

Chemistry and Origin of the Chilean Nitrate Deposits

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ABSTRACT

The Chilean nitrate deposits are one of the world's most unique and puzzling mineral deposits. They occur in the northern coastal desert region of Chile over a north-south range of approximately 700 km and over an east-west distance of 10–150 km as an almost continuous deposit of sodium nitrate and other soluble salts. It is the only substantial concentration of sodium nitrate anywhere in the world other than possible one or more small dry lakes in northern Africa. It is also the only solid phase deposit containing water soluble iodate, perchlorate and chromate ions. Sodium chloride and sodium sulfate occur in approximately the same quantity as the sodium nitrate, and there are smaller quantities of potassium, magnesium, boron and lithium. No bromine is present.

Many quite diverse theories have been presented in an attempt to explain the origin of the deposit, but all of them appear to have serious problems. Based upon some recent experimental data on catalytic nitrogen oxidation, a new theory is proposed in this paper. First, it is suggested that the more common ions in the deposit: sodium, potassium, magnesium, calcium, lithium, chloride, sulfate, borate and carbonate came from salars, thermal springs and the leaching of the adjacent

terrain, and were transported to the lower valleys through rivers, faults and underground aquifers. Once such water was in the salar aquifer, it evaporated. The extremely hygroscopic nature of the sodium nitrate, with recurring and persistent fogs, high water table and sporadic rain result in a net capillary movement of the solutions to the surface in some of the lower land areas, allowing evaporation to occur. Periodic partial leaching of the top meter or so of soil from the sporadic rains, followed by renewed capillary activity, continue to thoroughly mix, evaporate and spread the deposit. Wind action, however, is the principal means of redistributing the salts to cover the terrain fairly uniformly.

The nitrate and other less common elements require multiplicity of theories to explain their origin. Recent studies have indicated that desert soils of various types have the ability to photo-catalytically fix oxides of nitrogen from the air. This mechanism would have been especially active in the high Atacama elevations and with the clear skies of the Chilean desert. It is suggested that this photo oxidation, assisted by moisture from the frequent fogs, probably resulted in the accumulation of iodides and perchlorates.

INTRODUCTION

The Northern Chile sodium nitrate, or "caliche" deposit, represents one of the truly large saline (water soluble mineral) occurrences in the world. The author estimates that based upon current mining data and government records it contains over a billion tons of sodium nitrate, slightly less sodium chloride, and perhaps twice that amount of sodium sulfate. Potassium nitrate, magnesium sulfate and boric acid may total about 100 million tons each, while the iodine and sodium perchlorate content are both about five million tons. The deposit area averages approximately 700 km in a north-south direction, by 30 km in an east-west direction. The ore is generally most concentrated from one to five meters below the surface but is at about half strength in the overburden, and there are very small amounts of nitrate and the other salts to a considerable depth.

Various high grade zones of this deposit have been commercially extracted since the 1800s, and for many years this production represented the world's only large commercial source of nitrates for gun powder, fertilizer and chemicals. Areas having medium grade ores are still being mined, and "salitre" has remained a major industry for northern Chile. A great deal has been written about the deposit, and a recent paper (Erickson, 1981) presents a comprehensive review of the geology of the area, the deposit and theories of its origin.

The deposit is not only large but contains a unique collection of minerals with very little evidence of their source or how they were emplaced. Nitrates, for instance, are common in nature, but there have been only one or two other non-guano deposits reported anywhere in the world. Even though nitric acid, nitric oxides and ammonia are known to be minor constituents of the air, and a common constituent of soils from nitrogen reducing-bac-

terial, plants, algae, etc., nitrate salts (except from bird or bat guano) have nowhere else accumulated to an appreciable concentration or tonnage.

In a similar manner, iodine is a common constituent of oceanic waters, plants and animals and occurs in dilute concentration (usually below 100 ppm) in some brines. There are a few small occurrences of silver and copper iodide, but nowhere else has it been reported as a solid soluble mineral or in any substantial concentration. Furthermore, its oxidation state in the caliche deposits is as the iodate ion, an unusually high (and generally unstable) form.

Perchlorate is also present in the deposit in significant quantities. As with the iodate it is not found anywhere else and is in a high oxidation state. Chromate is the final unusual soluble salt in the deposit and is also unique to this location. Its oxidation state is likewise uncommon, because its form in chromite (the most common ore) and other minerals is usually as the chromium ion.

From a physical viewpoint the deposit is equally perplexing. There is very little uniformity as to grade, location or ratio of the constituent minerals. The sodium nitrate can vary from a fraction of one percent to pure crystalline NaNO_3 , and from high grade ore on the surface to traces many meters below it. It can occur equally on hills, in gullies or depressions, in fractured bedrock, or in porous conglomerate. It can be most concentrated adjacent to salars, or far from them, and occurs fairly continuously over a surprisingly large area. It is found at elevations varying from 1000 to 4000 meters and is definitely not the customary saline dry lake bed, or solar evaporated crystalline deposit.

DESCRIPTION OF THE DEPOSIT

An attempt will be made to abstract the more pertinent geological and topographical description of the deposit and its environment that have previously been reported (Eriksen, 1981). For more complete detail this paper should be consulted. Some of the author's data has also been added to these descriptions.

Location. The nitrate deposit is in the Atacama Desert of northern Chile, west of the Andes Mountains and east of the coastal range in broad, gentle valleys. Most of the deposit is in the provinces of Tarapacá and Antofagasta, although it extends in isolated areas in all directions, including into the coastal Desert of Peru. It varies from a few kilometers to 150 km in width in an east-west direction and extends north-south for about 700 km. The northern-most occurrences in Tarapacá are largely restricted to a narrow band along the east side of the Coastal Range, whereas to the south, they spread more extensively in the Coastal Range, Central Valley and Andean Front. Non-commercial nitrate deposits and nitrate-rich soils are much more widespread than the com-

mercial or potentially commercial deposits. Much of the Coastal Range is encrusted with nitrate-bearing, saline-cemented regolith, commonly ranging from a few tens of centimeters to a meter or two in thickness. Near-surface fractured bedrock also contains veins and may be impregnated by saline minerals. Low-grade nitrate ore, containing 1–7 percent NaNO_3 , probably forms an almost continuous band, 10–30 km wide, along the center and eastern side of the Coastal Range throughout the region of the nitrate fields. Scattered occurrences occur over a much greater distance.

Most of the commercial nitrate deposits are at altitudes less than 2,000 m, but those east of Aguas Blancas extend upward to altitudes of about 3,000 m. The deposits in the vicinity of Salar de Maricunga, which has not been exploited, are near 4,000 m.

The general terrain in northern Chile varies from west to east: 1) a relatively low Coastal Range with a maximum width of 50 km, with some wave cut cliffs of 1000 m, and whose peaks are generally less than 2,000 m in altitude; 2) a longitudinal depression or Central Valley, called the Pampa del Tamarugal (It is broadest and deepest in northern Antofagasta and southern Tarapacá provinces. The Central Valley consists of two major north-south segments, the Pampa del Tamarugal in the north and a similar basin to the south, centering at Aguas Blancas. The two segments are separated by the broad transverse Baquedano Valley); and 3) the high Andes Mountains, a plateau about 4000 m in altitude with many volcanic peaks. The elevation differences and profile in the nitrate area is generalized in Figure 1.

Geology. The Andes Mountains in the north of Chile contain hundreds of well preserved volcanic cones. Only a few of them are known to have erupted in historic time, but many show fumarolic activity, and there are abundant hot springs. In Tarapacá Province the Andean Front is marked by gentle slopes that merge with the Pampa del Tamarugal, whereas southward, longitudinal front ranges and valleys separate the Andean plateau from the Central Valley.

Northern Chile is underlain chiefly by sedimentary and volcanic rocks of Jurassic and Cretaceous age, covered extensively by volcanic rocks and associated unconsolidated sediments of Tertiary and Quaternary age. The Andean Front has a thick cover of alluvial sediments and interbedded ash-flow tuffs. The Central Valley contains a generally porous fill of alluvium and interbedded lake sediments that are as much as 900 m thick in the Pampa del Tamarugal. The Coastal Range is mantled with saline-cemented regolith consisting chiefly of fragmental rock material admixed with windblown silt and sand. The windblown material consists chiefly of fine volcanic ash and eroded playa sediments. The only known saline deposits in the older rocks of the region are anhydrite beds in marine sedimentary rocks of Late Jurassic age ex-

