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COMPUTER STUDIES OF THE COMPOSITION OF CHILEAN NITRATE ORES: DATA REDUCTION, BASIC STATISTICS AND CORRELATION ANALYSIS.

by

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Computer Studies
of
The Composition of Chilean Nitrate Ores
I: Data Reduction, Basic Statistics and Correlation Analysis

By Bernardo F. Grossling and George E. Ericksen

Abstract

Electronic computer studies were made on a suite of 815 chemical analyses of soluble salines in nitrate ores, representing monthly averages of ores treated by the two largest nitrate plants in Chile from 1932 to 1967. A package statistical program, STATPAC, of the U.S. Geological Survey was utilized: 1) to estimate the abundance of sodium not reported in the analyses, 2) to determine the soluble-insoluble ratio, 3) to calculate the basic statistics, and 4) to investigate the correlation between the saline constituents. The statistical average composition of the soluble salines in these nitrate ores, estimated to be a close approximation of the average of Chilean ores as a whole, is as follows (in weight percent; the standard deviation is given in parenthesis):
NO_3 6.29(±0.60), Cl 4.58(±1.26), SO_4 10(±3.16), IO_3 0.060(±0.012), ClO_4 0.028(±0.012), B_5O_9 0.50(±0.11), Na 6.90(±1.19), K 0.73(±0.36), Ca 1.81(±0.55), Mg 0.46(±0.28), percentage of solubles 31.36(±5.69).

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The analyses do not give the true abundance of salines of low solubility such as anhydrite, which commonly makes up several percent of the nitrate ore, nor of several other saline ions occurring in minor or trace amounts which together generally do not make up more than a percent or two. Tables are presented for the significant correlations between relative abundances of the constituents, which give a clue to the mineralogical composition of the nitrate ore. However, the analysis of these correlation studies has not yet been completed.

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List of Symbols

Symbol	Explanation
M	mass of an ore sample
a	mass of insoluble part of an ore sample
b	mass of soluble part of an ore sample
s	soluble ratio, b/M
m_i	molecular weight of i-th ion
v_i	valence of i-th ion
c_i	concentration of the i-th ion in the soluble part of the ore sample, but referred to the total mass, $i = 1, 2, \ldots, r$
c_i'	concentration of the i-th ion in the soluble part of the ore sample
$c_i'(*)$	concentration of the i-th ion in the soluble part of the ore sample that remains after the following assumptions: a) omitting the Cl ions and the amount of Na required for them to form $NaCl$, b) omitting the IO_3 ions and the amount of Ca

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Symbol	Explanation
	required to form $Ca(IO_3)_2$, and c) omitting all the remaining Ca ions and a stoichiometrically equivalent amount of SO_4 to form $CaSO_4$
$c'_i(\alpha *)$	concentration of the i-th ion in the soluble part of the ore sample that remains after the assumptions a), b), and c) above, and also the assumption: d) omitting an amount α percent of the NO_3 ions and the amount of Na required to form this amount of $NaNO_3$
$g(*)$	scaling factor, equal to $\overset{(*)}{\Sigma} c'_i/\Sigma c'_i$, where the summations refer to i = 1, 2, 3, 4, 5, 6, 17, 8, 9, and 18, and the c'_i terms in the summation sign with the (*) symbol above are the values modified as indicated in this listing for the $c'_i(*)$ symbol
$g(\alpha *)$	scaling factor, equal to $\overset{(*)}{\Sigma} c'_i/\overset{(\alpha *)}{\Sigma} c'_i$, where the summations refer to i = 1, 2, 3, 4, 5, 6, 17, 8, 9, and 18, and the c'_i terms in a): the summation sign with (*) above are the c'_i values modified as indicated for the $c'_i(*)$ symbol, and in b): the summation sign with (α*) above are the c'_i values modified as indicated for the $c'_i(\alpha *)$ symbol

Concentrations directly determined by Anglo-Lautaro

c_1	concentration of NO_3 in the soluble part, but referred to the total sample
c_2	concentration of the Cl in the soluble part, but referred to the total sample, and not including the Cl occurring as ClO_4 ion

Symbol	Explanation
c_3	concentration of the SO_4 in the soluble part, but referred to the total sample
c_4	concentration of the Mg in the soluble part, but referred to the total sample
c_5	concentration of the Ca in the soluble part, but referred to the total sample
c_6	concentration of the K in the soluble part, but referred to the total sample
c_7	concentration of the B in the soluble part, but referred to the total sample
c_8	concentration of the ClO_4 in the soluble part, but referred to the total sample
c_9	concentration of the IO_3 in the soluble part, but referred to the total sample
c_{10}	concentration of the H_2O in the total sample
Derived concentrations in Anglo-Lautaro data	
c_{11}	calculated concentration of $NaNO_3$, based on the NO_3 in the soluble part, but referred to the total sample
c_{12}	calculated concentration of $NaCl$, based on the Cl in the soluble part, but referred to the total sample, and not including the Cl occurring as ClO_4 ion
c_{13}	calculated concentration of Na_2SO_4, based on the SO_4 in the soluble part, but referred to the total sample
c_{14}	calculated concentration of $Na_2B_4O_7$, based on the B in the soluble part, but referred to the total sample

Symbol	Explanation
c_{15}	calculated concentration of $KClO_4$, based on the ClO_4 in the soluble part, but referred to the total sample; the amount of K is simply a calculated value and not part of K determined by analysis
c_{16}	calculated concentration of I, based on the IO_3 in the soluble part, but referred to the total sample
Other concentrations	
c_{17}	calculated concentration of B_5O_9, based on the B in the soluble part, but referred to the total sample
c_{18}	calculated concentration of the Na in the soluble part, but referred to the total sample
Mineral assemblage	
A_j	designation of j-th mineral, $j = 1, 2, \ldots, k$
$\{A_j\}$	mineral assemblage in soluble part
A_1	$NaCl$ (Halite)
A_2	KCl (Sylvite)
A_3	$NaNO_3$ (Soda-niter)
A_4	KNO_3 (Niter)
A_5	$Na_3(NO_3)(SO_4)\cdot H_2O$ (Darapskite)
A_6	$K_3Na_7Mg_2(SO_4)_6(NO_3)_2\cdot H_2O$ (Humberstonite)
A_7	Na_2SO_4 (Thenardite)
A_8	$CaSO_4$ (Anhydrite)
A_9	$2CaSO_4\cdot(H_2O)$ (Bassanite)
A_{10}	$CaSO_4\cdot 2H_2O$ (Gypsum)

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Symbol	Explanation
A_{11}	$MgSO_4 \cdot H_2O$ (Kieserite)
A_{12}	$MgSO_4 \cdot 7H_2O$ (Epsomite)
A_{13}	$Na_2Ca(SO_4)_2$ (Glauberite)
A_{14}	$Na_2Mg(SO_4)_2 \cdot 4H_2O$ (Bloedite)
A_{15}	$K_3Na(SO_4)_2$ (Aphthitalite)
A_{16}	$K_2Mg(SO_4)_2 \cdot 6H_2O$ (Picromerite)
A_{17}	$Ca(IO_3)_2$ (Lautarite)
A_{18}	$KClO_4$
A_{19}	$NaCaB_5O_9 \cdot 8H_2O$ (Ulexite)
A_{20}	$NaCaB_5O_9 \cdot 5H_2O$ (Probertite)
A_{21}	$CaMgB_6O_{11} \cdot 6H_2O$ (Hydroboracite)
A_{22}	H_2O (Water of crystallization)
Mineral concentrations	
x_j	concentration of the j-th mineral in the soluble part, but referred to the total sample
x'_j	concentration of the j-th mineral in the soluble part
x_1	$NaCl$ concentration
x_2	KCl concentration
x_3	$NaNO_3$ concentration
x_4	KNO_3 concentration
x_5	$Na_3(NO_3)(SO_3) \cdot H_2O$ concentration
x_6	$K_3Na_7Mg_2(SO_4)_6(NO_3)_2 \cdot 6H_2O$ concentration
x_7	Na_2SO_4 concentration
x_8	$CaSO_4$ concentration

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Symbol	Explanation
x_9	$2CaSO_4 \cdot (H_2O)$ concentration
x_{10}	$CaSO_4 \cdot 2H_2O$ concentration
x_{11}	$MgSO_4 \cdot H_2O$ concentration
x_{12}	$MgSO_4 \cdot 7H_2O$ concentration
x_{13}	$Na_2Ca(SO_4)_2$ concentration
x_{14}	$Na_2Mg(SO_4)_2 \cdot 4H_2O$ concentration
x_{15}	$K_3Na(SO_4)_2$ concentration
x_{16}	$K_2Mg(SO_4)_2 \cdot 6H_2O$ concentration
x_{17}	$Ca(IO_3)_2$ concentration
x_{18}	$KClO_4$ concentration
x_{19}	$NaCaB_5O_9 \cdot 8H_2O$ concentration
x_{20}	$NaCaB_5O_9 \cdot 5H_2O$ concentration
x_{21}	$CaMgB_6O_{11} \cdot 6H_2O$ concentration
x_{22}	H_2O concentration

Other Symbols

a_{ij}	mass of i-th ion per unit of mass of mineral A_j

Introduction

Statistical and other calculations on a large suite of chemical analyses of Chilean nitrate ores were undertaken to study the manner of variation of the concentrations of the saline components and their interrelations, and to assist in establishing the mineralogy of the nitrate deposits and their origin. The suite of analyses was provided by the Anglo-Lautaro Nitrate Corporation (hereafter called Anglo-Lautaro), and consist of 815 monthly average analyses of nitrate ores, treated during 1932-1967 at the company's two processing plants in Chile, María Elena and Pedro de Valdivia, which by far are the largest to have been in operation in Chile. The calculations were made with the IBM 360/65 electronic computer of the U.S. Geological Survey, Washington, D.C., utilizing for the data reduction and statistical calculations the computer package known as STATPAC.

The main steps of the computer study are as follows:

1) Reduction of the reported data to establish the chemical components actually determined in the nitrate ore; thus eliminating certain arbitrary assumptions about the presence of chemical compounds reported in the analyses, but which may not necessarily be present in the ore.
2) Calculation of the concentration of sodium, which is not reported in the analyses, although it is the principal cation in the salines.
3) Estimation of percentage of soluble salines.
4) Calculation of the concentrations of the saline components referred to the soluble part. We note here that only the soluble part of the ore was chemically analyzed, but in the Anglo-Lautaro data the concentrations are referred to the total sample as 100 percent.
5) Determination of the basic statistics--mean, range, and standard deviation--of the original data, and of the reduced data referred both to the total ore and to the soluble fraction.
6) Study of the distribution functions of the various ions, in particular whether they are best represented by normal, lognormal or other distributions.
7) Search for meaningful correlations between the abundances of the component ions that may give clues to their association in certain minerals.

A later paper will further study the mineral assemblage and the mineral abundances in the ores by means of theoretical models on the same data.

In our investigation, to facilitate the formulation of quantitative relationships, we have resorted to a concise mathematical-like notation to designate the various quantities, as shown in the *List of symbols*.

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Previous Work

Although tens of thousands of chemical analyses of nitrate ore have been made by the many nitrate companies that have operated in Chile, relatively few analyses have been published, probably less than 50, and not one of them can be considered to be representative of the nitrate deposits as a whole or even of a single nitrate field. Most of the published analyses were made before 1920, which include those of Darapsky (1900), Semper and Michels (1908), Penrose (1910), and Whitehead (1920), are cited most frequently in later publications. The most recently published analyses are by Ericksen (1963) and Ericksen and Mrose (1970). Most analyses cite 'calculated' compounds that actually have not been found as such in the nitrate ore; among these are $CaCl_2$, $MgCl_2$, $KClO_4$, $Na_2B_4O_7$, NaI, $NaIO_3$, and $Ca(NO_3)_2$.

The only comprehensive mineralogical studies of the salines in the Chilean nitrate deposits are those of Wetzel (1923, 1924, 1928, and 1932) and current studies by Ericksen and Mrose. Yet, most of the minerals now known to be possible constituents (see Table 1) had already been identified in various publications prior to Wetzel's investigations. Several other minerals that have been reported only on the basis of chemical analyses have yet to be actually identified.

General Features of the Chilean Nitrate Deposits

The Chilean nitrate deposits, unique in many respects, consist of highly soluble salines that cement or impregnate near surface soils and rocks. Some of the iodate, nitrate and chromate minerals are unique to the Chilean deposits, as is the presence of the perchlorate ion (ClO_4) whose source as a mineral has not yet been identified. The deposits contain large amounts of nitrate (NO_3) in concentrations much greater than elsewhere in the world. The exploitable reserves of ore of the entire nitrate region, presently requiring a minimum grade of 7 percent of $NaNO_3$, are estimated at more than 200 million tons of contained $NaNO_3$ (written communication Servicio de Minas de Chile, 1963). The deposits also contain comparable amounts of $NaCl$ and Na_2SO_4; and much smaller amounts of recoverable iodine and boron, although commercially very significant in terms of world consumption.

The nitrate deposits are found in the Atacama Desert of northern Chile, said to be the driest desert in the world, in a region some 700 km long extending from about Lat. 19°30'S. to Lat. 26°S. (Fig. 1).

Figure 1 near here.

The Atacama Desert region is characterized by a Coastal Range and a discontinuous Central Valley. The high Andes Mountains are to the east where the climate is far less dry. The nitrate deposits are found in the Coastal Range, most typically on broad, gentle, debris-covered slopes facing the Central Valley; in broad valleys at the east side of the Central Valley, and locally in hills and valleys interrupting the Central Valley.

Figure 1.--Index map of northern Chile, showing nitrate fields.

