

Study of the Phase Chemistry of the Salar de Atacama Brine

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ABSTRACT

In order to study the phase chemistry of the Salar de Atacama brine as it evaporates, and to determine the crystallization characteristics of potassium, magnesium and lithium salts, a complete solar evaporation sequence was made. The data came primarily from model studies employing small metal pans (1 to 3 meters in diameter) sitting on the surface of the Salar. Laboratory evaporation tests were also run. The data collected represent nearly six years of solar evaporation experiments.

The Salar de Atacama brine constitutes a complex multicom-

ponent system saturated in sodium chloride. The ions present in this brine are Na, K, Li, Mg, Ca, B, SO₄ and Cl. An Autenrieth type diagram was used to correlate all the brine data and to illustrate the changes in concentration of the components through the evaporation process. It was observed that seasonal conditions (summer and winter) largely influence the crystallization path of the potassium and magnesium salts due to the presence of lithium in the brine.

INTRODUCTION

The brines from the Salar de Atacama, (Chile) are solutions saturated in sodium chloride with a total dissolved solids content of about 28%, and an average density of 1,226 g/l (at 20°C). The elements present in this brine are Na, K, Li, Mg, Ca, B, SO₄ and Cl. Also Rb, Cs and Br can be found in a few parts per million.

The chemistry of this brine in the process of concentration by solar evaporation has been thoroughly studied for more than six years in order to define the crystallization path, and to determine the crystallization characteristics of the potassium, magnesium and lithium salts. The purpose of this particular study was to get the basic information necessary to design a process for the recovery of potassium, lithium and boric acid from the brines of the Salar de Atacama. Experimental work was done at the Salar de Atacama itself and also some tests were run in the laboratory. In this paper we present the data collected from the experiments carried out during the last three years. These experiments were done using a brine from a zone called Km-20, which is probably going to be the brine feed to the future solar ponds to be constructed on the Salar.

EXPERIMENTAL WORK

In order to know the composition of the brine over the whole Salar nucleus, a fairly extensive sampling survey was performed. It was found that the chemical composi-

tion of the brine is nearly uniform around the central nucleus (Ide, 1978). The average brine composition is shown in Table 1.

To study the phase chemistry of the Salar de Atacama brine in the solar evaporation process, five small metallic pans (1 to 3 meters diameter, and 0.4 to 0.6 meters height) were placed in an area of the Salar. Their side-walls and bottoms were not insulated.

The concentration range in each pan was defined initially by assuming a quinary system considering only the five major components of the brine: sodium, potassium, magnesium, sulfate and chloride. Using the Janecke dia-

TABLE 1
Average Brine Composition in the Nucleus of the
Salar de Atacama

Element	(g/l)
Na	93.18
K	21.95
Li	1.96
Mg	12.26
Ca	0.30
SO ₄	23.29
Cl	192.00
B	0.84
Density	1,226.

Chemical analyses showed that boron is present in this brine as borate and boric acid.

gram for this quinary system at 25°C, it was possible to design five evaporation stages, as shown in Table 2.

The evaporation process was controlled by measuring the free board of the pans. Once the desired evaporation percent (in volume) in the pans was reached, samples of the final brine and salts were taken for chemical analysis. Also the density and temperature of the brine were recorded. Then the brine was moved to a smaller pan and the salt removed. Figure 1 presents the magnesium concentration (MgCl_2 , moles/1000 moles H_2O) reached in the brine for a given volume reduction (%).

The results obtained from this projected evaporation showed that the Salar de Atacama brine behaves differently from this quinary system. Therefore, it was necessary to define a true depositional sequence in order to recover more potassium from the crystallized salts and to study the field of the double salts. For these purposes the number of evaporation stages was increased (8) for a series of summer experiments, and also the final evaporation value (%) for each stage was changed.

It was observed that the refractive index (R.I.) reading of a concentrating brine has a high degree of correlation with its magnesium ion concentration (Figure 2), and so this fact was used to monitor the evaporation process in the pans. The use of the density to control the evaporation was found inappropriate because once the brines reaches values above 1,300 g/l, the density does not

change significantly as the brine concentration increases (Figure 3).

