

Geology and Origin of the Chilean Nitrate Deposits

GEOLOGICAL SURVEY PROFESSIONAL PAPER 1188

*Prepared in cooperation with the
Instituto de Investigaciones
Geológicas de Chile*



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By GEORGE E. ERICKSEN

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*A discussion of the characteristic features
of the nitrate deposits and the sources and modes
of accumulation of their saline components*



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CONTENTS

	Page
Abstract	1
Introduction	1
Location	2
Acknowledgments	3
Geomorphology	3
Climate, vegetation, and soil microorganisms	8
Geology of the nitrate deposits	12
Topographic setting	12
Structural features	14
Chemical and mineralogical composition	19
Origin of the nitrate deposits	20
Discussion of theories	21
Sources of the saline components	23
Nitrate	24
Halogens	26
Sulfate	28
Borate, chromate, and dichromate	29
Alkali and alkaline-earth metals	30
Accumulation and enrichment of the saline components	30
Conclusions	31
References cited	32

ILLUSTRATIONS

	Page
FIGURE 1. Index map of northern Chile, showing location of nitrate deposits	2
2-4. Landsat images showing—	
2. Nitrate region in northern Antofagasta and southern Tarapacá Provinces and the major physiographic units of northern Chile	4
3. Distribution of principal nitrate workings in the Tocopilla and Baquedano districts	5
4. Deeply incised transverse valleys of probable late Miocene to Quaternary age cutting across the northern Pampa del Tamarugal	7
5, 6. Aerial photographs of nitrate workings—	
5. In the northern part of the Tarapacá district	9
6. At Oficina North Lagunas	12
7. Photograph showing underground nitrate workings at the northern end of the Tarapacá district ...	13
8, 9. Topographic maps of—	
8. Northern Tarapacá district, showing distribution of nitrate workings along the eastern margin of the Coastal Range	14
9. Baquedano district, showing areas of exploitable or potentially exploitable nitrate deposits ...	14
10. Diagram showing characteristic layering of an alluvial-type nitrate deposit	15
11-17. Photographs of—	
11. Layer of friable high-purity humberstonite at Oficina Alemania, Taltal district	16
12. Rajo San Martín, a nitrate mine in the Taltal district	16
13. Bedrock caliche, consisting of impregnations and veins of caliche blanco in rhyolite tuff ...	17
14. Polygonal surface of costra, Tarapacá district	17
15. Saline-cemented, nitrate-rich sand dike in alluvial-type caliche, northern Tarapacá district ...	18
16. Newly formed desiccation polygons in nitrate ore, Tarapacá district	18
17. Losa cakes embedded in powdery chuca, Tarapacá district	19

TABLES

	Page
TABLE 1. Chemical composition of water-soluble saline components in selected nitrate ores and high-purity veins from the nitrate deposits in northern Chile -----	20
2. Saline minerals of the Chilean nitrate deposits -----	21

GEOLOGY AND ORIGIN OF THE CHILEAN NITRATE DEPOSITS

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ABSTRACT

The unique nitrate-rich caliche deposits in the Atacama Desert of northern Chile owe their existence to an environment favorable to accumulation and preservation of the deposits, rather than to any unusual source of the saline materials. The essential conditions are: (1) extremely arid climate similar to that of the present-day Atacama Desert; (2) slow accumulation during late Tertiary and Quaternary time; and (3) paucity of nitrate-utilizing plants and soil microorganisms. The wide distribution of the deposits without systematic relationship to topography or rock type can be explained only by atmospheric transport and deposition. The saline constituents are chiefly those that have been found widely in the atmosphere in other parts of the world; in the nearly rainless Atacama Desert they have accumulated at or near the sites of the deposits chiefly as dry fallout and as solutions in condensate droplets from low clouds or fogs and dew prevalent during the winter. These saline materials were later leached, redistributed, and enriched in the highly soluble components, such as nitrate, at deeper soil levels and in soils on lower hillsides by fog condensate and water from infrequent rains. Ore-grade nitrate deposits evidently formed in three ways: (1) slow accumulation on old land surfaces that have had little or no modification since the Miocene; (2) accumulation on lower hillsides and at breaks in slopes as the result of leaching and redeposition by rainwater; and (3) accumulation in salt pans and saline ponds.

Although some of the saline materials in the nitrate deposits may have come from distant sources, I believe that most were from local sources, chiefly spray and evaporation from the nearby Pacific Ocean and from volcanic emissions in the nearby Andes Mountains. The nutrient-rich Humboldt Current may have been a major source of ammonia, oxides of nitrogen, and iodine, which were transformed to nitrate (NO_3^-) and iodate (IO_3^-) by photochemical reactions, particularly ozone reactions, in the lower atmosphere and at soil surfaces. Similar reactions may have transformed chloride to perchlorate (ClO_4^-), an ubiquitous minor constituent of the nitrate ore. The soils of the nitrate fields, though having an extremely low level of biological activity, do have populations of microorganisms capable of nitrogen fixation, nitrification, and ammonification. These organisms may have contributed to the formation of some of the nitrate, particularly in near-surface soils where condensate from winter fogs is sufficient to support growths of blue-green algae and other microorganisms. Chloride and sulfate, which together with nitrate are the dominant anions of the nitrate deposits, also

are chiefly of oceanic origin, but significant amounts may have been supplied during times of intense volcanism in the nearby Andes. The principal cations, sodium, potassium, magnesium, and calcium, were supplied by sea spray, by wind-blown dust from saline soils and playas in the Atacama Desert, and by volcanic emissions in the Andes. Small amounts of these cations and widespread trace amounts of chromate (CrO_4^{2-}) may have been derived by chemical weathering of soils and rocks in the nitrate fields. Boron, which is a widespread minor element, is of volcanic origin.

INTRODUCTION

The origin of the Chilean nitrate deposits has been a recurrent subject of discussion for more than 100 years, but none of the many theories proposed has found general acceptance. The proliferation of theories has been chiefly the result of three factors: (1) a scarcity of accurate geological descriptions of the deposits; (2) a tendency on the part of some authors to ignore geological data that would make their theories untenable; and (3) scarcity of information about processes that might form or supply large quantities of nitrate in a desert environment. Disagreement about the origin has persisted, as is shown by different theories published since 1960: (1) Mueller (1960, 1968) repropounded the theory of Singewald and Miller (1916) that postulates accumulation by capillary migration and evaporation of ground water at the margins of salars¹; (2) Wetzel (1961) reaffirmed his proposal, published in several reports (for example, Wetzel, 1932), that the deposits accumulated as saline-rich mudflows; (3) Fiestas (1966) reaffirmed his proposal (Fiestas, 1922) that the saline components were formed by reaction of clouds of volcanic acids with the rocks and soils of the nitrate fields; and (4) Claridge and Campbell (1968) and Ericksen (1975, 1979) proposed the deposition of atmospheric saline materials at or near the sites of the deposits.

¹ Salt pans or salt-encrusted playas are called "salars" in Chile and neighboring countries. A usage followed in this report.

The single most important factor in the accumulation of the nitrate deposits in the Atacama Desert has been the exceptional long-term aridity of this region. As will be shown, the region has been a desert at least since the middle Tertiary, and some of its landforms may date from early Tertiary. Nitrate-rich soils occur locally in some of the other deserts of the world, but the presence of widespread exploitable nitrate deposits is unique to the Atacama Desert. This special feature of the Atacama Desert undoubtedly reflects the long period of time available for accumulation of the deposits. In contrast, nitrate deposits that might have formed in other deserts during intervals of extreme aridity would have tended to be destroyed during intervals of increased rainfall.

This report will show that the Chilean nitrate deposits probably formed by slow accumulation of the saline components by deposition from the atmosphere of materials from diverse sources. However, local rather than distant sources predominated, and among these, the nearby ocean was probably the most important. Emanations and rocks from widespread volcanism in the northern Chilean Andes Mountains were also important sources of some saline components. Photochemical reactions in the atmosphere probably played a role in the formation of nitrate, sulfate, iodate, and perchlorate, all of which are constituents of the deposits.

LOCATION

The nitrate deposits are in the Atacama Desert of northern Chile, which lies west of the Andes Mountains and which is said to be the driest desert of the world. Most of the deposits are in the two northernmost provinces of Tarapacá and Antofagasta (fig. 1). During the heyday of the nitrate industry, in the latter part of the 19th century and early part of the 20th century, the nitrate deposits were exploited in five major centers or districts (fig. 1): Tarapacá, Tocopilla, Baquedano, Aguas Blancas, and Taltal.

Most of the commercial nitrate deposits are along the eastern side of the Coastal Range, in a band generally ranging from a few kilometers to about 30 km in width, between long $69^{\circ}30'$ W. and 70° W. (fig. 1). They extend from about lat $19^{\circ}30'$ S. to 26° S., a distance of about 700 km. The northernmost deposits in Tarapacá are largely restricted to a narrow band along the east side of the Coastal Range, whereas to the south, they spread out more extensively in the Coastal Range, Central Valley, and Andean Front. Noncommercial nitrate deposits and nitrate-rich soils are much more widespread than the commercial or potentially commercial deposits shown

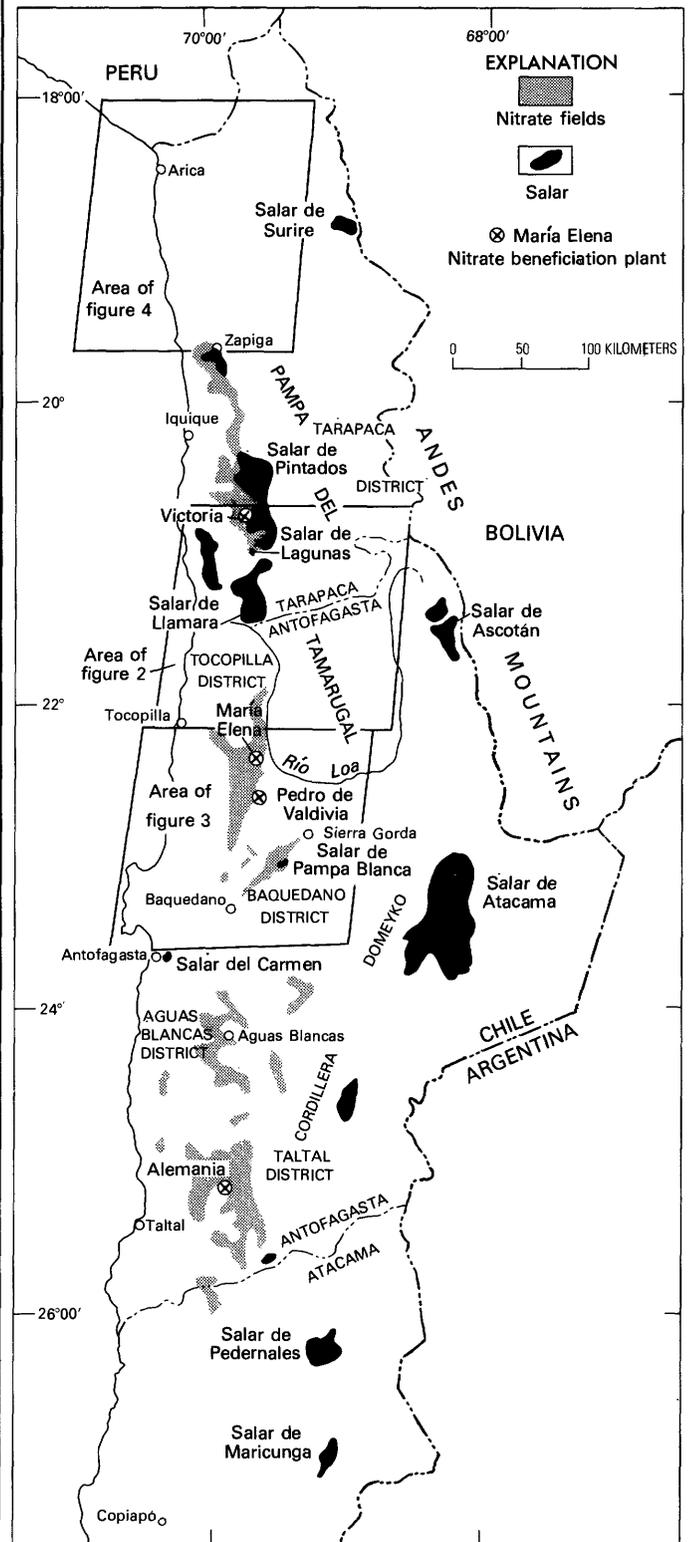


FIGURE 1.—Index map of northern Chile, showing location of nitrate deposits, as shown by mining-claim maps of the Servicio de Minas del Estado, and areas covered by Landsat images (figs. 2–4).

in figure 1. 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 veinlets and impregnations of 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 nitrate fields shown in figure 1. The only major gap in this band of nitrate deposits is in southern Tarapacá Province, where Salar de Llamara and associated clay playas interrupt the Coastal Range.

Low-grade nitrate deposits are known in the coastal desert of Peru several hundred kilometers north of the Chilean border (Portaro, 1935, 1936), and saline-rich soils probably occur elsewhere in the coastal desert of southern Peru. Commercial deposits have not been found there, nor have they been found in Chile north of Pampa de Tana (fig. 4). The reason for an absence of commercial deposits in these areas is not known, but climatic variations and the ages of the land surfaces could have been factors that inhibited accumulation of large amounts of nitrate-rich saline materials.

Most of the commercial nitrate deposits are at altitudes of less than 2,000 m, but those east of Aguas Blancas (fig. 1) extend upwards to altitudes of about 3,000 m. The deposits in the vicinity of Salar de Maricunga, which have not been exploited, are near 4,000 m in altitude and are the highest known nitrate deposits in northern Chile. This sector of the high Andes is exceptionally arid, having an annual precipitation of about 50 mm, mostly as snow; it undoubtedly has more extensive nitrate deposits and nitrate-rich soils than have been reported.

ACKNOWLEDGMENTS

The field and laboratory investigations on which this report is based were carried out as part of a cooperative project between the Instituto de Investigaciones Geológicas (IIG) of Chile and the U.S. Geological Survey. The work began in 1961 under the auspices of the United States Technical Aid Program (AID) of the U.S. Department of State. The principal field investigations were made in 1962, with the support of the United Nations Special Fund, and led to a report on the saline resources of northern Chile (Erickson, 1963). Many other short-term field studies from 1964 to 1979 were made in coop-

eration with the IIG and other government agencies in Chile, including the Corporación de Fomento and the Universidad del Norte in Antofagasta. The field studies have been facilitated in many ways by the nitrate-producing companies, especially the Anglo-Lautaro Nitrate Corp., the former owner of Oficinas (Oficina is the name applied to the beneficiation plant and town site) María Elena and Pedro de Valdivia, the Cia. Salitrera de Tarapacá y Antofagasta, the former operator of Oficina Victoria, and the Sociedad Química y Minera de Chile, the government corporation that took over these three oficinas in the early 1970's. These three plants are the largest of the more than 100 plants that formerly operated in northern Chile and are the only ones still in operation in 1979. Oficina Victoria closed at the end of 1979.

Many people have assisted or contributed to the field and laboratory investigations. Special thanks are given to Carlos Ruiz F., former Director of the Instituto de Investigaciones Geológicas of Chile and to Enrique Colzani, General Manager, and Henry B. Suhr, Chief Experimental Chemist, Oficinas María Elena and Pedro de Valdivia, all of whom have given enthusiastic support to the investigations. Special thanks also are given to Roy E. Cameron, formerly of the Jet Propulsion Laboratory, California Institute of Technology, for information about his studies of soil microorganisms in the Atacama Desert. Several geologists of the IIG made notable contributions to the investigations. Nelson Bravo and Jaime Sayez assisted during early fieldwork. Guillermo Chong, now Professor of Geology, Universidad del Norte, prepared the nitrate claim maps on which figure 9 of this report is based and collaborated in field investigations in 1967 and 1977. Mauricio Tabac, Fernando Munizaga, and Hernán Cusicanqui collaborated in laboratory studies of the nitrate ores. The many other people in Chile who contributed information or helped to make the field studies pleasant and efficient are too numerous to be mentioned individually.