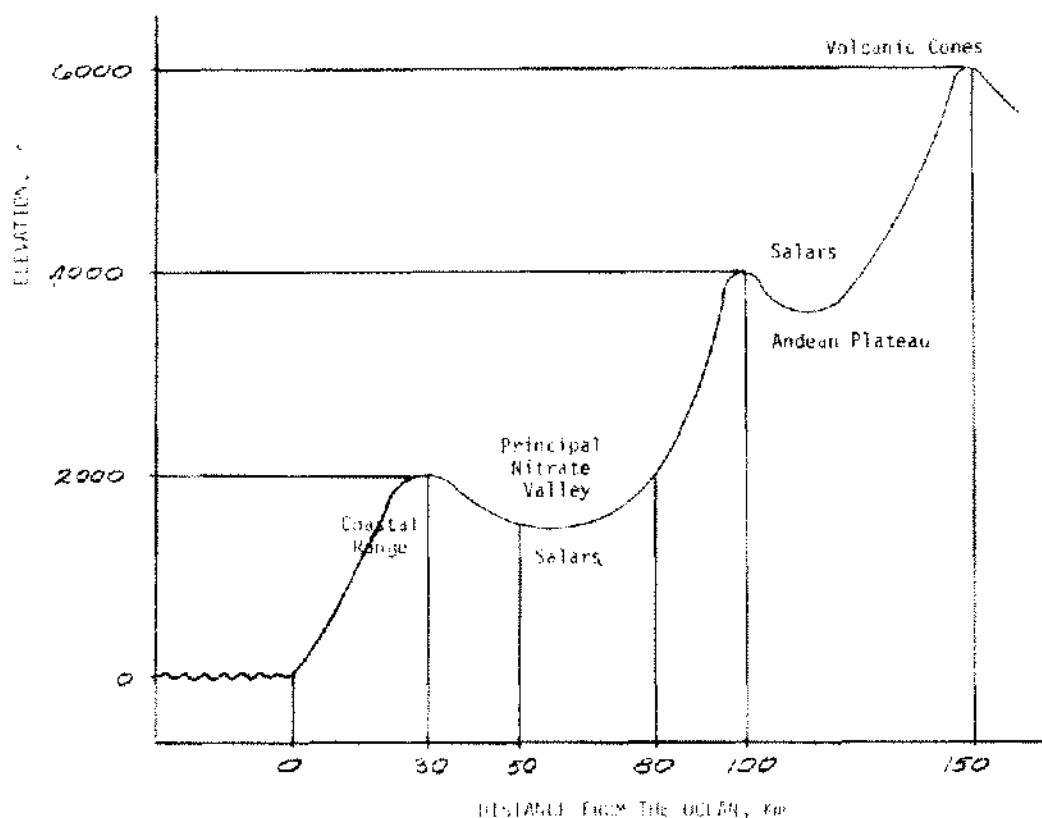


Figure 1. Typical elevation profile in the nitrate deposit area

posed in the Central Range, and an outcropping of rock salt of Cretaceous to early Tertiary age near San Pedro de Atacama.

The Atacama Desert has had an extremely arid, nearly rainless climate since at least Miocene time, and some of the Miocene and even earlier Tertiary landforms have been preserved with little modification. Other areas have been somewhat modified by late Tertiary and Quaternary block faulting. Additional modification by stream erosion has been slight, attesting to the aridity of the climate since early Tertiary time. Infilling of the Central Valley, which became a depression as the result of uplift of the Coastal Range and Andes, began in Oligocene time and was largely completed by the end of middle Miocene time. The deep transverse valleys in northern Tarapacá and Baquedano were formed after middle Miocene time by streams from the Andes that cut across the Central Valley. The Andean uplift has continued until the present, accompanied by the ejection of huge amounts of volcanic material, chiefly of rhyolitic composition during the Miocene and Pliocene, and of andesitic composition during Quaternary time.

Northern Chile during the late Tertiary and Quaternary time contained many saline lakes within the closed basins. Such lakes evidently formed at times of exceptionally high rainfall and runoff from the Andes, but

small saline lakes and ponds also occurred in closed basins of the Coastal Range that were interconnected by recent faults serving as conduits carrying water from the Central Valley. The central region was the site of a large perennial lake of probable late Tertiary age.

About 100 closed basins now exist in northern Chile, many of which contain salars or dry lakes in their lowermost parts and have prominent shoreline features. Shallow playa lakes now form in the Atacama Desert only at places along the western margin of the Pampa del Tamarugal at times of exceptionally heavy rainfall in the Andes. These lakes may form only once or twice in a 10-year period and last from a few days to several weeks.

CLIMATE, VEGETATION AND SOIL MICROORGANISMS

The Atacama Desert is claimed to be one of the driest in the world, averaging an annual rainfall of less than a millimeter in the areas where the nitrate deposits are most prevalent, and in any given part of the desert, measurable rainfall (1 mm or more) may be as infrequent as once every 5 to 20 years. Heavy rainfall of a centimeter or more may take place only a few times each century. Such rains may continue intermittently for several days and have an aggregate precipitation of several centimeters.

Because rainwater soaks into the ground with little or no runoff, gullying is minimal, and even some of the large valleys lack well-defined stream courses. Because of salt cementing and moisture adsorption, most surfaces are relatively stable and give rise to dense dust clouds only during very strong, turbulent winds. Sand dunes are fairly uncommon, and most of the region is devoid of plant growth. Plants are found only along streams, in a few areas where the ground water table is near the surface, and on hills along the coast that receive abundant fog condensate.

Rainfall shows a general increase with altitude, and the lowest limit of regular or seasonal precipitation is at altitudes of 2,500 to 3,000 m in some areas along the Andean Front. In this region, the rains are commonly associated with thunderstorms. Parts of the Tarapacá Province (above 4,000 m) can have up to 276 mm moisture, while in the Andes of central Antofagasta the moisture does not exceed 50 mm, chiefly as snow during the winter months. Because of the prevalence of snow, which tends to sublime rather than melt, this region is nearly as arid as the Atacama Desert.

One of the unusual features of the Atacama Desert is the presence of widespread, relatively abundant ground water supplies, commonly not more than 10–50 meters below the surface. The ground water occurs in the alluvium of the Central Valley as well as in other valleys along the Andean Front and the Coastal Range. The soil is generally porous from the water level to the surface. Ground water is recharged chiefly by runoff from the Andes and by slow infiltration along recent faults that connect the basins with higher ground.

Dense coastal fogs or low clouds, locally known as *camanchaca*, sweep inland from the Pacific Ocean, covering the nitrate area nearly every night during the winter months of June to August, and usually precipitating some condensate on the soil surface. At times of the most prevalent fogs the condensate may be sufficient to moisten soil to depths of a millimeter or two, and exceptionally heavy fogs cause deeper moistening of the soil. The amount of water deposited in this way is perhaps a few millimeters per month, and it is largely evaporated the following day. However, the near-surface soil moisture probably remains relatively high during the cool winter months. The fogs in most areas generally do not extend farther east than the Central Valley but do fairly completely cover the nitrate zone.

The Atacama Desert is characterized by ocean breezes during the morning that alternate with easterly winds from the Andes during the afternoon and night. Along the coast, south to southwesterly winds dominate, whereas inland the winds are more variable in direction. The winds are generally somewhat confined to the Valley area. Because of this, wind-transported material tends to be spread rather evenly over the desert, instead of form-

ing duneal accumulations. Wind erosional features are in many places more predominant than those from water erosion.

Recent studies have indicated that few soils in the Atacama Desert have bacteria or microflora populations capable of nitrogen fixation. The microbial activity in most of the dry soils is exceedingly low, a requisite for preservation of the nitrate. The soils contain a variety of species of bacteria, actinomycetes, molds and algae, but populations are generally several orders of magnitude less than in soils of milder deserts. Laboratory cultures show considerable diversity in types and growth rates of microflora populations and capacity of ammonification and nitrification. Bacteria and actinomycetes are generally the most abundant microorganisms present, and near the salars there is sporadic evidence of sulfate reducing bacteria.

Nostoc muscorum, a well-known nitrogen-fixing, blue-green algae, was found in mud from the edge of a saline pond in Salar de Bellavista near Oficina Victoria. It has also been found in the coastal desert of Peru where winter fogs are most prevalent and where fog condensate is somewhat greater than it is in the Atacama Desert. Such filamentous blue-green algae are photoautotrophic-requiring only oxygen, light and inorganic substances for their life processes, and many species have the ability to fix atmospheric nitrogen.

STRUCTURAL FEATURES OF THE NITRATE DEPOSITS

Nitrate deposits occur fairly uniformly from the tops of hills and ridges to the centers of the broad valleys, but the richest deposits that have been worked from the earliest period tend to be on the lower slopes of hills. Nevertheless, high-grade deposits also are found in broad, debris-filled valleys and basins and in nearly flat to gently undulating terrain. Several salars, in addition to those in the Baquedano district, have nitrate-rich crusts, and the crusts of at least two—Salar del Carmen and Salar de Lagunas—are actively receiving increments of new nitrate-rich saline material by capillary evaporation of near-surface saline ground water.

The general caliche (nitrate) deposits show characteristic features that reflect the original structures of the host rocks and other structures that formed later during accumulation and enrichment of the deposits. The deposits are in all types of porous rocks and unconsolidated sediments without showing any systematic variation in their mineral content. They occur as veins or impregnated zones in such diverse rock types as granitic intrusions, andesite and rhyolite flows and tuff layers, limestone, sandstone and shale. The most widespread deposits are those in which the saline minerals form a cement within unconsolidated regolith. Saline minerals were deposited

in original openings—pores, cavities and fractures—in the host rock and in new openings formed by the force of crystallization. The nitrate deposit is in the region of active faults, and mineral layers have been extensively fractured in the vicinities of faults.

The nitrate ores show great local and regional variations in chemical composition, so it is difficult to estimate the composition of an average or typical ore. Perhaps the best estimates are those based on large tonnages of ore treated by the nitrate-beneficiation plants (Table 1). Higher grade nitrate ores, mined selectively during earlier days, contained two or three times as much nitrate as do the present ores, and some contained 50 percent or more sodium nitrate. Some of the minerals present are shown in Table 2.