There is a marked change in the air temperature from "summer" (September to March) to "winter" (April to August); in summer it varies approximately between 18° and 35°C, and in winter between -1° and 20°C. These changes in temperature affect the crystallization path. The chemical analyses of the evaporating brines and of the crystallized salts on the pans show that variations of temperature during day and night, and during a season, and the presence of lithium in the brine, play an important role in the composition of the salts to be obtained through the evaporation process.

The composition (in percent) of the salts that crystallize in the different evaporation stages defined by the magnesium content (R.I.), for a summer and winter run (batch), are shown in Tables 3 & 4, respectively. In the first case, the brine temperature varied between 20° and 35°C, and for winter, between 3° and 15°C.

The nature of the crystallized salts was confirmed by x-ray diffraction. In some cases it was not possible by this method to detect the magnesium salts inferred by the chemical analyses.

PHASE CHEMISTRY

The ions present in the original brine constitute a complex multi-component system that can be looked upon as a quinary system considering only sodium, potassium, magnesium, sulfate and chloride. The rest of the elements represent only a low percent of the total dissolved solids, and can be ignored.

Based on this assumption, the behavior of this brine through the evaporation process could be analyzed using the phase diagram of the above mentioned quinary system. One of the most commonly used is the Janecke diagram (Garrett, 1978), as shown in Figures 4 and 5. The curves plotted on these diagrams (crystallization path) represent a summer and winter sequence of evaporations,

TABLE 2
Projected Solar Evaporation
(Accumulative %)

Stage	NaCl	K	Mg	SO_4	H_2O (*)
First	70.50	0	0	0	56.0
Second	86.20	40.3	0	0	71.9
Third	96.40	76.9	6.5	37.2	82.9
Fourth	98.95	89.8	22.8	84.0	87.9
Fifth	99.85	99.1	35.8	89.6	92.1

(*) Evaporated water

TABLE 3
Summer Salts Composition
(Weight percent)

MgCl_2 M/1000 M H_2O	Halite	Sylvite	Carnallite	Kainite	KLiSO_4	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
5.36	—	—	—	—	—	—
11.50	98.5	1.5	0	0	0	0
21.00	75.3	24.7	0	0	0	0
27.55	67.3	25.9	0	0	6.8	0
28.44	52.4	11.0	3.9	0	31.8	0
31.83	58.7	13.3	0	4.1	24.0	0
40.10	52.1	19.3	0	0	28.6	0
48.93	21.3	0	0	67.7	0	11.0
85.41	15.1	7.7	44.2	0	0	33.0