GEOMORPHOLOGY

The dominant physiographic provinces of northern Chile are, from west to east: 1) a relatively low Coastal Range, whose peaks are generally less than 2,000 m in altitude; 2) a longitudinal depression or Central Valley, called the Pampa del Tamarugal where it is broadest and deepest in northern Antofagasta and southern Tarapacá provinces; and 3) the high Andes Mountains (fig. 1). The elongate Coastal Range has a maximum width of about 50

km; the western margin is marked by a wave-cut cliff having a maximum height of about 1,000 m | (fig. 2). The Central Valley consists of two major segments, the Pampa del Tamarugal in the north

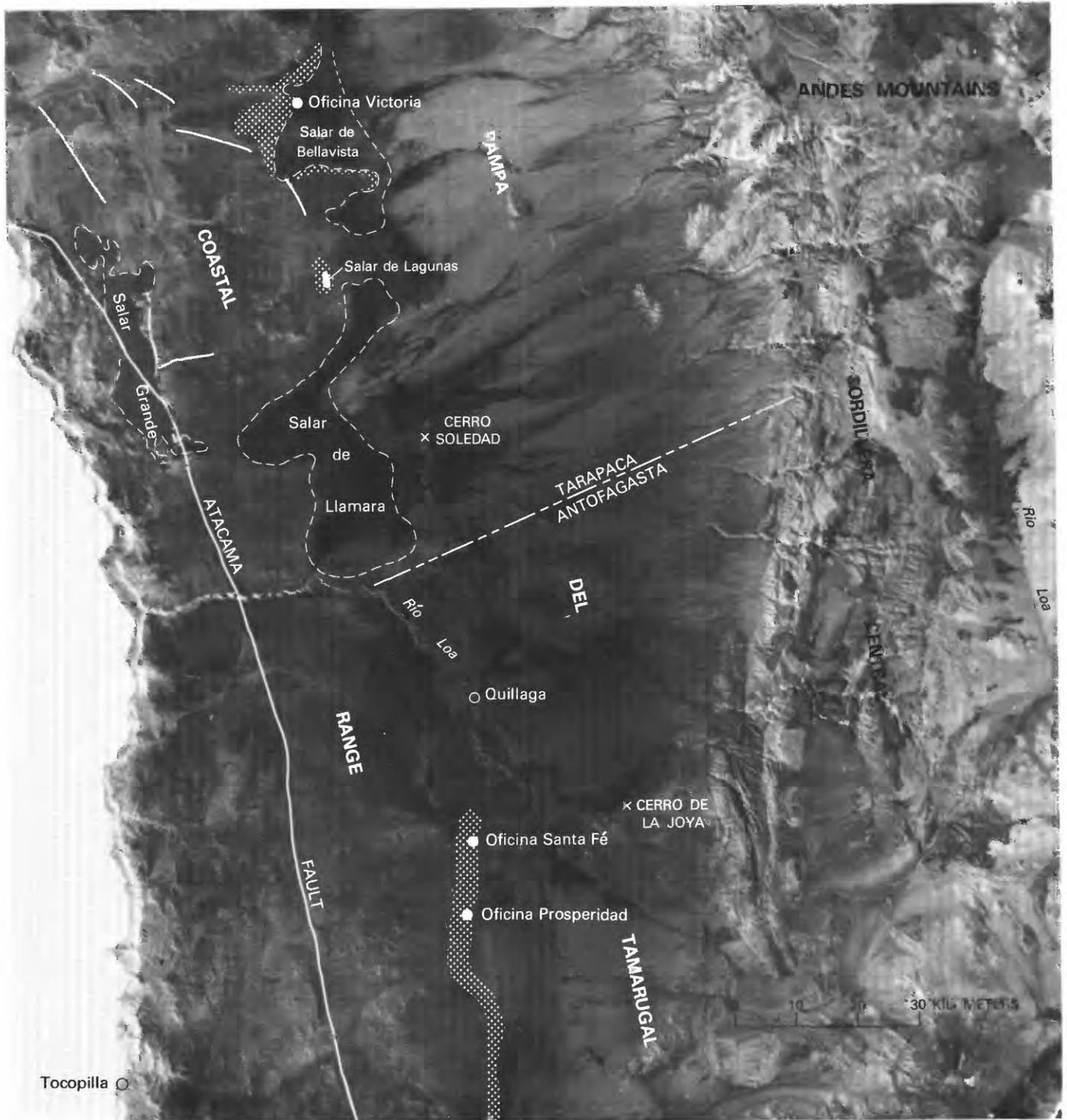


FIGURE 2.—Landsat image of the nitrate region in northern Antofagasta and southern Tarapacá Provinces, showing the major physiographic units of northern Chile: the Coastal Range, which has low relief and subdued topography; the broad Central Valley, which here is called the Pampa del Tamarugal; and the high Andes Mountains, including one of the high front ranges, the Cordillera Central. The coast is marked by a prominent wave-cut cliff and the Andean Front, by thick piedmont sediments. Principal nitrate workings (stippled), salars (outlined by dashed line), and selected recent faults are shown. Figure 1 shows area covered by image. Image No. 1244-14060, March 24, 1973.

and a longitudinal basin to the south, centering at Aguas Blancas, west of the Cordillera Domeyko (fig. 1). The two segments are separated by a broad transverse alluvial valley, herein referred to as the Baquedano valley, extending from Sierra Gorda

through Baquedano, and ending at Salar del Carmen (figs. 1 and 3). High-grade nitrate deposits have been worked extensively in this valley between Sierra Gorda and Baquedano (fig. 3).

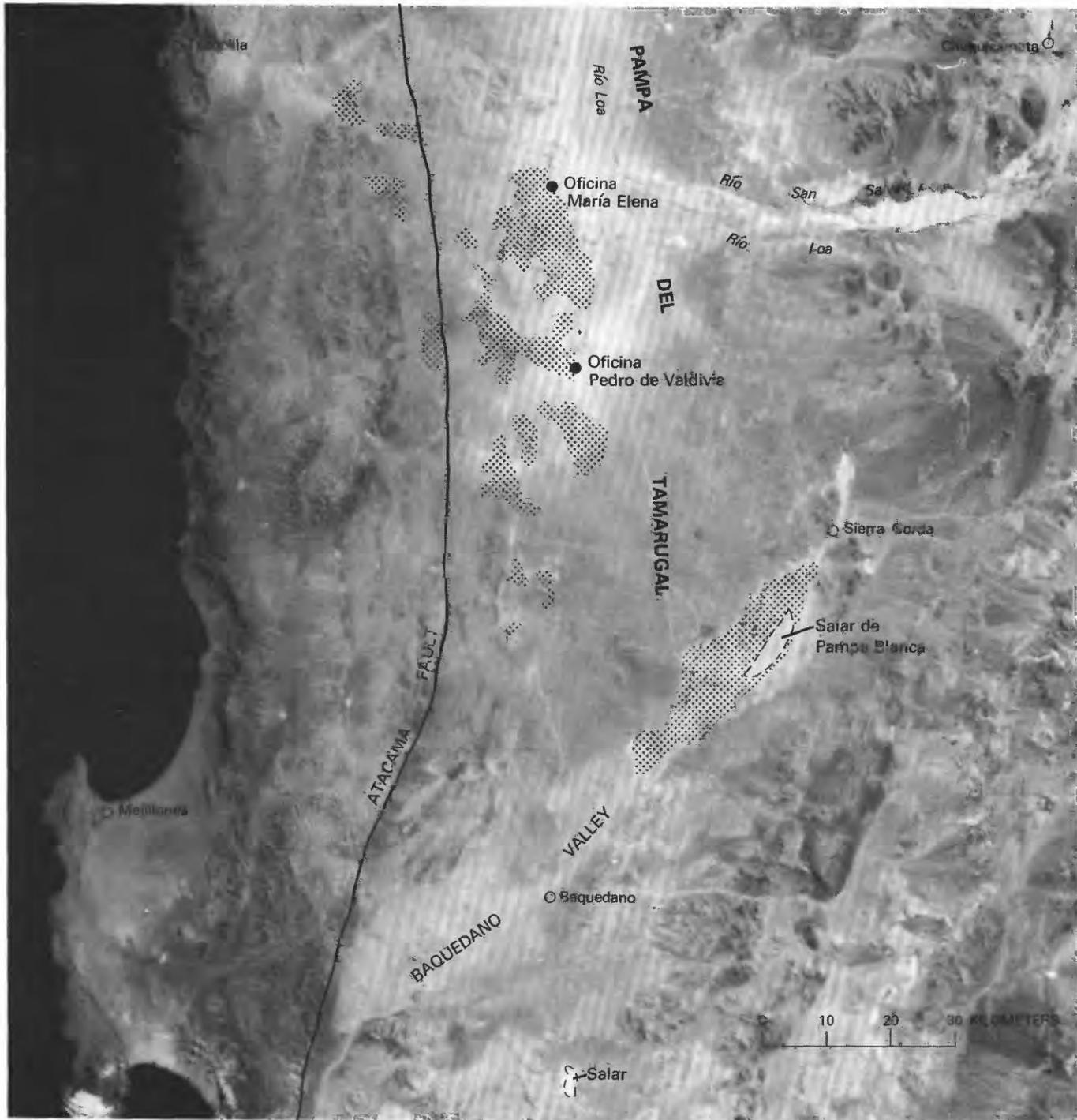


FIGURE 3.—Landsat image showing distribution of principal nitrate workings (stippled) in the Tocopilla and Baquedano districts. Unnamed salar south of Baquedano is in northernmost part of the Aguas Blancas basin, a segment of the longitudinal valley separated from the Pampa del Tamarugal by the oblique-trending Baquedano valley. Area covered by image is shown in figure 1. Image No. 1244-14062, March 24, 1973.

The Central Valley generally shows a rounded profile, having margins that merge with piedmont aprons along the Coastal Range and the Andean Front (fig. 3). However, in the latitude of the Tarapacá nitrate district (fig. 1), the Pampa del Tamarugal slopes westward and ends abruptly at the Coastal Range. The Andes Mountains consist of a plateau about 4,000 m in altitude, on which are hundreds of well-preserved volcanic cones. Only a few of the volcanoes are known to have erupted in historic time; some of these and a few others, not known to have erupted in historic time, now show fumarolic activity. In Tarapacá Province, the Andean Front is marked by gentle slopes that merge with the Pampa del Tamarugal, whereas southward, longitudinal front ranges—Cordillera Central (fig. 2) and Cordillera Domeyko (fig. 1)—and valleys separate the Andean plateau from the Central Valley.

Northern Chile is underlain chiefly by sedimentary, plutonic, and volcanic rocks of Jurassic and Cretaceous age, covered extensively by volcanic rocks and associated unconsolidated sediments of Tertiary and Quaternary age. The older rocks are best exposed in the Coastal Range and in the longitudinal ranges along the Andean Front. Upper Tertiary and Quaternary volcanic rocks are most extensive in the Andean region. The gently sloping Andean Front has a thick cover of piedmont sediments (fig. 2) and interbedded ash-flow tuffs. The Central Valley contains a fill of alluvium and interbedded lacustrine sediments that is as much as 900 m thick in the Pampa del Tamarugal, southern Tarapacá Province (Mordóovich, 1965). The Coastal Range is mantled with saline-cemented regolith consisting chiefly of fragmental rock material admixed with windblown silt and sand. Some of the windblown material is characteristically reddish-brown and consists chiefly of fine volcanic ash and eroded playa sediments. Closed basins in the Coastal Range contain fill consisting of alluvium and interbedded lacustrine sediments. The only known saline deposits in the older rocks of the region are anhydrite beds in marine sedimentary rocks of Late Jurassic age exposed in the Coastal Range, and layers and domal masses of rock salt in a sequence of terrestrial clastic sedimentary rocks of Cretaceous to early Tertiary age in the basin of Salar de Atacama (fig. 1).

The Atacama Desert has had an extremely arid, nearly rainless climate at least since Miocene time, and some of the Miocene and even earlier Tertiary landforms have been preserved with little modifica-

tion. For example, the Coastal Range north of Antofagasta (fig. 3) is considered to be an early Tertiary erosion surface, the Coastal Tarapacá Pediplain (Mortimer and Sarič, 1972, 1975), that has 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 (Mortimer and Sarič, 1975). The Miocene surface of the Central Valley is well preserved as the broad flat pampas—Pampa de Tana and others (fig. 4)—between the deep transverse valleys in northern Tarapacá Province. In southern Tarapacá, this surface is covered with alluvial fans from the Andes and by salars and playas crowded along the western side of the Pampa del Tamarugal (fig. 2). The deep transverse valleys in northern Tarapacá (fig. 4) were formed after middle Miocene time by streams from the Andes that cut across areas where the fill in the Central Valley overtopped the Coastal Range (Mortimer and Sarič, 1975). The Andean uplift, which began in the Oligocene, has continued until the present. It has been accompanied by 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 has been a region dominated by internal drainage during late Tertiary and Quaternary time, and saline lakes formerly existed in many of the closed basins. Such lakes were most prevalent in the Pampa del Tamarugal and the Aguas Blancas basin, where they 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 lacustrine and playa sediments of these former lakes include layers of diatomite and anhydrite. Diatomite is particularly widespread in the Pampa del Tamarugal in northern Antofagasta and southern Tarapacá Provinces, and a thick sequence of interbedded clastic lacustrine sediments and diatomite is well exposed along the Río Loa. This region was the site of a large perennial lake of probable late Tertiary age that Brüggén (1950) named Lago Soledad.

About 100 closed basins now exist in northern Chile, many of which contain salars or clay playas in their lowermost parts (Stoertz and Ericksen,

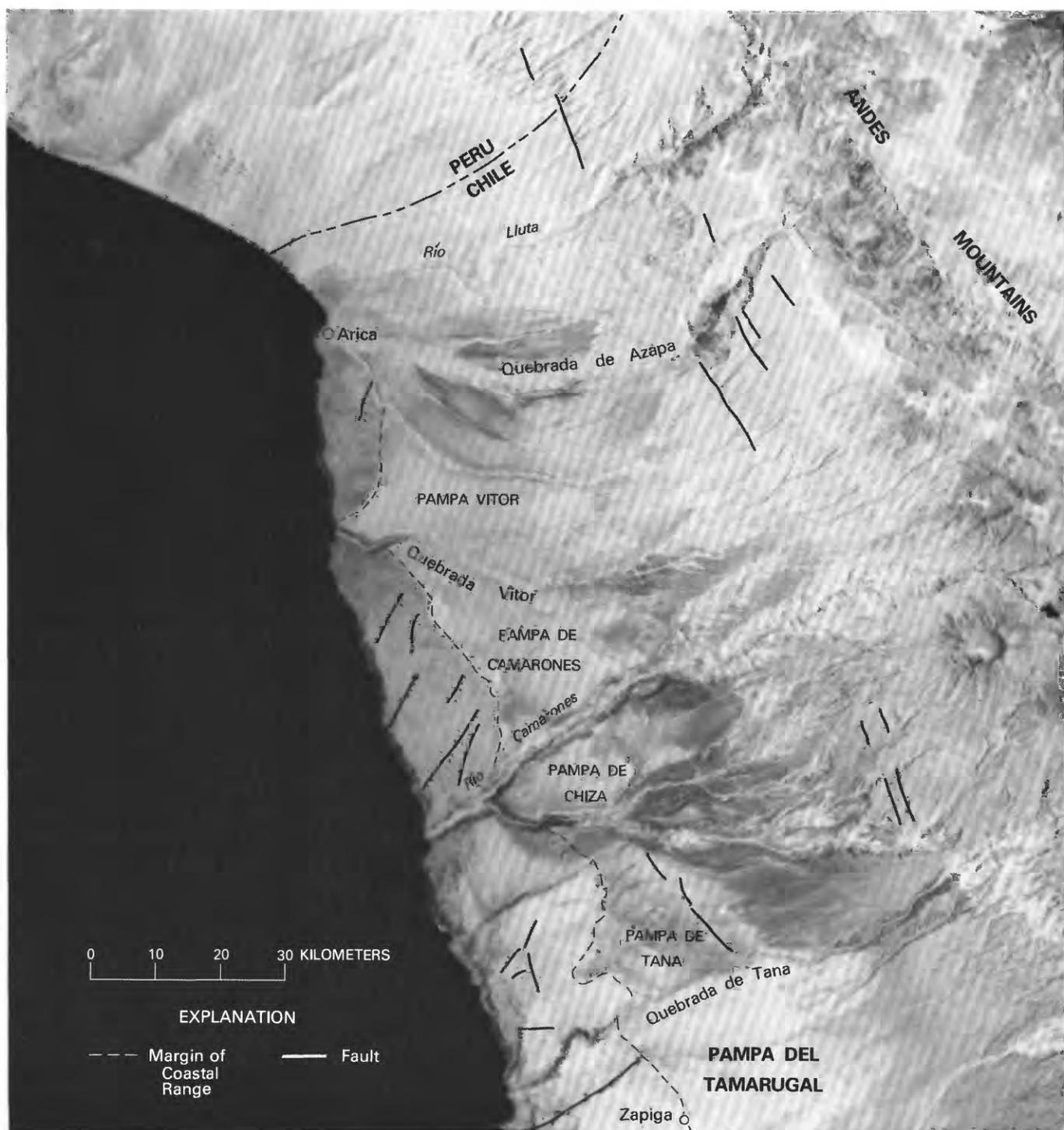


FIGURE 4.—Landsat image showing deeply incised transverse valleys of probable late Miocene to Quaternary age cutting across the northern Pampa del Tamarugal (flat pampas between the valleys are remnants) and the Coastal Range. Low-grade unworked nitrate deposits occur in the western part of the Pampa de Tana, a gentle, westward-sloping surface of probable Miocene age. Area covered by image is shown in figure 1. Image No. 1155-14102, Dec. 25, 1972.

1974). Only a few of these basins in the Andean Mountains now contain perennial saline lakes, but many others now having salars contained lakes during the Pleistocene, as indicated by prominent shoreline features. Shallow playa lakes now form in the Atacama Desert only at places along the western

margin of the Pampa del Tamarugal in southern Tarapacá Province at times of exceptionally heavy rainfall in the Andes. These lakes may form only once or twice in a given 10-year period and last from a few days to several weeks.

CLIMATE, VEGETATION, AND SOIL MICROORGANISMS

The Atacama Desert is the driest of the world's deserts; average annual rainfall is probably 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 rainfalls 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, gulying is minimal, and even some of the large valleys lack well-defined stream courses. The absence of recent stream erosion has given rise to the smoothed or rounded topography (fig. 5), and hills, gullies, and valleys of an earlier erosion cycle are now covered or choked with debris from nearby bedrock, mixed or covered with windblown dust and sand. Curiously, even the dust-covered surfaces are relatively stable and give rise to dense dust clouds only during very strong or turbulent winds. Sand dunes are absent in most of the desert; a single dune field occurs east of Salar de Pintados (fig. 1), and a few large dunes are found along the coast and in the Coastal Range. Most of the region is devoid of plant growth; plants are found only along streams in areas in the Central Valley 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 along the Andean Front. The lowest limit of regular or seasonal rainfall is at altitudes of 2,500 to 3,000 m along the Andean Front east of the Pampa del Tamarugal (Fuenzalida, 1965). In this region, the rains take place chiefly during the summer months of January–March and commonly are associated with violent thunderstorms. The maximum rainfall is in the Andean Highlands at altitudes of 4,000 m and above. Rainfall is greatest in the northern part of the province of Tarapacá, decreasing southward into Antofagasta, and then again increasing southward into Atacama. Fuenzalida (1965) reported the average annual rainfall in the northeasternmost

part of the Tarapacá Province (above 4,000 m) to be 276 mm, whereas that in the Andes of central Antofagasta does not exceed 50 mm. In southern Antofagasta and northern Atacama Provinces, precipitation is chiefly snow during the winter months of June–September, and annual precipitation is probably not significantly greater than that in central and northern Antofagasta Province. However, because of the prevalence of snow, which tends to sublimate rather than melt, this region of the Andes appears to be nearly as arid as the Atacama Desert. This arid climate favored the accumulation of the nitrate deposits known to exist in the Andean Highlands near Salar de Maricunga (fig 1).