PRIOR THEORIES OF ORIGIN

Theories on the origin of the Chilean nitrate deposit are based upon a large variety of possible mineralization methods, such as: (1) decay of seaweed and other marine organisms in waters and marshes of partially cut off inland arms of the sea (for the iodine content of the deposit) and bacterial decay and nitrification of plant and animal remains (for the nitrate); (2) leaching of guano on the margins of saline lakes, inland arms of the sea, or salars; (3) nitrification and fixation of atmospheric nitrogen by bacteria in the soil; (4) reaction of atmospheric nitric acid from electrical discharge in the dense winter fogs, or from gases in the atmosphere with feldspatic igneous rocks; (5) accumulation of nitrogen compounds of volcanic origin (ammonia, nitrogen oxides or nitric acid); (6) minerals from diverse sources accumulated in the sub-surface saline waters and brines of salars or in the soils of the

TABLE 2

Saline Minerals of the Chilean Nitrate Deposits

HALIDES:	
Halite, NaCl	
NITRATES:	
Soda niter, NaNO ₃	
Niter, KNO ₃	
Darapskite, Na ₃ (SO ₄)(NO ₃) · H ₂ O	
Humberstonite, K ₃ Na ₇ Mg ₂ (SO ₄) ₆ (NO ₃) ₂ · 6H ₂ O	
IODATES AND CHROMATES:	
Lautarite, Ca(IO ₃) ₂	
Bruggenite, Ca(IO ₃) ₂ · H ₂ O	
Dietzeite, Ca ₂ (IO ₃) ₂ (CrO ₄)	
Tarapacaita, K ₂ CrO ₄	
Lopezite, K ₂ Cr ₂ O ₇	
BORATES:	
Ulexite, NaCaB ₅ O ₉ · 8H ₂ O	
Probertite, NaCaB ₅ O ₉ · 5H ₂ O	
Ginorite, Ca ₂ B ₁₄ O ₂₃ · 8H ₂ O	
Hydroboracite, CaMgB ₆ O ₁₁ · 6H ₂ O	
Kaliborite, HKMg ₃ B ₁₂ O ₁₆ (OH) ₁₀ · 4H ₂ O	
Colemanite, Ca ₂ B ₅ O ₁₁ · 5H ₂ O	
SULFATES:	
Thenardite, Na ₂ SO ₄	
Glauberite, Na ₂ Ca(SO ₄) ₂	
Bloedite, Na ₂ Mg(SO ₄) ₂ · 4H ₂ O	
Kieserite, MgSO ₄ · H ₂ O	
Epsomite, MgSO ₄ · 7H ₂ O	
Gypsum, CaSO ₄ · 2H ₂ O	
Anhydrite, CaSO ₄	
Bassanite, 2CaSO ₄ · H ₂ O	
Polyhalite, K ₂ Ca ₂ Mg(SO ₄) ₄ · 2H ₂ O	

TABLE 1

Typical Analyses of Chilean Nitrate Ore and Two Possible Source Brines

	Nitrate Ore, wt., %		Salar de Atacama Typical wt., %		Ocean Water, ppm*	
	Maria Elena Typical	Range Currently Mined				
NaNO ₃	7.7	6-10	Na	7.9	Na	10,600
Na ₂ SO ₄	10.9	6-15	SO ₄	1.8	Stas SO ₄	900
NaCl	6.3	6-10	Cl	15.9	Cl	19,000
K	0.5	0.4-1	K	1.8	K	380
Mg	0.4	0.2-0.8	Mg	0.9	Mg	1,300
Ca	1.5	1-2.5	Ca	0.03	Ca	400
Li	0.004	—	Li	0.14	Li	0.2
IO ₃	0.06	0.04-0.08	I	trace	I	0.05
ClO ₄	0.03	0.02-0.04	ClO ₄	—	Sr	8
B ₄ O ₇	0.4	0.3-1	B ₄ O ₇	0.3	B	4.8
PO ₄	0.1	—	NO ₃	0.012	N(as NO ₃)	0.8
CO ₃	1.0	0.5-2	CO ₃	0.003	C(as HCO ₃)	28
H ₂ O	1.5	1.1-2	H ₂ O	71.2	Br	65
					F	1.3

*Reference 2.

nitrate fields; and (7) from ocean spray and atmospheric gases.

Two facets of the Chilean nitrate deposits have somewhat independently dominated these various theories. The first centers on the unusual minerals that are present, and the second is based upon their unusual placement and location throughout the mineralized area. The former feature has encouraged speculation on sources such as oceanic (for the iodine); inland lakes or salars (because of the lack of bromine, which is present in sea water); volcanic (to explain the boron, etc.); from guano or bacteria, algae or plants (to explain the nitrate), and others. However, most theorists have been more concerned about the second feature (location). They have suggested volcanic ash or gases, atmospheric condensate or sea spray to explain why the deposit so uniformly covers a wide area of uneven terrain. The most recent review proposes that the atmospheric gas-sea spray mechanism is the correct one. This theory shall consequently be considered as a basis for comparison.

Proof and Tests for any Theory. To the extent possible, any theory of origin should be capable of being tested and verified by experimental evidence. However, it can be assumed that such "verification" will be limited at best for this deposit because of its complexity. As a second requirement, any theory must meet the test of accounting for all of the deposits, or lack of them, where the conditions of the theory would also be operable. For instance, ideally it should also explain the small North African nitrate occurrences, and in similar near-volcanic, near-coastal deserts it should equally explain the lack of other nitrate deposits.

The Ocean Spray Theory. The atmospheric fallout-ocean spray theory gives considerable problems from both of these criteria. First, some of the minerals in the nitrate deposit have been reported in atmospheric gases, dust or spray, but not all of them. Boron, lithium, chromium, etc. had to come from other sources. If the importance of the air deposition mechanism is to lay down the deposit evenly and everywhere, how did these missing minerals join the air-deposited ones? Also, what happened to the other seawater minerals (bromine, cesium, rubidium, strontium, etc.)? Further, most atmospheric gases and condensate contain some ammonia (Bremblecombe, 1982), and there is none in this deposit. The lack of bromine (a major component of seawater) in the deposit is particularly hard to explain, and the ratios of salts in the deposit are totally wrong for seawater, seawater spray, or even typical rainwater, dew or fog. Finally, chlorate and iodate have never been reported in any analyses of rain, fog, dew or aerosols, so how did they happen to deposit on the land in only this area?

Even more troublesome, however, is the lack of generality of the theory. There are many deserts near oceans throughout the world, and all have been with their

present desert climate for at least 10,000 years (since the most recent ice age). Many of these deserts are much older. If the seawater spray theory applies to the Atacama Desert, it should equally apply to all of the others. Thus, even in the youngest deserts, when considering 200,000 years as the age of the nitrate deposit, 10,000/200,000, or $1/20$ of the Atacama formation time should result in about 50 million tons of NaNO_3 , NaCl and Na_2SO_4 ; 5 million tons of potassium nitrate, borax and magnesium sulfate; and 250,000 tons of iodine and sodium perchlorate. Thus, many other deserts should have major quantities of these compounds, according to the spray theory, and yet no such deposits or occurrences of any detectable concentration of NO_3^- , IO_3^- , or ClO_4^- exists anywhere else, and very few deserts have appreciable groupings of the other components.

It might be argued that greater rainfall in the other deserts precluded this accumulation. However, all of the deserts have some closed drainage basins where the concentration of these ions would be that much greater. But again, none exists. It might also be said that organics ("humic acid") in these wetter deserts have destroyed the NO_3^- , IO_3^- and ClO_4^- . This could be true, but the I^- , Cl^- , Na^+ , Mg^{2+} , K^+ , SO_4^{2-} , $\text{B}_4\text{O}_7^{2-}$, etc. would have persisted. Again, there is no such deposit of I^- , or of the Atacama ratio and proportional concentration of the other ions anywhere else. Finally, the North African nitrate deposits are 400 miles inland, and it is hard to visualize the sea spray carrying that far and selectively to these small locations. Basically, it seems inconceivable that such a broadly applicable mechanism as atmospheric fallout and sea spray would not have left at least some small trace of IO_3^- , ClO_4^- and NO_3^- somewhere else in the world if it were truly capable of forming the immense Chilean nitrate deposit.

One possible set of experimental data is used for the air-spray theory: the analysis of condensate from fog on the Antofagasta coast near (30 km) the nitrate deposit. The ratio of salts in the fog condensate are similar to surface, or low-grade, nitrate ore except for a moderate bicarbonate content. However, the present nitrate operations generate tremendous amounts of dust that generally drifts toward the ocean in the afternoon and early evenings. In the late evenings or morning the fogs form and move inland. The particulate matter or aerosol that the fogs have seen the most of is thus the nitrate plants' dust, and it appears that that is what they are laden with. Also, there is no bromine in this condensate, as there is in all seawater spray, snow, dew and rainwater reported elsewhere, further implying that dust was the main source of its salts.

The lack of any precedence or clues to the ore formation concept is fairly general to all of the proposed nitrate theories. Each has some facets that could explain specific unusual aspects of the Chilean nitrate deposit, but none

has either any direct proof or can explain why the Chilean deposit is the only major one of its kind.

PROPOSED THEORY OF ORIGIN

Unique Features of the Deposit and Area. Before proposing a new theory on the origin of the Chilean nitrate deposit the more pertinent features of the caliche and its environment will be reviewed. Perhaps the most important is the extreme dryness of the area, and the long period that it has been dry. It has been speculated that a generally arid climate has persisted for as much as 15 million years, but this does not seem reasonable as the formation time for such a soluble and fragile deposit. Because there is no age dating data available, a more conservative figure of 200,000 years will be used in this paper. This would still allow a slow or sporadic mechanism for the mineral formation or accumulation to have accounted for the immense caliche deposit, or for a deposition process to have taken place long ago and the deposit to have survived, at least in part, for the intervening years. Most other desert areas do not have quite as long an unchanged history.

Next in importance is the close presence of a highly mineralized and volcanic region. The nitrate deposit is adjacent to, and part of, one of the world's major copper and other metal mining areas. These deposits contain major oxidized zones with, in addition to the common sulfate, hydroxide, oxide, etc. minerals, seams of copper nitrate and copper and silver iodides (Palache, 1951).