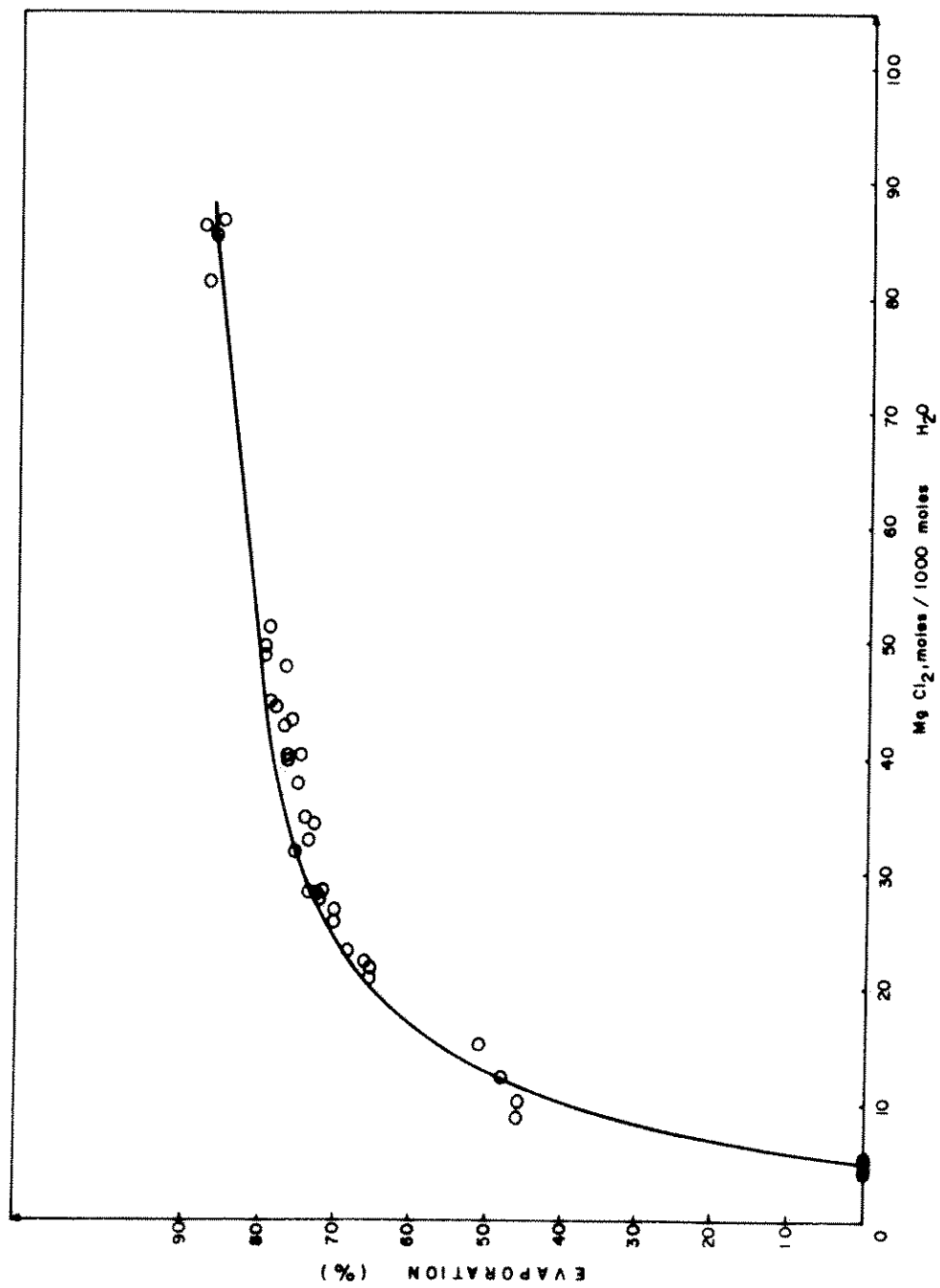


Figure 1. Brine evaporation

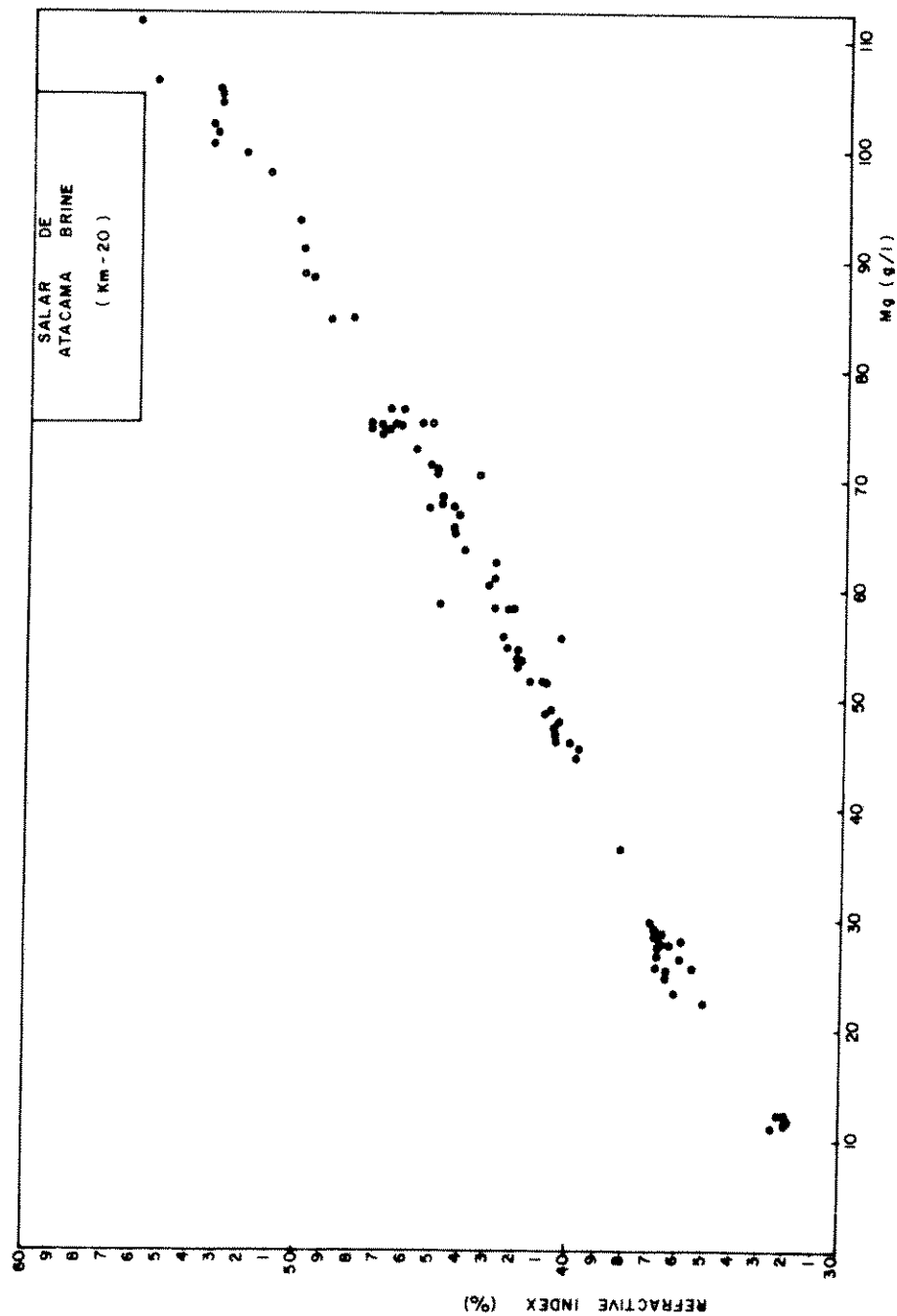


Figure 2. Correlation between magnesium concentration and refractive index.