Infrequent heavy rains in the Atacama Desert result in flash floods that may cause local flooding of low areas, mudflows, cutting of sharp gullies, and damage to buildings and roads. Hawxhurst (1926) reported torrential rains and floods in the Pampa del Tamarugal in the years 1819, 1823, 1852, 1859, 1878, 1884, 1905, and 1911. Evidently, flooding during some of those years was due to runoff from the Andes, which Hawxhurst does not distinguish from flooding due to rains in the Atacama Desert. He further stated that heavy rainfall and flooding in 1911 caused suspension of railroad service and operation of nitrate plants, and that considerable amounts of sodium nitrate in open storage piles were washed away. No other records of heavy rains in the Atacama Desert are available, but rains are reported to have destroyed unprotected stocks of nitrate in the Taltal district at least once during the present century.

One of the unusual features of the Atacama Desert is the presence of widespread, relatively abundant ground-water supplies, commonly not more than a few meters to a few tens of meters below the surface. The ground water occurs in the alluvium of the Central Valley as well as in that of dry valleys along the Andean Front and in the Coastal Range. This ground water, which is recharged chiefly by runoff from the Andes after heavy rains and by slow infiltration from valleys along the Andean Front, has been a major source of water for nitrate-beneficiation plants since the earliest days of the nitrate industry. The ground water in dry valleys and closed basins in the Coastal Range, particularly in the region of the nitrate deposits of southern Tarapacá Province (fig. 1), evidently is recharged by inflow along recent faults that connect the basins to the Pampa del Tamarugal.

Dense coastal fogs or low clouds, locally known as *camanchaca*, sweep inland from the Pacific

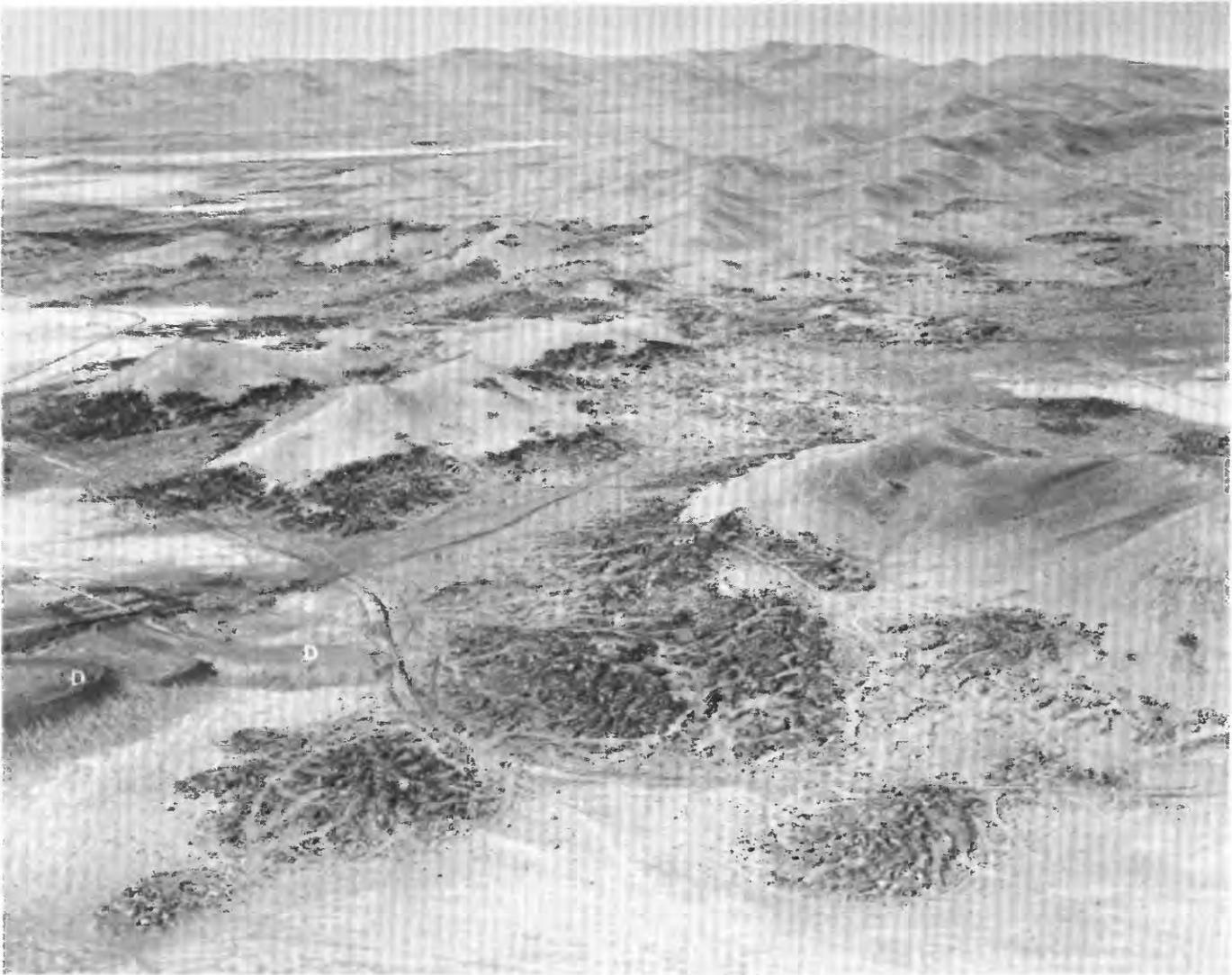


FIGURE 5.—Aerial view of nitrate workings in the northern part of the Tarapacá district. Nitrate ore mined in this area was chiefly of bedrock type, consisting of veins and impregnations of saline minerals in strongly fractured andesite. Waste dumps (D) of ore treated at Oficina Barcelona can be seen in left foreground.

Ocean, covering the Coastal Range nearly every night during the winter months of June to August, at times precipitating considerable amounts of water as condensate. The camanchaca of the nitrate region is typically a distinct cloud layer a few hundred meters thick, the bottom of which is several hundred meters above sea level. 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 soil and the formation of tiny rivulets of water on hard-rock surfaces and paved roads. The amount of water precipitated in this way is perhaps a few millimeters per month. Relative humidity is high in the Coastal Range, and considerable quantities of water also are precipitated as dew during the winter nights. Even though moisture precipitated at night is largely evaporated the following day, the near-surface soil

moisture probably remains relatively high during the cool winter months. The effect of such moisture is greatest near the coast, where it is sufficient to support local sparse plant growth, particularly on high hills facing the ocean. The fogs generally do not extend east of the Coastal Range, and the Central Valley is singularly free of fog or of cloud cover.

The coastal fogs of northern Chile contain saline material and they may have been important sources of constituents of the nitrate deposits. A 2-liter sample of fog condensate² from the crest of the

² Collected in July 1962, on frames having tightly strung nylon fibers, during an investigation by the Universidad del Norte into the feasibility of extracting water from fog for domestic and agricultural uses. It was found that frames 1-2 m on the side and strung with closely spaced nylon fibers were able to collect several liters of water from dense, wind-driven fog in a single night. Condensation was due chiefly to vibration of the nylon fibers as the fog moved across them.

coastal range, a few kilometers east of the city of Antofagasta, was found to contain 162 mg/l of dissolved salts, as follows (Ericksen, 1963):

	mg/l
Cl ⁻ -----	46
SO ₄ ⁻² -----	32
NO ₃ ⁻ -----	19
HCO ₃ ⁻ -----	15
Na ⁺ -----	30
Ca ⁺² -----	12
Mg ⁺² -----	6
K ⁺ -----	1
SiO ₂ -----	1

These constituents are considered to be chiefly of oceanic origin, having been ejected into the atmosphere in sea spray (see Blanchard and Woodcock, 1957), but part may have been contaminants from the atmosphere over Antofagasta and saline dust from the Atacama Desert. Although this single sample does not justify an estimate of quantities of saline material that might be precipitated in the nitrate fields, it does show that the fog contains the major constituents of nitrate ore in quantities sufficiently large to make it a potential major source of these constituents.

Temperatures are low in the Atacama Desert, in comparison with those in other deserts at low latitudes and altitudes. They also are relatively uniform throughout the year. An isothermal map by Almeyda Arroyo (in Fuenzalida, 1966) shows the average annual temperature of most of the Coastal Range in the region of the nitrate deposits to be 18° to 20°C. The average annual temperature in Iquique is 17.9°C, in Antofagasta, 16.6°C, and in Taltal, 17.7°C (Fuenzalida, 1965). The average daily temperature in Iquique ranges from about 21°C in January, the hottest month, to 15.5°C in August, the coldest month, a difference of only 5.5°C. In contrast to the Coastal Range, the Central Valley shows greater fluctuation in daily temperature and has lower relative humidity. For example, at Canchones, a government experimental farm at the northeast corner of Salar de Pintados (fig. 1), the mean annual temperature is 16.7°C, whereas the hottest month, February, averages 21.2°C, and the coldest, June, 12.9°C (Fuenzalida, 1965). The greatest fluctuation in daily temperatures here is during the period July to September, when minimum night temperature is near freezing and maximum day temperature is near 30°C.

Wind patterns and drainage are significant, in that they favor retention of saline material carried

into the Atacama Desert by wind and streams. This accounts in part for the exceptional saline accumulations that are more prevalent here than in other deserts. Wind is now the dominant agent of erosion and deposition, and wind transport and deposition of saline dust probably have been important processes in formation of the nitrate deposits. The Atacama Desert is characterized by onshore westerly winds during the day that alternate with easterly breezes from the Andes during the night. Along the coast, south to southwesterly winds dominate, whereas inland, the winds are more variable in direction. Because of variable wind directions, wind-transported material tends to be spread rather evenly over the desert, instead of forming dunal accumulations.

Vegetation is absent in much of the Atacama Desert, and the typical barren landscape is very different from that of most other deserts. Hardy shrubs grow sparsely only on hillsides where fog condensate is heaviest, particularly near the tops of the highest ridges and hills along the coast. Some areas near the coast have a sparse cover of *Tillandsia*, a Spanish moss that spreads over the otherwise barren soil. *Tillandsia* is an air plant, having rootlets that function as anchorage in young plants but that generally are absent in older plants. Shrubs and salt grass grow in areas in the Pampa del Tamarugal subject to occasional flooding by runoff from the Andes or where the ground-water table is within a few tens of centimeters of the surface. Tamarugo trees, a type of mesquite (*Prosopis*), are reported to have once covered large areas of the Pampa del Tamarugal where the ground-water table is shallow, but during the early days of the nitrate industry they were used as fuel, and the pampa was almost completely stripped of the trees. In the late 1930's or early 1940's, the government of Chile started a very successful reforestation program by planting Tamarugo and Algarrobo (also a type of mesquite) trees in the Salar de Pintados. The trees are planted in holes dug through the thin hard salt crust into underlying moist sediments.

The recent discovery that soils in the Atacama Desert have microflora populations capable of nitrogen fixation as well as nitrification and ammonification³ (Cameron and others, 1965, 1966; Cameron,

³ Nitrogen fixation is the conversion of elemental atmospheric nitrogen to ammonia and other nitrogen compounds, chiefly by activity of specialized bacteria and blue-green algae in soils; ammonification is the conversion of proteins and other organic compounds to ammonia, water, and carbon dioxide by many types of bacteria, actinomycetes, and molds; nitrification is the oxidation of ammonium to nitrite and nitrate by specialized bacteria.

1969, and Cameron, written commun., 1966, 1967, 1968) invites speculation about the role of microorganisms in the formation of the nitrate deposits. Unfortunately, the investigations are not sufficiently detailed to support quantitative estimates of the significance of microorganisms in formation of the nitrate, but they do show that microbial activity in the dry soils of the Atacama Desert is exceedingly low, a requisite for preservation of the nitrate. On the other hand, activity might be great at soil surfaces subject to frequent wetting by fog condensate during winter months, and during such periods of high microbial activity, significant quantities of nitrate could have been formed or consumed.

Investigation of soil microflora of the Atacama Desert was undertaken as part of a more extensive study of desert microorganisms supported by the National Aeronautics and Space Administration (NASA) and carried out under the direction of Roy E. Cameron who was then with the Jet Propulsion Laboratory (JPL), California Institute of Technology. I had the opportunity to accompany Cameron during part of a field investigation in northern Chile in 1965 and through correspondence with him was able to keep abreast of information gathered in subsequent laboratory studies. The information presented here is based on published and unpublished data of Cameron and his colleagues at JPL and on studies undertaken under JPL contract by W. B. Bollen (unpub. data, 1967, 1968) of Oregon State University and by E. E. Staffeldt (unpub. data, 1967, 1968) of New Mexico State University. Prior to the work of Cameron and his colleagues, relatively little was known about soil microorganisms in the Atacama Desert. Darwin (1890) mentioned the presence of the yellow lichen *Cladonia* on loose sand of the Coastal Range near Iquique, where winter fogs are prevalent. Schwabe (1960a, b) reported on blue-green algae in soils near Antofagasta.

The dry soils of the Atacama Desert 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. In this respect, the soils are most similar to the relatively barren soils of Antarctica, where nitrate-rich saline complexes are known to have accumulated (Claridge and Campbell, 1968). Laboratory cultures of soils of the Atacama Desert show considerable diversity in types and growth rates of microflora populations and capacity for ammonification and nitrification. Bacteria and actinomycetes

are generally the most abundant microorganisms present. Incubation periods in most laboratory cultures of soils from this area were many days rather than the 48 hours or less for soils from less arid deserts (Cameron and others, 1966). Some of the soils were found to have high nitrifying capacity but little or no ammonifying capacity, whereas others show the reverse (W. B. Bollen, unpub. data, 1967). Presumably, some other soils have both ammonifying and nitrifying capacity. Cameron (written commun., 1967) reported that some of the soils tested had the capacity for sulfate reduction.

The filamentous blue-green algae are among the more intriguing of the microflora in the soils of the Atacama Desert because they are photoautotrophic—requiring only oxygen, light, and inorganic substances for their life processes—an ability that is essential for significant microbial activity in the organic-deficient soils of this region. Furthermore, many species have the ability to fix atmospheric nitrogen. The favored habitats of these algae are the surfaces of wet or moist soils, and they may exist symbiotically with fungi in lichens. *Nostoc muscorum*, a well-known nitrogen-fixing blue-green alga, was found in saline material and mud from the edge of a saline pond in Salar de Bellavista near Oficina Victoria (figs. 1 and 2) (R. E. Cameron, written commun., 1966). It has been found in the coastal desert of Peru where winter fogs are most prevalent (Dawson, 1963) and where fog condensate is somewhat greater than it is in the Atacama Desert. *Nostoc* has not been reported from the desert soils of northern Chile, but it could occur undetected locally and might have been more widespread in times past, when fog condensate may have been greater.

Cameron and Blank (1966) summarized information about desert habitats of algae, indicating that favored sites for growth of algae in deserts were the undersides of translucent rock fragments, such as chalcedony, and beneath thin salt crusts where soil moisture is retained and yet light is available for photosynthesis. Algae are known to occur in such habitats in the Atacama Desert (Schwabe, 1960a, b). Residual algal colonies such as these serve as reservoirs from which spreading could take place to form extensive algal crusts on soil surfaces after rains (Cameron and Blank, 1966) and perhaps at times of high moisture due to accumulation of fog condensate.

Blue-green algae also are abundant in saline ponds associated with salt pans in the nitrate region of northern Chile, and we may assume that they also

were abundant in former saline lakes and ponds in this region. The two saline ponds for which chemical analyses are listed on page 31 have abundant algae and associated microflora in a nitrate-rich brine. In addition to *Nostoc muscorum*, samples of saline material and mud from the pond in Salar de Bellavista, collected in 1965, were found to contain *Schizothrix calcicola*, an alga having the ability to utilize ammonia as its sole source of nitrogen (R. E. Cameron, written commun., 1966). Whether these species and associated microorganisms have had any significant effect on the formation of the nitrate in these ponds is not known. However, the presence of a nitrogen-fixing species suggests the possibility of significant amounts of nitrate being formed in such ponds and in moist soils at margins of ponds and lakes at present and in the past.

GEOLOGY OF THE NITRATE DEPOSITS

TOPOGRAPHIC SETTING

The nitrate fields (fig. 1) are typically in areas of low relief characterized by rounded hills and ridges and by broad, shallow, debris-filled valleys. Nitrate deposits occur in all topographic positions from tops of hills and ridges to the centers of the broad valleys, but the richest deposits that have been worked most extensively tend to be on the lower slopes of hills (fig. 5). Nevertheless, high-grade deposits also are found in broad debris-filled valleys and basins (fig. 6) and in nearly flat to

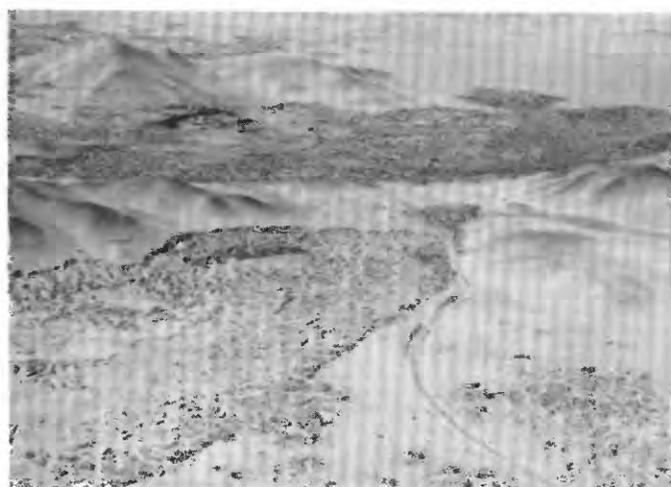


FIGURE 6.—Aerial view of nitrate workings at Oficina North Lagunas (ruins of former beneficiation plant can be seen at base of hill in background), near Salar de Lagunas at the southern end of the Tarapacá district. Nitrate ore here is chiefly saline-cemented regolith.

gently undulating terrain (fig. 7). Most of the nitrate fields in the Tarapacá and Tocopilla nitrate districts (fig. 1) are in gently inclined piedmont plains and steeper rocky slopes along the eastern side of the Coastal Range. They either end abruptly near the margin of a salar or playa along the western side of the Pampa del Tamarugal, typical of the Tarapacá district (fig. 8), or merge with valley fill without a perceptible break, as in the Tocopilla district (fig. 3). However, the topographically lowermost deposits in the Tocopilla district tend to occur along the zone where the lacustrine deposits that extend over the Pampa del Tamarugal intersect or interfinger with the piedmont deposits covering the gentle eastern slopes of the Coastal Range.