Also, in the high Andean plateau above, or in parts of the caliche deposit, there are extremely large saline deposits (salars) containing all of the common minerals in the caliche, and smaller amounts of nitrate and iodate (Chong, 1974). These salars have solutions and/or solid phases of NaCl , Na_2SO_4 , KCl , MgSO_4 , $\text{Na}_2\text{B}_4\text{O}_7$ and LiCl in similar, but somewhat different ratios than found in the caliche deposit. (See Table 8.) Presently flowing hot springs feed considerable quantities of these salts to the salars and local rivers annually (Lahsen, 1976). Table 1 lists the composition of brines in the largest of these salars.

Perhaps the most unique feature of the Chilean nitrate deposit is the dense fogs that roll over the area many late evenings or mornings in the winter. When the fogs burn off by mid-day the weather is generally sunny, bright and clear with high evaporation rates. The high altitude (1,000–4,000 m) and very clear air makes for particularly intense radiant energy. According to anthropologists there is evidence of the Lomas Indian culture in the Atacama Desert, indicating that the heavy fogs that currently support this culture in Peru previously existed in the nitrate area. Also, remains of the Baquedero and other indian cultures indicate cycles of climate with more moisture, vegetation and a higher ground water table than at

present (Hease, 1981). The Tamarugo tree reportedly has tap roots up to 10 m in length and has in recorded history flourished, thus further indicating high water tables. This tree has seed pods that are edible by domestic animals and probably helped support the Baquedero Indians who were hunters and gathered in one of the nitrate areas. Other tribes, such as the Chiuchin Complex (Druss, 1981) in the Rio Loa River basin (which travels through the nitrate deposit) were also hunters. Both are known to have periodically occupied and left these areas, presumably for reasons of climatic and vegetation change.

There is fairly general ground water under or adjacent to the nitrate deposit, and it is not very deep. Table 3 lists the chemical analysis of six fairly typical wells in the Central Valley, and Table 4 provides data on a number of older wells. It is thought that the aquifers are fed from the snows and springs of the Andes through river beds and fault structures. The ground water under the nitrate deposits is slightly basic, and the ratios $\text{Na}:\text{K}$, $\text{Na}:\text{Mg}$, $\text{K}:\text{Li}$, $\text{Cl}:\text{SO}_4$ and $\text{Cl}:\text{I}$ are very similar to the ratio of salts in the ore. Because its content of nitrate, the most soluble salt, is low it could not have obtained its minerals from leaching the caliche salts. Its similar mineral ratio thus leads to the speculation that such underground water could have supplied all the caliche minerals except for the NO_3^- , ClO_4^- and IO_3^- in the deposit. The waters are also somewhat typical of thermal spring or volcanic basin waters in that area, with their high lithium and boron content.

Another unusual feature of the caliche deposit is that much of it occurs in areas where there is considerable porosity in the soil down to and well past the underlying aquifer. There are also some areas of nitrates occurring in fractured rock, but most areas have no seams of clay, shale, silt or other impervious material until well below the nitrate deposit and/or the underlying aquifer. The surface zone in these areas consist of a fraction to several meters of finer grained material, but even it is quite porous. Table 5 lists a typical drilling log for the caliche and underlying soil structure, and Table 6 for a nearby water well. These were from the northern zone of the deposit (near Of. Victoria) but are essentially identical to the more central region (Maria Elena and Pedro de Valdivia), where current mining is taking place.

The structure of the deposit itself is very unusual in its mineral placement and composition. Cross sections of a typical portion of the deposit in two areas are shown in Figures 2 and 3. Table 7 lists a typical mineral analysis of a drill hole. This area is in fairly gently rolling hills, but similar ore patterns exist even in locations with much higher terrain and greater elevation differences. The patterns of ore variation, somewhat random overburden, ore thickness and the depth of the ore, are quite typical. There is little relationship of surface elevation to these

TABLE 3
Water Well Analyses in the Northern Nitrate Area*

Well Data	Humberstone	Baquedano		Ing. Pineda	
	#1	#3	#7	#8	#1 #2
Ground elevation, meters	NI	NI	1,070.19	1,065	NI NI
Static water level, meters	33.10	51.60	53.19	49.50	48.88 49.05
Total well depth, meters	106.5	105.25	92.25	81.00	197.00 127.80
Yield, gal/min	1110	634	951	555	1030 1585
Water Analysis, ppm					
Ca	254	295	281	360	154 —
Mg	47	69	53	60	19 —
Na	541	454	468	690	NA —
K	71	55	44	90	NA —
Li	NA	8.8	8.3	NA	NA —
Cl	960	1,030	950	1,200	221 —
SO ₄	499	454	474	540	477 —
NO ₃	NA	3.2	3.8	NA	2.5 —
F	NA	0.3	0.5	NA	0.6 —
HCO ₃	84	133	134	70	—
B	NA	22	22	60	NA —
pH	NA	7.2	7.8	NA	7.2 —

*Analysis for Baquedano #3 and #7 were performed by USGS, July, 1953. All other data received from Ministerio de Obras Publicas, Direccion de Reigo, Inquique. NI = No Information; NA = Not Analyzed.

factors, and rich, thick ore can occur equally on top of an elevated area, or ridge, or at its bottom. However, the top of the mining grade ore does follow the surface elevation quite well, even though there is considerable variation in the thickness of the "overburden." There is much less correlation to the base of the ore zone with surface elevation because of the cumulative variation in both of the overlying zones. This ore structure would require a fairly uniform depositional method that was reasonably independent of the surface elevation.

The ore grade, on the other hand, is very uneven. There is a rapid change in the sodium nitrate content, and in the ratio of minerals both laterally and vertically. Quite different ratios of the nitrate to sulfate, magnesium, potash, etc. are noted in different areas of the deposit. If the minerals came from the ocean spray or from gases, their composition must have changed very rapidly on a random basis (i.e. not seasonally or episodically) and have been quite different in different areas of the deposit.

The ore analyses show a reasonably sharp cutoff of the nitrate within four to six meters or so from the surface, but traces of the mineralization occurs to a considerable depth. The sodium sulfate, and probably the sodium chloride, appears to persist to a slightly greater depth than the sodium nitrate. Small quantities of the minerals presumably continue down to the water table.

The chemical composition of the nitrate ore is perhaps its most unusual feature. An analysis of composite ore samples from operating mines and an individual sample for a more complete analysis have been given in Table 1. The salt ratios for several possible ore sources are shown

in Table 8. The water soluble ions are seen to be Na^+ , K^+ , Mg^{2+} , Li^+ , Ca^{2+} , NO_3^- , SO_4^{2-} , Cl^- , IO_3^- , $\text{B}_4\text{O}_7^{2-}$, ClO_4^- and CrO_4^{2-} . The K^+ , $\text{B}_4\text{O}_7^{2-}$ and IO_3^- are present in the currently mined ore as sparingly water-soluble salts, as is all of the Ca^{2+} . There appears to be some CaCO_3 and CaSO_4 throughout the ore, and small quantities of calcium phosphate. There is some clay, generally a weathered montmorillonite. The remainder of the caliche is volcanic ash, tuff, silica and other predominately volcanic or windblown minerals.

Several materials are conspicuous for their absence in the nitrate deposit. First, there are no organic components present. In most saline deposits, either as solids or brines, there is considerable organic matter. It is usually broadly classified as "humates" and represents the trace quantities of organic material that has been concentrated through evaporation of the originally more dilute mineral-containing solutions. However, the nitrates, iodates, perchlorates and chromates would oxidize and destroy any organics that were originally present and would in turn suffer a corresponding loss while doing the oxidation.

There is also in the deposit almost no bromine, which is a major component of seawater. There is likewise none in the Salar de Atacama, nor has there been any reported in other adjacent salars, rivers or hot springs. Because bromine is always present in seawater spray, rain and snow (Bloch, 1972) its absence fairly well eliminates the possibility of seawater being the source of the deposit. Similarly, there are no ammonium salts in the deposit, and trace quantities of ammonia are always present along

TABLE 4
Typical Water Well Data in the Northern Nitrate Area*

Location (Nitrate Plant)	No. of wells	Well Depth, m.	Water Table, m.	Elevation, m.	Production gal/min	Water Quality
Constancia	5	50	46	1115	1.3	Brackish
	6	60	55	1118	2.0	Brackish
Ramiriz	1	60	56	1085	2.2	Brackish
	2	55	53	1092	1.8	Brackish
Santiago	1	56	53	1090	3.3	Brackish
Miapocho	2	56	51	1075	3.5	Brackish
San Donato	1	60	47	1063	1.1	Brackish
	2	65	60	1070	1.2	Brackish
San Jose	1	34	31	1054	4.0	Drinkable
Keryma	1	38	36	1045	1.3	Brackish
	2	60	57	1038	0.8	Brackish
Pena Chica	1	34	32	1036	1.5	Brackish
	2	36	33	1043	4.7	Brackish
Huberstone	2	36	31	1037	3.8	Brackish
(La Palma)	3	35	31.5	1028	2.8	Brackish
Cala Cafa	1	35	32	1032	4.2	Brackish
Buen Retiro	1	26.5	22.5	1025	1.1	Brackish
Carmen Bajo	1	33	31	—	not working	—
	2	33	31	1020	4.4	Brackish
San Manuel	1	22	20.5	1023	1.0	Brackish
Sara	1	22	20	1018	1.5	Brackish
	2	22	20	—	not used	—
Sebastapol	1	8.3	5	950	5.0	Brackish
Cholita	1	13	9	950	1.2	Brackish
	2	13	9	950	1.2	Brackish
Paposo	5 wells		3 to 23	983	N.D.	Brackish
San Enrique	1	27	25	960	N.D.	Brackish
Peruana	1	32	30	950	N.D.	Brackish
San Pedro	4 wells	30 avg.	25 avg.	933	5.8 total	Brackish
Santa Elena	3 wells	10	9	1013	2.4 total	Brackish
Virginia	1 South	15	9	993	0.6	Drinkable
	2 East	19	11.5	1019	0.3	Drinkable
Galinzo	2 wells	12.5	10	976	5.0	N.D.
Tarapoco		27	24	186	3.0 total	N.D.
Felisa	2 wells	12.5	10	176	5.6	Sweet
		17	10	196	8.3	Sweet
Baquedano	1	N.D.	35	1032	476.5	Sweet

*Data from local records prior to 1930, except for Baquedano.

with nitrate in atmospheric gases, also eliminating this as a possible source.

