposition fluxes of $\sim 20\ \text{mg of N m}^{-2}\text{yr}^{-1}$ from NO_3^- for remote ocean islands and south Pacific surface waters, in agreement with results given in Warneck (2000) for pristine oceanic atmospheres. Approximately half this NO_3^- flux is thought to be via dry deposition ($\sim 10\ \text{mg of N m}^{-2}\text{yr}^{-1}$). Modeling of regional continental NO_3^- concentrations and deposition rates is more complex because NO_3^- concentrations depend largely on the proximity of NO_x sources and deposition rates that vary with local meteorology and physiography (Dentener and Crutzen 1994; Adams et al. 1999; Holland et al. 1999; Levy et al. 1999). In the preindustrial atmosphere, the main NO_x sources were soil emissions from denitrification, nitrification, natural biomass burning, lightning, and stratospheric mixing of NO_x generated by N_2O photolysis (Holland et al. 1999). The respective magnitudes of these sources would have been influenced by the presence of the Amazon basin (biomass burning, soil exhalation) and the Andean range (stratospheric mixing, lightning), which may have given rise to additional NO_3^- influxes to the Atacama Desert. A detailed estimate of the relative importance of these regions for local NO_3^- fluxes is difficult because of uncertainties in the amount and type of biomass burning and overall uncertainties in lightning and stratospheric fluxes (Holland et al. 1999). In addition, the effective removal by wet and dry deposition in the Andean range of NO_3^- produced in the Amazon basin should limit the influence of this region on NO_3^- reaching the Atacama. These factors were considered in the global nitrogen deposition model of Holland et al. (1999) in which estimated global preindustrial nitrogen fluxes in continental regions were based on land and plant types, local emission

inventories, and global circulation and precipitation. Nitrate fluxes to desert regions in the southern hemisphere were estimated to be between 21 and 84 mg N m⁻² yr⁻¹ with an average of 44 mg N m⁻² yr⁻¹, with approximately half of this flux attributed to dry deposition (22 mg N m⁻² yr⁻¹). If marine and continental air masses are about equally represented on average in the region, then these deposition models would imply a total dry deposition NO₃⁻ flux to the Atacama Desert surface of 16 mg N m² yr⁻¹.

5.2. Accumulation Rate of NO₃⁻_{atm} by Wet Deposition

Because measurable precipitation in the Atacama Desert can occur as rarely as once a century (Ericksen 1983), the contribution of NO₃⁻_{atm} from rainout or washout is considered negligible. However, the upwelling of nutrient rich, cold bottom water off the Chilean coast intensifies the aridity in the Atacama by condensing water vapor from oceanic air and generates heavy fogs called “camanchaca.” Camanchaca occurs up to 189 d annually in some areas (Cereceda and Schemenauer 1991), with central Chile averaging 45 d, and the fog has been repeatedly suggested as a possible source of the NO₃⁻ in the nitrate deposits (Searl and Rankin 1993; Berger and Cooke 1997; Rech et al. 2003). In latitudes south of 30° S, the occurrence of fog decreases because of atmospheric subsidence created by the South Pacific anticyclone. This, combined with the Coastal Cordillera barrier, limits fog reaching the region of the nitrate deposits to only ~15 d annually (Cereceda and Schemenauer 1991). To evaluate this potential source of dissolved ions in the Atacama Desert requires an estimation of fog water deposition rates and the concentrations of soluble ions in the fog water.