On the whole, the richest nitrate ore in northern Chile is in the fields of the Tarapacá district. These fields were the chief source of nitrate produced prior to the 1870's. The first nitrate-beneficiation plants were built in the vicinity of Zapiga (fig. 8) between 1810 and 1812 (Bermudez, 1963). The most extensively worked deposits in this district include those in a narrow band along the eastern margin of the Coastal Range (fig. 8) and those within the Coastal Range south of this area (fig. 1), where a generally undulating terrain is marked by several closed basins. In the latter area, the richest nitrate deposits tend to be at the margins of the basins, but rich deposits also occur on the floors of some basins and in the nearly flat uplands between basins. Salar are found in the central parts of a few of these basins, and the nitrate deposits are on the hillsides marginal to them. Rich deposits also occur in several islandlike bedrock hills, 10–20 m high, within but near, the western sides of playas and salars along the western side of the Pampa del Tamarugal in the northern part of the Tarapacá district. Some of these hills have been worked extensively for nitrate ore from near the level of the playa or salar to the hill-top.

The nitrate deposits of the Baquedano nitrate district are distinctly different topographically from those in Tarapacá, as can be seen in figure 9. These deposits are nearly continuous along the broad debris-filled valley from Baquedano to Sierra Gorda, a distance of about 60 km. They occur along the valley bottom, where the nitrate layer is locally exposed in the 1–3-m-high walls of a recent stream channel, and in the gently sloping valley sides for horizontal distances of as much as 10 km and vertical distances of 100–200 m from this stream channel. Scattered deposits also are found in an undulating upland area between this valley and the north-trending valley to

the west (fig. 9), which connects with the Pampa del Tamarugal. Both the salars shown in figure 9—Pampa Blanca and Lina—contain nitrate-rich saline crusts that formerly were exploited as nitrate ore. These ores evidently were relatively low grade and generally less than 50 cm thick but because they lacked overburden, they could be mined at low cost.

Nitrate deposits also have been found on hilltops and in high valleys far from other known deposits and from any possible source of saline materials in ground water or in former lakes. Some of the deposits at the east side of the Aguas Blancas district (fig. 1) are of this type. They are high on the west flank of the Cordillera Domeyko, and seem isolated from the known deposits to the west. However, this isolation may be more apparent than real; deposits in this poorly explored area probably are much more

widespread than indicated in figure 1, and nitrate-rich soils may be even more widespread. Cerro Peineta, a flat-topped mountain in the southern part of the Taltal district, is unusual in having an isolated nitrate deposit at its top, several hundred meters above the surrounding terrain. This deposit has been cited as an example of a nitrate deposit that could have formed only by atmospheric deposition of the saline components (Brüggen, 1938).

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 (fig. 1)—are actively receiving increments of new nitrate-rich saline material by capillary evaporation of near-surface saline ground water. Salar del Carmen was mined in the latter part of the 19th century, when nitrate-rich efflores-



FIGURE 7.—Underground nitrate workings at the northern end of the Tarapacá district. Near-horizontal discontinuous layers of relatively pure saline material occur in limestone and interbedded shale 5–10 m below the surface. Shallow layers and veins of this material were mined in open-cut in foreground; tunnels from this cut connect shafts marked by isolated waste piles.

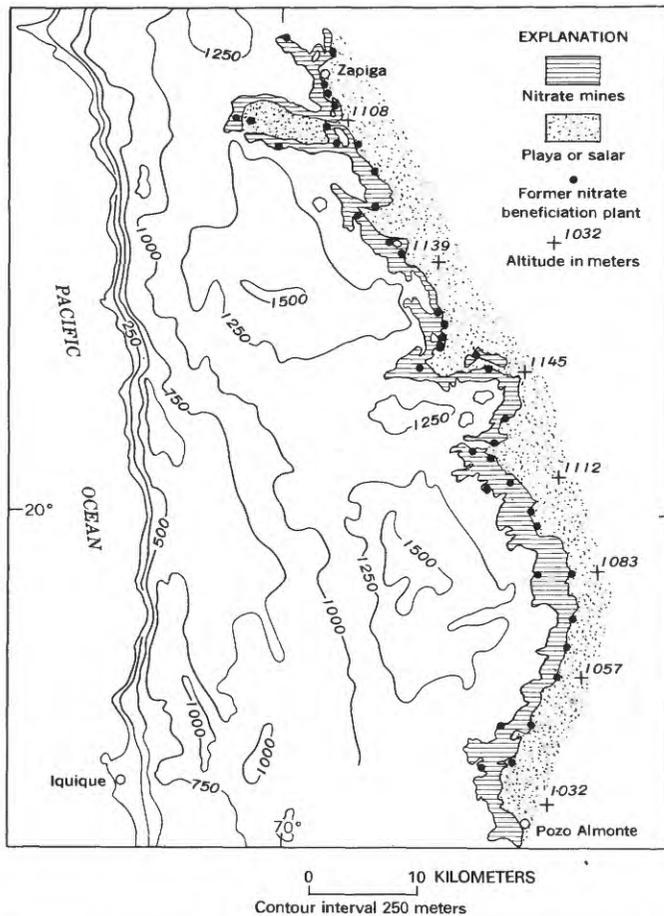


FIGURE 8.—Topographic map of the northern Tarapacá district, showing distribution of nitrate workings along the eastern margin of the Coastal Range. Deposits here were the first to be worked in the early 19th century and on the average contain the richest nitrate ore in northern Chile. From unpublished map prepared by the Instituto de Investigaciones Geológicas of Chile.

cences that reformed in some old mine areas were harvested periodically (Whitehead, 1920). The nitrate-rich crusts of two or three small salars in the Aguas Blancas district also have been mined.

STRUCTURAL FEATURES

The nitrate deposits show characteristic features that reflect original structures in the host rocks and other structures that formed later, during accumulation and enrichment of the deposits. The deposits are in all types of rocks and unconsolidated sediments in the Coastal Range and Central Valley without showing any systematic variation in content of the saline components or of trace elements in these components. Nitrate and other saline minerals occur as veins or impregnations in such diverse rock types as granitic intrusions, andesite and rhyolite

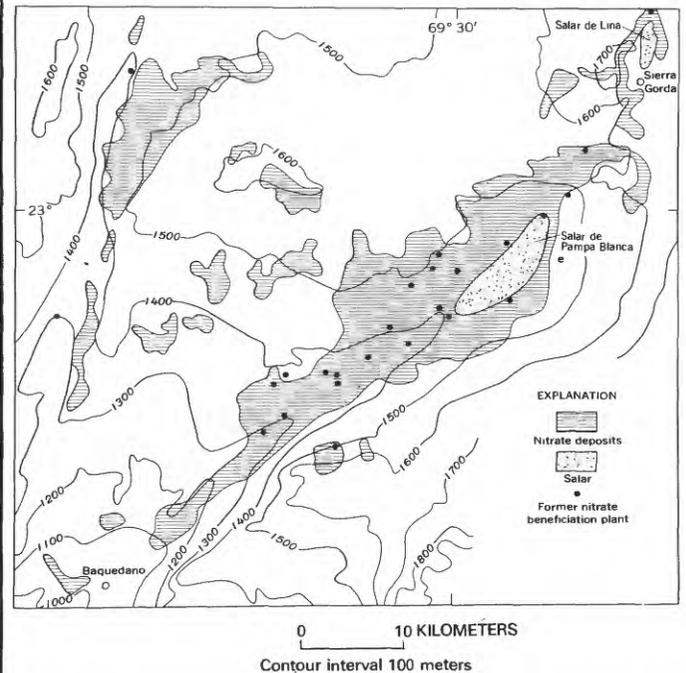


FIGURE 9.—Topographic map of the Baquedano district, showing areas of exploitable or potentially exploitable nitrate deposits. Most of the nitrate workings, indicated by distribution of beneficiation plants, are in the broad valley extending from Baquedano to Sierra Gorda. Prepared from topographic maps of the Instituto Geográfico Militar (scale 1:50,000) and unpublished nitrate mine-claim maps of the Servicio de Minería of Chile.

flows and tuff layers, limestone, sandstone, and shale. The most widespread deposits are those in which the saline minerals form a cement in unconsolidated regolith. Saline minerals were deposited in original openings—pores, cavities, and fractures—in the host rock and in new openings formed by force of crystallization. Features such as compositional layering, veins of high-purity saline minerals, sand dikes, solution cavities, desiccation polygons, and gypseous cakes (*losa*) resulted from processes of solution and redeposition. The nitrate fields are in a region of active faults, and nitrate layers have been extensively fractured in the vicinities of faults.

Two major types of nitrate ore (called *caliche*⁴ in Chile) can be recognized, one in which the saline minerals occur chiefly as a cement in regolith and the other in which they form impregnations, veins, and irregular masses in porous or fractured bedrock. For convenience of discussion, the two types

⁴ *Caliche* is now considered to be a nitrate ore having a minimum grade of about 7 percent NaNO_3 , the approximate cutoff grade for the operating beneficiation plants. Formerly, higher grade nitrate ore was mined (earlier in this century minimum grades were generally about 15 percent NaNO_3), and lower grade material was not considered to be *caliche*.

are referred to as alluvial caliche and bedrock caliche. Alluvial caliche generally rests on poorly cemented or uncemented rock debris similar to that within the caliche itself, whereas bedrock caliche gives way downward to less fractured or more impervious rock relatively free of saline minerals. The typical alluvial-type nitrate deposit is considered to be made up of several layers (fig. 10)—**chuca**, **costra**, **caliche**, **conjelo**, and **coba**—each having characteristic chemical and physical features. Distribution of the saline minerals in these layers is in part determined by their solubilities and is consistent with selective leaching of surface material and reprecipitation at deeper soil levels.

Chuca and **costra** constitute the overburden of the alluvial-type nitrate deposit. Chuca is the powdery to poorly cemented surface layer, generally 10–30 cm thick, consisting of silt, sand, and rock fragments, variable though generally abundant gypsum or anhydrite, and small amounts of other saline minerals. It consists of the surface soil, from which most of the water-soluble saline minerals have been leached, and admixed windblown material. Saline materials leached from this layer have been redeposited to enrich underlying or downslope caliche and to form veins and mantos of high-purity saline materials in preexisting caliche. At many places, the chuca contains a layer of hard to soft white saline material a few centimeters to about 50 cm thick (fig. 11), which consists chiefly of either relatively insoluble gypsum and anhydrite or of soluble sulfates such as thenardite, bloedite, and humberstonite. The hard material is brittle and breaks with a conchoidal fracture; it has the appearance of having formed as a gel. It weathers to a soft friable material. Costra consists either of a hard and brittle material similar to the underlying caliche, or of poorly cemented friable material that appears transitional between chuca and caliche. Contacts between costra and chuca are generally sharp, and although those of costra and caliche tend to be gradational, they also may be sharp, as shown in figure 12. Costra is generally 1/2–2 m thick, but locally it may be thinner or even absent. Some nitrate fields characteristically have poorly cemented costra several meters thick, and thicknesses of as much as 12 m have been observed.

Alluvial-type caliche is generally 1–3 m thick, but material as thin as 50 cm and as thick as 5 m has been mined locally. Veins and layers of high-purity, white nitrate-rich saline material (called **caliche blanco** by the miners) are widespread in the alluvial-type caliche of some fields or areas, but

relatively rare in others. They generally range from 10–50 cm in thickness. Layers of caliche blanco are generally at the base of the caliche layer, perhaps the level of deepest penetration by rainwater. Most alluvial-type caliche is somewhat porous and contains irregular to slitlike cavities as much as 20 cm in longest dimension. Such cavities commonly contain well-developed crystals of saline minerals. Pebbles may have halos of fine-grained, white, saline material, as much as a centimeter thick, some of which show desiccation cracks. The caliche layer typically shows considerable variation in physical character and chemical composition in short horizontal distances. These variations seem to be the result of a combination of factors, including the physical

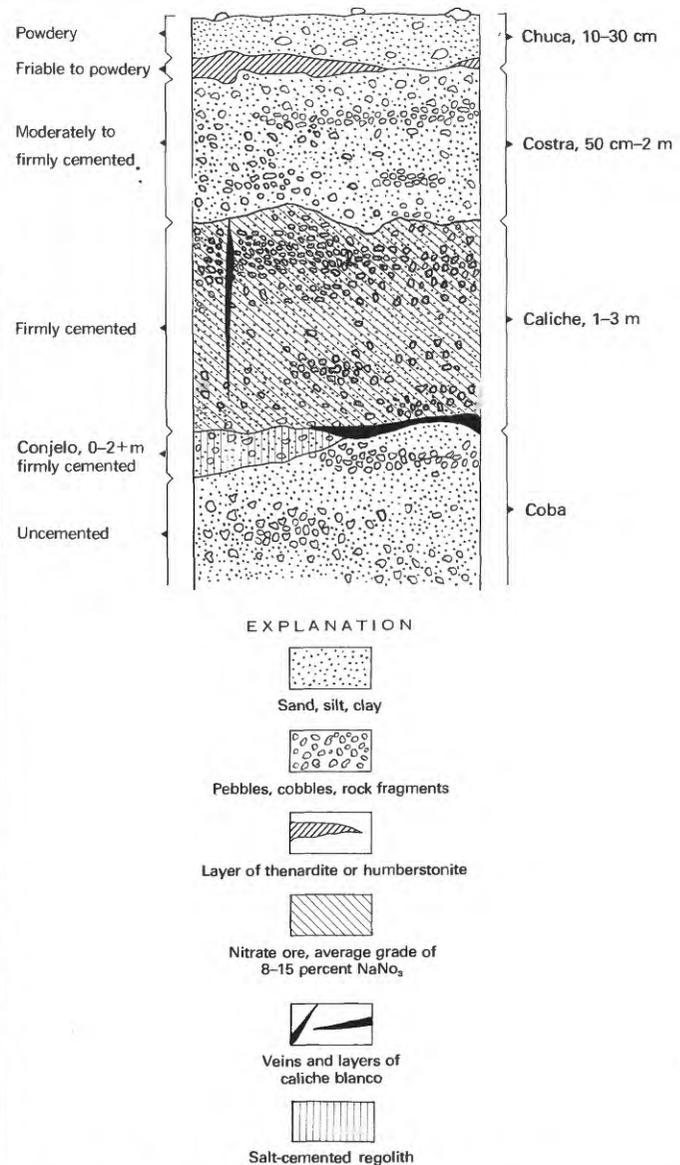


FIGURE 10.—Characteristic layering of an alluvial-type nitrate deposit.

nature and porosity of the host rock, configuration of the land surface, and degree of erosion, leaching, and redeposition of the saline minerals by rainwater.

Alluvial-type caliche either grades downward into **conjelo**, which is saline-cemented regolith containing little NaNO_3 , or into **coba**, which is loose uncemented regolith (fig. 10). Conjelo, where present, grades downward into **coba**. Conjelo was not observed in this study, and thicknesses are not reported in the literature. Presumably, maximum thicknesses are not more than a meter or two. Isolated lenses and pods of firmly cemented conjelo or caliche have been found in the **coba** below the caliche, but evidently these are relatively rare. Both **coba** and **conjelo** are dry, although some **coba** has been reported to be slightly moist (Brüggen, 1938). The contact between caliche and **coba** is relatively sharp, generally changing from hard nitrate ore to soft uncemented material in a few centimeters.

Bedrock caliche consists of saline impregnations in porous rock and of veins and layers of caliche blanco along fractures in otherwise massive or poorly bedded rocks such as ash-flow tuffs (fig. 13) and along bedding planes and in crosscutting fractures in layered sedimentary rocks. Such veins and layers, which generally range from a few centimeters to several tens of centimeters in thickness, formed along incipient cracks and narrow fissures



FIGURE 11.—Layer of friable high-purity humberstonite 10–30 cm thick, overlain by 10–30 cm of sandy rocky soil (**chuca**). Oficina Alemania, Taltal district. Ore pile to right contains large chunks of humberstonite.

that were gradually forced open by the crystallizing saline minerals. Where carried to the extreme, such a process transforms strongly fractured bedrock into a mosaic of isolated rock fragments in a matrix of caliche blanco.

Layers of caliche blanco in bedrock are generally at depths of 3–6 m. They are most extensive in thin-bedded, near-horizontal, stratified rocks such as a sequence of Jurassic limestone and interbedded shale and sandstone that occurs in the northern Tarapacá district (fig. 7). In a given nitrate field, the layers tend to be at a relatively constant depth and, like layers of caliche blanco in alluvial-type caliche, tend to be parallel or subparallel to the land surface. Because of the depth and difficulty of removing the bedrock overburden, much of this type of nitrate ore was formerly mined in shafts and interconnecting tunnels, such as those shown in figure 7.