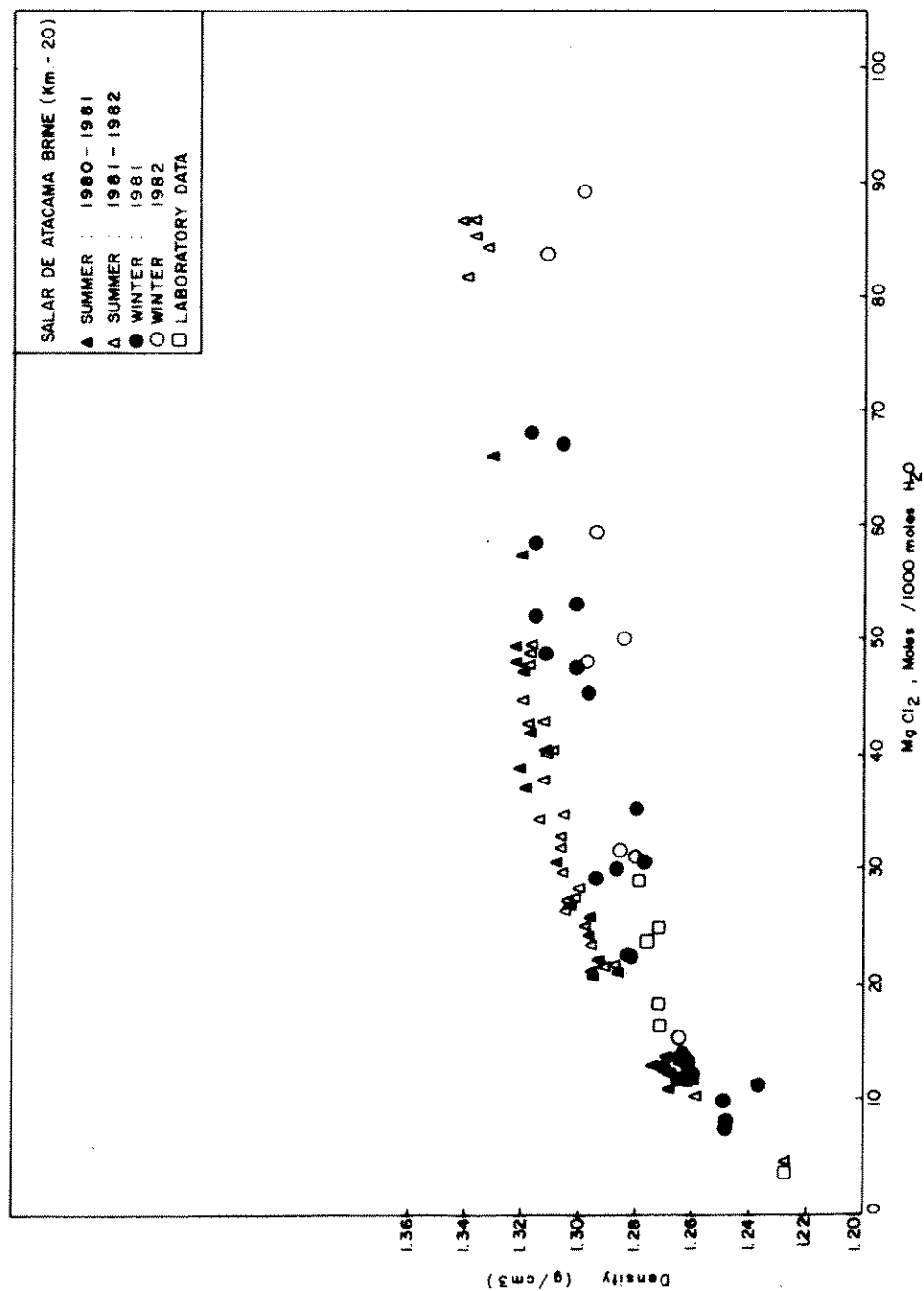


Figure 3. Density of evaporating brine

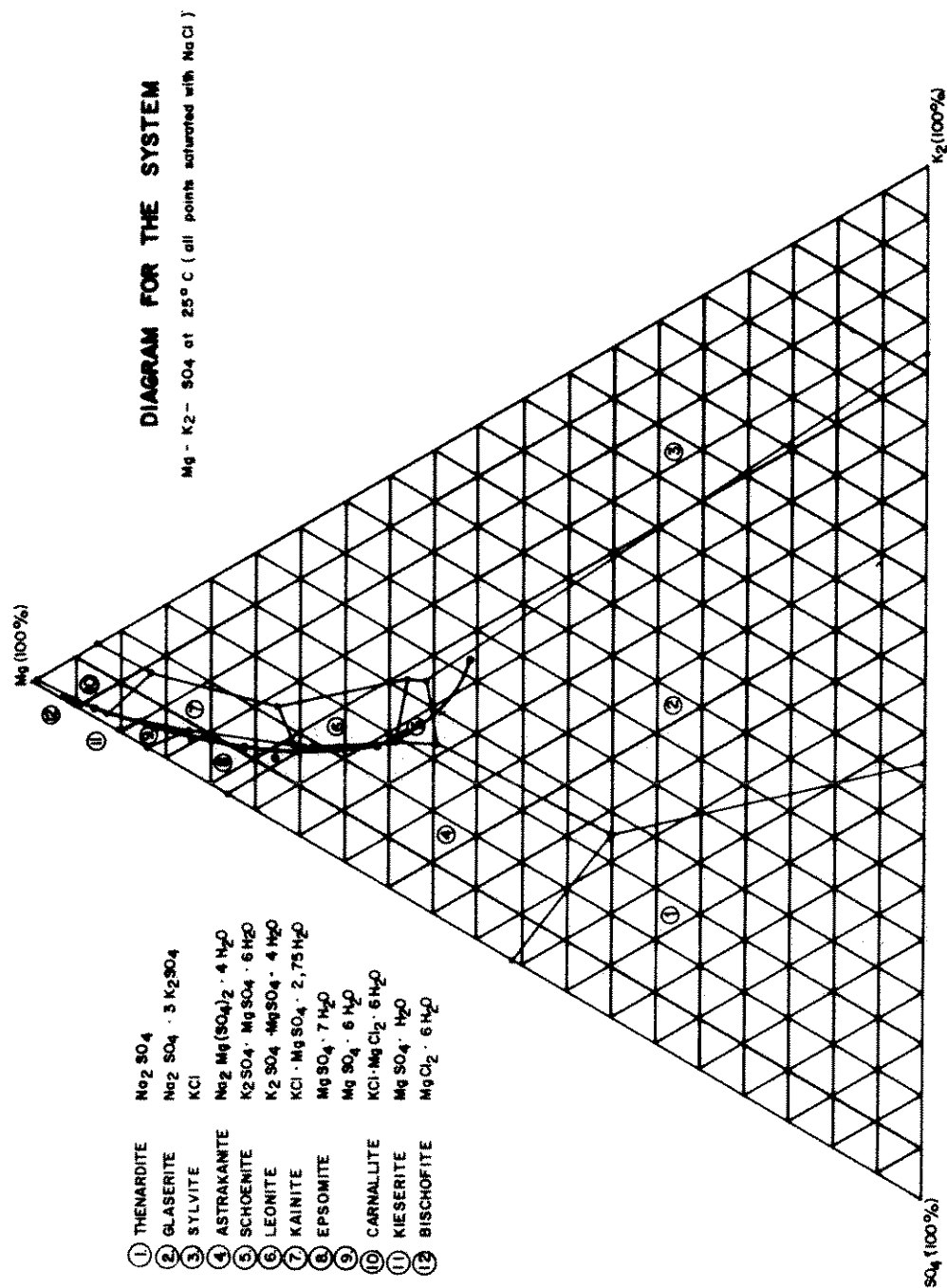


Figure 4. Solar evaporation path of Salar de Atacama brine at summer

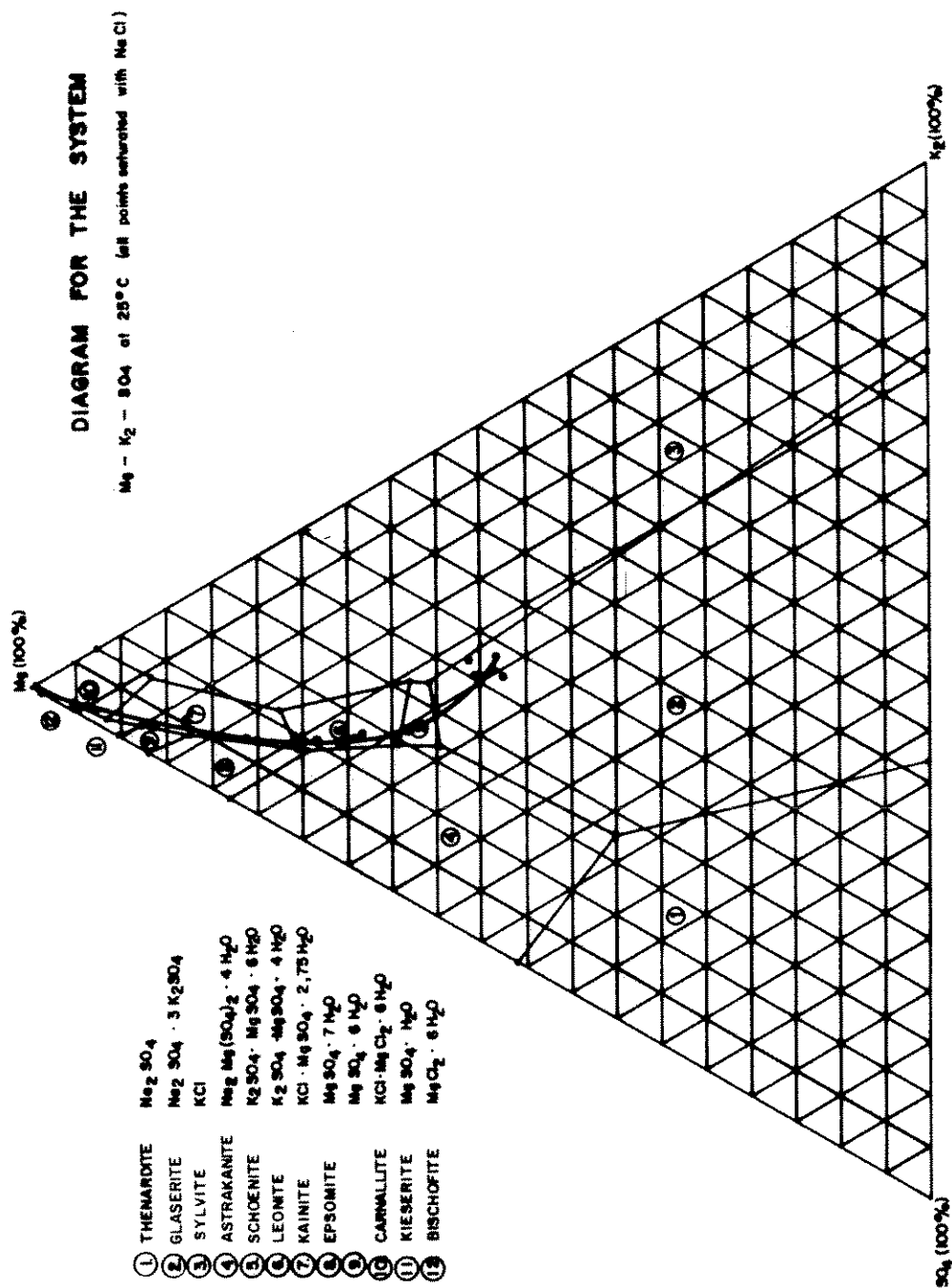


Figure 5. Solar evaporation path of Salar de Atacama brine at winter

TABLE 4
Winter Salts Composition
(Weight percent)

MgCl ₂ M/1000 M H ₂ O	Halite	Sylvite	Schoenite	Kainite	Carnallite	Li ₂ SO ₄ · H ₂ O	H ₃ BO ₃
5.36	—	—	—	—	—	—	—
9.00	100.0	0	0	0	0	0	0
30.97	59.3	22.2	17.3	0.8	0.4	0	0
49.18	32.8	2.0	14.7	47.2	3.3	0	0
58.55	15.4	0.3	9.8	26.9	47.6	0	0
89.39	9.8	7.4	0	1.3	48.0	33.5	0
107.17	16.2	8.1	0	4.1	15.4	47.2	9.0

respectively. The data for the curves are shown in Tables 5 and 6.

It is convenient to note that these curves are shown plotted on phase diagrams for experiments run at 25°C, which is not the case for the experiments run in the Salar (non-isothermal evaporations), and also the diagram does not take into account the presence of lithium. The