The virtual absence of vegetation in the region simplifies deposition velocities to gravitational settling since resistance from leaves and shrubs is zero. For fog droplets having a typical diameter of ~ 10 μm, a liquid water content of 1.5 g m⁻³ and a deposition velocity of 3 cm s⁻¹, the amount of fog water deposited to the desert surface would be ~0.2 L day⁻¹ m⁻² (Seinfeld and Pandis 1998). This rate will be slightly higher for hillsides, but for our purposes, a flat terrain approximation is satisfactory. A single fog-water sample collected east of Antofagasta, Chile contained Cl⁻, NO₃⁻, and SO₄⁻² concentrations of 46, 19, and 32 mg/kg, respectively (Ericksen 1981). However, in a separate study at El Tofo (inner coastal range) these same anion concentrations in fog were only 4.5, 0.75 and 5.9 mg/kg (Schemenauer and Cereceda 1992). Fog water from both sites contained detectable amounts of sea salt, but the authors also noted the possible influence of anthropogenic emissions on NO₃⁻ and SO₄⁻² concentrations, as well as the possible contribution of local dust that is highly enriched in both NO₃⁻ and SO₄⁻². Vong et al. (1997) analyzed northern hemisphere marine cloud water and found Cl⁻, NO₃⁻, and SO₄⁻² concentrations of 15, 0.9, and 4.6 mg/kg, which they considered to represent background marine cloud concentrations. Much of the fog invading the inland Chilean valleys is orographic fog, originating from stratocumulus clouds in the Pacific Ocean intercepting the coastal range (Cereceda et al. 2002). This observation, combined with the lack of data from Chilean fog samples unaffected by local or distant anthropogenic sources, prompts us to use the marine cloud-water con-

centrations of Vong et al. (1997). These data result in a fog NO₃⁻ deposition flux of approximately 0.5 mg N m² yr⁻¹, which is much smaller than the NO₃⁻_{atm} dry deposition flux.

5.3. Accumulation Time Estimates for NO₃

The Atacama Desert nitrate ore deposits are located primarily on the eastern side of the Coastal range in an area that is approximately 700 km long and 30 km wide, which would represent the minimum deposition area (21000 km²) (Ericksen 1983). A larger area encompassing the entire watershed could be considered as the deposition area if it is assumed that the NO₃⁻ was redistributed and concentrated locally by hydrologic or eolian processes. The total estimated wet (fog) and dry deposition flux of 16.5 mg N m²yr⁻¹ (as NO₃⁻) spread over the estimated area of the nitrate ore deposits (21000 km²) could account for ~350 metric tons of NO₃⁻-N annually. The amount of high-grade nitrate ore in the Atacama Desert is estimated to have been around 33 million metric tons (as N) and the more widespread low-grade deposits are perhaps twice this amount (Ericksen 1983), for a total of approximately 100 Mt as N. The $\Delta^{17}\text{O}$ data indicate that approximately 75% of the total (75 million tons of NO₃⁻-N) is derived directly from NO₃⁻_{atm} deposition, which would require a minimum of 214,000 yr to accumulate in the area of the major deposits. The required time would be shorter if the NO₃⁻ was accumulated over a larger area and then concentrated in the deposits via postdeposition redistribution, or it could be longer if the estimates of NO₃⁻ reserves are biased to exclude large amounts of material with low (non-economic) concentrations.

The hyper-arid conditions of the Atacama Desert are estimated to have existed for at least 6 million years and perhaps as long as 15 million years (Alpers and Brimhall 1988; Hartley and Chong 2002), which is more than sufficient time to accommodate our deposition estimates. It is possible that the 214,000 yrs. underestimates by a factor of two, or perhaps even by an order of magnitude, the actual time required to accumulate the NO₃⁻ because of uncertainties in the deposition rates, the air masses trajectories and estimates of the NO₃⁻ reservoir in so large an area. In addition, this timeframe is based on the assumption that all deposited NO₃⁻ is retained in the soil and that no net loss by wind erosion or denitrification has occurred. $\delta^{15}\text{N}$ values indicate that denitrification is not a major sink for NO₃⁻ in the Atacama Desert (Böhlke et al. 1997), which is reasonable given the lack of water, yet wind erosion in deserts is considered significant (Reheis and Kihl 1995). The importance of wind erosion for NO₃⁻_{atm} accumulation depends on the rate at which NO₃⁻ is leached and transported downward below the exposed surface. The fogs and rare precipitation events, which only contribute a small fraction of the total NO₃⁻_{atm} deposition rate, may play an important role in moving NO₃⁻ below the surface. The arid conditions also are punctuated by brief periods of heavy rainfall (Vargas et al. 2000) and perhaps longer periods (10³ to 10⁴ years or longer) of overall decreased aridity. These conditions may have helped create vertical salt zonation based on solubility differences, and they may have periodically diminished the NO₃⁻ salt deposits by leaching them into ground water or to deeper horizons in the unsaturated zone. If our estimates are correct, then it is possible that the modern (preexploitation) nitrate ore fields represented

only a small fraction of the total accumulation of atmospheric NO_3^- since hyperarid conditions were established in the region and that large reservoirs of NO_3^- either exist in the subsurface or have been removed.