The nitrate fields are characterized by large and small desiccation polygons that formed and continue to form in response to volumetric changes related to slow leaching and redeposition of the saline minerals. Small polygons generally do not penetrate deeper than the upper part of the caliche layer, as shown in figure 14, but the large polygons, which are several meters in diameter, may extend to the bottom of the layer. Marginal fractures of the large polygons generally have a filling of saline-cemented sand and silt a few centimeters to several tens of centimeters



FIGURE 12.—Rajo San Martín, a nitrate mine in the Taltal district that was active at the time this photograph was taken in 1962. The working face shows a sharp contact (marked by hammer) of hard massive caliche and overlying **costra**, which here is slightly porous and relatively soft. A 20–30-cm layer of unconsolidated **chuca** on top of the **costra** was removed before mining.

thick, which have been called sand dikes (Ericksen, 1963). The sand dikes (fig. 15) commonly are richer in nitrate than is the alluvial caliche in which they occur, which reflects enrichment due to selective leaching of nitrate from near-surface soil or caliche and redeposition as cementing material in the dikes. Some of the sand dikes and narrow fissures without dikes contain narrow veins of caliche blanco. Large polygons, which continue to form in the nitrate fields today, are marked by depressions in soft *chuca* (fig. 16).

One of the unusual surface manifestations of prolonged slow leaching is the formation of hard spheroidal cakes of anhydrite, called *losa*, embedded in powdery *chuca* (fig. 17). These cakes evidently are the end product of processes of desiccation and leaching that first formed small polygons such as those shown in figure 14.

Abundant chalcedony nodules in some of the nitrate fields, notably those of the Taltal district, have been the subject of much discussion and specu-



FIGURE 13.—Bedrock **caliche**, consisting of impregnations and veins of **caliche blanco** in rhyolite tuff, exposed in an open-pit nitrate mine in the Taltal district. The veins from this locality were found to contain about 99 percent NaNO_3 , the highest nitrate content reported from northern Chile.

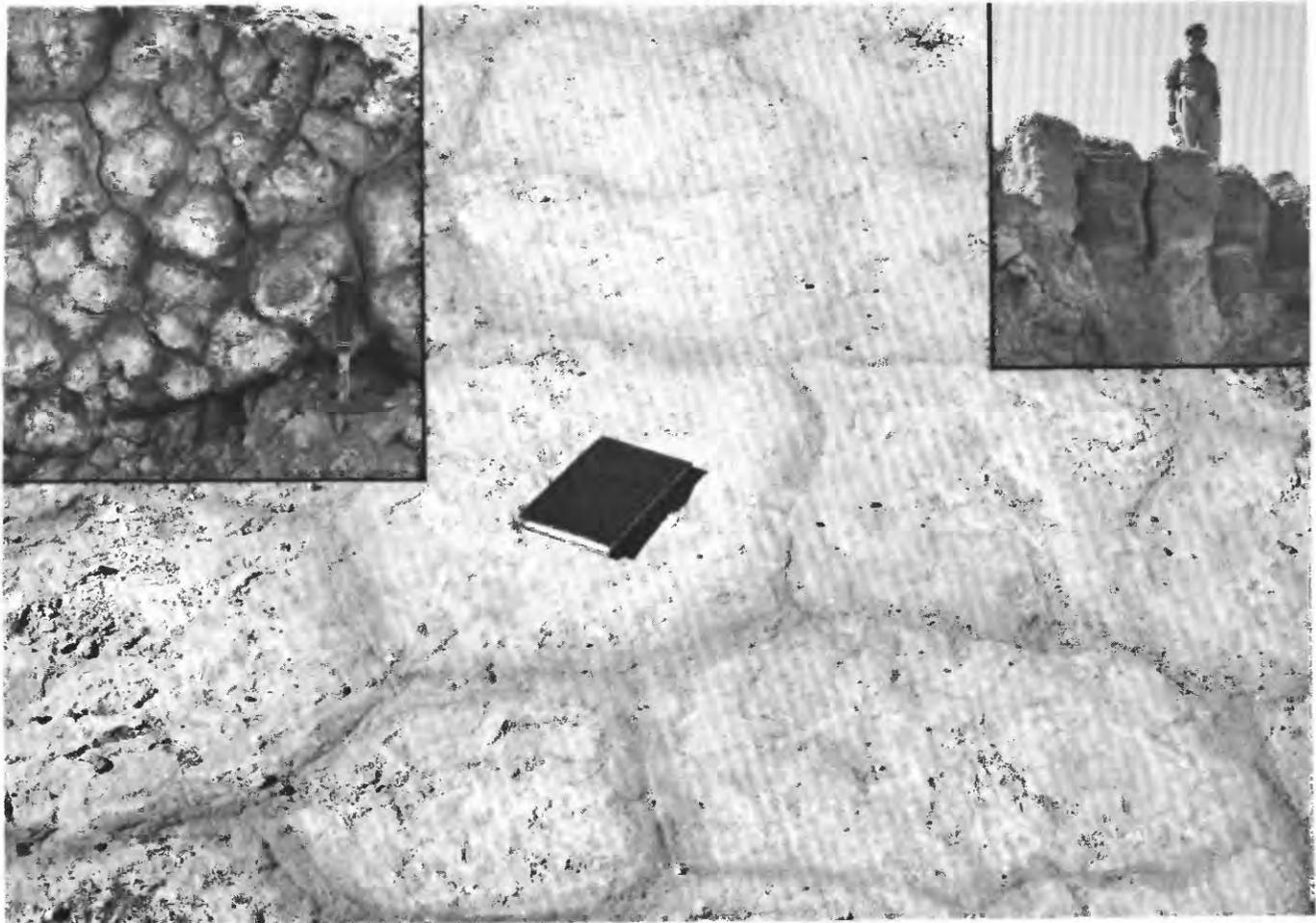


FIGURE 14.—Polygonal surface of **costra**, Tarapacá district, which has been swept free of the surface covering (**chuca**) along a mine-access road. Inset on left shows nodular underside of 50–75-cm-thick slab of hard polygonal **costra**; inset on right shows section of leached soft polygonal **costra** in which polygonal fractures terminate in the underlying **caliche**.



FIGURE 15.—Saline-cemented, nitrate-rich sand dike in alluvial-type caliche, northern Tarapacá district. These dikes generally are somewhat richer in nitrate than is the enclosing caliche. Note parallel sides of dike indicating that the structure is a former open fissure; sides of other dikes are more irregular because of sloughing of material from the sides of the open fissure.

lation. They occur as small, convolute, flattened nodules and fragments of tan, pink, and white chalcedony and are locally so abundant that they form a desert pavement. Nitrate miners have long considered abundant chalcedony to be an indicator of rich nitrate ore. Several authors (Ochsenius, 1887-88; Sundt, 1919; Wetzel, 1928) suggested that the chalcedony is the residual product of in situ decomposition of feldspathic rocks that liberated the sodium, potassium, magnesium, and calcium in the saline minerals of the nitrate deposits. The literature does not give a clue to any other source of these chalcedony nodules, but early in our studies we found veins of vuggy lamellar chalcedony in rhyolite ash-flow tuff in the eastern part of the Taltal district that were being weathered to form a desert pavement identical with the pavements of chalcedony fragments seen elsewhere in the district (Ericksen, 1963). Evidently, these veins formed by thermal-spring activity in the ash flows shortly after they were emplaced. Wind erosion of the relatively soft tuff exposed the veins which then disintegrated, and the fragments spread in their vicinity. In turn, the fragments were spread more widely by mudflows and runoff at times of exceptionally heavy rains. They accumulated on some old surfaces that were favorable sites for slow accumulation of rich nitrate

ore, which led the miners to believe that chalcedony was an indication of such ore.

Feathers and mummified bodies of birds, masses of bird guano, and even egg fragments have been found in the nitrate fields, some in the caliche layer, a meter or more below the surface. The remains of both land birds and sea birds have been found. The presence of masses of guano and of eggs indicates that some areas of the nitrate fields were favored nesting or roosting grounds for certain birds. Some guano appears to be very old and has been cemented by saline minerals of the nitrate ore. Other guano is uncemented and obviously more recent. Masses of saline-cemented guano a meter or two in diameter and as much as 50 cm thick are particularly abundant in the nitrate fields near Oficina Alemania, Taltal district (fig. 1). Wetzel (1925) described bird remains in the region of Toco (Tocopilla district) and identified a mummified sea bird as being of the genus *Thalassidroma*. Nitrate miners have reported that small land birds have been blasted alive out of nitrate ore during mining. They evidently live in crevices and cavities in the ore. Sea birds now occasionally fly into the nitrate region, and Brügggen (1938) mentioned sea birds as having nesting grounds in some of the nitrate fields. It seems unlikely that sea birds would now occupy nesting grounds far from the coast, but they may have done



FIGURE 16.—Newly formed desiccation polygons in nitrate ore, Tarapacá district; fissures at the margins of the polygons are marked by depressions in the *chuca*.

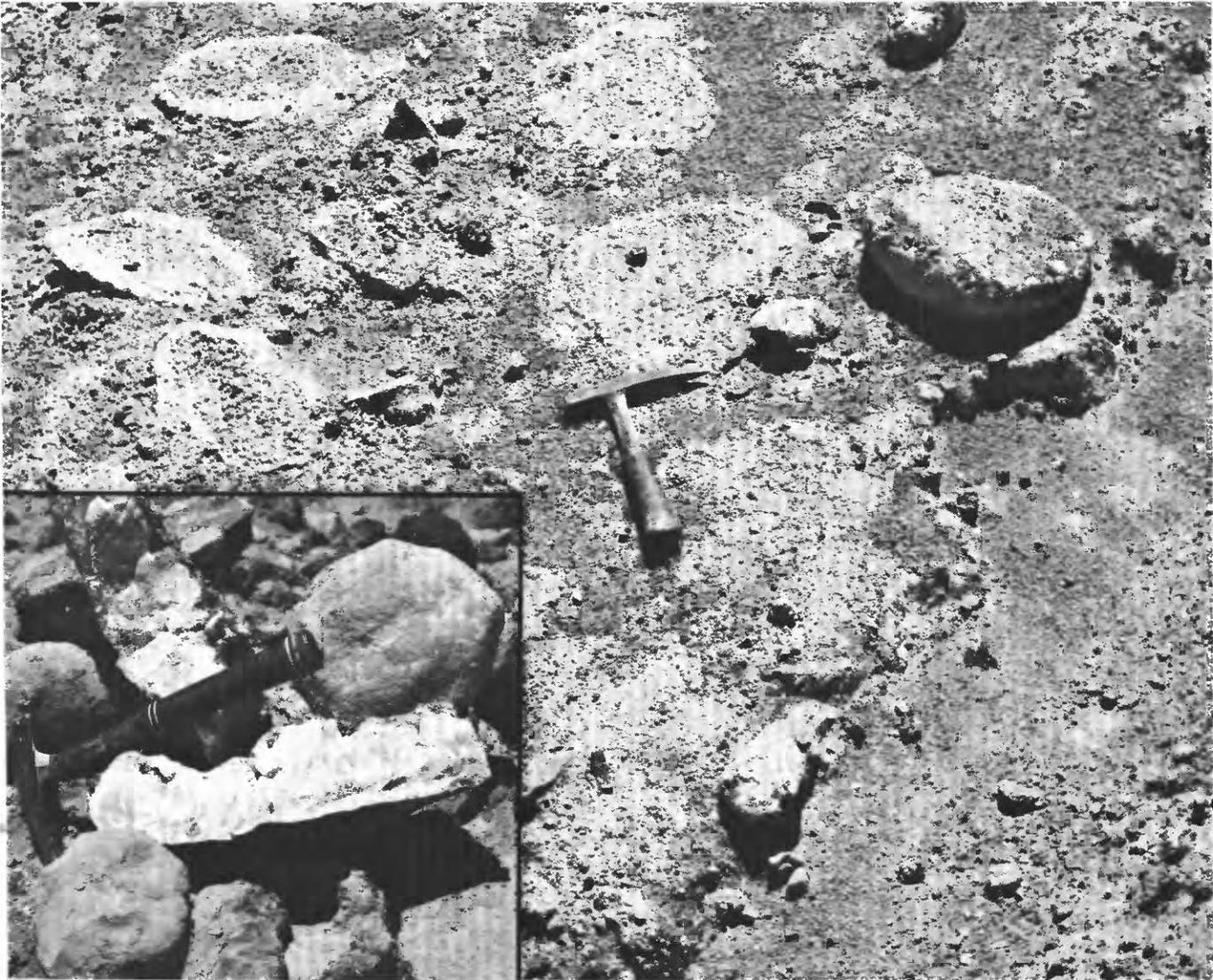


FIGURE 17.—Losa cakes embedded in powdery chuya, Tarapacá district. Cakes show typical oblate spheroidal form, and consist chiefly of tan anhydrite cut by veinlets of white anhydrite deposited in shrinkage cracks, as can be seen in broken cakes in inset. Tops of cakes tend to be smoothly rounded, whereas bottoms are nodular or jagged.

so in the past when lakes were present in the Atacama Desert (see p. 6).

CHEMICAL AND MINERALOGICAL COMPOSITION

The nitrate deposits are unique not only in having a high concentration of nitrate (table 1), but also in having exploitable iodate, an extremely high iodine/bromine ratio, and the only known naturally occurring perchlorate ion (ClO_4^-).⁵ The several iodate minerals are unique to the deposits, as are the potassium chromate and dichromate minerals (table 2).

⁵The perchlorate ion has an exceptionally high oxidation potential and is not known to form by any natural chemical process, which has led some reviewers of this report to express doubt that it exists in the Chilean

nitrate deposits. However, the evidence for widespread perchlorate in nitrate ore is overwhelming, and it clearly does exist, even though neither its mode of formation nor its mineral identity is known. Conventional chemical analyses of nitrate ore, in which perchlorate is determined by an oxidation-reduction reaction, show ubiquitous perchlorate in amounts similar to those shown by the analyses in table 1. Also, end-product nitrate produced from the ore contains perchlorate, and one nitrate plant reportedly experimented in the production of potassium perchlorate earlier in this century. To test the validity of the conventional chemical analyses of nitrate ore and to determine possible interference of the other highly oxidized ions nitrate and iodate, John Marinenko of the U.S. Geological Survey devised a colorimetric method of determining perchlorate in the presence of these ions. He found that a sample of rich ore from a nitrate field in northern Antofagasta Province, a region known for exceptionally high perchlorate, contains 0.73 percent ClO_4^- . An on-going mineralogical study of this sample and other samples of nitrate ore from the same region has not yet shown the presence of a perchlorate mineral, but potassium perchlorate was formed during fractional crystallization experiments, by Mary E. Mrose (U.S. Geological Survey) and by me, of solutions of these ores. We now can only estimate that the perchlorate is present either as finely crystalline potassium perchlorate or as a contaminating ion in the crystal structure of other saline minerals.

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.

One of the problems of estimating chemical composition of the nitrate ores is the lack of complete chemical analyses of the saline constituents. Nearly all analyses, including those cited in table 1, show only the saline components that are dissolved by hot water. As a consequence, the analyses show low values for constituents such as sulfate, calcium, borate, and iodate, which occur in part in minerals of low solubility.

Of the many saline minerals present (table 2), halite, the only halide mineral, and soda niter are by far the most abundant, being the dominant minerals in nearly all nitrate ore. Although the total sulfate may equal or exceed nitrate (table 1), it is contained in several minerals, and any single sulfate mineral is rarely more abundant than soda niter. The most abundant sulfate minerals are glauberite, bloedite, gypsum, and anhydrite. Also abundant are the sulfate-nitrate minerals, darapskite, and humberstonite. Thenardite, which is an abundant mineral in other desert saline deposits, is rare or absent in the nitrate ore because it is unstable in solutions

from which soda niter precipitates (Erickson and Mrose, 1970). Ulexite is the dominant boron mineral.

ORIGIN OF THE NITRATE DEPOSITS

The diversity of ideas about the origin of the Chilean nitrate deposits may be taken as an indication of the complexity of the problem and the scantiness or obscurity of direct evidence about the sources of the saline components and their modes of accumulation and concentration. The origin is neither simple nor obvious. Although the saline materials in the deposits clearly accumulated as the result of atmospheric transport and deposition, the major sources or modes of formation of these materials remain obscure. This is particularly true for the nitrate, iodate, perchlorate, and chromate ions. Nevertheless, the presence of widespread nitrate-rich saline soils in the Atacama Desert and their scarcity or absence in other deserts should be a result of the unique characteristic of this desert—the long existence of a nearly rainless climate. This factor has favored the accumulation and preservation of the highly soluble saline minerals in the nitrate deposits. Other factors of importance are wind and hydrologic regimens that favored accumulation and retention of saline materials within the Atacama Desert, the proximity of the Pacific Ocean, a probable source of significant amounts of saline materials, and widespread volcanic activity in the nearby Andes during late Tertiary and Quaternary time, a source of additional saline material.

TABLE 1.—Chemical composition of water-soluble saline components in selected nitrate ores and high-purity veins from the nitrate deposits in northern Chile

[Composition in weight percent. Based on total sample; insoluble residue not cited in analyses. Recalculated to facilitate comparison of analyses from different sources. Ions shown are the principal chemical components of nitrate ore, except for boron, which exists largely as ulexite $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$]

	1	2	3	4	5	6	7	8
NO_3^- -----	6.35	6.66	17.67	8.77	72.15	32.63	44.46	49.65
Cl^- -----	3.87	7.07	11.11	4.73	.07	21.84	14.97	12.92
SO_4^{2-} -----	6.60	12.43	3.47	2.69	.10	8.30	2.38	2.72
IO_3^- -----	.061	.068	.004	.04	----	.04	.14	.08
ClO_4^- -----	.035	.027	.57	.4	.04	.25	----	.56
B -----	.10	.17	.02	.06	----	.05	----	.12
Na^{+*} -----	6.2	8.9	13.8	6.4	----	----	----	----
K^+ -----	.56	.61	.95	.28	----	.32	1.12	6.89
Mg^{+2} -----	.15	.73	----	----	.01	.93	.28	.27
Ca^{+2} -----	1.15	2.27	1.06	1.00	.05	.32	.36	.14
H_2O -----	1.74	1.08	1.87	4.87	1.52	3.40	.79	----

1. Average grade of 5.97 million tons of nitrate ore treated at Oficina Pedro de Valdivia during 12-month period, July 1, 1935-June 30, 1936. Furnished by Anglo-Lautaro Nitrate Corp.
2. Average grade of 6.27 million tons of nitrate ore treated at Oficina María Elena, July 1, 1951-June 30, 1952. Furnished by Anglo-Lautaro Nitrate Corp.
- 3-4. Channel samples of selected parts of nitrate ore layer from two localities at Oficina Humberstone. Analyses by Empresa Salitrera Victoria of samples collected by Instituto de Investigaciones Geológicas of Chile.
5. Oficina Lautaro; specimen of caliche blanco analyzed at Oficina Victoria, 1964.
6. Oficina Santa Fé; specimen of caliche blanco analyzed at Oficina María Elena, 1966.
7. Oficina Argentina; specimen of caliche blanco (Semper and Michels, 1908).
8. Tarapacá district; specimen of caliche blanco (Penrose, 1910).