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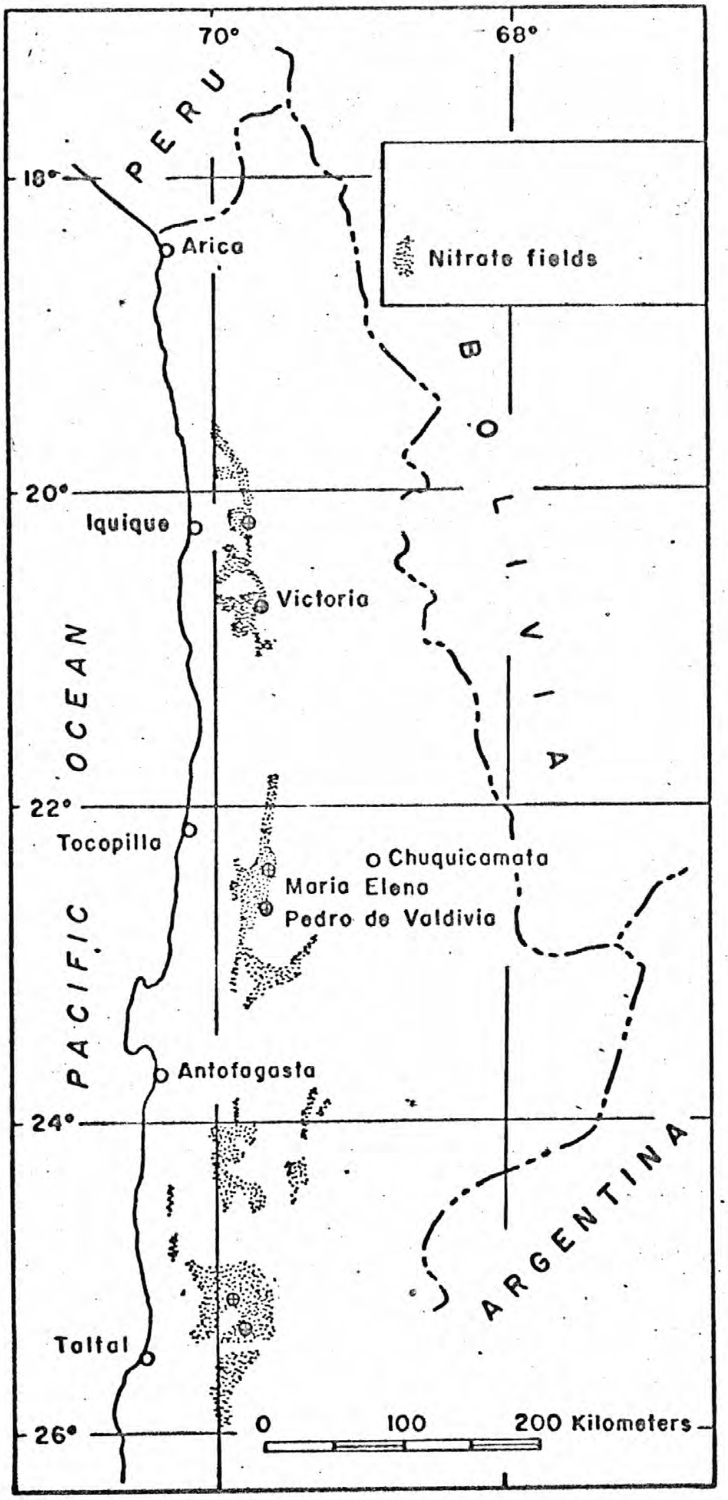

Figure 1.--Index map of northern Chile, showing nitrate fields.

The extreme aridity of the Atacama Desert was probably the single most important factor in the accumulation and preservation of the highly-soluble saline minerals of the nitrate deposits. Records indicate that the average annual rainfall in the nitrate region presently is less than 10 mm. Nevertheless, the question of the origin of the nitrate deposits is still perplexing, and no theory of origin has been proposed so far that is entirely satisfactory. This is in spite of the many scientists who have tried for more than 100 years to account for the origin of the deposits and have discussed them in many publications.

The nitrate deposits consist of saline-impregnated regolith and bedrock in which locally occur irregular masses, veins, and layers of high-purity salines, as much as a meter thick (Figure 2). They are found at or near the ground surface, generally not extending to depths of more than 5 m. Usually, the layer of exploitable nitrate ore is 1-3 m thick and is covered by 1/2 to 2 m of low-grade or barren material. The nitrate and associated saline minerals occupy original pores, cavities, and fractures in alluvium, soil, and bedrock, as well as additional spaces probably opened by forces induced by the crystallization of the salines (Figure 3). As a result, the saline content of the typical nitrate ore is greater than would be expected if deposition were restricted to original pores and cavities in the host rock. Generally, the layer of nitrate ore is underlain by uncemented alluvium or by compact bedrock. At places, the lower boundary of the nitrate ore is gradational whereas at others it is abrupt.

Figure 2.--Nitrate ore in Pedro de Valdivia, consisting of alluvium cemented with saline minerals.

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Figure 2.--Nitrate ore in Pedro de Valdivia, consisting of alluvium cemented with saline minerals.

Figure 3.--Saline-filled tabular cracks probably pried open by forces of crystallization.

Figure 3.--Saline-filled tabular cracks probably pried open by forces of crystallization.

Horizontal and vertical local variations of mineralogical and chemical composition are large. Because of this variability it is difficult to determine the average composition, and more so to relate the composition to geologic factors. Yet, it is apparent that the nitrate ores exhibit a certain degree of uniformity throughout the entire nitrate region. Furthermore, selective mining in given areas yields ores of relatively uniform composition, as indicated by the suite of analyses on which this report is based.

The suite of saline minerals found in the Chilean nitrate deposits is more complex than that in most evaporite deposits elsewhere. In addition to Cl^-, SO_4^{--}, Na^+, Ca^{++}, Mg^{++}, K^+, and B, which are common in other saline deposits, the Chilean deposits also contain NO_3^-, IO_3^-, CrO_4^-, $Cr_2O_7^-$, and ClO_4^-, which are rare or absent in saline deposits elsewhere. The minerals listed in Table 1 probably account for more than 98 percent of the saline minerals in the nitrate ore. Investigations of Ericksen and Mrose indicate the presence of several other minerals, which in part at least may be minerals heretofore not described in the literature. Furthermore, crystallization experiments on saline solutions made from high-sulphate nitrate ores show that mirabilite ($Na_2SO_4 \cdot 10H_2O$), aphthitalite ($K_3Na(SO_4)_2$), and picromerite ($K_2Mg(SO_4)_2 \cdot 6H_2O$) crystallize upon evaporation, and thus one might expect to find these minerals in the nitrate deposits.

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Table 1.--Saline Minerals of the Nitrate Deposits of Chile

(after Ericksen and Mrose, 1970)

Halite	$NaCl$	Glauberite	$Na_2Ca(SO_4)_2$
Soda-niter	$NaNO_3$	Bloedite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$
Niter	KNO_3	Lautarite	$Ca(IO_3)_2$
Darapskite	$Na_3(NO_3)(SO_4) \cdot H_2O$	Ulexite	$NaCaB_5O_9 \cdot 8H_2O$
Humberstonite	$K_3Na_7Mg_2(SO_4)_6(NO_3)_2 \cdot 6H_2O$	Probertite	$NaCaB_5O_9 \cdot 5H_2O$
Thenardite	Na_2SO_4	Hydroboracite	$CaMgB_6O_{11} \cdot 6H_2O$
Anhydrite	$CaSO_4$	Ginorite	$Ca_2B_{14}O_{23} \cdot 8H_2O$
Bassanite	$2CaSO_4 \cdot H_2O$	Kaliborite	$HKMg_2B_{12}O_{16}(OH)_{10} \cdot 4H_2O$
Gypsum	$CaSO_4 \cdot 2H_2O$	Dietzeite	$Ca_2(IO_3)_2(CrO_4)$
Kieserite	$MgSO_4 \cdot H_2O$	Lopezite	$K_2(Cr_2O_7)$
Epsomite	$MgSO_4 \cdot 7H_2O$	Tarapacaite	K_2CrO_4

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Analytical procedure and significance of the Anglo-Lautaro chemical analyses

The following outline of the mining, sampling, and chemical analysis methods employed at the María Elena and Pedro de Valdivia plants is relevant to the understanding of the chemical data used in our computer study:

1) The nitrate deposits are selectively mined to yield an ore averaging about 8 percent $NaNO_3$. Broken ore, in fragments of up to nearly 2 m in diameter, is hauled to the plant where it is crushed to a size of about 1/2 in. or less; very fine material is screened and processed separately. The crushed screened ore is automatically and continuously sampled, to provide a main sample, as it moves by conveyor belt from the crushing plant to the leaching vats, where the nitrate is extracted by a recirculated brine (called *agua vieja*) at about 40°C.

2) The main sample collected each day, amounting to several hundred pounds, is sent to the chemical laboratory for analysis. The procedure for analyzing the ore fines obtained by screening is the same as for the main sample, and both results are combined to give the daily average composition of ore treated.

3) Each daily sample is pulverized and a standard amount is taken for analysis. It is then dried at about 110°C to determine the H_2O content by the weight loss.

4) The dried sample is treated with a large excess of cold water and the resultant mixture is heated in a beaker for 4 hrs at 40-50°C.

5) The mixture is then brought quickly to the boiling point and immediately filtered.

6) The insoluble residue, consisting of rock particles and saline minerals of low solubility, such as gypsum, is discarded.

7) The filtrate is chemically analyzed for the following substances: NO_3, Cl, SO_4, Mg, Ca, K, B, ClO_4, and I.

8) Part of these substances are recalculated to certain assumed compounds, whereby the following constituents are reported: $NaNO_3$, $NaCl$, Na_2SO_4, Mg, Ca, K, $Na_2B_4O_7$, $KClO_4$, I, and H_2O. These substances in the soluble part of the ore are given as concentrations referred to the total sample as 100 percent.

9) Sodium (Na), the most abundant cation of the saline minerals in the nitrate ore, was not determined by analysis. The calculated amount of Na shown in the Anglo-Lautaro data, as occurring in the hypothetical compounds $NaNO_3$, $NaCl$, Na_2SO_4, and $Na_2B_4O_7$, differs from the true amount of Na present by the equivalent cumulative amount of K, Mg, and Ca that substitute for Na in these and other compounds in the nitrate ore. The Na can be determined by calculation of the stoichiometric ratios of the cations and anions present.

The insoluble matrix, more abundant than the soluble salines in all the samples, was not analyzed--it consists of rock fragments, gravel, sand, silt and clay and lesser amounts of saline minerals of low solubility such as gypsum and anhydrite. The actual proportion of insoluble material in each sample is not available.

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The Anglo-Lautaro analyses provided for our study are monthly averages of the daily analyses of the soluble fraction of nitrate treated during the period July 1932 to June 1967. Each monthly analysis represents hundreds of thousands of tons of ore; for example, during the early days of operation of María Elena, some 400,000 to 500,000 metric tons of nitrate ore were treated each month, which increased over the years to 500,000 to 600,000 tons in the 1950's and 1960's. In the early days, the plant at Pedro de Valdivia, somewhat larger than that at María Elena, treated about 600,000 metric tons of ore per month, and later as much as 900,000 tons per month.

COMPUTER CALCULATIONS AND STATISTICAL METHODOLOGY USED

Reduction of the Data

For the computer studies of the Chilean nitrate ores, it is necessary to recast the chemical analyses so that they reflect the ions and elements actually determined in the chemical analyses. Thus, the concentrations of H_2O, Mg, Ca, and K remain the same as reported in the chemical analyses. We have recalculated the other reported concentrations as follows: $NaNO_3$ as NO_3, $NaCl$ as Cl, Na_2SO_4 as SO_4, $Na_2B_4O_7$ as B_5O_9, $KClO_4$ as ClO_4, and I as IO_3.

The concentration c_1 of NO_3 is obtained from the concentration c_{11} of $NaNO_3$ as follows

$$\begin{aligned} c_1 &= c_{11}\cdot(62.008/85.005) \\ &= 0.72946\ c_{11}. \end{aligned} \qquad (1)$$

The concentration c_2 of Cl is obtained from the concentration c_{12} of $NaCl$ as follows

$$\begin{aligned} c_2 &= c_{12}\cdot(35.457/58.454) \\ &= 0.60658\ c_{12}. \end{aligned} \tag{2}$$

The concentration c_3 of SO_4 is obtained from the concentration c_{13} of Na_2SO_4 as follows

$$\begin{aligned} c_3 &= c_{13}\cdot(96.066/142.060) \\ &= 0.67624\ c_{13}. \end{aligned} \tag{3}$$

The concentration c_{17} of B_5O_9 is obtained from the concentration c_{14} of $Na_2B_4O_7$, for equal amounts of B, as follows

$$\begin{aligned} c_{17} &= c_{14}\cdot \frac{4 \times 10.82}{201.274} \cdot \frac{198.10}{5 \times 10.82} \\ &= 0.78738\ c_{14}. \end{aligned} \tag{4}$$

The concentration of c_7 of B is obtained from the concentration c_{14} of $Na_2B_4O_7$ as follows

$$\begin{aligned} c_7 &= c_{14}\cdot(43.280/201.274) \\ &= 0.21503\ c_{14}. \end{aligned} \tag{5}$$

The concentration c_8 of ClO_4 is obtained from the concentration c_{15} of $KClO_4$ as follows

$$\begin{aligned} c_8 &= c_{15}\cdot(99.457/138.557) \\ &= 0.71781\ c_{15}. \end{aligned} \tag{6}$$

The concentration c_9 of IO_3 is obtained from the concentration c_{16} of I as follows

$$\begin{aligned} c_9 &= c_{16}\cdot(174.91/126.91) \\ &= 1.37822\ c_{16}. \end{aligned} \tag{7}$$

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Estimation of the concentration of *Na*

Of all the ions that are present in the soluble part of the ore in more than trace amounts, only the concentration of *Na* was not determined in the Anglo-Lautaro chemical analyses. However, *Na* can be calculated from the equality of the weight ratios of the total cations and anions. Such equality stems from two considerations: 1) the solution on which the chemical analyses is performed is a fully ionized solution and, 2) there are no other significant ions in the solutions aside from *Na* and those analyzed.

The cations present are Mg^{+2}, Ca^{+2}, K^{+1} and Na^{+1}, the concentrations of which we have denoted by the symbols c_4, c_5, c_6, and c_{18}, respectively. The anions present are NO_3^{-1}, Cl^{-1}, $(SO_4)^{-2}$, $(ClO_4)^{-1}$, $(IO_3)^{-1}$, and $(B_5O_9)^{-3}$[1], the concentrations of which we have denoted by the symbols c_1, c_2, c_3, c_8, c_9, and c_{17}, respectively.

The equivalent weights of positive and negative ions are related by the equation

$$\Sigma \frac{\upsilon_i c_i(+)}{m_i} = \Sigma \frac{\upsilon_i c_i(-)}{m_i} , \tag{8}$$

where m_i denotes the molecular weight and υ_i the valence of the i-th ion, $c_i(+)$ the concentration of an i-th positive ion, and $c_i(-)$ that of a negative. The summation on the left side of (8) is for the positive ions, and on the right, for the negative ions.

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[1] This ion is not necessarily present in the solution; it is, however, the most abundant borate ion in the nitrate ore and is therefore utilized in the calculations here.