5.4. Accumulation Rates of Other Salts in the Atacama Desert

The isotopic evidence and NO_3^- atm deposition calculations indicate that the accumulation of atmospheric particles is the major source of the NO_3^- and SO_4^{2-} in the Atacama Desert nitrate ore fields. An additional check on this conclusion is to estimate what the expected anion ratios should be for atmospheric deposition and compare those ratios with the observed ratios in the deposits. Submicron aerosols in clean marine air contain approximately equal molar amounts of Cl^- , sea salt SO_4^{2-} , and nss- SO_4^{2-} , but only about one tenth as much NO_3^- atm (Sievering et al. 1999). Preanthropogenic continental aerosol anion ratios are more difficult to assess because of the anthropogenic influences in modern studies. One approach is to adopt anion ratios from Andean ice core data. These cores span the past 20000 yr and represent the anion composition of high-elevation, east-to-west moving air masses. Anion data from the Sajama ice cap in the Bolivian Andes east of the Atacama Desert exhibit some variability on 1000 yr timescales, but average molar ratios of $\text{NO}_3^-/\text{Cl}^-$ and $\text{NO}_3^-/\text{SO}_4^{2-}$ are roughly 2:1 and 1:2 respectively (Thompson et al. 1998; Thompson et al. 2000). As a first approximation, assuming half continental and half oceanic sources for the air masses (see above), one might expect bulk ratios of $\text{NO}_3^-/\text{Cl}^-$ and $\text{NO}_3^-/\text{SO}_4^{2-}$ to be ~ 1.0 and 0.3 , respectively, in the Atacama Desert.

Data compiled by Grossling and Ericksen (1971) and Erickson (1981) indicate $\text{NO}_3^-/\text{Cl}^-$ and $\text{NO}_3^-/\text{SO}_4^{2-}$ molar ratios in the bulk nitrate ores are around 1.27 and 1.03, respectively (Table 3). The apparent relative enrichment of NO_3^- over Cl^- and SO_4^{2-} in the ores may simply be an artifact since the salt ratios compiled for the nitrate ore layers may not represent the total salt ratios in the region. For example, failure to include some of the non-soluble sulfate phases such as CaSO_4 that occur above the nitrate ores could explain the difference in the

$\text{NO}_3^-/\text{SO}_4^{2-}$ ratios. Another uncertainty is the degree to which wind erosion has fractionated the various salts. Because Cl^- and NO_3^- are more readily leached below the surface, surficial gypsum and anhydrite may be more susceptible to erosion, with the result that SO_4^{2-} may be selectively transported out of the region by wind. Therefore, the bulk anion composition of the ores is considered reasonably consistent with an atmospheric source for much of the NO_3^- , SO_4^{2-} , and Cl^- , as suggested by Böhlke et al. (1997). Acknowledging the atmospheric source of NO_3^- while simultaneously discounting the importance of nss- SO_4^{2-} and Cl^- deposition (Rech et al. 2003) would appear to be unsupported by these data.