Theory on the Origin of the NaCl , Na^+ , K^+ , Mg^{2+} , Li^+ , Cl^- , SO_4^{2-} and $\text{B}_4\text{O}_7^{2-}$ in the Deposit. The so-called "common ions" listed above would appear to need no esoteric theory to explain their presence in the nitrate caliche. There are major sources of them in salars in the Andean Plateau, in thermal springs in the Andes and in the ground water underneath the caliche deposit. The transport of these ions from the salars to the Central Valley can be easily visualized, as a similar transport has occurred in many basins throughout the world. For instance, there is evidence of leakage from the Salar de Atacama within the period of the nitrate deposit's formation. This could have accounted for the somewhat unusual lithium content, as well as most of the other "common"

minerals in the nitrate deposit. Also, there are mineralized thermal springs feeding into the ground water at the present time (e.g., the Tatio geyser, etc.). Considering that the very large upper and lower structure salt masses and brine deposit in Searles Lake, California can be mostly accounted for from thermal springs and river water flowing for about 35,000 years (Garrett, 1959) from the Sierra Nevada Mountains, it would appear to be quite simple for the much larger Atacama basin, and the much longer time-of-formation period to account for these salts in the nitrate deposit. The ratios of minerals in the Salar de Atacama are not the same as the ground water analyses under the nitrate deposits, but because all of the salars and mineral water occurrences have somewhat different compositions, the ground water should be a blending of the various sources that feed it. This blended

TABLE 5
Typical Nitrate Ore Bore-Hole Log

Interval	Lithology
0-0.5-m	Brown, mostly aggregates of sand and silt in soluble salt matrix. Some transparent clear soluble mineral. Some transparent clear soluble mineral. Also volcanics, 5-6 varieties, fine-grained.
0.5-0.9	Cuttings tannish grey, similar to above, but particles in aggregates are coarser. 60% of matrix is soluble mineral.
0.9-1.30	Color tannish, light grey, as above, but considerable iron staining? Fine particles.
1.30-1.70	As above, with more coarse sand size particles. Light grey.
1.70-2.10	Tan and white aggregates of fine sand and silt with substantial free medium sized sand. Some aggregates disintegrated in water quickly, others slowly.
2.10-2.50	Unconsolidated material at 2.10-2.30-m. Thin beds, sand size, light grey. Continued aggregates of fine-coarse volcanic materials. Five different textures and colors, in a matrix of soluble material. Noticeably more tuffaceous rocks.
2.50-2.90	Unconsolidated material at 2.70-m., sand size grains. Color brown-grey, as above, with some clear saline minerals present. Much less tuffaceous material.
2.90-3.30	Color is light brown grey and as above but with fewer clear soluble crystals and fragments.
3.30-3.70	Unconsolidated material at 3.40-3.62-m. Grey fine sand—silt particles in matrix of white-grey-tan opaque materials 50% +. Particles are volcanic, as above.
3.70-4.90	Unconsolidated material at 3.70-3.90-m. Color light brown-grey as above but with 10% coarse fragments of volcanics. Many of the particles are in very fine silt range.
4.90-5.70	Color as above. Sand-gravel sized volcanic fragments with subordinated cemented aggregates. (>50%). Much soluble material in fines.
5.70-7.80	Color as above. Gravel and sand sized volcanics with 50% fines. Salines present only as fine grains.
7.80-8.60	Unconsolidated material commencing at 8.20-m. Fine sand and silt predominate with gravel sized particles. Fines largely clear and transparent.
8.60-10.60	Fines with 10% gravel sized particles, showing rounded corners. Fine grained volcanics; some tuffaceous aggregates.
10.60-11.80	80% fine grained, with 20% coarse fragments. Some rounded surfaces, of fine grained volcanics, 4-5 varieties, some tuffaceous aggregates. Fines mostly tuffaceous or fine transparent-opaque white grains.

TABLE 5 (continued)
Typical Nitrate Ore Bore-Hole Log

Interval	Lithology
11.80-15.60	Medium sand-silt sized fine grained volcanics, some small gravel fragments with rounded corners. Several thin beds tuffaceous material.
15.60-27.60	Fine tuffaceous material with some silt, sand and gravel of fine grained volcanics.
27.60-33.60	30% tuffaceous fines, 50% fragments of pebbles, 20% gravel, mostly dark grey fine grained volcanics.
33.60-42.60	50% tuffaceous fines, 50% gravel with some sand.
42.60-51.60	50% tuffaceous fines, 50% gravel, sand and silt. Six types of fine grained volcanics present.
51.60-54.60	40% tuffaceous fines, 60% gravel, sand and fine sand. Some rounding of corners of the gravel. Six varieties of fine grained volcanics. Some silty sand with pebbles, followed by sand, tuffaceous seams and ending in sand with pebbles.
54.60-64.60	Silty sand with coarse gravel sized particles and thin seams of tuff.
64.60-67.60	60% fine tuffaceous material. Remainder sand, fragments of gravel, and gravel. Six varieties of fine grained volcanics. Some gypsum present.

TABLE 6
Water Well Drillers Log

Pena Chica Well	Depth	Lithology
	1-4 m.	Medium sand and gravel (to 20-mm). Subordinate fines, little clay. Sand very angular with little rounding; 50% quartz.
	7-9	Sand, subordinate gravel with thin layers of clay.
	9-12	Clays with subordinate silt. Clays gypsiferous.
	12½-15½	Sand, medium, very well sorted. Grains mostly angular, approximately 20% quartz, all angular. Some indication of frosting of some quartz.
	15½-17	Silt in clay. Clay in part appears admixed with the silt.
	17-21	Silt with admixed clay. Layers of clay commencing at 18 m., .25 m apart.
	21-36	Sand with coarse sand.
	36-56	Sand with fine gravel.
	56-80	Sand with a little clay.
	80-86½	Conglomerate, fine sand.
	86½-99	Gravel with sand.
	99½-106½	Sand with a little clay.

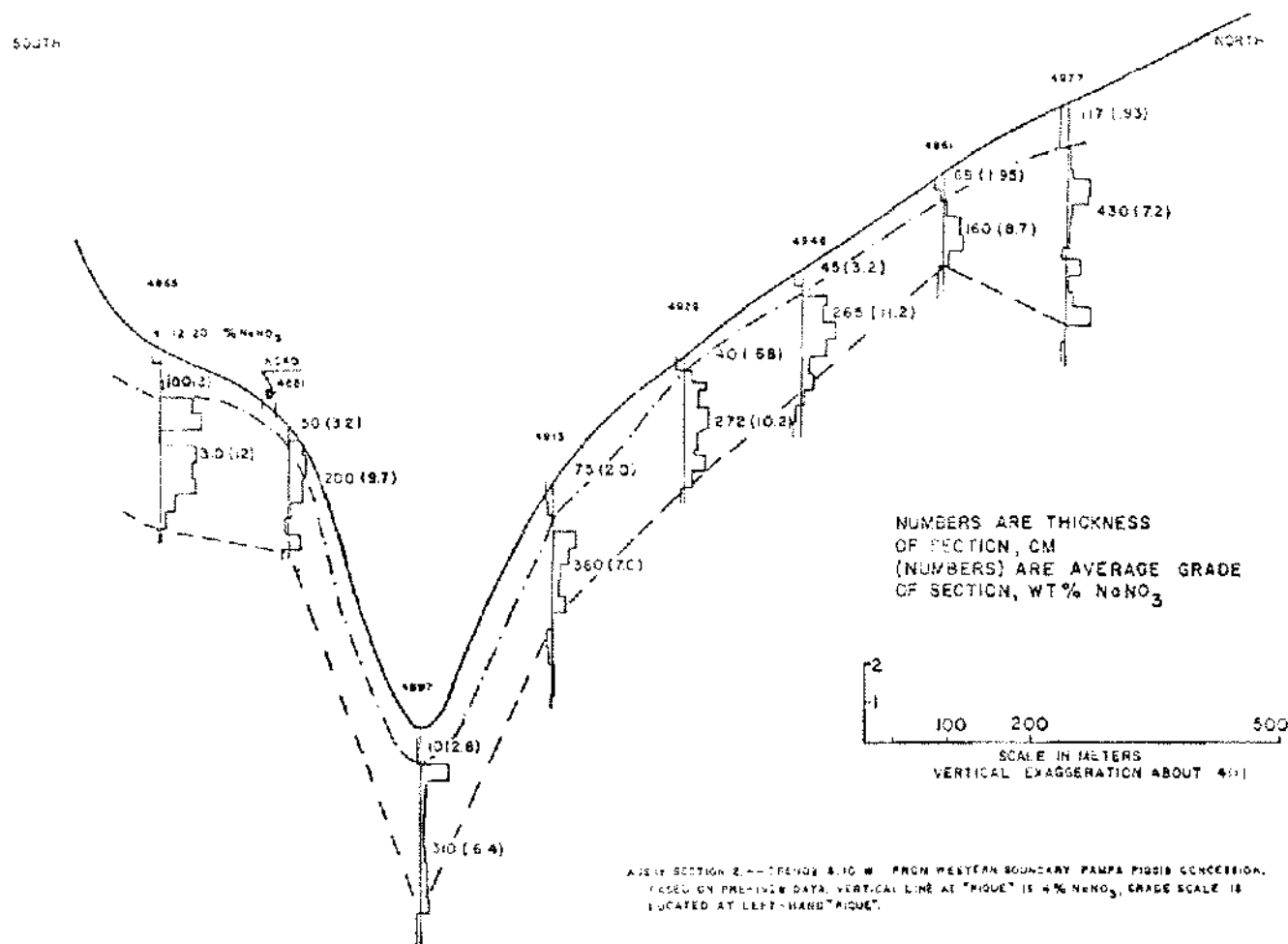


Figure 2. North-South section at Pampa Pissis

water, with local differences in various areas, would thus appear to be a logical candidate to have supplied the common minerals in the deposit.