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The application of (8) to the ionic solution of the nitrate ore gives

$$\frac{2c_4}{24.32} + \frac{2c_5}{40.08} + \frac{c_6}{39.100} + \frac{c_{18}}{22.997} = \frac{c_1}{62.008} + \frac{c_2}{35.457} + \frac{2c_3}{96.066} + \frac{c_8}{99.457} + \frac{c_9}{174.91} + \frac{3c_{17}}{198.100} . \tag{9}$$

In this equation all the c_i except that corresponding to *Na*, namely c_{18}, are known, and hence c_{18} can readily be determined. After consideration of equations (1) to (7), except (5), we have

$$\begin{aligned} c_{18} = {} & 0.27054\ c_{11} + 0.39342\ c_{12} + 0.32376\ c_{13} \\ & + 0.16598\ c_{15} + 0.18121\ c_{16} + 0.27422\ c_{14} \\ & - 1.89120\ c_4 - 1.14756\ c_5 - 0.58816\ c_6 . \end{aligned} \tag{10}$$

We note here that the hypothetical amount of *Na* reported in the Anglo-Lautaro data corresponds to only four of the terms in formula (10), namely

$$\begin{aligned} (c_{18})_{\text{assumed}} = {} & 0.27054\ c_{11} + 0.39342\ c_{12} \\ & + 0.32376\ c_{13} + 0.22852\ c_{14} , \end{aligned} \tag{11}$$

and moreover, the coefficient of c_{14} is different.

Estimation of the percentage of solubles

To obtain the total mass of the soluble part we should add to the masses of Mg, Ca, K, Na, NO_3, Cl, SO_4, ClO_4, IO_3, and B_5O_9, that of the water in the soluble part. In the ore, water exists as humidity and in hydrated minerals known to occur both in the soluble and insoluble fractions. However, we only have the concentration of water in the total sample. As a first approximation, we will assume that the amount of water in the soluble saline minerals is negligible, and thus water is ignored in calculating the soluble-insoluble ratio. The water of crystallization will be examined later, in the linear programming study of the mineral species that may be present in the nitrate ores.

The soluble ratio is given by

$$b/M = c_1 + c_2 + c_3 + c_4 + c_5 + c_6 + c_8 + c_9 + c_{17} + c_{18}, \qquad (12)$$

where M is the total mass and b that of the soluble part, and expressing c_1 in terms of c_{11}, c_2 of c_{12}, c_3 of c_{13}, c_8 of c_{15}, c_9 of c_{16}, c_{17} of c_{14} and considering equation (10), we have

$$\begin{aligned} s = b/M &= c_{11} + c_{12} + c_{13} - 0.89120\ c_4 - 0.14756\ c_5 \\ &+ 0.41184\ c_6 + 1.06160\ c_{14} + 0.88379\ c_{15} \qquad (13) \\ &+ 1.55943\ c_{16}. \end{aligned}$$

Therefore, the soluble-insoluble ratio is

$$b/a = (b/M)/(1 - b/M), \qquad (14)$$

where a is the mass of the insoluble part of the sample. The percentage of solubles is equal to $s \times 100$.

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The concentration c_i' of the i-th ion referred to the soluble fraction is

$$c_i' = \left(1 + \frac{a}{b}\right)c_i. \tag{15}$$

Ad-Hoc Assumptions About the Occurrence of Certain Chemical Substances

As a means of investigation of the interrelations of the chemical components in the nitrate ore, after computer reduction of the Anglo-Lautaro original chemical data, we have made various alternative assumptions about the existence of certain chemical substances in the nitrate ore. This has been done in a systematic manner so that each step in the calculations can be evaluated as to its legitimacy or adequacy in explaining mineralogical composition.

First, we will assume: 1) that all the Cl ions occur as $NaCl$, 2) that all the IO_3 ions occur as $Ca(IO_3)_2$, and 3) that the remaining Ca ions occur as $CaSO_4$. In this manner it is possible to compute the concentrations of the remaining Na, SO_4, and other ions, referring them to the soluble part of the ore after omitting the amounts of Cl-, Na-, IO_3-, Ca-, and SO_4-ions in the above mentioned chemical substances.

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To facilitate the formulation of quantitative relationships we will adopt a simple and compact notation. The symbol (*) attached to an ionic concentration denotes the concentration of that ion after taking into consideration the assumptions described in the previous paragraph. For instance, $c_1'(*)$ denotes the concentration of the NO_3 ion in the soluble part of the ore, after omitting all the Cl-, IO_3-, and Ca-ions, to the extent permitted by the amounts of Na-, Ca-, and SO_4-ions present, and the amounts of Na- and SO_4-ions required to form $NaCl$, $Ca(IO_3)_2$, and $CaSO_4$.

The $c_i'(*)$ for $i = 1, 4, 6, 17$, and 8 are the same as the corresponding c_i', but the $c_i'(*)$ are referred to the soluble part less $NaCl$, $Ca(IO_3)_2$, and $CaSO_4$ as 100 percent. The scaling factor for c_i' to obtain $c_i'(*)$ is $g(*) = \Sigma c_i'/\overset{(*)}{\Sigma c_i'}$.

As to $c_2'(*)$, that is, the concentration of Cl, it is necessary to distinguish between two cases, namely

a) if $c_{18}' \geq 0.64859\ c_2'$, then (16)

$$\left. \begin{aligned} &c_2'(*) = 0, \text{ and} \\ &c_{18}' \rightarrow c_{18}' - 0.64859\ c_2', \text{ and} \end{aligned} \right\} \quad (17)$$

b) if $c_{18}' < 0.64859\ c_2'$, then (18)

$$\left. \begin{aligned} &c_2'(*) = g(*)\ (c_2' - 1.54181\ c_{18}'), \text{ and} \\ &c_{18}'(*) = 0. \end{aligned} \right\} \quad (19)$$

In case a) the amount of Na is more than sufficient for the Cl, and vice versa in case b).

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As to $c_9'(*)$, that is, the concentration of IO_3, two cases must be distinguished, namely

c) if $c_5' \geq 0.11457\ c_9'$, then (20)

$$\left.\begin{aligned} & c_9'(*) = 0, \text{ and} \\ & c_5' \rightarrow (c_5' - 0.11457\ c_9') \end{aligned}\right\} \qquad (21)$$

d) if $c_5' < 0.11457\ c_9'$, then (22)

$$\left.\begin{aligned} & c_5'(*) = 0, \text{ and} \\ & c_5'(*) = g(*)(c_9' - 8.72804\ c_5'). \end{aligned}\right\} \qquad (23)$$

Any remaining Ca is now assigned to SO_4 to form $CaSO_4$. Then the continuation of case c) above is as follows

e) if $c_3' \geq 2.39686\ (c_5' - 0.11457\ c_9')$, then (24)

$$\left.\begin{aligned} & c_5'(*) = 0, \text{ and} \\ & c_3'(*) = g(*)\{c_3' - 2.39686\ (c_5' - 0.11457\ c_9')\}. \end{aligned}\right\} \qquad (25)$$

Next, it is postulated that a percentage α of the amount of NO_3 exists as $NaNO_3$. The symbol $(\alpha *)$ attached to an ion concentration will denote the concentration (by weight) of that ion after removal of α percent $NaNO_3$, and of Cl, IO_3, and Ca as described above.

The $c_i'(\alpha *)$ for i = 2, 3, 4, 5, 6, 17, 8, and 9 are the same as the corresponding $c_i'(*)$, but the $c_i'(\alpha *)$ are referred to the soluble part less $NaCl$, $Ca(IO_3)_2$, $CaSO_4$, and $NaNO_3$. The scaling factor for c_i' to obtain $c_i'(\alpha *)$ is $g(\alpha *) = \Sigma c_i'^{(\alpha *)}/\Sigma c_i'$.

Two possibilities exist for the interrelation between $c_1'(\alpha*)$ and $c_{18}'(\alpha*)$, which follow after the alternative a) above. If

f) $c_{18}' - 0.64859\ c_2' \geq 0.37087\ \alpha c_1'$, then (26)

$$\left.\begin{array}{l} c_1'(\alpha*) = 0, \text{ and} \\ c_{18}'(\alpha*) = g(\alpha*)(c_{18}' - 0.64859\ c_2' - 0.37087\ \alpha c_1'), \end{array}\right\} \quad (27)$$

and

g) if $c_{18}' - 0.64859\ c_2' < 0.37087\ \alpha c_i'$, then (28)

$$\left.\begin{array}{l} c_{18}'(\alpha*) = 0, \text{ and} \\ c_1'(\alpha*) = g(\alpha*)(c_1' - 2.69635\ c_{18}'). \end{array}\right\} \quad (29)$$

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Calculation of the frequency distributions

To study the manner of distribution of the values of the variates x_i for example, we have calculated their frequency distributions using the STATPAC program. In this program the computer produces a printout of the histograms in which the frequencies in each interval are rounded to the nearest integral percentage value, and also gives the midpoint value for each interval. The computer determines the range of a variate, namely max x_i - min x_i, and subdivides it into equal intervals of length C determined from the formula

$$\frac{\max x_i - \min x_i}{C} = 2.5 + 3.322 \log n_i, \tag{30}$$

where n_i is the number of values in the sample. This formula is the same as Sturges rule (1926), but with a constant 1.5 added to the number of classes. Moreover, in the computer program the calculated number of classes, as given by the formula above, is rounded to the next higher integer.

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Correlation between variates

Statistical correlations between the variates, as determined in this study, may exist that can give clues to the presence or dominance of certain minerals, and to the manner of formation of the nitrate deposits. The fact that in a given mineral the component ions enter in definite proportions tends to introduce correlations among the abundances of these ions in the ore. If in the soluble part of the ore an ion, say I_i, were to occur only in a mineral A_j which also would contain another ion, say I_k, and if furthermore I_k would not occur in any other mineral in the ore, then the ratio between their concentrations, $c_i^{\prime}:c_j^{\prime}$, would be a constant. That is, the ratio would be independent of the amount of the mineral A_j present. Moreover, the ratio would correspond to the ratio of the two ions in the mineral A_j. Such a simple condition is not likely to hold for any sample of nitrate ore, and certainly does not hold for composite samples such as those on which the present study is based. Each of the ions reported in the Anglo-Lautaro data--with the possible exceptions of Cl, ClO_4, and IO_3, each of which may occur in only one mineral--enters into two or more minerals. Consequently, exact constant ratios among the various abundances should not be expected.

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To examine the correlation between the statistical abundance of the concentrations of the ions and the soluble ratio s we have used the product-moment correlation coefficient, namely

$$r = \frac{\sum_{k=1}^{n} (y_{k,i} - \bar{y}_i)(y_{k,j} - \bar{y}_j)}{\left[\left\{\sum_{k=1}^{n} (y_{k,i} - \bar{y}_i)\right\}^2 \left\{\sum_{k=1}^{n} (y_{k,j} - \bar{y}_j)^2\right\}\right]^{1/2}} \tag{30}$$

where $y_{k,i}$ is the k-th value of the y_i variant, $\bar{y}_i$ is the average value of $y_{k,i}$ in the statistical sample, and similarly for $y_{k,j}$ and $\bar{y}_j$; and where n is the number of pairs of values $y_{k,i}$ and $y_{k,j}$ in the statistical sample. In the above formula the variates $y_{k,i}$ and $y_{k,j}$ represent the concentrations of a pair of ions in the nitrate ore, or the concentration of one of the ions and the soluble ratio s.

Before proceeding, we should note some of the properties of the correlation coefficient r. The value of r is confined to the range $-1 \leq r \leq 1$. The extreme value $r = + 1$ indicates a perfect positive correlation; that is, the ratio between the two variates, taking the mean as datum, has exactly the same value for each pair of values in the statistical sample. The other extreme, namely $r = - 1$, indicates also a constant ratio, but the variations are of different sign.

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Intermediate values, that is $-1 < r < 1$, indicate various degrees of statistical correlation. The closer $|r|$ is to the value one, the more perfect the correlation. The value $r = 0$ corresponds to the lowest degree of correlation. However, even if two variates are totally unrelated the value of r in a statistical sample only rarely would attain the value zero. Nevertheless, the larger the statistical sample, the closer to zero should be the correlation coefficient of two unrelated variates. That is, the distribution of the sample correlation coefficient r for a zero population correlation coefficient ρ is a distribution about the value $r = 0$ which becomes narrower as n increases.

In examining the various correlation coefficients between pairs of variates, as displayed in the correlation matrix, we would like to dismiss those low correlations which can reasonably be attributed to statistical fluctuations of two unrelated variables. Moreover, we are not too concerned with the error of assigning a zero correlation to two variables with a low correlation. When $\rho = 0$ the frequency distribution of r has a variance equal to $1/(n - 1)$, and tends fairly rapidly with increasing n to the normal form. For the normal distribution, using a two-tail test, 99.9 percent of the values are contained within the range $-3.2905 \leq r \leq 3.2905$, in units of standard deviation. For the María Elena statistical sample we have $n = 414$, and for Pedro de Valdivia, $n = 401$; giving the values 0.0492 and 0.05 for the standard deviations of the approximating normal distribution. Therefore, if the variates are independent of each other, 99.9 percent of the sample values should be contained in the ranges

$$- 0.162 \leq r \leq 0.162,$$

and

$$- 0.164 \leq r \leq 0.164,$$

for the María Elena and Pedro de Valdivia samples, respectively.

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The confidence limits of the correlation coefficient for a confidence coefficient of 0.95 and $n = 400$, (Pearson and Hartley, 1966, p. 148) are listed in Table 2. These are rather narrow limits because of the large sample size. Hence, any sample correlation coefficient greater in absolute value than 0.162 and 0.164 for María Elena and Pedro de Valdivia, respectively, is statistically significant. As we shall see, the difficulty lies in how to interpret geologically these statistically significant correlations.

The handling of more complex situations requires investigating functional relationships of the type

$$p_i = f(\{p_k\}), \tag{31}$$

where p_i represents the concentration of a particular ion of interest, and where $\{p_k\}$ represents the set of remaining concentrations. The statistical tool to carry out this more sophisticated analysis is multiple correlation analysis. As is usual, the functional dependence in (31) will be assumed to be linear in the p_k.

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Table 2.--Confidence Limits of the Correlation Coefficient, for $n = 400$ and a Confidence Coefficient of 0.95[1]

r	ρ_A	ρ_B
1.0	1.0	1.0
0.8	0.77	0.83
0.6	0.53	0.66
0.4	0.32	0.48
0.2	0.11	0.29
0	-0.1	0.1
-0.2	-0.29	-0.11
-0.4	-0.48	-0.32
-0.6	-0.66	-0.53
-0.8	-0.83	-0.77
-1.0	-1.0	-1.0

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[1] Biometrika Tables for Statisticians, vol. I, E.S. Pearson and H. O. Hartley, editors, 1966, p. 148.