Substantial amounts of iodate and perchlorate salts also are present in the Atacama Desert nitrate ores. Grossling and Ericksen (1971) estimate that the average bulk nitrate ores have molar ratios of $\text{IO}_3^-/\text{NO}_3^- = 0.0034$; $\text{ClO}_4^-/\text{NO}_3^- = 0.0028$ (Table 3). Iodate is the only aerosol iodine species that is not volatile and it is formed through gas phase oxidation of IO by O_3 in a process that resembles the NO_x cycle (Chatfield and Crutzen 1990). There is little anthropogenic IO_3^- in comparison to natural IO_3^- in modern aerosols, which have IO_3^- concentrations ranging from 1 to 7 ng m^{-3} (Wimschneider and Heumann 1995; Baker et al. 2001). Combining those concentrations with preindustrial estimates of $\sim 20 \text{ ng m}^{-3}$ of NO_3^- atm (Duce et al. 1991; Warneck 2000) would give $\text{IO}_3^-/\text{NO}_3^-$ molar ratios of 0.002 to 0.013, similar to the bulk ratios in the Atacama Desert nitrate ores, consistent with the IO_3^- in the ores being mainly the result of photochemistry and subsequent atmospheric deposition. Because of its interaction with O_3 , the O isotopic composition of IO_3^- might indicate its origin; however, the absence of significant $\Delta^{17}\text{O}$ would not necessarily exclude photochemistry because exchange between IO_3^- and water is rapid (Gramsjaeger and Murmann 1983).

Perchlorate is perhaps even more interesting with respect to the origins of the salts. No measurements of ClO_4^- concentrations in aerosol have been made to our knowledge. However, several authors have suggested the possibility of stratospheric production of aerosol ClO_4^- through the reaction of perchloric acid or ClO on stratospheric SO_4^{2-} aerosols (Jaegle et al. 1996; Murphy and Thomson 2000). ClO chemistry is remarkably similar to NO_x chemistry, with rapid photolysis and O_3 oxidation sequences, which prompted Lyons to propose the existence of substantial $\Delta^{17}\text{O}$ values in stratospheric ClO (Lyons 2001). There is no known source of tropospheric ClO_4^- or other geologic mechanism known to produce substantial amounts of ClO_4^- . Therefore, if the O isotopic composition of ClO_4^- salts could be shown to have non-zero $\Delta^{17}\text{O}$ values, then it might be concluded either that some of the Atacama Desert salts are from stratospheric aerosols (Ericksen 1983) or that there is an unknown source of tropospheric or terrestrial ClO_4^- . Investigations on the isotopic composition of both these compounds should be carried out.

6. CONCLUSIONS

The O isotopic composition ($\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\Delta^{17}\text{O}$) of NO_3^- and SO_4^{2-} in the nitrate mineral deposits of the Atacama Desert have confirmed that the main source of these anions is the long term accumulation of NO_3^- and SO_4^{2-} produced by photochemical reactions in the atmo-

Table 3. Average composition of soluble salts in nitrate ores of the Atacama Desert (data from Grossling and Ericksen, 1971) derived from 815 analyses representing monthly averages from 1932 to 1967 for ores treated by the two largest nitrate production plants (Oficina Pedro de Valdivia and Oficina Maria Elena). Relatively insoluble phases containing Ca^{+2} , SO_4^{2-} , $\text{B}_5\text{O}_9^{-3}$, and IO_3^- may be underestimated.

Soluble component	Fraction in ore (wt. %)	Mole ratio with respect to Cl^-
Cl^-	4.58	1
SO_4^{2-}	10.00	0.806
NO_3^-	6.29	0.786
$\text{B}_5\text{O}_9^{-3}$	0.50	0.020
IO_3^-	0.060	0.0027
ClO_4^-	0.028	0.0022
Na^+	6.90	2.33
Ca^{+2}	1.81	0.35
Mg^{+2}	0.46	0.15
K^+	0.73	0.14
Sum	31.36	

sphere. The deposits represent accumulation of submicron particles transported in the free troposphere and removed primarily by dry deposition. Variation in $\text{NO}_3^- \Delta^{17}\text{O}$ values is most likely the result of mixing of NO_3^- derived from microbial nitrification with the atmospheric photochemical source. Comparative data from the Mojave Desert indicate that the photochemical NO_3^- isotope signature is well preserved in the driest surficial environments that are almost lifeless, whereas the microbial NO_3^- isotope signature becomes dominant rapidly with increasing moisture, biologic activity, and N cycling. The SO_4^{2-} isotope data indicate a large fraction of the SO_4^{2-} is derived from atmospheric nss- SO_4^{2-} that is produced by heterogeneous and homogeneous oxidation of SO_2 . However, a more complete study of SO_4^{2-} O isotopes based on location and depth should be undertaken to assess the importance of aerosol deliquescence and other surface reaction properties on $\text{SO}_4^{2-} \Delta^{17}\text{O}$ values.