* Not determined in conventional analyses by nitrate companies of northern Chile. Calculated by author on basis of equivalent weights of reported components. Estimated to be within 1 percent of correct value.

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 Brüggenite, Ca(IO ₃) ₂ ·H ₂ O Dietzeite, Ca ₂ (IO ₃) ₂ (CrO ₄) Tarapacaite, 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 ₂₈ ·8H ₂ O Hydroboracite, CaMgB ₃ O ₁₁ ·6H ₂ O Kaliborite, HKMg ₂ B ₁₂ O ₁₈ (OH) ₁₀ ·4H 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

DISCUSSION OF THEORIES

Discussions of origin have been concerned largely with sources of the nitrate and with the mode of accumulation of the deposits. The sources of the other saline components generally have been assumed to be those most compatible with the presumed source of nitrate.

The following sources of nitrate have been proposed: (1) Decay of seaweed and other marine vegetation in waters and marshes of partially cutoff inland arms of the sea (Forbes, 1861; Noellner, 1867; Flagg, 1874; Müntz, 1887; Müntz and Marcano, 1885) or of vegetation in saline lakes of continental origin (Sieveking, 1887); (2) nitrification and leaching of seabird guano at the margins of saline lakes (J. C. Hillinger, 1860⁶), inland arms of the sea (Penrose, 1910), or salars (Gautier, 1894), or accumulation of windblown ammoniacal particulate matter and gas from extensive guano deposits that were presumed to have existed formerly along the coast of northern Chile (Ochsenius, 1887–88, 1888, 1903; Brügggen, 1928, 1938); (3) bacterial decay of plant and animal remains during Tertiary and Qua-

ternary time when a less arid climate supported abundant vegetation in northern Chile (Plagemann, 1897–98), or of ancient plant material in soils (Newton, 1896); (4) nitrification and fixation of atmospheric nitrogen by bacteria in soil (Gale, 1912, 1917; Brügggen, 1938); (5) reaction of atmospheric nitric acid with feldspathic igneous rocks of the nitrate fields (Pissis, 1878; Sundt, 1904, 1911, 1917, 1921; Wetzel, 1924, 1926, 1928, 1932, 1961; Knoche, 1930, 1939). Pissis and Wetzel suggested that the nitrate ion formed by electrical discharge in the dense winter fogs (camanchaca); Sundt proposed diverse sources for nitrate and ammonia in the atmosphere, and Knoche suggested formation by reaction of atmospheric nitrogen with ozone; (6) accumulation of nitrogen compounds of volcanic origin (ammonia, nitrogen oxides, or nitric acid) in gases associated with intense volcanism in the Andes (de Kalb, 1916; Feistas, 1922, 1966; Steinman, 1925), and nitrate salts leached either from volcanic rocks of Jurassic age (Whitehead, 1920) or from rhyolitic ash-flow tuffs of late Tertiary and Quaternary age (Ericksen, 1961); (7) nitrate from diverse sources accumulated in the subsurface saline waters and brines of salars (Singewald and Miller, 1916; Mueller, 1960, 1968) or in the soils of the nitrate fields (Hofseth, 1931; Claridge and Campbell, 1968; Ericksen, 1975, 1979).

According to these theories, the saline constituents of the deposits were supplied by: (1) Evaporation

⁶ Referred to in many publications about the nitrate deposits as a report in the "Anuario Nacional de Perú." The original report concerning mineral deposits in Tarapacá was published in the newspaper "Comercio" and cited by A. G. Leubel in his book "El Perú en 1860 o sea anuario nacional." No further information is available on the book or the newspaper.

of saline waters at the margins of inland arms of the sea or saline lakes, or within such bodies of water or marshes that subsequently evaporated to dryness. Charles Darwin, who visited the nitrate fields of Tarapacá in July 1835 during the famous voyage of the *Beagle*, was the first to suggest that the deposits were formed at the margin of an inland arm of the sea (Darwin, 1890); (2) capillary migration of subsurface saline water and brine from salars into soils and fractured rock of nearby hillsides where the saline materials were deposited by capillary evaporation, first proposed by Singewald and Miller (1916) and then repropoed by Mueller (1960); (3) accumulation in soils of the nitrate fields by fallout or washout from the atmosphere and by reactions of atmospheric constituents with these soils, first proposed by Pissis (1878); and (4) accumulation of saline-rich mudflows, first proposed by Wetzel in 1924 (Wetzel, 1924) and discussed in several subsequent papers (Wetzel, 1926, 1928, 1932, 1961). Wetzel has been the only adherent of this proposed mode of accumulation of the nitrate deposits.

Many authors have proposed special chemical or biological reactions in the soils of the nitrate fields to form the saline constituents of the deposits, as well as special mechanisms for concentrating the widespread saline materials to form commercial nitrate deposits. The reaction of nitrate and other atmospheric constituents with feldspathic rocks was favored by many authors (for example, see Pissis, 1878; Sundt, 1919; Wetzel, 1928) as the chief source of the principal cations Na, K, Mg, and Ca in the saline minerals of the deposits. Brüggén (1928, 1938) suggested that the deposits formed at a time when rainfall was sufficient to support widespread though sparse plants in the Atacama Desert and that symbiotic bacteria associated with roots of legumes caused fixation of atmospheric nitrogen and nitrification of ammonia from guano deposits. Most of the theories for accumulation by deposition or reaction of atmospheric constituents at the sites of the deposits also proposed that leaching by rainwater and movement of solutions downslope enriched the nitrate to produce the high-grade deposits that are so common on the lower parts of hills (for example, see Brüggén, 1938).

Theories suggesting formation of the deposits at the margins of salars, lakes, or inland arms of the sea are based chiefly on the distribution of nitrate workings in Tarapacá Province, which tend to be along the eastern side of the Coastal Range near salars and playas in the Pampa del Tamarugal (fig.

1). Indeed, the positions of these workings are suggestive of accumulation at a lake margin or within the capillary fringe of near-surface saline water or brine at the margins of salars. However, moist capillary fringes are not evident at the margins of present-day salars, even where the water level is virtually at the surface, and there is no reason to suspect that deposition of saline material in capillary-fringe zones of salars has been a significant process in the formation of the nitrate deposits. Moist capillary-fringe zones may have existed at the margins of former saline lakes in the Atacama Desert, but they would have been restricted to relatively narrow zones at the lake margins, and capillary evaporation and deposition of saline material would have been restricted to the soils of these narrow zones. Most of the nitrate deposits are far from such zones. On the other hand, former saline lakes in the Pampa del Tamarugal (see p. 6) might have contributed significant quantities of saline material to nitrate deposits by evaporation of shallow marginal waters and of windblown spray. Isolated small saline lakes and ponds in the Coastal Range, which were fed by ground-water inflow along faults connecting them to the Pampa del Tamarugal (see p. 6), also may have received saline materials that infrequent rains leached from nearby nitrate-rich saline soils and preexisting nitrate deposits. Such nitrate-rich saline materials would have been redeposited in the ponds as they evaporated to dryness. The nitrate region has been above sea level since before the nitrate deposits began to form; consequently, none of the saline materials in the deposits originated in inland arms of the sea.

Pissis (1878) was the first to suggest that an atmospheric source of the saline components was the only way the geographic and topographic distribution of the deposits could be adequately explained. His arguments are as valid today as they were a century ago. His evidence for an atmospheric source was chiefly the presence of nitrate deposits on hills where they could not have been formed in or near a lake, arm of the sea, or marsh. Sundt (1911) and Brüggén (1928) also noted that the existence of these deposits presented insurmountable difficulties to any mode of accumulation of the saline material other than deposition from the atmosphere. They both cited nitrate fields high on hills and at great distances from salars as examples of accumulations that could not have formed by migration and evaporation of subsurface saline water at margins of salars (Singewald and Miller, 1916). Rich (1941, 1942) noted that the distribution of the nitrate de-

posits could not be adequately explained by the theory of Singewald and Miller. Brügger (1938) pointed out that Wetzel (1932) was in error in supposing that mudflows had anything to do with accumulation of the nitrate deposits. Wetzel had suggested accumulation of saline mudflows in an attempt to explain the fragmental nature of the saline components of nitrate ore, which he discovered in microscopic examination of thin sections (Wetzel, 1924), and a peculiar layering that he observed in alluvial-type nitrate deposits (Wetzel, 1926, 1928). Evidently, Wetzel failed to recognize that the fragmental texture could be caused by repeated partial solution and redeposition of the saline components as they migrated through the soils to form the enriched nitrate deposits, and that the layering was a primary structure in the alluvium rather than a feature related to accumulation of the nitrate deposits.

Some of the proposed sources of the nitrate are untenable on the basis of present-day geological and chemical knowledge or did not yield a significant part of the nitrate in the deposits. The soils of the nitrate fields do not show any widespread concentration of phosphatic material indicating the presence of former guano deposits that might have been the source of nitrate. Some nitrate may have originated as ammonia released from seabird guano along the coast, as suggested by Brügger (1938), but the amount probably was small because the guano deposits are small in comparison with the nitrate deposits. Ammonia and ammonium compounds are known products of volcanic emissions, but the amounts are small compared with those of sulfate, sulfur dioxide, and chloride (for example, see White and Waring, 1963). Nitrate has been found in water-soluble saline material in ash-flow tuffs of Pliocene age in northern Chile (Ericksen, 1961), but whether this nitrate is an original constituent, perhaps formed by oxidation of primary ammonia, or a later contaminant is uncertain. Whitehead (1920) suggested that volcanic rocks of Jurassic age in northern Chile contained concentrations of nitrate that were leached and redeposited to form the nitrate deposits. His theory was based on the occurrence of rich nitrate ore along certain tuffaceous horizons in a Jurassic volcanic sequence exposed in nitrate fields in the eastern part of the Aguas Blancas district. However, later work (Brügger, 1938; Ericksen, 1963) has shown that the nitrate deposits are unrelated to rock type, and that the fortuitous relationship observed by Whitehead was probably due to porosity of the tuff rather than to its composition.

Feistas (1922) first proposed that the nitrate deposits formed by reaction of soil and rock in the nitrate fields with acids in clouds of volcanic gases. This proposal was based on his spectrographic studies of nitrate ores, which showed a wide variety and great abundance of rock-forming elements. Evidently Feistas failed to recognize that these elements were contained in the rock and soil of the nitrate ore as well as in the saline components. Feistas (1966) reiterated his theory after a visit to southern Peru and proposed that the acid-bearing volcanic clouds originated near the city of Arequipa in southern Peru and swept northward in Peru and southward into Chile. In both papers, Feistas proposed some rather fanciful geological processes. For example, in the 1966 paper, he concluded that dune fields in southern Peru mark the paths of the corrosive acid clouds and that the famous *sillar*, or ash-flow tuff, near Arequipa was the final product of the most intensive leaching by volcanic acids.

SOURCES OF THE SALINE COMPONENTS

In a recent paper (Ericksen, 1979), I suggested that the nitrate deposits could have formed by normal atmospheric deposition of the major constituents in periods of 100,000 to 200,000 years, if it were assumed that none of these constituents was removed from the nitrate fields by rainwater leaching or was destroyed by microbial activity. These estimates were based on investigations of atmospheric trace constituents conducted by many investigators in the 1950's and 1960's (for example, see Eriksson, 1960; Robinson and Robbins, 1970a, b). Additional investigations in the 1970's cast doubt on earlier estimates of atmospheric concentrations of natural particulate and reactive gaseous compounds of nitrogen and sulfur, indicating that these estimates are too high by at least an order of magnitude (for example, see Noxon, 1975, 1978; Granat and others, 1976; Söderlund and Svensson, 1976; Busenberg and Langway, 1979; Crutzen, 1979). As a consequence, it does not seem possible that the nitrate deposits could have accumulated by atmospheric deposition of saline constituents whose concentrations here are not greater than world averages for clean air; therefore, local sources must increase these constituents.

The local sources of the saline constituents are those that supply these constituents to the atmosphere elsewhere; they include evaporation and spray from the ocean surface and from former saline lakes in the Atacama Desert, gaseous and particulate matter from volcanic activity in the Andes, windblown

dust, biological activity in soils, and photochemical reactions or electrical discharge in the atmosphere. I assume that saline constituents from these sources have been accumulating at the sites of the nitrate deposits at least since mid-Miocene time, 10–15 million years ago, when infilling of the Central Valley had been largely completed (see p. 6). Although the climate of the Atacama Desert has been extremely arid throughout late Tertiary and Quaternary time, there undoubtedly have been intervals of climatic change when increased rainfalls greatly modified or destroyed preexisting nitrate deposits.

Although some of the saline material in the deposits may have been transported from distant sources, as has been suggested for saline materials in dry Antarctic soils (Claridge and Campbell, 1968), most probably came from local sources. Sea salts, ejected from the ocean surface chiefly in bubble spray (Blanchard and Woodcock, 1957; Bloch and Luecke, 1972), are carried inland as solutions in fog droplets and as dry particulate matter remaining after evaporation of the spray. The amounts deposited in dry fallout and in rainwater may be considerable (for example, see Junge and Gustafson, 1957; Eriksson, 1952a, b, 1959, 1959–1960). As I have pointed out (p. 10), the coastal fog of northern Chile contains saline materials and may be an important source of some of the saline constituents of the nitrate deposits. The hundreds of volcanoes that were active in the northern Chilean Andes at various times during late Tertiary and Quaternary time may have supplied large amounts of gaseous materials and dust containing compounds such as SO_2 , H_2SO_4 , NaCl , NH_3 , and NH_4Cl that could have been important sources of sulfate and chloride. The associated volcanic rocks contain considerable amounts of saline materials that are leached by rainwater and carried by ground water and streams into the Atacama Desert (Erickson, 1963); there, they accumulated in former lakes and today are being deposited in playa lakes and salars. Rocks of the nitrate fields show evidence of corrosion by the saline minerals in the soils; such evidence chiefly consists of pits and cavities on the undersides of rock fragments that have lain in one position on saline soil surfaces for many thousands or tens of thousands of years. However, chemical weathering is extremely slow in the Atacama Desert, and it is unlikely that it produced more than small amounts of the saline constituents of the nitrate deposits.

Recent investigations undertaken primarily to evaluate the effects of atmospheric anthropogenic contaminants such as fluoro-chloromethanes and

oxides of nitrogen on stratospheric ozone (McElroy and McConnell, 1971; Crutzen, 1974a; Wofsy and McElroy, 1974; Cicerone and others, 1974; Molina and Rowland, 1974; Rowland and Molina, 1975; McElroy and others, 1976) show many reactions in the atmosphere that could have formed significant amounts of nitrate and other oxidized saline components of the nitrate deposits. Tropospheric reactions involving ozone (O_3) and photochemically dissociated water (HO_2^- , OH^-) probably have been of prime importance in the formation of nitrate from gaseous nitrogen oxides and ammonia (Levy, 1972; Crutzen, 1974b; Chameides, 1975, 1978; Simonaitis and Heicklen, 1975; Chameides and Stedman, 1977). Similar reactions involving gaseous chlorine and iodine in the atmosphere may have formed perchlorate and iodate, although such reactions have not yet been identified as occurring in the atmosphere. Ozone and other gas-phase reactants are formed in the atmosphere by ultraviolet radiation, the dominant process in the stratosphere, by a variety of photochemical reactions involving oxides of nitrogen, methane, and carbon monoxide, and by lightning during thunderstorms (for example, see Crutzen, 1979; Chameides, 1975, 1978; Noxon, 1976; Griffing, 1977). A discussion of these and other atmospheric photochemical reactions is beyond the scope of this report, but their diversity has been indicated by Anderson (1976) who cited 250 gas-phase reactions of possible importance in the atmosphere.

NITRATE

Nitrogen (N_2) is a chemically unreactive atmospheric gas that is fixed or combined into natural organic and inorganic compounds by microbial activity in soils and water and by photochemical processes in the atmosphere (for example, see Söderlund and Svensson, 1976). Of the global nitrogen cycle, 90–97 percent involves exchange of organically fixed nitrogen in soil and water, whereas only 3–10 percent involves fixation of atmospheric nitrogen (Ross-wall, 1976). Microbial fixation of atmospheric nitrogen is chiefly by symbiotic bacteria of certain leguminous plants, by autotrophic bacteria, and by certain blue-green algae (for example, see Söderlund and Svensson, 1976; Griffing, 1977). Fixation of nitrogen in the troposphere is chiefly due to thunderstorm activity, wherein temperatures in lightning flashes are high enough to cause formation of nitrogen oxides (Noxon, 1976, 1978; Crutzen, 1979).