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COMPUTER RESULTS AND THEIR INTERPRETATION

Basic statistics of the analytical data

The basic statistics--range, mean, and standard deviation--calculated by the electronic computer a) from the chemical analyses as reported by Anglo-Lautaro are given in Table 3, and b) from the analyses reduced to show the component ions in the nitrate ore, in Table 4. When the percentages are referred to the soluble part as 100 percent, the statistics are those shown in Table 5. The ranges and means shown in these tables can be considered as the average bulk composition of Chilean nitrate ores, and for any large tonnage of ore that might be extracted the composition would tend to fall within the ranges given.

The estimated ore reserves of 200 million metric tons of contained $NaNO_3$, previously mentioned, would be expected to have an average composition that would fall within the ranges indicated in Tables 3 and 4.

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The coefficient of variation, that is the ratio of the standard deviation to the mean value of a variate, can be used to compare the variability of the various chemical components of the nitrate ore. In Table 6 are listed the values of that coefficient for the concentrations referred to the soluble part, arranged by increasing value, for the María Elena and Pedro de Valdivia data. Of the four most abundant substances--Na, SO_4, Cl and NO_3--three--Na, SO_4, and NO_3--exhibit the three smallest coefficients of variation. Na is the substance that exhibits the smallest variations--namely its standard deviation amounts to only 7.2 percent and 6.7 percent of the mean for the María Elena and Pedro de Valdivia data, respectively. By comparison, the coefficient of variation of the percentage of solubles is 0.143 for María Elena, and 0.080 for Pedro de Valdivia.

An average of the mean values of ores treated at the two plants, as shown in Table 4, is probably as near to the bulk composition of soluble salines in Chilean nitrate ore as is possible to estimate. These average values are summarized in Table 7.

Table 3.--Summary statistics of the chemical analyses as reported by Anglo-Lautaro

Reported Substance	Nitrate Plant[1]	Weight Percentages Referred to Total Sample		
		Range	Mean	Standard Deviation
$NaNO_3$	ME	5.55-11.12	8.64	±0.67
	PV	7.40-10.37	8.61	±0.46
$NaCl$	ME	4.56-15.21	9.38	±1.97
	PV	4.02-7.56	5.72	±0.70
Na_2SO_4	ME	10.05-29.99	18.92	±4.31
	PV	5.98-16.20	10.62	±1.89
I_2	ME	0.015-0.064	0.042	±0.007
	PV	0.016-0.070	0.044	±0.006
$KClO_4$	ME	0.019-0.086	0.040	±0.008
	PV	0.010-0.093	0.041	±0.013
$Na_2B_4O_7$	ME	0.41-1.04	0.73	±0.12
	PV	0.27-1.03	0.55	±0.09
K	ME	0.41-1.90	0.86	±0.32
	PV	0.25-1.31	0.60	±0.16
Ca	ME	1.10-3.54	2.22	±0.45
	PV	0.73-2.41	1.41	±0.31
Mg	ME	0.15-1.30	0.72	±0.27
	PV	0.06-0.51	0.20	±0.07
H_2O	ME	0.42-2.62	1.14	±0.27
	PV	1.05-2.57	1.74	±0.23

[1] ME = María Elena, PV = Pedro de Valdivia

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Table 4.--Summary statistics of the chemical analyses of Anglo-Lautaro, reduced to actual constituents of the nitrate ore

Substance	Nitrate Plant[1]	Weight Percentage Referred to Total Sample Range	Mean	Standard Deviation
NO_3	ME	4.05-8.11	6.30	±0.49
	PV	5.40-7.56	6.28	±0.34
Cl	ME	2.77-9.23	5.69	±1.19
	PV	2.44-4.59	3.47	±0.42
SO_4	ME	6.80-20.28	12.80	±2.91
	PV	4.04-10.96	7.20	±1.23
IO_3	ME	0.021-0.088	0.058	±0.009
	PV	0.022-0.096	0.061	±0.008
ClO_4	ME	0.014-0.062	0.028	±0.006
	PV	0.007-0.067	0.029	±0.010
B_5O_9	ME	0.32-0.82	0.58	±0.09
	PV	0.021-0.81	0.43	±0.07
Na	ME	5.17-10.83	7.95	±1.04
	PV	3.92-7.09	5.85	±0.57
K	ME	0.41-1.90	0.86	±0.32
	PV	0.25-1.31	0.60	±0.16
Ca	ME	1.10-3.54	2.22	±0.45
	PV	0.73-2.41	1.41	±0.31
Mg	ME	0.15-1.30	0.72	±0.27
	PV	0.06-0.51	0.20	±0.07

[1] ME = María Elena, PV = Pedro de Valdivia

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Table 4.--Summary statistics of the chemical analyses of Anglo-Lautaro, reduced to actual constituents of the nitrate ore

(Continued)

Substance	Nitrate Plant[1]	Weight Percentage Referred to Total Sample		
		Range	Mean	Standard Deviation
H_2O	ME	0.42-2.62	1.14	±0.27
	PV	1.05-2.57	1.74	±0.23
Soluble salines	ME	23.90-47.77	37.21	±5.31
	PV	21.28-32.08	25.52	±2.05

[1] ME = María Elena, PV = Pedro de Valdivia

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Table 5.--Summary statistics of the chemical analyses of Anglo-Lautaro, reduced to actual constituents, but referred to the soluble part of nitrate ore as 100 percent

		Weight Percentage Referred to Soluble Part		
Substance	Nitrate Plant[1]	Range	Mean	Standard Deviation
NO_3	ME	10.58-25.30	17.23	±2.29
	PV	19.98-29.15	24.70	±1.73
Cl	ME	9.76-20.76	15.27	±2.46
	PV	9.98-18.69	13.63	±1.60
SO_4	ME	25.77-43.26	34.11	±3.78
	PV	18.79-35.11	28.06	±3.04
IO_3	ME	0.044-0.307	0.160	±0.036
	PV	0.075-0.442	0.240	±0.035
ClO_4	ME	0.038-0.221	0.078	±0.022
	PV	0.026-0.307	0.120	±0.040
B_5O_9	ME	1.05-2.37	1.56	±0.24
	PV	0.79-3.14	1.70	±0.31
Na	ME	16.35-24.88	21.45	±1.54
	PV	16.79-26.24	22.94	±1.53
K	ME	1.10-4.51	2.29	±0.70
	PV	1.13-4.97	2.34	±0.62
Ca	ME	3.55-9.02	5.96	±0.91
	PV	3.32-10.34	5.50	±1.04

[1] ME = María Elena, PV = Pedro de Valdivia

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Table 5.--Summary statistics of the chemical analyses of Anglo-Lautaro, reduced to actual constituents, but referred to the soluble part of nitrate ore as 100 percent

(Continued)

Substance	Nitrate Plant[1]	Weight Percentage Referred to Soluble Part Range	Mean	Standard Deviation
Mg	ME	0.58-3.02	1.88	±0.49
	PV	0.23-2.17	0.77	±0.27
H_2O	ME	0.94-7.11	3.17	±1.08
	PV	4.31-10.81	6.87	±1.06

[1] ME = María Elena, PV = Pedro de Valdivia

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Table 6.--Coefficients of variation of the c_i' and b/M

For María Elena		For Pedro de Valdivia	
Substance	Coefficient	Substance	Coefficient
Na	0.072	Na	0.067
SO_4	0.111	NO_3	0.070
NO_3	0.133	SO_4	0.108
Ca	0.153	Cl	0.117
B_5O_9	0.154	IO_3	0.146
Cl	0.161	H_2O	0.154
IO_3	0.225	B_5O_9	0.182
Mg	0.261	Ca	0.189
ClO_4	0.282	K	0.265
K	0.306	ClO_4	0.333
H_2O	0.341	Mg	0.351

Quantity	Coefficient	Quantity	Coefficient
b/M	0.143	b/M	0.080

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Table 7.--Average composition of soluble salines in Chilean nitrate ore

Substance	Weight Percent	Standard Deviation
NO_3	6.29	±0.60
Cl	4.58	±1.26
SO_4	10.00	±3.16
IO_3	0.060	±0.012
ClO_4	0.028	±0.012
B_5O_9	0.50	±0.11
Na	6.90	±1.19
K	0.73	±0.36
Ca	1.81	±0.55
Mg	0.46	±0.28
H_2O	1.44	±0.36

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The statistics for the percentage of soluble salines in the nitrate ore, calculated according to equation (13) which disregards as a first approximation the water which may be present in the soluble part, is shown in the last two rows of Table 4. The large variations of the percentage of solubles in the suite of samples--namely 23.90 to 37.21 percent in María Elena and 21.28 to 32.08 percent in Pedro de Valdivia--undoubtedly obscure relationships among the abundances of certain saline components. The rather large mean percentage of solubles in the ore, namely 37.21 and 25.52 in María Elena and Pedro de Valdivia, respectively, indicates that the saline minerals of the nitrate ores were deposited not only in an original porosity of the insoluble matrix, but also in openings developed by crystallization forces.

The manner of statistical distribution of the concentrations--more precisely, their frequency distribution functions--can give important clues as to the complexity of the mechanisms accounting for the sample to sample concentration variations. Of special interest is whether these functions are distinctly unimodal, or whether they exhibit several maxima. When the concentration range of a certain ion is subdivided into equal intervals and when the concentrations of individual samples are classified in accordance to these intervals, the frequency distribution function becomes a histogram. For our data we have determined the latter as explained in an earlier section of this paper.

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Figure 4 shows the histograms of the concentrations, referred to the total sample, of the various ions and also the histogram of the percentage of solubles for Pedro de Valdivia and María Elena. First, we note that the histograms are distinctly unimodal for the following ions: Mg, K, B, NO_3, IO_3, and Ca; and also for the percentage of solubles. The histogram for IO_3 is particularly narrow. On the other hand, the histograms are distinctly multimodal for the following ions: Cl, Na, ClO_4, and SO_4.

By comparison, the histograms for María Elena are in general more complex. The only distinctly unimodal histograms are those for the concentrations of ClO_4, NO_3 and to a less extent for Na and Cl. The histograms are distinctly multimodal for the concentrations of Mg, B, SO_4, Ca, K, and IO_3, and also for the percentage of solubles.

Similar relationships are observed when the concentrations referred to the total soluble are considered, as shown in Figure 5. Again, the histograms for María Elena are, in general, more complex than for Pedro de Valdivia. For Pedro de Valdivia the bimodal distribution of the Cl concentration referred to the total sample becomes practically a uniform distribution when instead it is referred to the total soluble; and the distribution of ClO_4 referred to the total soluble becomes unimodal. For María Elena the histogram for the concentration of NO_3 becomes broader, and that for Cl acquires a distinctive bimodal character.

Figures 4 and 5 near here.

Figure 4.--Histograms for the concentrations of various ions in the soluble part of the ore, referred to the total soluble, for Pedro de Valdivia and María Elena.

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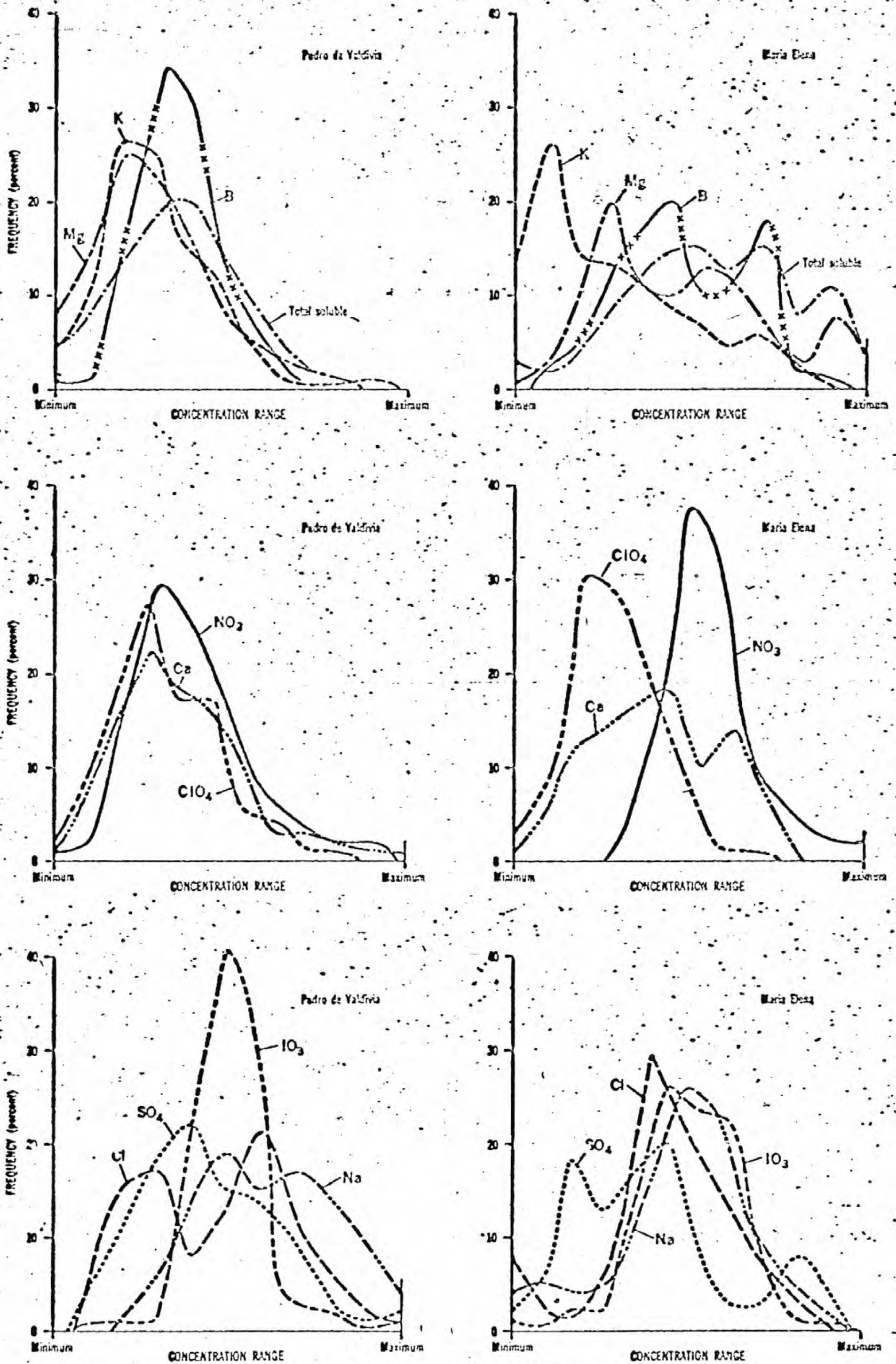

Figure 4.--Histograms for the concentrations of various ions in the soluble part of the ore, referred to the total soluble, for Pedro de Valdivia and María Elena.