These findings are important for a variety of fields in biogeochemistry. In the Atacama Desert, $\Delta^{17}\text{O}$ values represent a preserved isotopic signature of atmospheric processes that occurred over hundreds of thousands to millions of years. If future isotopic measurements could be coupled with detailed dating studies, it is possible that new insights would be obtained about atmospheric processes dating back millions of years, where few proxies are currently available. In paleoclimate studies using ice cores, where in situ nitrification is limited and annual deposition is isolated in ice layers, $\text{NO}_3^- \Delta^{17}\text{O}$ variations might indicate shifts in atmospheric oxidative pathways. This principle also may be applied to extraterrestrial planetary studies where, for example, investigations of atmosphere/regolith interactions utilizing mass independent isotopic compositions have raised new questions about the evolution of the Martian atmosphere (Farquhar et al. 2000; Farquhar and Thiemens 2000). The existence of NO_3^- in the Martian regolith has been proposed theoretically (Yung and DeMore 1999) and confirmed by analyses (Grady et al. 1995) and isotopic analyses of future returned samples may provide information on the ancient Martian atmosphere unattainable by other means.

Measurements of the complete O isotopic composition of NO_3^- are useful not only for tracing atmospheric/photochemical processes but also for probing the influence of biologic processes on NO_3^- formation. In natural systems on Earth, NO_3^- formation is mainly the result of photochemistry ($\Delta^{17}\text{O} > 0$) or biologic nitrification ($\Delta^{17}\text{O} = 0$). The Atacama Desert is commonly studied as a model for the Martian surface, and it is possible that $\Delta^{17}\text{O}$ measurements could be used to identify products of nitrification by biologic processes in extraterrestrial samples as well, making this a potentially important planetary biomarker. On Earth, $\text{NO}_3^- \Delta^{17}\text{O}$ values can provide a measure of the contribution of $\text{NO}_3^-_{\text{atm}}$ deposition in aquatic systems where a variety of natural and anthropogenic NO_3^- sources are present. For example, this would be useful in northern hemisphere countries concerned with the effects of N deposition associated with fossil fuel burning. This study has highlighted the importance of examining all three stable isotopes of oxygen in studies concerned with interactions between atmospheric and terrestrial/biosphere processes.

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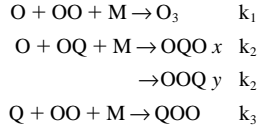
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APPENDIX

Ozone $\Delta^{17}\text{O}$ values can be calculated knowing the rates of formation and destruction of the various isotopomers. The photolysis rates for each isotopomer are assumed to be approximately equal given their quantum nature and it is in the recombination process that isotopic partitioning occurs. The three possible ozone isotopomer production channels are



Where Q is either ^{17}O or ^{18}O , x/y is the branching ratio for the OQ + O reaction which can form symmetric OQO (x) or asymmetric QOO (y) ozone molecules, and k 's are the measured rate coefficients. The rates of formation are then

$$d/dt[\text{OQO}] + [\text{QOO}] = k_2[\text{OQ}][\text{O}] + k_3[\text{OO}][\text{Q}] \quad (17)$$

$$d/dt[\text{OOO}] = k_1[\text{OO}][\text{O}] \quad (18)$$

In calculating the isotopic composition of the bulk ozone it is not necessary to differentiate between the symmetric and asymmetric branching ratio since $x + y = 1$, but this has been done by other investigators interested in symmetric/asymmetric enrichments. Dividing (17) by (18), assuming steady state ($d/dt = 0$) gives

$$([\text{OQO}] + [\text{QOO}])/[\text{OOO}] = k_2/k_1[\text{OQ}]/[\text{OO}] + k_3/k_1[\text{Q}]/[\text{O}]$$