The immense Salar de Atacama is above the eastern center of the nitrate area, with basement rocks of rhyolite tuffs about 7.5 million years old. It is filled with 350 m of solid salt (NaCl), the upper part of which is porous and contains a brine with high concentrations of Na, K, Mg, Li, Cl, SO_4 , B_4O_7 , small quantities of NO_3 and traces of I. However, the San Pedro river alone would have provided its entire potassium content in 200,000 years at its present flow rate and mineralization, yet based upon other known inputs and a salt balance, this river probably did not provide more than one seventh of the potash. This would imply that a great deal of the entering potassium must have escaped. The basin closure is 300 m above the present surface, so overflow might not account for very much, if any, of the mineral loss. There are known faults connecting to the south and west, however, and even though no outlets or downstream springs are known, it would appear that this is the most probable

method of brine (and potash, etc.) removal from the basin. In the highly faulted Andean deserts, such brine-carrying faults and aquifers have long been credited with supplying the rather abundant ground water in the lower nitrate desert valleys. If this is the case, other upper salars also should have contributed strong brines to the nitrate deposits in a similar manner.

The entire nitrate valley is a fairly closed basin for ground water, with only one river outlet to the ocean between Zapigo to Taltal. This drainage appears to have a very limited water-carrying capacity. Based upon the Central Valley water table being much higher than the Rio Loa pass through the Coastal Range, the ground water release over or through the Coastal Range appears to be slow and difficult. Thus, the reservoir occupied by the under-the-surface aquifer in the area's very porous soil is immense and may very well have been primarily discharged by surface evaporation. The mineral carrying and concentrating capacity of the ground water and lower salars is large enough to have supplied all of the "common" minerals to the nitrate deposits.

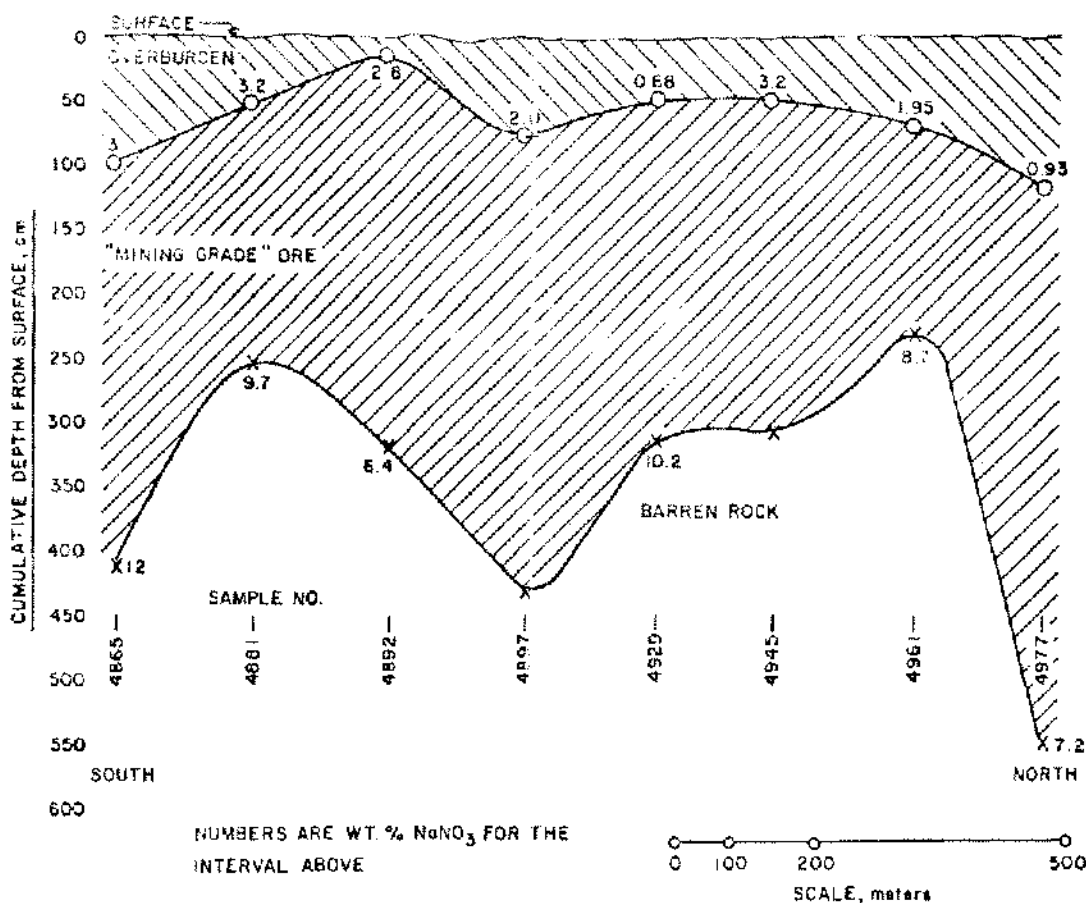


Figure 3. Pampa Pissis pit logs, trend 510°W from western boundry

Theory of the Origin of the Sodium Nitrate. Recent studies have indicated that a catalytic photochemical oxidation of atmospheric nitrogen is possible. Certain sands and rocks appear to photochemically convert small amounts of the nitrogen and oxygen in the air to nitric oxide: $N_2 + 2O_2 + h\nu \rightarrow 2NO_2$. A small amount of heated and sterilized soil or sand was placed into tubes and exposed to sunlight (Schrauzer, 1981). The solids were then washed with dilute acid, and the solution was analyzed by a micro Kjeldahl procedure. Clays, shales, limestone and dolomite showed little or no activity, while sand containing titanium dioxide, iron oxides, etc. had a catalytic effect. Typically, 0.14 μ moles of NO_2 were formed by exposing 10 g of sand to (July) sunlight for five days. Controls with no irradiation gave no yield, and further tests indicated that silica, aluminum silicates, etc. were not active. However, even small quantities of the metallic oxides (TiO_2 , Fe_2O_3 , etc.) resulted in considerable photo oxidizing activity. This data would indicate the production of about 2 to 20 Kg of NO_2 per year per acre, or 5 to 50 Kg $NaNO_3$ per year per acre, or 30,000 to 300,000 tons per year for the deposit area. This could have generated the estimated one billion tons of $NaNO_3$

in the deposit in 3,000 to 30,000 years if none of the NO_2 volatilized, was reduced by organics or was otherwise lost from the deposit.

The previously described experiment was performed on dry heat-sterilized and vacuum-degassed sands, and with an analytical procedure that could not differentiate which nitrogen compound was formed. Because no water was present it is difficult to accept the author's conclusion that ammonia was the product of the photochemical reaction. However, previous experiments (Bickley, 1979) appear to show conclusively that nitric oxide is the normal end product of photolysis on TiO_2 surfaces under atmospheric or oxidizing conditions. Similar studies performed later (Kuliev, 1981) also produced nitric oxide.

This mechanism would thus appear to be fairly well established as a possible nitrate producer under the highly unusual conditions of the Atacama Desert. There is no vegetation or bacteria to reduce the nitrate, and with the fogs, enough moisture exists for nitrate formation and accumulation. The high altitude and unusually clear skies provide a high radiation intensity, and the predominant surface area is rocks or sand that would have good catalytic activity. There is little pure silica, clay or sedimen-