Figure 5.--Histograms for the concentrations of various ions in the soluble part of the ore, referred to the total sample, for Pedro de Valdivia and María Elena.

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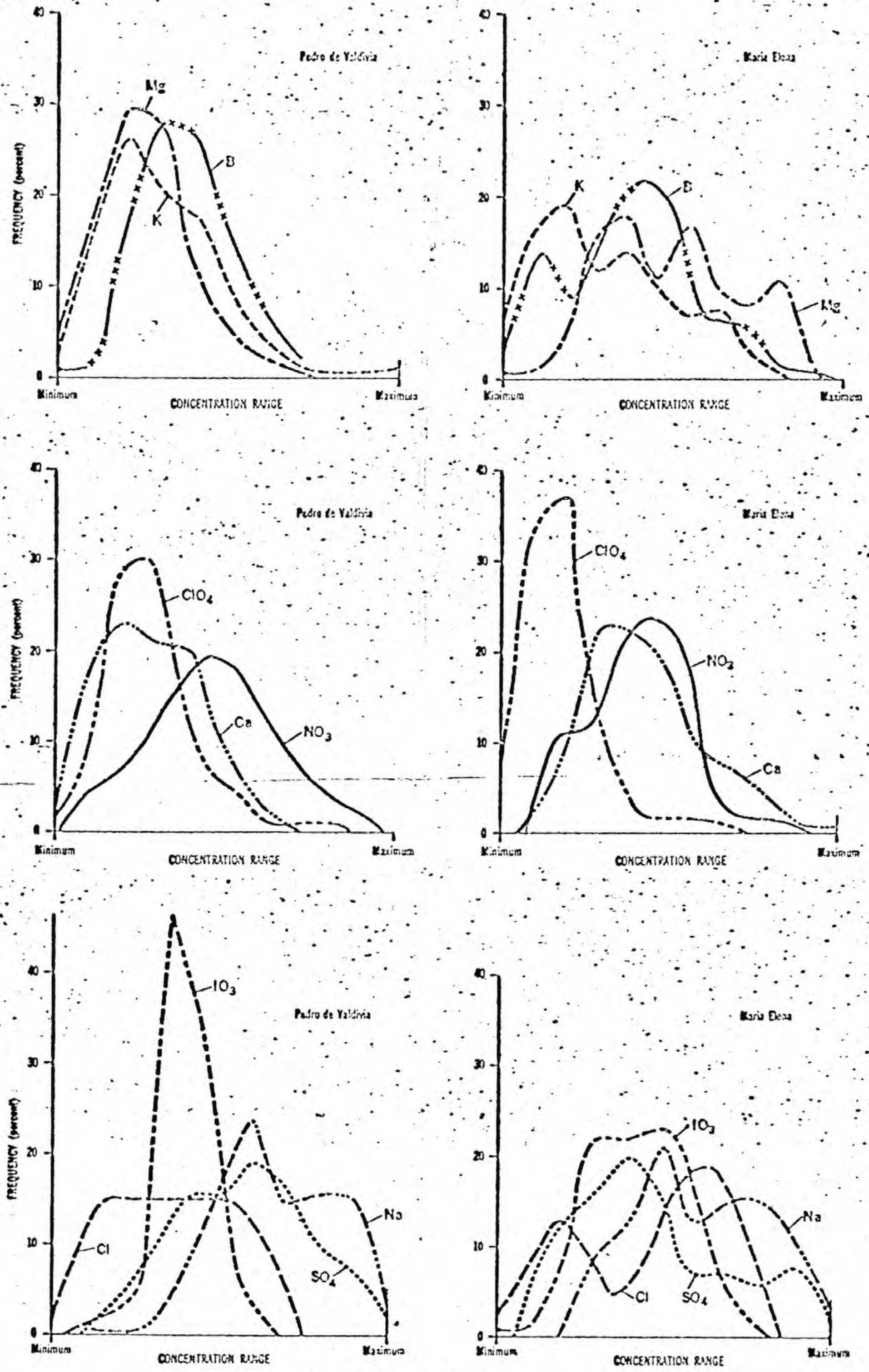

Figure 5.--Histograms for the concentrations of various ions in the soluble part of the ore, referred to the total sample, for Pedro de Valdivia and María Elena.

The above-described relationships reflect a relatively uniform ore type at Pedro de Valdivia and a much more variable type at María Elena. The variability of the soluble ratio for the María Elena ores may be related to basic differences between high-sulfate and low-sulfate ores which in turn may be due to several factors: 1) degree of leaching and secondary enrichment; 2) amount of pore space developed by the crystallization (there is no fundamental difference between the host rock of the two areas); and 3) variability in the composition of the solutions from which the nitrate ores first formed.

Time Variations of the Ion Concentrations and of the Soluble Ratio

An important issue is the role of the time of sampling--that is, the manner of variation of the concentrations of the component ions and of the soluble ratio during the period of exploitation of a given nitrate field. Such time variations should reflect both the desirability and the availability of nitrate ore of a certain grade--the Chilean nitrate deposits vary greatly in composition even over short distances, and the grade of ore sought has changed with time as a result of changes in the treatment processes and in the economics of production.

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Before examining the actual time variations observed in the Anglo-Lautaro data, we will explain first the two extreme manners of time variability which may be visualized a priori: 1) concentrations that fluctuate randomly during the exploitation, exhibiting no definite time trends, or 2) concentrations that exhibit definite trends of variation with time. A lack of a definite time trend would occur if either of the two following conditions were met: a) the ores treated at the plant are taken at random from deposits statistically uniform in composition, even though the local variations in composition may be as great as in the Chilean nitrate deposits, or b) if nearly the full range of variability is already displayed in distances which are not much greater than the average shift of the mining points from month to month. On the other hand, a definite time trend is apt to occur if either of the two following conditions is met: a) if there is zoning and regional changes of the concentration of the saline components in the ore deposits, which take place in distances greater than the month to month shift of the mining points, or b) if increasingly greater selectivity of ore grade is required by progressive changes of efficiency of the treatment process or of cost factors.

For such a study and using our computer results, we have plotted the time variations of the concentrations of NO_3, Cl, SO_4, K, and Mg and that of the percentage of solubles as indicated in Figures 6 and 7 for María Elena and Pedro de Valdivia, respectively. A comparison of the time variations of the concentrations of SO_4, Cl, and NO_3, and that of the percentage of solubles for a) María Elena and b) Pedro de Valdivia is given in Figure 8. A logarithmic scale was used for plotting the value of the quantities in order to compare the relative rather than the absolute variations. Moreover, rather than plotting the month to month averages, we have plotted only the yearly range, that is, the range from maximum to minimum value during each year. Even though the data is thus greatly condensed, this simplification has served to disclose major trends, as we shall see. Also, to facilitate the comparisons, we have calculated the correlation coefficients, Tables 8 and 9, between the c_i' and c_i, that is between the concentrations referred to the soluble part and to the total, and the percent of solubles.

Figures 6, 7 and 8 near here.

The percentage of solubles for María Elena (Figure 6) exhibit well defined trends encompassing periods of several years. The percentage of NO_3 in the total ore is much steadier, fluctuating about a mean value of 6.3 percent, than it is in the soluble part, which presents wider fluctuations as can be seen in Figure 6. The concentration of the NO_3 in the soluble part correlates negatively with the soluble ratio, a high correlation coefficient -0.863 (Table 8). Thus, the amount of NO_3 in the total ore is about constant, essentially independent of the percent of soluble material.

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Figure 6.--Time variations of the concentrations of NO_3, Cl, SO_4, K, and Mg, and that of the percent of solubles for María Elena.

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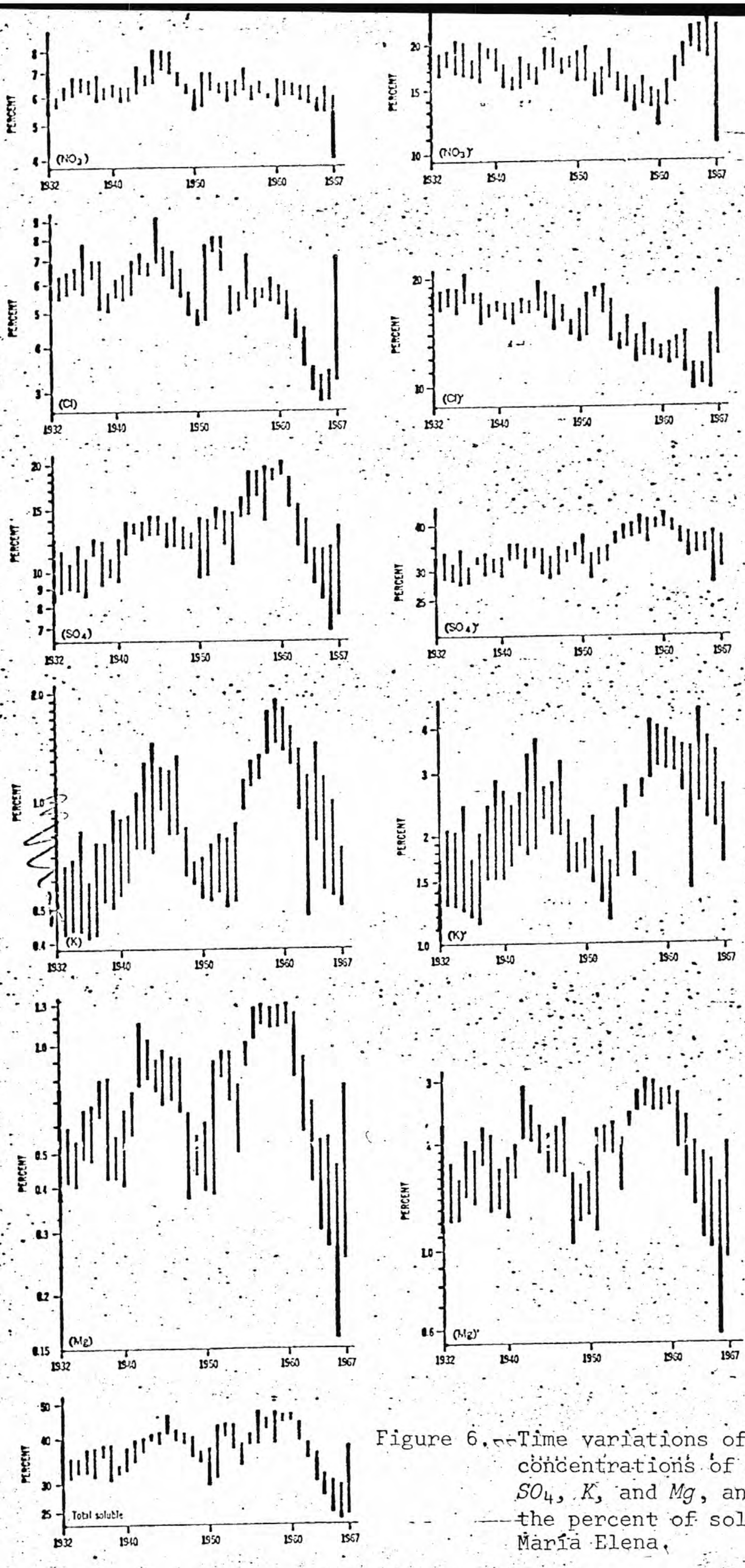

Figure 6.--Time variations of the concentrations of NO_3, Cl, SO_4, K, and Mg, and that of the percent of solubles for María Elena.

Figure 7.--Time variations of the concentrations of NO_3, Cl, SO_4, K, and Mg, and that of the percent of solubles for Pedro de Valdivia.

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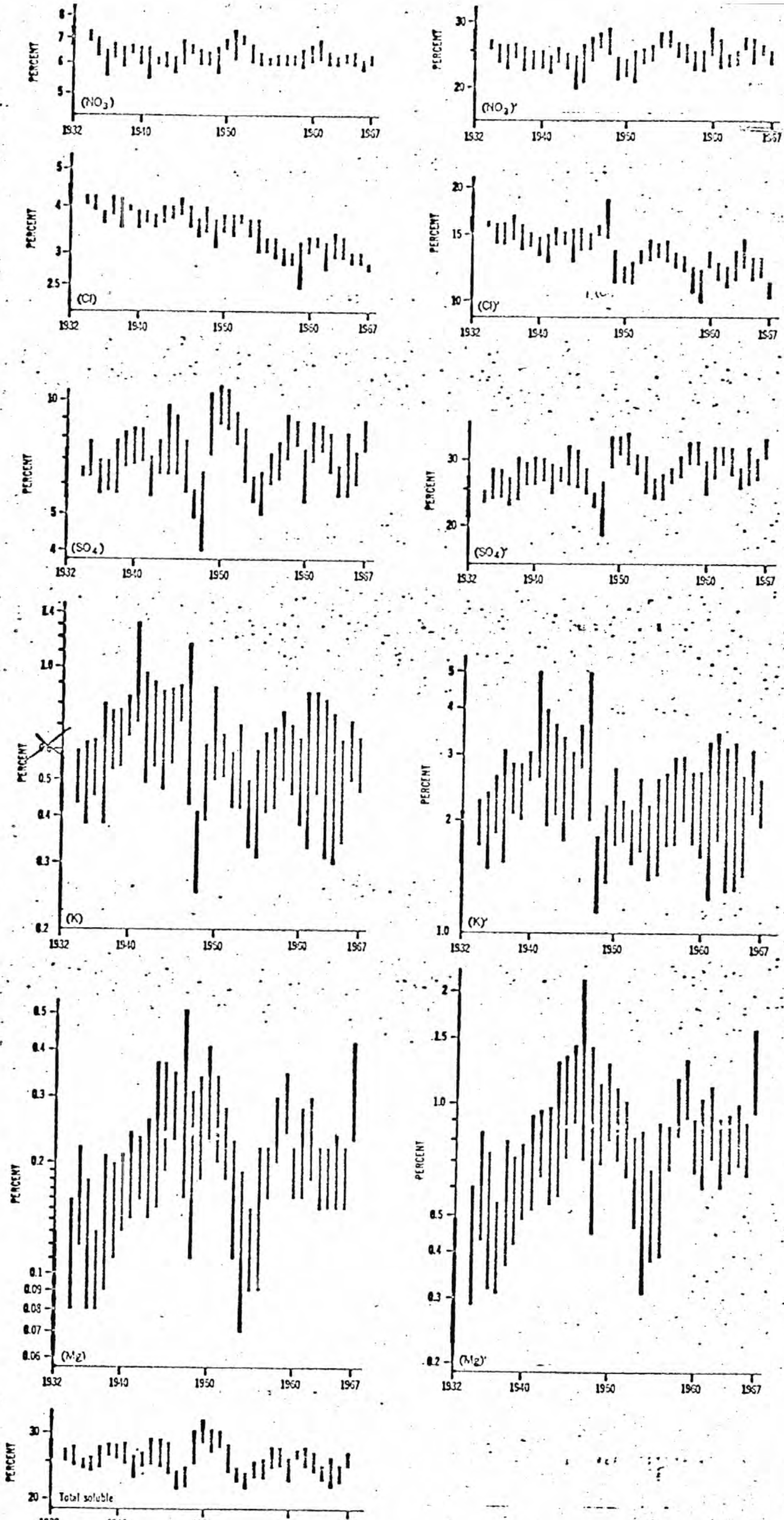

Figure 7.--Time variations of the concentrations of NO_3, Cl, SO_4, K, and Mg, and that of the precent of solubles for Pedro de Valdivia.