The isotopic exchange between $\text{O}_3(\text{P})$ and O_2 ($\text{Q} + \text{O}_2 \leftrightarrow \text{OQ} + \text{O}$) is many orders of magnitude faster than the O_3 production rate and it therefore determines the $[\text{Q}]/[\text{O}]$ ratio. The equilibrium constant (K_{eq}) for this exchange has been measured for Q = ^{18}O ($1.94\exp(32/T)$) and calculated for Q = ^{17}O ($1.97(16/T)$) (Kaye and

Strobel 1983). The normalized rate ratios of $k_{2n} = k_2/k_1$ and $k_{3n} = k_3/k_1$ have been measured by Mauersberger (1999) for ^{18}O ($k_{2n} = 1.27$, $k_{3n} = 0.93$) and for ^{17}O ($k_{2n} = 1.17$, $k_{3n} = 1.03$) giving

$$([\text{OQO}] + [\text{QOO}])/[\text{OOO}] = (k_{2n} + k_{3n}(K_{\text{eq}})^{-1})[\text{OQ}]/[\text{OO}]$$

$$\begin{aligned} \frac{([\text{OQO}] + [\text{QOO}])/[\text{OOO}]}{[\text{QO}]/[\text{OO}]} &= \frac{[\text{QO}]/[\text{OO}]_{\text{O}_3}}{[\text{QO}]/[\text{OO}]_{\text{O}_3}} = \frac{2}{3} (k_{2n} + k_{3n}(K_{\text{eq}})^{-1}) \\ &= 1.133 \text{ }^{18}\text{O} = 1.110 \text{ }^{17}\text{O} \quad (19) \end{aligned}$$

The left-hand side of (19) takes the form of R/R in the familiar isotope delta formula (1) with product ozone as the sample and the initial O_3 as the reference. Statistically only 2/3 of the O_3 molecules generated from conversion of OQO + QOO (19, middle) will contain Q, hence the balancing factor of 2/3 on the right-hand side of (19). Using (1) and (2) gives $\delta^{18}\text{O} = 133\%$, $\delta^{17}\text{O} = 110\%$ and $\Delta^{17}\text{O} = 40.8\%$.

The rate constants used above (k_{n2}, k_{n3}) were determined at low pressure (200 Torr) relative to tropospheric conditions. The experimental data on the pressure and temperature dependence of ozone $\Delta^{17}\text{O}$ values is more applicable, and is useful in examining the magnitude of ozone $\Delta^{17}\text{O}$ variations under tropospheric conditions. A second order polynomial fit of the pressure dependency data from Morton (1990) yields $\delta^{18}\text{O} = -1.1385p^2 + 2.3185p + 11.559$ and $\delta^{17}\text{O} = -0.8979p^2 + 1.8069p + 10.3$, where p is the log of pressure in Torr. The temperature data (adjusted for isotopic exchange), also from Morton et al. (1990), give linear fits relative to T (K): $\delta^{18}\text{O} = 0.035T + 4$ and $\delta^{17}\text{O} = 0.0243T + 3.7667$. For surface pressure of 1 ATM (760 Torr) and temperature of 298K, $\Delta^{17}\text{O}$ values of 34.8‰ and 34.7‰ are generated respectively. Temperature variations with altitude in the boundary layer ($\sim 3\text{km}$) are typically ± 10 K resulting in a maximum $\sim 1.5\%$ $\Delta^{17}\text{O}$ fluctuation and a similar value arises from the pressure variability. Since altitudinal changes in T and P effect $\Delta^{17}\text{O}$ in opposite directions, and only daytime T (ozone production) variations are considered, the P and T effect is on the order of 1‰. Since nitrate deposition to the Atacama is an annual average and integrated over thousands of years, the O_3 and $\text{NO}_3^-_{\text{atm}}$ $\Delta^{17}\text{O}$ values can be considered constant at $\sim 35\%$ and 24‰, respectively.