Fixed nitrogen compounds that have been detected in the atmosphere including the gaseous forms ni-

trous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3), and ammonia (NH_3); compounds such as $(NH_4)_2SO_4$, $NaNO_3$, and HNO_3 occurring as particulate material and as solutions in rainwater; and nitrogen-bearing organic substances such as proteins, amines, and amino acids (for example, see Eriksson, 1952a; Junge, 1958b; Visser, 1961; Jones 1971; Levy, 1972; Söderlund and Svensson, 1976; Griffing, 1977; Noxon, 1978). Nitrous oxide is formed by anaerobic decay of organic materials on the earth's surface, chiefly on continents but also at the ocean surface (Koblentz-Mishke and others, 1970; Junge and Hahn, 1971; Hahn, 1974; McElroy and others, 1976; Griffing, 1977). Nitric oxide and nitrogen dioxide, which are the principal reactive odd nitrogen oxide molecules (NO_x) in the atmosphere, are formed by photochemical reactions involving ozone (for example, see Georgii, 1963; Nicolet, 1970) and by electrical discharge in thunderstorms (Noxon, 1976; Griffing, 1977; Dubin and Zipf, 1977). Nitrate is concentrated in thin organic films at the ocean surface (Wilson, 1959; Williams, 1967; Barger and Garrett, 1970; Barker and Zeitlin, 1972), which are ejected into the atmosphere in bubble-spray (MacIntyre, 1970). The chief source of ammonia is considered to be biological processes in continental soils (for example, see Georgii and Müller, 1974), but the sea surface may be the source of considerable amounts of ammonia or ammonium compounds in areas of high biological activity. For example, Bloch and Luecke (1970) reported a relatively high concentration of ammonium (NH_4^+) in seawater bubble-spray, showing as much as 100 ppm compared with 0.1 ppm in seawater. They suggested that nitrate in the Chilean deposits formed from such oceanic ammonium that was oxidized photochemically in the atmosphere. Photochemical oxidation of NH_3 in the troposphere, chiefly by reaction with OH^- molecules produced by reaction of ozone with water vapor or by other photochemical reactions, may be an important source of tropospheric NO_x (Junge, 1958b; Levy, 1972; Crutzen, 1974b; Chameides, 1975).

Nitrous oxide (N_2O), which is the most abundant of the fixed nitrogen compounds in the atmosphere (about 250 ppbv), is a relatively unreactive gas in the troposphere, but is the major source of NO_x in the stratosphere (for example, see Griffing, 1977). Reaction of N_2O in the stratosphere with the electronically excited oxygen atom $O(^1D)$ is rapid and probably is the major process in the formation of stratospheric NO_x (Nicolet, 1970; McElroy and McConnell, 1971). NO_x formed in the stratosphere

may be carried to the troposphere by mixing of tropospheric and stratospheric air. The reaction of N_2O and $O(^1D)$ is of little importance in the troposphere because $O(^1D)$, which forms by photodissociation of ozone by ultraviolet light, is sparse in the troposphere (Levy, 1972).

The principal source or sources of the nitrate in the Chilean nitrate deposits is uncertain, because average concentrations of NO_x , HNO_3 , and NH_3 in the atmosphere appear to be too low for these constituents to be the sole sources of the nitrate as I had formerly proposed (Ericksen, 1979). Estimates that indicated background concentrations of the NH_3 and NO_x in clean unpolluted air of 6 ppbv (parts per billion, vol/vol) and 3 ppbv, respectively (Robinson and Robbins, 1970a), were the basis of the estimate (McConnell, 1973) that worldwide annual deposition of NH_3-N and NO_3-N is about 2×10^{14} g. At this rate of deposition, and assuming that NO , NO_2 , and NH_3 were oxidized to NO_3 in the troposphere or at ground level, the nitrate in the deposits could have accumulated in about 200,000 years (Ericksen, 1979).

New estimates indicate that concentrations of NO_x in clean air are <0.1 to 1 ppbv (Chameides, 1978; Noxon, 1978; Huebert and Lazrus, 1978) and that removal rates are on the order of 10^{12} to 10^{13} g $N \text{ yr}^{-1}$ (Galbally and Roy, 1978; Crutzen, 1979). Concentrations of particulate nitrate in the troposphere are similar to NO_x (Huebert and Lazrus, 1978), and the natural global source of ammonia in the atmosphere is about 5×10^{13} g yr^{-1} (Dawson, 1977). Crutzen (1979) suggested that gas-phase reactions producing NO_x from NH_3 in the atmosphere would yield only about 10^{13} g $NO_x-N \text{ yr}^{-1}$, and that most NH_3 is removed from the troposphere by processes other than gas-phase reactions. On the basis of these estimates, the deposition rate of NO_x-N from the atmosphere would be at least an order of magnitude slower than that estimated by McConnell (1973), and the time required to form the nitrate deposits would be nearer to 2 million years than 200,000 years.

If, as I have suggested (p. 24), the nitrate deposits were formed during the past 10–15 million years, and if they have had a complex history of repeated deposition and destruction, a rate of deposition whereby the nitrate theoretically might accumulate in 200,000 years is reasonable, whereas I believe that a rate requiring 2 million years is not. Two factors must be considered: (1) Only part of the nitrate-bearing saline material that falls to the

ground surface moves downward into the soil—some may be carried away by wind, some may evaporate as a gas, HNO_3 or NO_2 , for example, and some may be washed away by rainwater. (2) Nitrate deposits once formed have probably been partly destroyed many times by exceptionally heavy rains or during periods of climatic change when rainfall was greater than it is at present. Also, as will be shown, the chloride in the deposits, which shows an abundance similar to that of the nitrate, has a rate of atmospheric deposition whereby it might accumulate in less than 200,000 years. I believe that the rates of accumulation of the chloride and the nitrate were similar. Therefore, local rich sources of fixed nitrogen compounds are probably more important in northern Chile than are the distant or normal sources of these compounds that account for average global concentrations. The most likely local source for NO_x , NH_3 , and organically fixed nitrogen, which through photochemical reactions or other processes might be transformed to nitrate, is the nutrient-rich water of the nearby Pacific Ocean. In addition, some ammonia may have been supplied by erupting volcanoes in the Andes, but to judge from the small amounts present in volcanic gases in other regions (for example, see Allen and Zies, 1923; White and Waring, 1963), the amounts transformed to nitrate in northern Chile are correspondingly small. Rhyolite ash-flow tuffs in the north Chilean Andes, which apparently contain small amounts of water-soluble nitrate (see p. 23), are evidently not sources of any significant amount of nitrate in the deposits. If these tuffs were important sources of nitrate or other water-soluble nitrogenous material, one would expect some of the many salars in this part of the Andes, which contain saline materials leached from these tuffs, to show abnormal concentrations of nitrate. Neither the saline crusts nor associated saline waters or brines in these salars contain unusual amounts of nitrate. Considerable amounts of nitrogen oxides may have been formed in Andean thunderstorms and carried westward to the Atacama Desert by wind and as solutions in streams and ground water.

The role of microorganisms in the formation of the nitrate deposits is difficult to evaluate, except that a general low level of microbial activity was essential to the preservation of the deposits. As has been pointed out (p. 11), microorganisms identified in the soils of the nitrate fields include species capable of nitrification and nitrogen fixation, and although these organisms are sparse in the dry desert soils today, they would be expected to multiply at times of greater-than-normal rainfall or coastal

fog. At such times, significant amounts of nitrate or organic nitrogen compounds, later oxidized to nitrate, may have been formed, particularly at soil surfaces where the content of soluble saline material is low and where autotrophic bacteria and blue-green algae would be most active. For example, more prevalent fogs in times past may have created conditions in the nitrate region similar to those of the well-known present-day *lomas* of the coastal desert of Peru where the condensate from winter fogs (June–August) is sufficient to support growth of a variety of lichens, mosses, grasses, tuberous plants, and drought-resistant bushes in areas that are essentially devoid of plants (except for sparse bushes) the rest of the year. Furthermore, during times of the heaviest fogs, the nitrogen-fixing blue-green alga *Nostoc* locally forms extensive mats on soil and dune sand (Dawson, 1963; Grolier and others, 1974). Although *lomas* do not exist today in the nitrate region of northern Chile, they probably have existed in past times of more prevalent coastal fogs. At such times, the higher plants and microorganisms both consumed and formed soil nitrates. Unfortunately, little is known about the salt content of the loma soils of Peru, so that direct comparison with soils in northern Chile is not possible.

HALOGENS

The only halogens occurring as distinct chemical components in the nitrate deposits are chloride (Cl^-), perchlorate (ClO_4^-), and iodate (IO_3^-). Only trace amounts of bromide (Br^-) have been reported. The presence of perchlorate, the relative abundance of iodate, and the paucity of bromine are unique features of the deposits.

Chlorine, bromine, and iodine occur in the atmosphere as the molecular gases Cl_2 , Br_2 , I_2 ; as the gaseous compounds HCl , ClO , HBr , and BrO ; as inorganic compounds such as NaCl and NH_4Cl ; and as halogen-bearing organic compounds (Eriksson, 1952b; Miyake and Tsunogai, 1963; Duce and others, 1963; Moyers and Duce, 1972a, b; MacIntyre, 1974; Wofsy and McElroy, 1974; Wofsy and others, 1975). Investigators generally agree that the ocean is the dominant source of these halogens, but considerable amounts of chlorine also are injected into the atmosphere by major volcanic eruptions (Ryan and Mukherjee, 1975). Both these sources may have contributed chloride to the nitrate deposits, but the oceanic source probably was dominant.

The relatively high I/Cl and I/Br ratios in marine aerosols and rainwater, much greater than those in

seawater (Duce and others, 1963; Miyake and Tsunogai, 1963; Moyers and Duce, 1972a, b; Seto and Duce, 1972), indicate somewhat different processes by which each element is added to the atmosphere. The chief source of chlorine in the atmosphere is probably NaCl in the sea spray (Blanchard and Woodcock, 1957), whereas iodine is released by evaporation of iodine gas from the ocean surface and as iodine-rich organic material of sea-surface films ejected in sea spray (Miyake and Tsunogai, 1963; MacIntyre, 1974). The ratio of Br/Cl in the marine atmosphere is similar to that in seawater (Moyers and Duce, 1972a), so that sea spray is probably the chief source of the bromine.

The global flux of gaseous chlorine and of chlorine as NaCl in sea spray to the atmosphere is much greater than that of the other principal anions, sulfate and nitrate, in the nitrate deposits. Wofsy and McElroy (1974) estimated a net global production of gaseous chlorine, chiefly of marine origin, to be about 2×10^{11} g yr⁻¹, whereas production of particulate chloride, chiefly as NaCl in ocean spray, is about 6×10^{15} g yr⁻¹. These authors suggested that HCl and ClO are the dominant gaseous compounds at ground level. Eriksson (1959) found a relatively high concentration of chloride in rainfall and dry fallout along continental margins, where annual rates of chloride deposition from the atmosphere are commonly greater than 2 g per m² and at places may exceed 10 g per m². Values are much lower in the interiors of continents, an indication of the importance of the ocean as a source of chloride. At rates such as these, the chloride in a typical nitrate field could have accumulated by atmospheric deposition in less than 200,000 years.

The oceans are the chief source of atmospheric iodine and probably the chief source of the iodine in the nitrate deposits. Iodine also occurs in volcanic gases and sublimates (Honda and others, 1966; Honda, 1970), but the amounts are small compared with those emitted from the ocean surface. MacIntyre (1974) suggested that organically bound iodine is the chief form of iodine in the atmosphere and that the principal source of this iodine is films on the sea surface that are rich in organic matter. He also pointed out that evaporation of iodine takes place at the sea surface but that the relative importance of this source of iodine is not known. Blanchard (1969) and Moyers and Duce (1972b) also suggested that organic-rich films on the sea surface were major sources of iodine in the atmosphere. Miyake and Tsunogai (1963) estimated that 99 percent of the iodine in the atmosphere was iodine that

evaporated from the ocean surface. According to these authors, the flux of iodine from the ocean to the atmosphere is about 5×10^{11} g I yr⁻¹, which would also be the rate of deposition if the observed concentration of gaseous iodine in the atmosphere were to be maintained. At such a rate of deposition, the iodine in the Chilean nitrate deposits would require about 3 million years to accumulate. As in the case of the nitrate, I believe this rate of deposition to be too slow and that organically bound iodine, ejected in bubble spray from the nutrient-rich coastal waters of northern Chile, is the principal source of the iodine in the nitrate deposits. Furthermore, the iodine, which occurs chiefly in calcium iodate minerals of low solubility, would not be as readily leached at times of relatively heavy rainfall and would tend to remain in the soils of the nitrate fields, whereas more soluble saline minerals would be leached.

Virtually all the iodine in the nitrate deposits occurs as the iodate ion (IO₃⁻); iodine as iodide (I⁻) is absent or occurs only in traces. Iodine released from the ocean surface, either as a gas or in organic compounds, probably is oxidized to iodate by photochemical reactions in the atmosphere and at soil surfaces in the nitrate fields. Iodate also occurs in seawater and is released to the atmosphere along with NaCl in bubble spray, but the amount is insignificant in comparison with the amount of iodine found in maritime air (Moyers and Duce, 1972b).

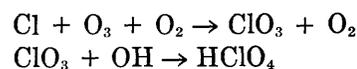
The absence of bromine in the nitrate deposits is difficult to explain. Unfortunately, only a few determinations of bromine have been made for saline materials of northern Chile, so that little is known about bromine distribution and variations in concentration. Several semiquantitative X-ray spectrographic analyses of nitrate ore by Harry J. Rose of the U.S. Geological Survey (written commun., 1968) showed all to contain less than 100 ppm bromine. Mueller (1960) reported his analysis of a specimen of nitrate ore from near Oficina Victoria (fig. 1) as showing 0.19 percent iodine (1,900 ppm) and 0.007 percent (70 ppm) bromine, giving an I/Br ratio of 27/1. Mueller also reported an analysis of a sample of saline crust (evidently high in NaCl) from a nearby salar as containing 0.005 percent (50 ppm) iodine and 0.011 percent (110 ppm) bromine, giving an I/Br ratio of 0.45. This I/Br ratio is considerably higher than ratios for continental evaporites and brines elsewhere and is several orders of magnitude higher than those for marine evaporites, (for example, see White and others, 1963; Stewart, 1963).

Bromine occurs in nature chiefly as bromide salts of magnesium, sodium, and potassium (Pourbaix and others, 1966). It occurs in the atmosphere as the gaseous form Br_2 , HBr , and BrO , and in association with particulate matter such as aerosols, cloud droplets, and sea salts (Wofsy and others, 1975), where these same gases are adsorbed or dissolved, or where the bromine occurs as the bromide ion (Br^-). Bromate, the analogue of iodate, is not known in nature, and perbromate, the analogue of perchlorate, is not known to form as a chemical compound (Latimer, 1952; Goldschmidt, 1958; Cotton and Wilkinson, 1966). Bromine occurs in soils in amounts averaging 6.5 ppm, chiefly in organic complexes (Rankama and Sahama, 1950).

Bromine is much more abundant than iodine in nearly all natural materials, so bromine must be eliminated during formation of the nitrate deposits. This elimination could be effected by processes at the sources of the saline materials, probably the ocean for iodine and bromine, in the atmosphere, and in the soils of the nitrate fields. Processes at the ocean surface cause a great enrichment of iodine in the marine atmosphere, relative to bromine and chlorine (Duce and others, 1963; Moyers and Duce, 1972a, b; Seto and Duce, 1972; Bloch and Leucke, 1972; MacIntyre, 1974). However, as indicated by the I/Br ratios for seawater and marine rainwater and aerosols (Duce and others, 1963), the bromine in the marine atmosphere is still more abundant than iodine, and additional bromine would have to be eliminated to account for the high I/Br ratios of the nitrate deposits, if the ocean is to be considered a major source of the iodine. The most likely means of separating bromine from iodine is through atmospheric photochemical processes that cause oxidation of iodine to iodate, which then may be dissolved in rain and fog droplets and removed from the atmosphere, whereas the bromine remains as a gas that becomes dispersed in the atmosphere. Wofsy and others (1975) suggested that HBr is the dominant bromine compound in the atmosphere and that it is produced by hydrolysis of bromine, chiefly in marine aerosols. These authors estimated annual emission of bromine to the atmosphere to be 1.1×10^{12} g Br yr^{-1} . They also suggested that the gaseous forms of bromine act as catalysts in the destruction of ozone and, consequently, remain unchanged in ozone reactions. Duce and others (1965) suggested that photochemical oxidation of the Br^- ion in the aerosols formed Br_2 , released to the atmosphere as a gas.

The perchlorate ion (ClO_4^-) is the most enigmatic component of the nitrate deposits because it has not

been detected in nature elsewhere and is not known to form by any natural process. However, perchlorate is an ubiquitous constituent that is reported in nearly all conventional chemical analyses of nitrate ore; in this study it has been identified as a chemical component in nitrate ore from northern Antofagasta province (see p. 20). The perchlorate in the nitrate deposits most probably formed in the atmosphere by photochemical reactions involving chlorine and ozone (Motoako Sato, oral commun., 1978). It has been proposed that chlorine-ozone reactions produce oxides of chlorine (ClO_x) in the stratosphere (for example, see Nicolet, 1975). Simonaitis and Hecklen (1975) proposed that perchloric acid could form in the stratosphere by the following photochemical reactions:



Gaseous chlorine, ozone, and OH^- from photodissociation of H_2O are present in the troposphere (for example, see Levy, 1972; Crutzen, 1974b; Chameides, 1975), and the same reactions might produce HClO_4 in the troposphere or even at ground level. Unfortunately, neither ClO_3 nor HClO_4 have been detected in the atmosphere, so their formation by photochemical reactions remains speculative.