Figure 8.--Comparison of the time variations of the concentrations of SO_4, Cl, and NO_3, and that of the percent of solubles for a) María Elena, and b) Pedro de Valdivia.

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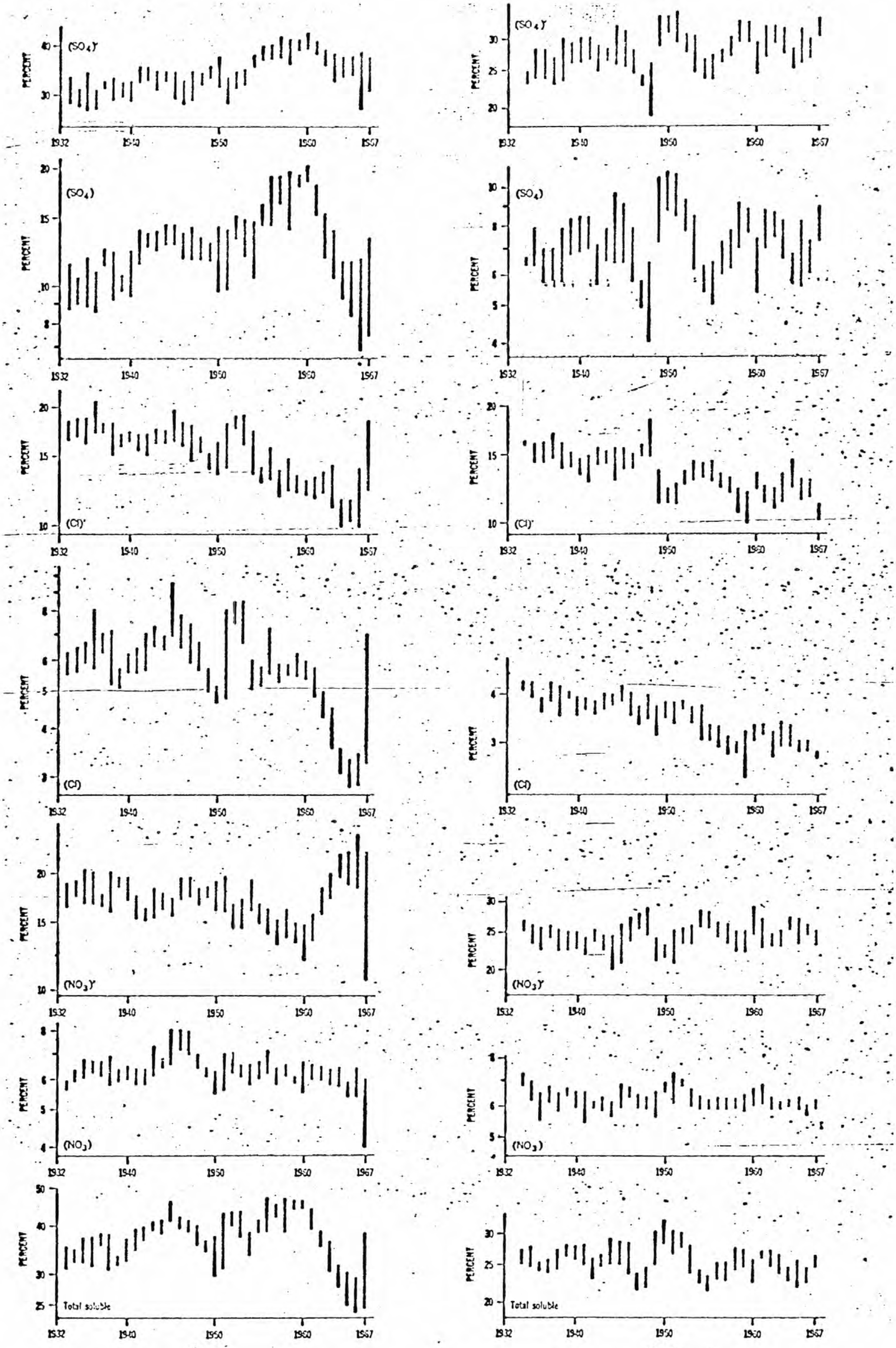

(a) (b)

Figure 8.--Comparison of the time variations of the concentrations of SO_4, Cl, and NO_3, and that of the percent of solubles for a) María Elena, and b) Pedro de Valdivia.

Table 8.--Correlation coefficients between the c_i''s and b/M

Concentration	Ion	M.E.	P.V.
c_{10}'	H_2O	-0.738	-0.508
c_1'	NO_3	-0.863	-0.752
c_2'	Cl	+0.054	-0.268
c_3'	SO_4	+0.530	+0.608
c_4'	Mg	+0.830	+0.123
c_5'	Ca	-0.013	+0.163
c_6'	K	+0.241	+0.007
c_{17}'	B_5O_9	-0.417	-0.409
c_8'	ClO_4	-0.597	-0.099
c_9'	IO_3	-0.748	-0.474
c_{18}'	Na	-0.383	-0.119

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Table 9.--Correlation coefficients between c_i and b/M

Concentration	Ion	M.E.	P.V.
c_{10}	H_2O	-0.370	+0.018
c_1	NO_3	+0.435	+0.503
c_2	Cl	+0.652	+0.386
c_3	SO_4	+0.897	+0.862
c_4	Mg	+0.914	+0.359
c_5	Ca	+0.694	+0.519
c_6	K	+0.621	+0.280
c_{17}	B_5O_9	+0.441	+0.030
c_8	ClO_4	-0.024	+0.154
c_9	IO_3	-0.152	+0.071
c_{18}	Na	+0.857	+0.734

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The percentage of Cl referred to the total ore for María Elena (Figure 6), that is c_2, fluctuates in accordance with the soluble ratio; but, when referred to the soluble part, that is c_2', the fluctuations are much smaller. Moreover, c_2' exhibits an almost linear downward trend, decreasing from about 18 percent in 1932 to about 11 percent in 1966. The value for 1967, the last year in the data, seems to be anomalous in that there is a sudden departure from the distinct trends of previous years. The small influence of the soluble ratio on c_2' is indicated by the very low correlation coefficient, namely +0.054.

The percentage of SO_4 referred to the total ore for María Elena (Figure 6), that is c_3, fluctuates in the same manner as the soluble ratio, but its percentage fluctuations are much greater than when the percentage of SO_4 is referred to the soluble part. In the latter case a trend of gradually increasing values can be distinguished ranging from about 30 percent in 1932 to about 36 percent in 1966. However, c_3' still exhibits a significant correlation of +0.530 with the soluble ratio.

The percentage of K referred to the total ore for María Elena, that is c_6, fluctuates in accordance with the percentage of solubles (correlation coefficient 0.621); but, when referred to the soluble part, that is c_6', the correlation with the percentage of solubles is lower (0.241) and the range of fluctuation is about the same.

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The percentage of Mg, both when referred to the total ore and to the soluble part for María Elena, fluctuates in excellent accordance with the percentage of solubles (correlation coefficients 0.914 and 0.830, respectively). However, the range of fluctuation is decreased when the percentage is referred to the soluble part.

The time trends for Pedro de Valdivia (Figure 7) differ somewhat from those described for María Elena. The percentage of solubles exhibits well defined fluctuations, encompassing several years, about a mean value of 25.5 percent. The percentage of NO_3 referred to the total ore, that is c_1, is much steadier. Its fluctuations resemble that of the soluble ratio, but are much smaller in relative values. The percentage of NO_3 referred to the soluble part, that is c_1', shows wider fluctuations than when referred to the total ore, a negative correlation, -0.752, with the soluble ratio.

The percentage of Cl referred to the total ore for Pedro de Valdivia (Figure 7), that is c_2, exhibits a well defined downward trend, from about 4.2 percent in 1932 to about 2.9 percent in 1967. When referred to the soluble part, that is c_2', the fluctuations are wider, correlating negatively (-0.268) with the soluble ratio.

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The percentage of SO_4 referred to the total ore of Pedro de Valdivia (Figure 7), that is c_3, shows wide fluctuations, that are similar but more exaggerated than the percentage fluctuations of the soluble ratio. When referred to the soluble part, c_3', on the other hand, the fluctuations are much diminished, although they still correlate positively (0.608) with the soluble ratio. The general trend of the percentage of SO_4 referred to the soluble part of the ore shows an increase from about 24 percent in 1932 to about 30 percent in 1967.

The percentage of K referred to the total ore part, for Pedro de Valdivia, that is c_6, correlates with the percentage of solubles with a coefficient of only 0.280; and very poorly (0.007) when referred to the soluble part.

The percentage of Mg referred to the total ore for Pedro de Valdivia, that is c_4, fluctuates in accordance with the percentage of solubles (correlation coefficient 0.359); but the correlation is decreased (0.123) when referred to the soluble part.

The manner of these variations for the 1932-1967 period, Figure 8, can be summarized as follows:

a) The amount of NO_3 in the soluble part of the ore is such that there is almost a constant percentage in the total ore.

b) The percentage of Cl in the soluble part of the ore, both when referred to the soluble part and to the total ore, exhibits a downward trend throughout the period.

c) In María Elena the percentage of Cl, (Figure 8a) when referred to the soluble part, exhibits a steadier downward trend than when referred to the total ore.

d) In Pedro de Valdivia the percentage of Cl, (Figure 8b), when referred to the total ore, exhibits a steadier downward trend than when referred to the soluble part.

e) The concentration of SO_4 referred to the soluble part of the ore shows an upward trend throughout the period, and exhibits a steadier trend than when referred to the total ore.

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Manner of Fluctuation of the Concentrations and of the Percentage of Solubles and Their Geologic Significance

The percentage of solubles fluctuates from place to place for various reasons which we would like to elucidate. Its coefficient of variation is 0.143 for the María Elena data, and 0.080 for the Pedro de Valdivia data. A satisfactory theory about the way in which the nitrate deposits come about should explain the manner of fluctuation of the percentage of solubles, and also how the variation of this percentage influences the concentrations of the various ions.

The field observation of the nitrate deposits points to the establishment of a host rock (fractured bedrock or rock debris) and its subsequent impregnation by salines. Hence, perhaps the more important factor in the fluctuation of the percentage of solubles may be the fluctuation of the original porosity of the host rock.

If the soluble materials occupy the pores of a pre-existing rock matrix, then the porosity of that matrix sets an upper limit to the soluble ratio. However, the field inspection of the nitrate ores reveals that the saline minerals not only fill the original pore space in the host rocks and soils, but have opened additional space by the pressures exerted by their crystallization. Thus, we may consider that the percentage of solubles of the nitrate ore is determined by the following factors: 1) amount of original porosity--either in pores, cavities, or fissures--in the host material, either fractured bedrock or rock debris; 2) degree of filling of the original porosity by saline minerals; 3) relative amount of additional space which may have been pried open by forces of crystallization; 4) degree of filling of this additional porosity by saline minerals; and 5) relative amount of salines of low solubility, chiefly anhydrite and gypsum, deposited together with the more soluble salines and which contribute to the insoluble portion of the ore.

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The importance of each of these factors probably varies greatly from place to place. A visual examination of the deposits demonstrates that the original porosity was an important factor, but that often a significant amount of additional porosity was developed by forces of crystallization. For example, horizontal veins or mantos in alluvium as well as in bedrock and containing nitrate ore are widespread in some areas. The field relations indicate that the nitrate layers crystallized inside the host rock, and not on the surface of the ground. The veins occupy spaces that could not remain open without a supporting filling of material. At places, such veins parallel the bedding in gently dipping bedrock, at others they pinch out at depth to emerge again on a bedding plane nearer to the ground surface. Such features clearly indicate that the crystallizing salts were able to lift the overburden. Many veins consist of isolated fragments of rock in a saline matrix, the relative positions of the fragments showing that they once were an original coherent rock mass that was pushed apart by the saline material as it crystallized in fractures.

The fluctuations of the chemical concentrations of the various substances in the water-soluble salines is even more difficult to explain. They are probably controlled by a complex set of factors different from those determining the fluctuation of the original porosity. If these two sets of factors were independent of each other, then the fluctuation of the concentrations in the soluble part should correlate poorly with the fluctuation of the percentage of solubles. Our computations of the correlation coefficients (Table 8) allows us to check the validity of such a condition. The correlation coefficient between a) concentration referred to soluble and b) percentage of solubles is positive and high only for SO_4 and Mg in María Elena, and SO_4 in Pedro de Valdivia. This suggests that a mineral having the SO_4 ion is instrumental in increasing the matrix porosity by its forces of crystallization. There is a marked contrast between the María Elena and Pedro de Valdivia data for the correlation coefficient between ion concentration and percentage of solubles for Mg referred to the soluble part, that is c_4'. In María Elena the correlation coefficient is +0.830, very high and positive, whereas in Pedro de Valdivia it is low, namely +0.123.

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That is, in principle we could view the formation of a nitrate deposit as involving the following three constructional steps:

1) establishment of a host material, either fractured bedrock or rock detritus,
2) establishment of soluble salines, that will constitute the 'input', and
3) 'blending' of the rock and soluble salines.

As used here, the work 'input' denotes a contribution of something put in, and the word 'blending' denotes the bringing together or bringing forth together two kinds of contributions. The 'input of rock-detritus' could denote an actual influx of detritus taking place simultaneously with the input of saline material, or pari passu with it; or it may denote a pre-existing layer of detrital material which is later permeated by saline-rich fluids.