TABLE 7
Chemical Analysis of Pampa Pissis Drill Cuttings

Hole No.	Sample	Meters	NaNO ₃ %	Na ₂ SO ₄ %	K %	Ca %	CO ₂ %	Insolu- ble %
4634-1	1	0 - 0.50	2.6	11.14	0.39	2.89	0.79	72.2
"	2	0.50- 0.90	12.7	6.60	1.03	1.52	1.62	73.5
"	3	0.90- 1.30	8.6	9.22	0.93	0.77	1.36	76.4
"	4	1.30- 1.70	10.6	3.57	0.82	0.92	1.02	79.1
"	5	1.70- 2.10	8.8	7.11	0.71	1.08	2.56	75.5
"	6	2.10- 2.50	5.1	1.06	0.22	1.08	1.51	69.9
"	7	2.50- 2.90	11.4	1.95	0.48	1.13	1.10	80.5
"	8	2.90- 3.30	8.7	4.24	1.35	0.75	3.23	79.2
"	9	3.30- 3.70	9.5	1.38	0.68	1.02	0.13	82.4
"	10	3.70- 4.10	4.2	2.88	0.86	1.02	0.87	85.4
"	11	4.10- 4.50	3.7	12.67	0.24	0.67	1.88	61.4
"	12	4.50- 4.90	6.3	7.94	0.34	0.45	2.07	68.5
"	13	4.90- 5.30	6.2	6.15	0.29	0.25	1.19	72.6
"	14	5.30- 5.70	10.1	2.16	0.11	0.20	2.21	95.6
"	15	5.70- 6.10	4.9	1.27	0.06	0.30	1.86	96.7
"	16	6.20- 6.60	2.5	2.73	0.29	0.25	0.97	96.7
"	17	6.60- 7.00	1.2	0.90	0.03	0.23	1.26	96.3
"	18	7.00- 7.40	1.1	0.95	0.13	0.27	2.04	96.4
"	19	7.40- 7.80	1.2	0.74	0.04	0.18	1.31	95.9
"	20	7.80- 8.20	1.1	0.85	0.21	0.18	3.24	96.4
"	21	8.20- 8.60	1.0	1.35	0.05	0.12	—	92.4
"	22	8.60- 9.00	1.0	2.22	0.04	0.10	—	95.2
"	23	9.00- 9.40	1.0	0.02	0.27	0.10	—	96.7
"	24	9.40- 9.80	1.0	0.18	0.03	0.10	—	96.2
"	25	9.80-10.20	1.0	0.21	0.00	0.09	—	96.6
"	26	10.20-10.60	1.0	0.18	0.02	0.08	—	96.6
"	27	10.60-11.00	1.0	0.19	0.00	0.07	—	96.8
"	28	11.00-11.40	1.0	0.10	0.01	0.06	—	96.5
"	29	11.40-11.80	1.0	2.28	0.05	0.05	—	95.6
"	30	11.80-12.20	1.0	0.23	0.05	0.16	—	94.5
"	31	12.60-15.60	1.0	0.52	0.03	0.19	—	96.1
"	32	15.60-18.60	1.0	0.39	0.02	0.15	—	96.8
"	33	18.60-21.60	0.5	1.11	0.02	0.32	—	96.2
"	34	21.60-24.60	0.5	1.41	0.02	0.34	—	95.8
"	35	24.60-27.60	0.9	0.52	0.02	0.18	—	96.2
"	36	27.60-30.60	0.3	1.87	0.02	0.08	—	96.8
"	37	30.60-33.60	0.1	0.21	0.02	0.06	—	96.7
"	38	33.60-36.60	0.1	0.21	0.01	0.06	—	96.7
"	39	36.60-37.90	0.1	0.23	0.01	0.09	—	96.1
"	40	37.90-39.60	0.1	0.14	0.02	0.07	—	97.1
"	41	39.60-42.60	0.1	0.26	0.02	0.07	—	96.3
"	42	42.60-45.60	0.1	0.15	0.01	0.05	—	96.5
"	43	45.60-48.60	0.1	0.76	0.02	0.06	—	96.2
"	44	48.60-51.60	0.1	0.17	0.01	0.07	—	95.2
"	45	51.60-54.60	0.0	0.006	0.00	0.04	0.26	95.7
"	46	54.60-57.60	0.0	0.00	0.00	0.04	0.23	96.3
"	49	63.60-66.60	0.6	0.29	0.01	0.07	4.80	96.3

tary type material on the surface. Finally, and by far most importantly, the frequent fogs that cover the area could wash the nitric oxide or nitrate from the catalytic surface, thus allowing the active sites to be re-exposed and capture the nitrate in solution where it could flow downward and accumulate. Thus, only areas with these, or similar, conditions could collect nitrates, and possibly form deposits. There are very few such areas in the world.

Once the nitric oxide formed it would oxidize to nitrate, as happens in commercial nitric acid plants. Again, moisture in the fog would be a necessity: $2\text{NO}_2 + \text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$.

The nitric acid that was formed would then slowly leach any rocks it contacted, such as with limestone:

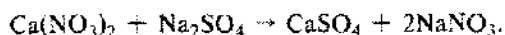


TABLE 8
Ratio of Several Ions in Chilean Nitrate and Various Possible Source Materials

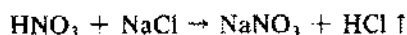
Ion Ratio	Chilean Nitrate Ore		Ground Water					
	Maria Elena, 1975 typical	Pedro de Valdivia, 1952 Avg.	Humberstone, Baquedano Average	Ing. Pineda	Salar de Atacama	Antofagasta Fog	Sea Water	Typical Rain Water
Na:K	17	11	8.3	—	4.3	30	28	3-10
Na:Mg	22	41	9.4	—	8.5	5	8.3	3
Cl:SO ₄	0.52	0.59	2.1	0.46	9.0	1.44	7.2	0.3-3
Cl:NO ₃	0.68	0.61	296	88	—	2.42	5·10 ⁵	—
Cl:B ₄ O ₇	8.9	10.8	8.3	—	71	—	10 ³	—
Cl:I	112	87	2.1	—	—	—	4·10 ⁵	10 ³
Cl:Br	> 3·10 ³	∞	∞	∞	∞	—	300	50-100

OBSERVATIONS: Groundwater under the deposit has a surprisingly similar ratio of ions to the nitrate ore, except for reduced quantities of nitrate and iodine. Also, the Antofagasta fog mineral ratios are quite similar to the ore. The salt content of ocean water and general (from other countries) rainwater, on the other hand, does not appear similar to the nitrate ore's ion ratios. This leads to the interesting speculation that a) the groundwater may have been the source of the ore's minerals (except nitrate) through capillary evaporation and evaporation in adjacent salars, and b) wind blown dust may have carried the nitrate ore salts to all parts of the deposit through direct placement and condensation of the fog.

Later, when the calcium nitrate contacted salt cake (Na₂SO₄) it would react to form gypsum and sodium nitrate:



There would also be some reaction with salt:



since hydrochloric acid is somewhat more volatile than nitric acid.

Much of the NO₂ or nitrate that was formed even in the Atacama Desert would be lost. Re-volatilization would represent the greatest loss, both from the original gas and from the initial dilute solutions. Although the nitrate area temperatures are not extremely high, some thermal driving off of nitrogen oxides from solids or liquids would be inevitable. Also, whatever small amount of organic matter there was in the soil would be oxidized, thus resulting in a further nitrate loss. As noted earlier, in most deserts of the world this would be enough to destroy all of the nitrate, because organic matter would be formed at a faster rate than the nitric oxide. This was probably also the case in most of the higher Andean areas. Only the non-vegetated and foggy zones could allow the nitrate to accumulate.

As a final means of nitrate loss, some could escape in solution through river drainage to the ocean. The sum total of all of these losses makes the possible 200,000 year deposit formation period appear to be compatible with the theoretically much faster formation time of the nitric oxide production experiments.

With this nitrate formation mechanism in mind it is interesting to see if it fits the known occurrences of nitrate elsewhere in the world. Nitrate has been reported in tuff-

aceous rocks in the Atacama Desert. Assuming the tuff to be photocatalytic, the comparatively large surface area would be a natural site for photochemical nitrate formation, and the nitrates could later be washed into the rock structure and then into the adjacent soil. However, wind-blown mineral dust could also account for the nitrate and the other soluble constituents present.

The North African nitrate deposits are in an area of water outcrops (i.e., a 100-mile line of oases in Libya near its small deposit) in an extremely arid portion of the Sahara Desert. It is not certain, but possibly ground fogs could occur near the water seepage area for part of the year. If so, this would provide the same mechanism for nitrate formation as in Chile, and thus lead to limited deposits. There is no vegetation, except near the water outcrops, and almost no rainfall (i.e., one storm typically with less than 10 mm moisture on about a 20-year average).

A similar situation may have occurred on the desert-like western side of the San Joaquin Valley in California. It has been reported that nitrate existed in the top four feet of the soil prior to the area being brought under irrigation. This nitrate could have resulted from bacterial action or plant debris, but with the heavy Tule fogs in the area, possibly it also could have been partly formed by photocatalytic nitrogen fixation. These speculated examples, and even the laboratory tests, are not conclusive as a mechanism for the occurrence of nitrate in the Chilean deposit, but the data fits reasonably well, and perhaps provides a plausible theory to explain these nitrate occurrences and why such a deposit has not been formed elsewhere.

Theory on the Origin of the Iodate. As puzzling as the nitrate source is, the iodate is even more unusual. People

have speculated that it came from seaweed or marine organisms. Others have claimed it originated from seawater spray or atmospheric gases; all would appear to be highly improbable. There is very little iodine in seawater, both in the surface layer and below (0.05 ppm), and in its spray. Iodide accumulation presumably from kelp and other marine organisms has occurred in a few brine supplies (usually containing 100 ppm of iodine or less) associated with petroleum reserves (where known marine life decomposition occurred).

Also, iodide is known to occur in some hot springs or magmatic sources. Because iodide salts are generally quite soluble, they would be expected to stay in solution and concentrate in evaporating waters. For instance, the brines of Searles Lake, California contain perhaps 100,000 tons of iodide (Garrett, 1959), which probably came from only one thermal spring over the past 35,000 years or so. There is a reasonable fraction of that in the Chilean caliche deposits, which probably had a much longer formation time, and was fed by more hot springs along the Andes.

Also, the Atacama Desert has a number of metallic iodide locations. For instance, marshite, CuI , is found at Chuquicamata, the gigantic copper mine above the east and center of the nitrate zone. Iodyrite, AgI , is found at Chancarrillo, Atacama and Carocoles, Antofagasta. Other iodide occurrences in the area have been reported. Such minerals may have been alteration products of the original ore or have originated from magmatic sources of iodine. Finally, the present ground water under the nitrate fields and the upper salar brines contain some iodide, probably originating from the mineral springs.