TABLE 5
Brine Composition—Summer
(mole %)

Mg	K ₂	SO ₄
49.2	26.9	23.8
58.0	16.2	25.8
60.8	13.1	26.1
64.7	11.1	24.2
67.9	9.6	22.5
72.1	6.8	21.1
75.6	6.7	17.7
82.4	3.0	14.5
86.9	1.6	11.5
93.2	0.4	6.4
95.6	0.3	4.1

TABLE 6
Brine Composition—Winter
(mole %)

Mg	K ₂	SO ₄
49.4	27.8	22.8
51.2	26.8	22.0
65.2	11.3	23.5
76.7	7.8	15.5
77.0	7.2	15.8
81.4	5.5	13.1
87.3	2.5	10.2
91.4	1.8	6.8
94.0	1.0	5.0
95.0	0.7	4.3
98.3	0.2	1.4

effect of this element is to displace the crystallization curve owing to the sulfate associated with lithium.

According to these diagrams, the sequence of crystallization should be: glaserite, schoenite, kainite, carnallite and bischofite, together with halite and sylvite. Neither glaserite nor bischofite were found in any of the crystallized salts; the rest of the other salts did appear through the evaporation process. Another difference with this crystallization sequence is the presence of lithium salts such as Li₂SO₄ · H₂O and KLiSO₄.

A representation of the type of salts that crystallize in winter and summer through the concentration process is given in Figure 6. Owing to changes in temperature that occur in the Salar it is not possible to define exactly the field of crystallization of these salts with these experiments.

To provide a more meaningful correlation of the phase chemistry data, an Autenrieth type diagram was used. In this diagram the concentration of the various ions in the brine have been plotted (Figures 7 to 16) as a function of the magnesium chloride concentration, for summer and winter conditions. In each brine sample, the total amount of sulfate was considered to be MgSO₄, and the residual magnesium was MgCl₂. However because Li₂SO₄ · H₂O and KLiSO₄ salts crystallize through the potash deposition sequence, the MgSO₄ are obviously merely arbitrarily defined amounts.