Correlation analyses of ionic abundances

In this section, as yet incomplete, the results of the correlation analyses will be presented, which will provide the background for the subsequent section on the mineralogy. Tables 10 to 18 that follow will form part of this section, and maybe others, as required.

Table 10.--Correlation matrix of the c_i values

(soluble part and insoluble part = 100 percent)

for María Elena

	c_{10} (H_2O)	c_1 (NO_3)	c_2 (Cl)	c_3 (SO_4)	c_4 (Mg)	c_5 (Ca)	c_6 (K)	c_7 (B)	c_8 (ClO_4)	c_9 (IO_3)	c_{18} (Na)
H_2O	1	-.160	-.299	-.307	-.322	-.397	-.128	-.278	.133	-.028	-.287
NO_3		1	.563	.121	.258	.145	.147	.445	.153	.178	.539
Cl			1	.268	.454	.276	-.041	.737	-.216	.177	.865
SO_4				1	.915	.738	.780	.126	.048	-.315	.593
Mg					1	.610	.727	.267	.039	-.158	.678
Ca						1	.483	.141	.030	-.379	.330
K							1	-.049	.187	-.204	.251
B								1	-.261	.290	.630
ClO_4									1	-.105	-.144
IO_3										1	.057
Na											1

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Table 11.--Correlation matrix of the c_i values (soluble part and insoluble part = 100 percent) for Pedro de Valdivia

	c_{10}	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9	c_{18}
	(H_2O)	(NO_3)	(Cl)	(SO_4)	(Mg)	(Ca)	(K)	(B)	(ClO_4)	(IO_3)	(Na)
H_2O	1	.258	.133	-.078	-.006	-.100	-.288	-.221	.166	-.058	.144
NO_3		1	.513	.123	-.007	-.060	-.115	-.191	.360	.232	.647
Cl			1	-.096	-.209	-.355	.174	-.237	.461	.098	.730
SO_4				1	.516	.772	.244	.122	-.103	-.025	.374
Mg					1	.473	.238	.175	.063	.070	-.134
Ca						1	.144	.051	-.191	-.044	-.145
K							1	.179	-.026	.008	.003
B								1	-.026	.065	-.091
ClO_4									1	.112	.306
IO_3										1	.087
Na											1

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Table 12.--Correlation matrix of the c'_i values

(components in soluble part = 100 percent)

for María Elena

	c'_1	c'_2	c'_3	c'_4	c'_5	c'_6	c'_7	c'_8	c'_9	c'_{18}
	(NO_3)	(Cl)	(SO_4)	(Mg)	(Ca)	(K)	(B)	(ClO_4)	(IO_3)	(Na)
c'_1	1	.040	-.677	-.792	-.101	-.204	.413	.632	.717	.427
c'_2		1	-.759	-.139	-.321	-.724	.533	-.318	.125	.687
c'_3			1	.635	.316	.651	-.699	-.172	-.573	-.796
c'_4				1	-.090	.417	-.479	-.443	-.595	-.521
c'_5					1	.087	-.229	.059	-.256	-.673
c'_6						1	-.464	.118	-.209	-.699
c'_7							1	.015	.492	.582
c'_8								1	.428	.020
c'_9									1	.472
c'_{18}										1

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Table 13--Correlation matrix of the c'_i values (components soluble part = 100 percent) for Pedro de Valdivia

	c'_1	c'_2	c'_3	c'_4	c'_5	c'_6	c'_7	c'_8	c'_9	c'_{18}
	(NO_3)	(Cl)	(SO_4)	(Mg)	(Ca)	(K)	(B)	(ClO_4)	(IO_3)	(Na)
c'_1	1	.449	-.825	-.211	-.389	-.216	.168	.298	.485	.379
c'_2		1	-.864	-.370	-.715	.055	-.126	.473	.187	.708
c'_3			1	.370	.680	.024	-.111	-.456	-.401	-.652
c'_4				1	.326	.174	.117	.040	.018	-.606
c'_5					1	.021	-.021	-.357	-.140	-.901
c'_6						1	.130	-.048	-.034	-.335
c'_7							1	.028	.256	-.103
c'_8								1	.163	.298
c'_9									1	.082
c'_{18}										1

Table 14.--Significant correlations between the c'_i values, (components in soluble part = 100 percent), for María Elena. Positive correlations shown above main diagonal, and negative, below

	c'_1 (NO_3)	c'_2 (Cl)	c'_3 (SO_4)	c'_4 (Mg)	c'_5 (Ca)	c'_6 (K)	c'_7 (B)	c'_8 (ClO_4)	c'_9 (IO_3)	c'_{18} (Na)
c'_1	1						.413	.632	.717	.427
c'_2		1					.533			.687
c'_3	-.677	-.759	1	.635	.316	.651				
c'_4	-.792			1		.417				
c'_5		-.321			1					
c'_6	-.204	-.724				1				
c'_7			-.699	-.479	-.229	-.464	1		.492	.582
c'_8			-.172	-.443				1	.428	
c'_9			-.573	-.595	-.256	-.209			1	.472
c'_{18}			-.796	-.521	-.673	-.699				1

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Table 15.--Significant correlations between the c'_i values, (components in soluble part = 100 percent), for Pedro de Valdivia. Positive correlations shown above main diagonal, and negative, below

	c'_1	c'_2	c'_3	c'_4	c'_5	c'_6	c'_7	c'_8	c'_9	c'_{18}
	(NO_3)	(Cl)	(SO_4)	(Mg)	(Ca)	(K)	(B)	(ClO_4)	(IO_3)	(Na)
c'_1	1	.449					.168	.298	.485	.379
c'_2		1						.473	.187	.708
c'_3	-.825	-.864	1	.370	.680					
c'_4	-.211	-.370		1	.326	.174				
c'_5	-.389	-.715			1					
c'_6	-.216					1				.335
c'_7							1		.256	
c'_8			-.456		-.357			1		.298
c'_9			-.401						1	
c'_{18}			-.652	-.606	-.901	-.335				1

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Table 16.--Non-significant correlations between the c_i' values, (components in soluble part = 100 percent), for María Elena

	c_1' (NO_3)	c_2' (Cl)	c_3' (SO_4)	c_4' (Mg)	c_5' (Ca)	c_6' (K)	c_7' (B)	c_8' (ClO_4)	c_9' (IO_3)	c_{18}' (Na)
c_1'	1	--			--					
c_2'		1		--					--	
c_3'			1							
c_4'				1	--					
c_5'					1	--		--		
c_6'						1		--		
c_7'							1	--		
c_8'								1		--
c_9'									1	
c_{18}'										1

NOTE: The non-significant correlations are denoted by the double dash symbols.

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Table 17.--Non-significant correlations between the c'_i values, (components in soluble part = 100 percent), for Pedro de Valdivia

	c'_1	c'_2	c'_3	c'_4	c'_5	c'_6	c'_7	c'_8	c'_9	c'_{18}
	(NO_3)	(Cl)	(SO_4)	(Mg)	(Ca)	(K)	(B)	(ClO_4)	(IO_3)	(Na)
c'_1	1									
c'_2		1					--			
c'_3			1			--	--			
c'_4				1			--	--	--	
c'_5					1	--	--		--	
c'_6						1	--	--	--	
c'_7							1	--		--
c'_8								1	--	
c'_9									1	--
c'_{18}										1

NOTE: The non-significant correlations are denoted by double dash symbols.

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Table 18.--Interrelations between ions chemically determined and minerals to be considered

Minerals to be considered	Ions chemically determined									
	NO_3	Cl	SO_4	IO_3	ClO_4	B_5O_9	Na	K	Ca	Mg
$NaCl$		×					×			
KCl		×						×		
$NaNO_3$	×						×			
KNO_3	×							×		
$Na_3(NO_3)(SO_4)\cdot H_2O$	×		×				×			
$K_3Na_7Mg_2(SO_4)_6(NO_3)_2\cdot H_2O$	×		×				×	×		×
Na_2SO_4			×				×			
$CaSO_4$			×						×	
$2CaSO_4\cdot(H_2O)$			×						×	
$CaSO_4\cdot 2H_2O$			×						×	
$MgSO_4\cdot H_2O$			×							×
$MgSO_4\cdot 7H_2O$			×							×
$Na_2Ca(SO_4)_2$			×				×		×	
$Na_2Mg(SO_4)_2\cdot 4H_2O$			×				×			×
$K_3Na(SO_4)_2$			×				×	×		
$K_2Mg(SO_4)_2\cdot 6H_2O$			×					×		×
$Ca(IO_3)_2$				×					×	
$KClO_4$					×			×		
$NaCaB_5O_9\cdot 8H_2O$						×	×		×	
$NaCaB_5O_9\cdot 5H_2O$						×	×		×	
$CaMgB_6O_{11}\cdot 6H_2O$						×			×	×

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Correlations among the abundances of ions in the soluble part of the nitrate ore, and their mineralogical significance

Because of the complex mineralogy of the Chilean nitrate ores and of the incompleteness of the analytical data, it is not possible to make a straightforward correlation of chemical and mineralogical composition. The possible relation of each of the saline components listed in Table 4, to minerals in the soluble part of the ore, is discussed below in the light of our computer calculations of frequency distributions and correlation coefficients.

A comparison of the histograms of the component ions in the soluble parts of nitrate ores suggest relations between the ions that, as a first approximation, can be interpreted as saline mineral associations and abundances. Such discussion is particularly valuable to formulate a linear programming computer model to estimate the mineral suites that best fit the chemical analyses, which is to be discussed in a subsequent paper.

The histograms (Figures 4 and 5) show that the distributions of the components of the Pedro de Valdivia ores differ markedly from those of the María Elena ores. The components of the Pedro de Valdivia ores tend to have rather narrow ranges represented by a single peak whereas several of those in the María Elena ores have bimodal or even trimodal distributions. We believe that these differences reflect variations in the mineralogy between the two mine areas. The Pedro de Valdivia ores are probably more characteristic of normal or typical nitrate ore. The greater complexity of the María Elena ores may be attributed to two factors: 1) production of low-sulfate ore prior to 1949 and high-sulfate ores since 1949 (Figure 7), and 2) because high-sulfate ores are more complex mineralogically than the low-sulfate ores, many of the components occur in two or more minerals in them.

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The anions that dominate the saline complex of the nitrate ores are NO_3^-, Cl^-, and SO_4^{--}, and from their relative abundances the major mineral suites that may be present can most easily be guessed. The abundance of sodium, the most abundant cation, should be directly related to these three anions. The abundances of other ions (Mg^{++}, Ca^{++}, K^+, $B_5O_9^{---}$, ClO_4^-, IO_3^-), which occur in much smaller amounts, are masked by the four dominant ions, and consequently their interrelations are more uncertain, as are the mineral types in which they occur.

Nitrate (NO_3^-).--The nitrate is contained in four minerals known to exist in the ore: soda-niter ($NaNO_3$), niter (KNO_3), darapskite ($Na_3(NO_3)(SO_4)\cdot H_2O$), and humberstonite ($K_3Na_7Mg_2(SO_4)_6(NO_3)_2\cdot 6H_2O$). X-ray powder diffraction studies by Ericksen and Mrose show that soda-niter is by far the most abundant nitrate-bearing mineral, probably accounting for 80 percent or more of the nitrate in the typical ore. Darapskite is widespread, but generally is present in far smaller amounts than $NaNO_3$. Niter and humberstonite in appreciable quantities have been found only locally.

From the shapes of the histograms (Figure 5) it can be suspected that a single mineral is the chief or only source of NO_3^- in the Pedro de Valdivia samples, whereas two or more minerals are the sources in the María Elena ores. Judging from our present knowledge of the mineralogy of these ores, it is fairly certain that $NaNO_3$ is the dominant source of NO_3^- in both ores. In the María Elena ores lesser amounts of NO_3^-, as indicated by secondary peaks in the histogram, are probably supplied by darapskite, humberstonite, and niter.

The correlation coefficients shown in Tables 7 to 9 for both Pedro de Valdivia and María Elena, do not show any strong relation between NO_3^- and the other ions present. When nitrate is referred to the soluble part as 100 percent (Tables 9 and 10) there appears to be a moderately strong negative correlation between NO_3^- and SO_4^{--}; which indicates that the abundances of these two substances tend to have an inverse relation. The ores of María Elena (Table 10) also show a moderately strong negative correlation between a) Mg^{++}, ClO_4^-, and IO_3^-, and b) NO_3^- suggesting that the substances in a) are more closely associated with sulfate and other ions than they are with nitrate. Two alternate explanations for this are: 1) the minerals containing NO_3^- and one or more of these ions are rare or absent, and 2) the abundance of NO_3^- is so much greater than of these and other ions that an existing relationship is obscured. The moderately large positive correlation between NO_3^- and H_2O (Tables 9 and 10) is more difficult to explain on the basis of the present available data.

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It should be pointed out that the close association between NO_3^- and Na^+, as indicated by the known mineralogy of the nitrate deposits, is obscured in the matrix of correlation coefficients by a similar positive correlation between Na^+ with Cl^- and SO_4^{--}.

Chlorine (Cl^-).--Halite ($NaCl$) is a major constituent and the only chloride mineral that has been identified in the Chilean nitrate deposits. The Cl^- for Pedro de Valdivia clearly shows a bimodal frequency distribution (Figure 4) when its concentration is referred to the total sample, and when it is referred to total soluble it shows a very uniform distribution. On the other hand, for María Elena the histograms for the concentration of Cl^- are slightly bimodal when referred to the total sample (Figure 4), and distinctly bimodal when referred to the total soluble (Figure 5). Because it is reasonably certain that halite is the only abundant chloride mineral in the nitrate ore, we conclude that the above-mentioned bimodal distributions of the abundance of Cl^- reflect two types of ore, one relatively low in halite and the other relatively high. It can be noted from the matrix of correlation coefficients for Pedro de Valdivia (Tables 7 to 10) that Cl^- shows a moderately strong positive correlation with Na^+ which is consistent with its occurrence in a single mineral. The María Elena ores (Tables 8 to 10) also show a moderately strong correlation between Cl^- and $B_5O_9^{---}$. The reason for this correlation is not known. Tables 9 and 10 show strong negative correlation values between Cl^- and SO_4^{--} in the ores at both plants, and between Cl^- and K^+ in María Elena only. Again, this indicates that high-chloride ores tend to be relatively low in sulfate, and vice versa.

K^+ is apparently unrelated to Cl^-, suggesting that sylvite, KCl, is sparse or absent in the ores. Other ions listed in Tables 9 and 10 vary independently with regard to Cl^-, as indicated by their low correlation coefficients.