Once the iodide was in the nitrate deposit, some unusual chemistry took place. The deposit is slightly basic and totally in an oxidized state (there is nitrate and no organic matter). This could have allowed a catalytic photochemical oxidation to take place that is well known in the laboratory (Fujishima, 1971):



The iodine formed would immediately react with the alkaline solution to produce OI^- :



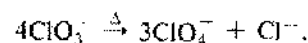
The OI^- would in turn react with additional iodine to form iodate:



The iodide ion that was produced along with the iodate would remain in the deposit for additional photo oxidation, and eventually all of the iodide would be in the iodate form. This iodide photochemical oxidation is a much studied, classical reaction (Adamson, 1975). The hyperiodate reaction is fast and automatic, while the iodate formation is slow. However, it is a normal end

result of I_2 and IO^- being present in solution together, making the entire sequence fairly plausible chemically (Pauling, 1975). The reason that it hasn't occurred elsewhere, such as at Searles Lake and in petroleum brines, is due to the presence of large amount of organic matter in these and all other sources which would immediately reduce the iodine and hyperiodate as it was formed. Also these solutions are generally slightly acidic. In the Chilean nitrate deposit there are no organics or other reducing agents, the solutions are basic, and therefore the iodate ion remains stable.

Theory on the Origin of the Perchlorate. The same theory that was applied to the iodate could account for the formation of perchlorate. The photochemical oxidation of chloride to chlorine is not as rapid or easily accomplished as the iodide reaction, but it does occur in the laboratory, has also been thoroughly studied and its energy requirements developed. Once any Cl_2 had been formed the same subsequent sequence of reactions would naturally occur, with one additional step. With moderate temperatures, or over a long time, chlorate would automatically convert into perchlorate:



The chloride photochemical oxidation requires much more energy to form and thus would occur less frequently than the iodide oxidation. This accounts for the more modest quantities of perchlorate that are present. The reasons for the exclusiveness of this deposit for these reactions compared to other chloride brine deposits are the same as for the iodate occurrence. However, the very high altitude and clear air probably also played a part in supplying the higher energy photons needed for this photochemical reaction.

Theory on the Origin of the Chromate. The origin of the small chromate content of the ore probably comes from one or both of two sources: 1) leaching of chromate containing rocks or ores, and 2) thermal springs. Other authors have suggested the leaching of shales containing about 100 ppm of chromate. The chromium ion would then be oxidized by the iodate or chlorate ions to the chromate state. The basic oxidizing nature of the nitrate brines would keep the chromium in the chromate (CrO_4^{2-}) form.

However, there is also an analogy once again with Searles Lake, which contains the U.S.'s largest reserve of tungsten as a dilute minor component. At least a fourth of its content came from a thermal spring feeding the lake (Garrett, 1959). It would be just as possible that the chromate (instead of tungsten) came from a Chilean hot spring feeding the nitrate deposit. It is unfortunate that its exact source is not known, but it is very easy to believe that this highly soluble and stable ion could be present in alkaline, oxidizing brines in this richly mineralized area.

METHOD OF ORE PLACEMENT AND DEPOSITION

This feature of the Chilean nitrate deposit has appeared to be the most troublesome to most investigators and consequently has led to the most unusual and speculative theories for its origin. Unfortunately, this theory, like the earlier ones, can find no means of proving the method of placement. However, it is proposed that capillary action and dust transport are both logical transport phenomena and could fully explain the minerals location.

The theory as stated to this point proposes that the nitrate in the deposit formed on the surface of "catalytic" rock or sand particles. Fog and the occasional rains washed it into the soil, water courses and playas. All of the other constituents came from rivers, volcanic springs and salars in the higher Andes. They drained into the nitrate valleys through rivers (Rio Loa, etc.), faults and fractures, aquifers and the occasional overflow of higher basins.

It is speculated that these factors led to a situation where conditions were ideal for surface (in the lower salars) and capillary evaporation to crystallize salts in some of their present locations. The nitrate salts are highly hygroscopic, and once deposited, during the foggy periods should have condensed enough moisture to have at least partially dissolved the surrounding salts. Upon re-drying, capillary motion would occur, and the salts would migrate to higher ground. In this manner the hygroscopic nitrates would help to provide moisture for all of the salts, thus aiding in mixing and spreading the minerals over the areas near salars and high water tables.

Examples of such capillary action are quite common in nature today, but on a smaller scale, and usually without the fog's assistance to increase the rate and completeness of transport. Underground waters have formed sodium carbonate-bicarbonate capillary "reefs" one to two meters high at the edge of Searles Lake. Salt solutions in many areas have generated one to two-meter-high capillary formations such as the "Devil's haystacks" in Death Valley and the massive salt heaves at the Salar de Atacama. A closer example is the low sand dunes a few km south of Of. Victoria in the Atacama Desert which have a $K\text{-}NaNO_3$ crust. The only source of these salts would be the nearby valleys or salars, such as the Salar de Belavista. Here the capillary migration and evaporation is quite easily seen, and this in a comparatively dry period. Similar effects are quite noticeable adjacent to the tailing ponds of the current nitrate operations, and in the formation of surface crusts by capillary action from the Salars del Carmen and de Lagunas.

The capillary transport of the minerals from the local salars and the ground water to the adjacent areas would depend largely upon an unusually porous soil structure

and a high ground water table. Tables 3 and 4 provide detail about the plant water source used by the nitrate operations (Oficians, or Of.) in one area. It is likely that this ground water structure is typical of the Central Valley. Ground water occurs extensively in the nitrate area, and the water table is high. Table 6 shows the soil structure of a water well in the same area. It is generally porous and has no impervious seams until below the water table. Also, it is predicted by archeologists that vegetation has cycled in the Central Valley. Various Indian cultures have prospered or declined, probably based upon the water table and the fog or rain density.

During periods of high water tables the upper soils would act as a wick, and the ground water would evaporate, bringing its salts with it. The various salts, including gypsum and limestone, would precipitate at or near the surface and slowly accumulate. With the hygroscopic nature of the nitrates assisting in providing more moisture at the surface, the capillary, or wick, distance would be greater, and more soils, including higher ground, would be effected. In this manner part of the nitrate area would act as an "upside down" salar, with the evaporation bringing mineral-laden waters up. Also, a few of the lower valleys would have been flooded intermittently, as they are now, and these salars would have assisted with the evaporation and mineral deposition.

A major difference with capillary rather than lake evaporation is that all of the salts would crystallize in the proportion that they exist in the water, and there would be no concentration of the more soluble ions. This accounts for the constantly present, more modest concentrations of gypsum and limestone, rather than the massive layers of these sparingly soluble minerals that normally form from the evaporation of sea water or large lake basins. It also explains the lack of salt layering, zoning and massive accumulation of individual minerals. Finally, such a water source would supply much lower concentrations of organic matter to consume nitrate than would salars.

In this manner, during periods of high water tables there would be an accumulation of salts at or near the ground surface. Later, rains would wash these salts down to their present levels. During the life of the deposit this cycle would have been repeated over and over, slowly accumulating the quantities of minerals that are present today. This cyclic repetition at times would also provide enough water in local zones to dissolve and recrystallize the salts, such that some segregation based upon relative solubility could have occurred. This would have accounted for the rapid change in chemical analysis of the ore over short intervals. However, the repeated accumulation cycle would have greatly smeared this effect, so that little evidence of fractional crystallization can be seen. Variable soil permeability would explain the differences in ore thickness and grade. Different fault paths,

fractures and water sources would explain the major mineral differences that occur in various areas. For instance, higher magnesium-containing water sources would have fed the nitrate areas with a higher magnesium content, and the same for locations with higher sulfates, etc.

For most of the deposit, however, the distance from the water source to the final mineral location is too great for capillary migration, and a second mechanism is needed to explain the distribution of the minerals so evenly throughout the deposit and for reaching many of the nitrate zones. It is proposed that this came about by the variable direction winds of the Atacama Desert. They generally stay within the basin, and there are comparatively infrequent winds out of the general nitrate area. Once the nitrate mineral deposit had formed on the surface of salars or capillary evaporation areas, the winds would blow some of it as dust randomly throughout the area. Some dust also would become trapped in the fogs, further assisting in the spreading effect. Once redeposited, the fog and rain would again wash it into the soil, just as the minerals from capillary migration. The exceedingly long formation time of the deposit would have allowed the wind and fog to aid the capillary action in spreading the minerals fairly uniformly over wide areas. Wind-blown erosional and depositional features are very apparent in the area, and it would be inescapable for the nitrate ore to be part of the windblown debris. Furthermore, minerals deposited on the surface of capillary structures are often light and powdery and would easily be windblown. Data such as the present fog condensate mineral composition are further evidence of such caliche dust pickup and eventual re-deposition.

SUMMARY

A theory is proposed for the formation of the Chilean nitrate deposit involving two sources of mineral supply and two methods of ore placements. It is suggested that the nitrate came from the photocatalytic oxidation of nitrogen on various sand and rock surfaces that exist widely in the area. Fogs then washed the oxides from the mineral surface and captured them in the soil, where they were oxidized further. Laboratory experiments have indicated this to be possible on rocks and sands containing titanium, iron, etc. at a sufficient rate to account for all of the nitrogen in the deposit. Iodides and chlorides in the deposit could also have been photo-oxidized in the slightly basic, organic-free, oxidizing solutions to form first the element and then iodate and perchlorate, respectively. Next, it is proposed that the other mineral constituents of the deposit were derived from hot springs and run-off water from the adjacent upper (volcanic) area of the Andes. They could have been transported to the salars in the nitrate ore areas, or the aquifers under them,

by rivers, faults, aquifers and occasional mineral-containing basin overflow.

This theory visualizes that the ore became placed in its present position by both the capillary action of brines rising through the very porous soil from high water tables to evaporate and deposit salts at the surface. It also formed and traveled by capillary action from salars and basins in the area. Periodic rains washed the salts to their present depth, and the cycle was repeated numerous times. The hygroscopic nature of nitrates greatly aided this movement. The active, variable direction, local winds were responsible for spreading windblown nitrate mineral dust fairly uniformly and completely over the entire nitrate area. Solution and capture of the mineral dust in the pervasive fogs of the Atacama Desert also aided in the comparatively uniform placement of the ore.

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