SULFATE

Sulfate compounds such as sulfuric acid (H_2SO_4) and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), occurring chiefly as particulates and as solutions in rainwater, and gaseous sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) are trace constituents of the atmosphere. The chief natural sources of gaseous sulfur compounds are biological decay of organic matter and volcanic emissions (see Granat and others, 1976), whereas most of the sulfate in the atmosphere is formed by photochemical oxidation and hydrolysis of the gaseous sulfur compounds and is supplied by sea spray (Eriksson, 1960; Gambell and Fisher, 1964; Goldhaber and Kaplan, 1974; Granat and others, 1976). Sulfate is removed from the atmosphere as dry fallout and as rainwater solutions of H_2SO_4 and sulfate compounds. Granat and others (1976) estimated the flux of natural sulfur compounds through the atmosphere to be 84×10^{12} g S yr^{-1} as compared with that of present-day anthropogenic sources of 65×10^{12} g S yr^{-1} . These authors suggested that H_2S formed by biological decay of plant material in the oceans, especially in estuaries and marshes at continental margins, and sulfur compounds in sea spray are the dominant natural

sources of atmospheric sulfur, contributing 34×10^{12} g S yr⁻¹ and 44×10^{12} g S yr⁻¹, respectively. They suggested that SO₂ and other compounds of sulfur originating in volcanic eruptions and fumaroles contribute only about 3×10^{12} g S yr⁻¹ to the atmosphere, and that other natural sources contribute an additional 3×10^{12} g S yr⁻¹. These estimates of the flux of sulfur through the atmosphere are less than previous estimates that natural emissions of gaseous sulfur compounds ranged from a low of 89×10^{12} g S yr⁻¹ to a high of 267×10^{12} g S yr⁻¹ (Eriksson, 1960; Junge, 1963; Robinson and Robbins, 1970b; Kellogg and others, 1972; Friend, 1973). Most investigators agree that the ocean is the major source of atmospheric sulfur and that volcanic sources are small by comparison (for example, see Eriksson, 1963; Friend, 1973; Stoiber and Jepsen, 1973; Cadle, 1975).

Granat and others (1976), after reviewing sources and fluxes of sulfur through the atmosphere, concluded that atmosphere deposition of sulfur compounds on land areas are equivalent to about 25×10^{12} g S yr⁻¹, which would be equivalent to about half a gram SO₄ per square meter of land surface. At such a rate of deposition, the accumulation of sulfate in the nitrate deposits would probably require at least a million years, rather than 100,000–200,000 years that I previously estimated (Ericksen, 1979), on the basis of a rate of deposition on the land of 165×10^{12} g S yr⁻¹ proposed by Eriksson (1963). The figure by Eriksson (1963) includes anthropogenic sulfur in the atmosphere, which he estimated to be only 1/10 of the emissions of sulfur from natural sources. Accumulation of sulfate over a time span of a million years is perhaps not unreasonable when it is considered that 10–15 million years have been available for formation of the nitrate deposits. However, the rate of accumulation of sulfate in the Atacama Desert probably has been much greater than the world average because of a greater local flux of sulfur to the atmosphere, chiefly H₂S gas and sea spray from the nearby nutrient-rich coastal waters of the Pacific ocean, and SO₂ and other sulfur compounds from the hundreds of volcanoes in the nearby Andes that were active at various times during late Tertiary and Quaternary time. Furthermore, the amount of sulfate in the nitrate deposits is similar to that of chloride, which might have accumulated in less than 200,000 years; these two components probably had similar rates of accumulation.

BORATE, CHROMATE, AND DICHROMATE

Boron in the nitrate deposits, occurring chiefly as ulexite, is probably of volcanic rather than oceanic origin. Gast and Thompson (1959) noted that the B/Cl ratio of rainwater was several times that of seawater, and they concluded that boric acid in the atmosphere was evaporated from the ocean surface. However, Nishimura and Tanaka (1972) presented experimental data that indicate the atmosphere to be supersaturated in boron with respect to seawater; these authors concluded that the oceans are sinks rather than sources of atmospheric boron. Perhaps the best evidence for a volcanic source of boron in the Chilean nitrate deposits is the abundant ulexite in salars of the Andean highlands, which consist chiefly of saline constituents supplied by recent volcanic emissions and thermal springs as well as those leached from nearby volcanic rocks of late Tertiary and Quaternary age. Salars in the Atacama Desert also contain local concentrations of ulexite deposited by water draining from the Andes (Ericksen, 1963).

Chromate (CrO₄⁻²) is a widespread trace constituent of nitrate ore, occurring sporadically throughout the nitrate fields in the so-called **caliche azufrado** (sulfurous caliche, in reference to its color) which together with small amounts in typical nitrate ore become concentrated and impart a yellow color to the leach solutions that are recycled in the processing of the nitrate ore. Maximum values for chromate in typical ore are probably a few parts per million (Ericksen, 1963), whereas the caliche azufrado may contain several percent of chromate. No obvious source exists for this chromate. For example, ultramafic igneous rocks, which are the richest sources of chromium, are absent in northern Chile. The most abundant igneous rocks of the area are granitic plutons and rhyolitic tuffs, which contain very little chromium (for example, see Krauskopf, 1967).

The most likely sources of the chromate are sedimentary rocks in the nitrate fields, principally shales that elsewhere commonly contain about 100 ppm Cr (Krauskopf, 1967; Connor and Shacklette, 1975). In the highly oxidizing environment of the nitrate deposits, trace amounts of chromium in these rocks may have been oxidized from the trivalent state (Cr⁺³), which tends to form insoluble oxides, to the relatively mobile hexavalent (Cr⁺⁶) state in CrO₄⁻². Rankama and Sahama (1950) suggested that formation of the relatively mobile chromate in the Chilean nitrate deposits was due to the high oxidation po-

tential of the deposits. Additional chromate might have been released to soils of the nitrate fields by decay of organic matter in sea spray or by decay of plants such as *Tillandsia* that exist in the nitrate fields (see p. 11). Shacklette and Conner (1973) reported *Tillandsia* ash as containing as much as 1,500 ppm Cr.

Dichromate ($\text{Cr}_2\text{O}_7^{-2}$), which is extremely sparse in the nitrate deposits, evidently formed chiefly by alteration of chromate. The transition of chromate to dichromate can be observed in vugs in the chromate-rich caliche azufrado. Also, grains of bright-orange dichromate slowly form in moist residues left by evaporation of solutions of caliche azufrado in the laboratory.

ALKALI AND ALKALINE-EARTH METALS

The alkali and alkaline-earth metals: sodium, potassium, magnesium, and calcium, which are the only cations in nitrate ore in more than trace amounts (table 1), show concentrations indicating that they come from diverse sources. The Na/Cl ratio of the nitrate ores is two to three times that of seawater, whereas the Mg/Cl ratio is only slightly greater than that of seawater. The K/Cl and Ca/Cl ratios are 10–30 times that of seawater, and although both these elements have been shown to be somewhat enriched in bubble-spray because of fractionation at the sea-air interface (for example, see Chesselet and others, 1972; Wilkniss and Bressan, 1972), the amount of enrichment is small compared with that required to form the nitrate deposits. On the other hand, Wilson (1959) suggested that an enrichment of K in organic films at the ocean surface, which are ejected by bubble-spray, might account for K in rainwater, known to be as much as 10 times the amount in seawater. Likens and others (1979) proposed that soil particles swept into the atmosphere by wind may release the cations Na^+ , K^+ , Mg^{+2} , and Ca^{+2} to rainwater solutions.

It may be inferred that the dominant sources of the cations in the nitrate deposits probably were (1) sea spray; (2) windblown saline dust resulting from wind erosion in the Atacama Desert, including erosion of former playas and salars; and (3) wind-transported ash and dust from volcanic eruptions in the Andes. Additional small amounts of these cations may have been derived from chemical weathering of rocks in the nitrate fields. Because of the enrichment processes that have affected the nitrate deposits, the varied solubility of the saline minerals present, and the paucity of analytical data for saline accumulations other than nitrate ore in northern

Chile, precise comparisons of the relative quantities of these cations from each of the above sources in the nitrate fields cannot be made. Nevertheless, the ocean clearly has been a major source of Na^+ and Mg^{+2} , as indicated by comparison of the ratios of these elements, relative to chlorine in the nitrate deposits and in seawater, the probable source of most of the chlorine, and windblown dust and volcanic ash, the major sources of Ca^{+2} and K^+ .

ACCUMULATION AND ENRICHMENT OF THE SALINE COMPONENTS

Most of the ore-grade nitrate deposits apparently formed in three ways: (1) slow accumulation on very old, flat to gently sloping or undulating land surfaces that have had little or no modification since Miocene time; (2) accumulation on lower hillslopes and breaks in slopes as the result of leaching by rainwater and downslope migration of solutions to sites of redeposition; and (3) accumulation of saline minerals in saltpans and saline ponds. Examples of accumulation on old surfaces are the deposits on uplands of the Coastal Range in Tarapacá and Antofagasta Provinces, which have been little modified since early Tertiary time; on old surfaces of the Central Valley such as that of Pampa de Tana in northern Tarapacá Province (fig. 4), of probable Miocene age; and in the Baquedano valley, where some of the deposits are in old stream gravels that probably date from early Tertiary time. Downslope migration of saline material is perhaps the most important process in the formation of the richest nitrate deposits, and nitrate workings along lower slopes of hills and at breaks in hillslopes can be seen throughout the nitrate region. Unusual nitrate deposits are found along the courses of old streams in the low range of rocky hills in the vicinity of the southwesternmost nitrate beneficiation plants in the Baquedano district (fig. 9), which are downhill from a broad, gently sloping area of lower-grade nitrate deposits. The richest deposits here are in the stream channel rather than on the nearby hillsides.

Nitrate-rich brines are now accumulating in ponds and salars in the nitrate region of northern Chile, and similar accumulations may have formed rich deposits in the past. Several salar crusts have been worked as nitrate ore. The best-known nitrate-rich salar is Salar del Carmen (fig. 1) where efflorescences of nitrate-bearing salts were harvested periodically during the latter part of the 19th century (Whitehead, 1920). Other nitrate-bearing salars have been mined in the Tarapacá, Baquedano, and

Aguas Blancas districts (fig. 1). Two ponds in the Tarapacá district, one in a valley at Oficina Jazpampa, about 2 km northwest of Zapiga (fig. 1), and the other in Salar de Bellavista near Oficina Victoria, were found to contain nitrate-rich brines, as shown by the following chemical analyses by the laboratory at Oficina María Elena, Sept. 1977:

	Pond, Oficina Jazpampa (ppm)	Pond, Salar de Bellavista (ppm)
NO ₃ ⁻ -----	13,700	4,280
Cl ⁻ -----	28,700	15,300
SO ₄ ⁻² -----	19,400	8,100
IO ₃ ⁻ -----	140	trace
ClO ₄ ⁻ -----	270	210
B -----	370	210
K ⁺ -----	1,550	770
Mg ⁺² -----	5,080	1,170

These brines are contaminated with old leach solutions draining from waste dumps at nearby nitrate beneficiation plants, which account for the exceptionally high nitrate, iodate, and perchlorate, admixed with brines or saline waters from salars. Although these ponds are anomalous in receiving these leach solutions, they indicate types of ponds that might have formed in the past in closed basins within the nitrate fields. Saline water and brine formed by rainwater leaching of surrounding nitrate deposits and saline-rich soils could have accumulated in such basins and evaporated to form nitrate-rich saline crusts. The nitrate efflorescences at Salar del Carmen evidently had such an origin.

The role of former ephemeral saline lakes in formation of the nitrate deposits is difficult to evaluate. However, some deposits were destroyed or prevented from forming by such lakes. For example, the absence of nitrate deposits in southernmost Tarapacá Province, the region of Salar de Llamara (fig. 1), is considered to be due to the presence of the former large lake of probable Pleistocene age, Lago Soledad, and to playa lakes that still form periodically there (Brüggen, 1938). The high-grade nitrate deposits at the margins of some of the playas and salars in the Pampa del Tamarugal, northern Tarapacá Province, do not extend down to playa or salar levels; rather, they terminate a few meters above these levels. I believe that the absence of nitrate deposits in this narrow band is due to leaching at the margins of late Pleistocene and Holocene ephemeral lakes. On the other hand, the persistence and abundance of high-grade nitrate deposits along the eastern side of the Coastal Range in the Tarapacá and Tocopilla nitrate districts, the region marginal to these ephemeral saline lakes, suggests that some of

the saline material here came from the lakes. Evaporation of shallow marginal waters and windblown spray of the lakes might have contributed significant quantities of saline materials to the nearby nitrate deposits, and microbial activity in the shallow waters and moist soils at the margins of the lakes may have formed nitrate.

The position of the nitrate caliche layer between leached surface material and underlying salt-free rock or regolith indicates deposition of the saline material in a zone where capillary evaporation takes place. The bottom of the caliche layer is probably the level of deepest penetration of water from the heaviest rains, whereas the leached overburden (costra) is in the zone of average penetration by the more frequent light rains. Penetration of rainwater to the deepest parts of the caliche is probably along major desiccation cracks, such as those shown in figure 16. The powdery surface layer (chuca) is affected by both rain and fog. Although workable nitrate-rich layers are generally less than 5 m below the surface, some are as deep as 12 m. At a few places, layers of caliche blanco have been found in relatively salt-free to salt-cemented regolith (coba or conjelo) beneath the normal near-surface caliche layer. Such a layer of caliche blanco was found at Oficina Virginia in the southern part of the Tarapacá district, 2–3 m below the normal caliche (F. H. Humberstone, oral commun., 1962). This layer is probably a remnant of a former nitrate deposit that was partially destroyed during a period of greater than normal rainfall. Small amounts of nitrate (0.1–1.0 percent NaNO₃) and other saline components of the nitrate deposits have been found to depths of as much as 66 m in unconsolidated regolith, as shown by drill-hole logs from nitrate fields east of Iquique (logs were made available by Dr. Donald Garrett, President, Saline Processors, Inc., 1977). These saline materials probably indicate deeper penetration by surface water or the former presence of saline ground water in areas where ground water does not now exist.

CONCLUSIONS

The geographic and topographic distribution of the Chilean nitrate deposits indicates atmospheric transport and deposition of the saline constituents and subsequent redistribution by rainwater at the sites of the deposits. The saline components in the deposits are chiefly those found worldwide in the atmosphere or those known to form by atmospheric photochemical processes; these components have been

deposited and preserved in the Atacama Desert because of the uniquely arid climate. Although some constituents may have been transported from distant sources, the greater part probably came from local sources such as the nearby Pacific Ocean and the volcanic rocks and the emissions from intense volcanic activity in the nearby Andean Highlands during late Tertiary and Quaternary time. A general low level of microbial activity in the dry soils of the Atacama Desert has been essential to preservation of the nitrate.

The following model for the formation of Chilean nitrate deposits is proposed:

(1) Long-term widespread accumulation of saline materials from the atmosphere in soils of the nearly rainless Atacama Desert, perhaps starting in middle Miocene time, 10–15 million years ago, and continuing until the present. Although a virtually rainless climate prevailed during this time, periodic heavy rains or rainy periods caused considerable leaching and redeposition of soluble saline materials and at times may have caused widespread destruction of former nitrate deposits.

(2) The saline components were transported by and deposited from the atmosphere chiefly as dry fallout and as fog-condensate solutions. These components included salts such as NaCl and NaNO₃, as well as gaseous or water-soluble constituents such as NH₃, HCl, H₂SO₄, and HNO₃ that reacted at the soil level to form the saline components in the deposits.

(3) Ore-grade nitrate deposits formed by: (a) accumulation of saline materials on very old, flat to gently inclined or undulating land surfaces, where rainwater dissolved the more soluble components such as nitrate and redeposited them at deeper soil levels; (b) accumulation of saline materials on hills, where they were dissolved by rainwater and moved to lower levels on hillslopes, typically at slope breaks and bottoms of hills; and (c) accumulation of nitrate-rich saline materials in salt pans and saline ponds.

(4) The principal sources of the saline components were: (a) sea spray and gases such as ammonia and iodine from the nearby Pacific Ocean; (b) volcanic rocks and emanations of active volcanoes in the Andes; (c) photochemical reactions in the atmosphere; (d) wind-transported saline materials derived from erosion of saline soils, pre-existing nitrate deposits, and salars in the Atacama Desert; and (e) atmospheric constituents that reacted with soils and rocks in the nitrate fields or that were transformed by soil microorganisms.

Different sources dominated for each of the saline constituents, as follows: (1) Nitrate probably was formed chiefly by photochemical oxidation of ammonia (NH₃) or the ammonium ion (NH₄⁺), gaseous nitrogen oxides NO and NO₂, and nitrogenous organic materials. The chief source of the ammonia and nitrogenous organic material probably was sea spray from the nearby Pacific ocean, whereas the nitrogen oxides were formed by oxidation of these substances, by nitrogen fixation during thunderstorms in the nearby Andes, and by mixing of stratospheric air containing NO and NO₂ formed by reaction of relatively abundant nitrous oxides (N₂O) with electronically excited oxygen atoms O(¹D); additional nitrate may have been formed at soil surfaces of the nitrate fields by nitrification of NH₃ and NH₄⁺ and nitrogen fixation by photoautotrophic bacteria and blue-green algae. (2) The principal source of NaCl was probably spray from the nearby Pacific Ocean, but significant amounts of NaCl or HCl may have been supplied by volcanic emanations in the Andes. (3) Sulfate originated as SO₂ in volcanic emanations, as water-soluble sulfate minerals in volcanic rocks of the Andes, and as SO₄⁻² or H₂S from seawater. (4) Essentially all the borate came from volcanic emanations and volcanic rocks in the Andes. (5) Perchlorate is considered to have formed by reactions of chlorine with ozone (O₃) in the troposphere and at ground level. (6) Iodine is chiefly of oceanic origin, as iodine-rich organic material ejected in bubble spray and as gaseous iodine formed by photochemical oxidation of iodide at the ocean surface; iodine was oxidized to iodate by photochemical reactions in the troposphere and at ground level. (7) The anomalously low bromine content of the nitrate deposits is attributed to atmospheric photochemical processes that favored formation of the gaseous forms of bromine, Br₂, HBr, BrO, which were lost in the atmosphere rather than accumulating as saline components of the nitrate deposits. (8) The alkali and alkaline-earth elements, sodium, potassium, calcium, and magnesium, which are the dominant cations of the saline minerals of the nitrate deposits, had diverse sources, including sea spray, airborne particulate matter related to Andean volcanism, and wind-transported saline dust from soils, salars, and playas in the Atacama Desert.

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