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Sulfate (SO_4^-).--The most abundant sulfate-bearing minerals of the average ore treated at Pedro de Valdivia are believed to be gypsum ($CaSO_4 \cdot 2H_2O$) and/or anhydrite ($CaSO_4$), darapskite ($Na_3(NO_3)(SO_4) \cdot H_2O$) and bloedite ($Na_2Mg(SO_4)_2 \cdot 4H_2O$). These minerals probably furnish most of the sulfate. Most nitrate ore contains little or no thenardite (Na_2SO_4), but it is possible that considerable amounts of thenardite occur in high-sulfate ores. However, some nitrate ores with a high content of SO_4^{--}, such as some of those treated at María Elena, may contain some. Other sulfate minerals present, but in unknown distribution and quantities, are humberstonite ($K_3Na_7Mg_2(SO_4)_6 \cdot (NO_3)_2 \cdot 6H_2O$), glauberite ($Na_2Ca(SO_4)_2$), epsomite ($MgSO_4 \cdot 2H_2O$), bassanite ($2CaSO_4 \cdot (H_2O)$), and kieserite ($MgSO_4 \cdot H_2O$). Humberstonite and glauberite are locally abundant, either as disseminated material in nitrate ore or as high-purity layers on top of nitrate ore.

The histograms for SO_4^{--} (Figures 4 and 5) show bimodal or trimodal forms that are believed to indicate several minerals as a source of sulfate. The correlation coefficients (Tables 9 and 10) indicate a moderately strong positive correlation between SO_4^{--} and Ca^{++} for Pedro de Valdivia ores, and between Mg^{++} and K^+ for María Elena ores. Ores of both plants show a moderately strong negative correlation between SO_4^{--} and Na^+ which is consistent with the known sparsity or absence of thenardite, $NaNO_3$, in typical nitrate ore. The sulfate is clearly related to Ca-bearing minerals such as gypsum and anhydrite at both plants, and to Mg- and K-bearing minerals such as humberstonite, epsomite, picromerite, $K_2Mg(SO_4)_2 \cdot 6H_2O$, and aphthitelite, in the high-sulfate ores of María Elena. The María Elena ores also show moderately strong negative correlations between SO_4^{--} both with B and IO_3^- for which we cannot give any explanation at present.

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Furthermore, solubility data and experimental crystallization tests by Ericksen and Mrose indicate that some of the nitrate should contain the minerals aphthitalite ($K_3Na(SO_4)_2$) and picromerite ($K_2Mg(SO_4)_2 \cdot 6H_2O$). Although these minerals have not yet been found they are included in our mineral suite for the computer model of the ore. Minor amounts of mirabilite ($Na_2SO_4 \cdot 10H_2O$) may also be present in some deposits; as it is very unstable and would dehydrate during sample preparation to thenardite; its presence would not be revealed by the chemical analyses.

Calcium (Ca^{++}).--The relatively insoluble calcium sulfate minerals gypsum and anhydrite are by far the most abundant calcium-bearing minerals of nitrate ore. They and the less abundant hemi-hydrate bassanite, probably supplied most of the Ca^{++} reported. Because of the low solubility of the $CaSO_4$ minerals, the Ca^{++} reported in the chemical analyses may represent only a fraction of the total $CaSO_4$ actually present in the ore. Relatively little calcium would be released by the far less abundant iodate and borate minerals. Glauberite provides only a little Ca^{++} because the solution of glauberite in water yields a solution of Na_2SO_4 and a residue of $CaSO_4$.

Calcium exhibits slightly asymmetrical broad histogram curves (Figures 4 and 5) that indicate a major source of gypsum and anhydrite. The asymmetry of the curve probably reflects additional calcium as supplied by iodate and borate minerals (see Table 1). For the Pedro de Valdivia ores, the correlation coefficient (Tables 9 and 10) show a moderately strong positive correlation between Ca^{++} and SO_4^{--}, and a very strong negative correlation between Ca^{++} and Na^{+}, which suggest that gypsum and anhydrite are a major source of calcium. In the María Elena ores, the correlation between Ca^{++} and Na^{+} is also negative, but there is a positive correlation between Ca^{++} and SO_4^{--}, which is small in comparison to that for Pedro de Valdivia. The concentration of Ca^{++} appears to be unrelated to concentrations of the other ions (Tables 9 and 10).

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Magnesium (Mg^{++}).--The magnesium-bearing minerals of the Chilean nitrate deposits, in contrast to the calcium-bearing minerals, are highly soluble. Hence, the weight percent of *Mg* reported should be a fairly accurate measure of the total *Mg* in the saline minerals of the ore, and furthermore this total provides a good control in determining the quantities of magnesium-bearing minerals actually present. The chief sources of the reported magnesium probably are bloedite, epsomite and humberstonite. Additional *Mg* may be yielded by kieserite, seemingly a sparse mineral in the Chilean nitrate deposits, and picromerite, a mineral that may be present though not yet identified in those deposits. Hydroboracite ($CaMgB_6O_{11}\cdot 6H_2O$), which occurs in trace amounts only, is the only relatively insoluble magnesium-bearing mineral known to exist in the Chilean nitrate deposits.

The frequency distributions of Mg^{++} are distinctly different for the ores of the two nitrate plants (Figures 4 and 5). The unimodal histograms for Mg^{++} for Pedro de Valdivia indicate a simple ore of relatively uniform content of magnesium that probably is supplied chiefly by a single mineral. In contrast, the María Elena ores show a complex trimodal distribution that probably indicates two or more types of ore and two or more minerals as the chief sources of the Mg^{++}. The correlation coefficients (Tables 9 and 10) indicate a moderate negative correlation between Mg^{++} and Na^{+} for ores of both plants and also a moderate negative correlation between Mg^{++} and IO_3^{-} for María Elena. Otherwise there seems to be little correlation between Mg^{++} and the other ions.

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The strong positive correlations of the concentration of Mg^{++} with Ca^{++}, K^{+}, and Na^{+}, are a curious feature for María Elena, (Table 8), when the concentrations referred to the total sample are considered.

It may be that Mg^{++} comes from several minerals that are not distributed uniformly, and because of the small concentration the relationships with other ions are obscure.

Potassium (K^{+}).--Like Mg^{++}, the K^{+} shows a fairly unimodal histogram for the Pedro de Valdivia ores and a trimodal one for the María Elena ores (Figures 4 and 5). Again, these curves suggest an ore of relative uniform chemical and mineralogical composition for Pedro de Valdivia, and two or more chemically mineralogically different ores for María Elena. The correlation coefficients for the Pedro de Valdivia ores (Table 9) indicate little relation between the concentration of K^{+} and that of the other ions. It is evident that the relationship of the small quantities of K^{+} is masked by the more abundant ions. The correlation coefficients for María Elena (Table 10) indicate a strong positive correlation between K^{+} and SO_4^{--}, and a strong negative correlation between K^{+} both with Cl^{-} and Na^{+}. This suggest one or more sulfate minerals as the chief sources of the K^{+}.

The minerals that apparently are the chief sources of K^+ reported in the analyses are niter and humberstonite. For the purposes of this study, we also consider that sylvite, aphthitalite and picromerite, are potential sources of some of the K^+, although they have not yet been recognized in the nitrate deposits. On the other hand, the amount of K^+ supplied by the rare minerals tarapacaite (K_2CrO_4) and lopezite ($K_2Cr_2O_7$), is insignificant, and their presence will not be allowed in the computer model.

Boron (B) or borate ($B_5O_9^{---}$).--X-ray powder diffraction studies by Ericksen and Mrose have shown that ulexite ($NaCaB_5O_9 \cdot 8H_2O$) is the most abundant boron-bearing mineral in the Chilean nitrate ores. We believe that most of the boron reported in the chemical analyses is supplied by this mineral, and lesser amounts by the other two borate minerals, namely probertite ($NaCaB_5O_9 \cdot 5H_2O$) and hydroboracite ($CaMgB_6O_{11} \cdot 6H_2O$). For the computer study we assume that the boron occurs only as the ion $B_5O_9^{---}$.

Because boron occurs chiefly or wholly in minerals that have low solubility in water, such as those above-mentioned, the amount of boron reported in the chemical analysis is only a part of the total boron in the ore. Judging from our mineralogical studies, some ores may contain several times as much boron as reported by the analyses, in others the boron reported is probably approximately equivalent to the total amount present in the ore. The frequency distributions shown by the histograms (Figures 4 and 5) are probably more indicative of the solubility of the boron minerals obtained by leaching the nitrate, rather than of the actual amount of boron present in the ore.

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Perchlorate (ClO_4^-).--The presence of the perchlorate ion in the Chilean nitrate ores is seemingly unique because, as far as we know, it does not occur naturally elsewhere in the world. It is found in all the Chilean nitrate ores. In individual ore samples it may reach several percent, much higher than the average values shown in the Anglo-Lautaro analyses.

No perchlorate-bearing mineral has been identified as yet. If such a mineral does exist, it is probably a relatively simple compound such as $KClO_4$, $NaClO_4$, $CaClO_4$ or their hydrated forms. The scant information on the solubility of perchlorate (Seidel, 1940, 1952) suggests that perchlorate crystallizing from water solutions may not form complex compounds with ions such as NO_3^-, Cl^-, and SO_4^{--}. On the other hand, substitution of ClO_4^- for NO_3^-, Cl^- or SO_4^{--} in one or more of the known minerals of the nitrate deposits is possible for the small quantities of ClO_4^- that generally are revealed by the analyses. The possibilities of substitution will be examined in terms of ionic sizes and coordination. However, such a source would be improbable for those ores reported to contain several percent ClO_4^-.

For the computer model it is assumed that the ClO_4^- occurs in a mineral having the composition $KClO_4$.

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The histograms (Figures 4 and 5) for ClO_4^- are fairly unimodal, which indicates one of the following conditions: 1) the ores of both plants have a rather uniform content of ClO_4^-, 2) the analyses of ClO_4 are too imprecise, inasmuch as the amount of ClO_4^- in the ore is of no importance in the treatment process, unless it is excessively high; or 3) the ClO_4^- occurs in a compound such as $KClO_4$ that has a low solubility. The correlation coefficients for Pedro de Valdivia ores do not show a significant correlation between the concentration of ClO_4^- and that of other ions. The coefficients for María Elena ores indicate a moderately strong positive correlation between ClO_4^- and both NO_3^- and Na^+, which may or may not be significant.

Iodate (IO_3^-).--A relatively high concentration of iodine is one of the unique features of the Chilean nitrate deposits. It occurs only as iodate ion IO_3^-. For the computer model, we assume that all the iodine in the nitrate ore is contained in the mineral lautarite ($Ca(IO_3)_2$). However, iodine may also occur in one or more calcium iodate minerals that are being studied by Ericksen and Mrose; but because of the small amounts of iodine present, it may not be possible to estimate additional quantities of iodine contained in other minerals. Furthermore, calcium iodate is a relatively insoluble mineral and the amount of iodate reported in the analyses is probably somewhat less than the total iodate in the ore, but generally this discrepancy would be expected to be small.

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The histograms for Pedro de Valdivia show relatively narrow frequency distributions for IO_3^-, and a broader unimodal distribution for María Elena. They suggest one of the following conditions: 1) the IO_3^- is contained chiefly in a single mineral that has a rather uniform distribution, 2) the IO_3^- occurs in a mineral of limited solubility and the quantity reported is a measure of solubility rather than a measure of the absolute amount of IO_3^- in the ore, or 3) the uniformity of IO_3^- content reflects an approximation of analytical results. In relation to 3) we note that only a portion of the iodine is extracted by the treatment process, so that an accurate measure of the IO_3 content may not be deemed to be necessary.

The correlation matrix for Pedro de Valdivia (Table 9) indicates that the correlations of the concentration of IO_3^- with the other ions is weak, except for a small positive relation between IO_3^- and NO_3^-, and a weak negative correlation between IO_3^- and SO_4^{--}. These relations may not be too significant. For the María Elena ores there is a strong positive correlation between IO_3^- and NO_3^-, and a moderate negative correlation between IO_3^- and both SO_4^{--} and Mg^{++}.

Sodium (Na^+).--The amount of sodium was not determined in the Anglo-Lautaro chemical analyses. Yet, it is known that Na^+ is the dominant cation, and that ordinarily it is present in sufficient quantities to more than satisfy the NO_3 to make $NaNO_3$. Numerous complete analyses of the nitrate ore have been made demonstrating that Na^+, Mg^{++}, Ca^{++}, and K^+ are the only cations that occur in nitrate ore in more than trace amounts. As previously explained, the sodium concentrations used in this have been calculated as part of our computer processing of the data.

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The sodium shows a distinctly bimodal frequency distribution in the ores treated by both plants (Figures 4 and 5). These distributions suggest that at least two types of ore characterized by different suites of *Na*-bearing minerals are present. The correlation coefficients (Tables 9 and 10) indicate a strong positive correlation between *Na* and *Cl* for ores of both plants, and a moderately strong negative correlation between *Na* and the following ions: SO_4^{--}, Mg^{++}, Ca^{++}, and K^+.

Water (H_2O).--Water occurs in the nitrate ore in three forms: as water of crystallization, as fluid inclusions in saline minerals, and as moisture. From the Anglo-Lautaro chemical data it does not seem to be possible to estimate the relative amounts of water present in each of these forms.

As a first approximation, in the second phase of this study which utilizes theoretical models, we will assume that all the water shown in the chemical analyses corresponds to water of crystallization in the soluble part of the ore. If the amount of water of crystallization required by the model calculation turns out to be smaller than that actually measured in the total sample, the balance could then be attributed to moisture in the soluble part, and to moisture and water of crystallization in the insoluble part. On the other hand, if the required amount of water of crystallization turns out to be greater than that actually measured in the total sample, then either the water loss from the hydrated minerals was incomplete during the drying process, or the amount of hydrated minerals selected by the model has to be corrected.

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The most likely sources of water of crystallization, upon heating to 110°C, are darapskite, bloedite and humberstonite, all of which become unstable at temperatures between 50° and 100°C. Some water would also be released from gypsum which starts to transform to $CaSO_4 \cdot H_2O$ at about 70°C (Zen, 1962). Other hydrated minerals that might be present in minor quantities would yield only a very small amount of water and are to be ignored in the present study.

Insoluble residue.--The insoluble residue, not reported in the Anglo-Lautaro data, consists of two types of material: 1) rock particles--rock fragments, pebbles, sand, silt, and clay--and 2) insoluble saline minerals, chiefly gypsum and anhydrite, but also small amounts of borates, iodates, and perchlorates may be present. The relative amounts of these two types of material are known to fluctuate widely.

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