Water in the brine was not measured directly. To calculate it, a summation of all the components was made, and then subtracted from the measured density. The most remarkable difference between summer and winter solar evaporation is that in summer lithium precipitates earlier, in the sulfate double salts field, as KLiSO₄ salt. Another difference is that lithium reaches a lower concentration in the brine in summer (10 g/l) than in winter (14 g/l). Also schoenite does not crystallize in summer. The Autenrieth representation illustrates the different behavior of the brine in summer and winter, as well as its differences with the quinary system Na, K, Mg, SO₄, Cl₂.

For more concentrated brines, above 80 moles MgCl₂/1000 moles H₂O, in which practically no sodium or potas-

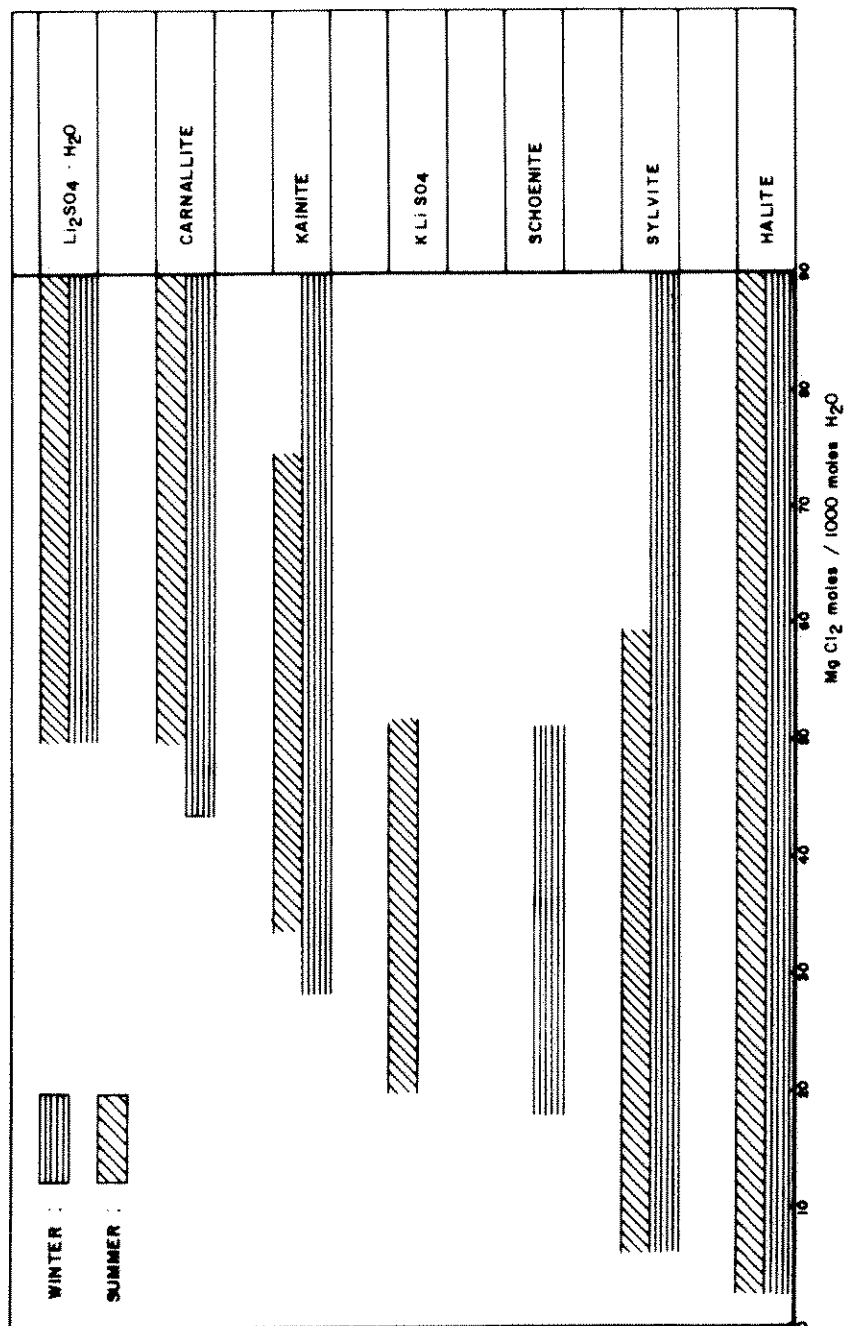


Figure 6. Typical salts crystallized in the evaporation process

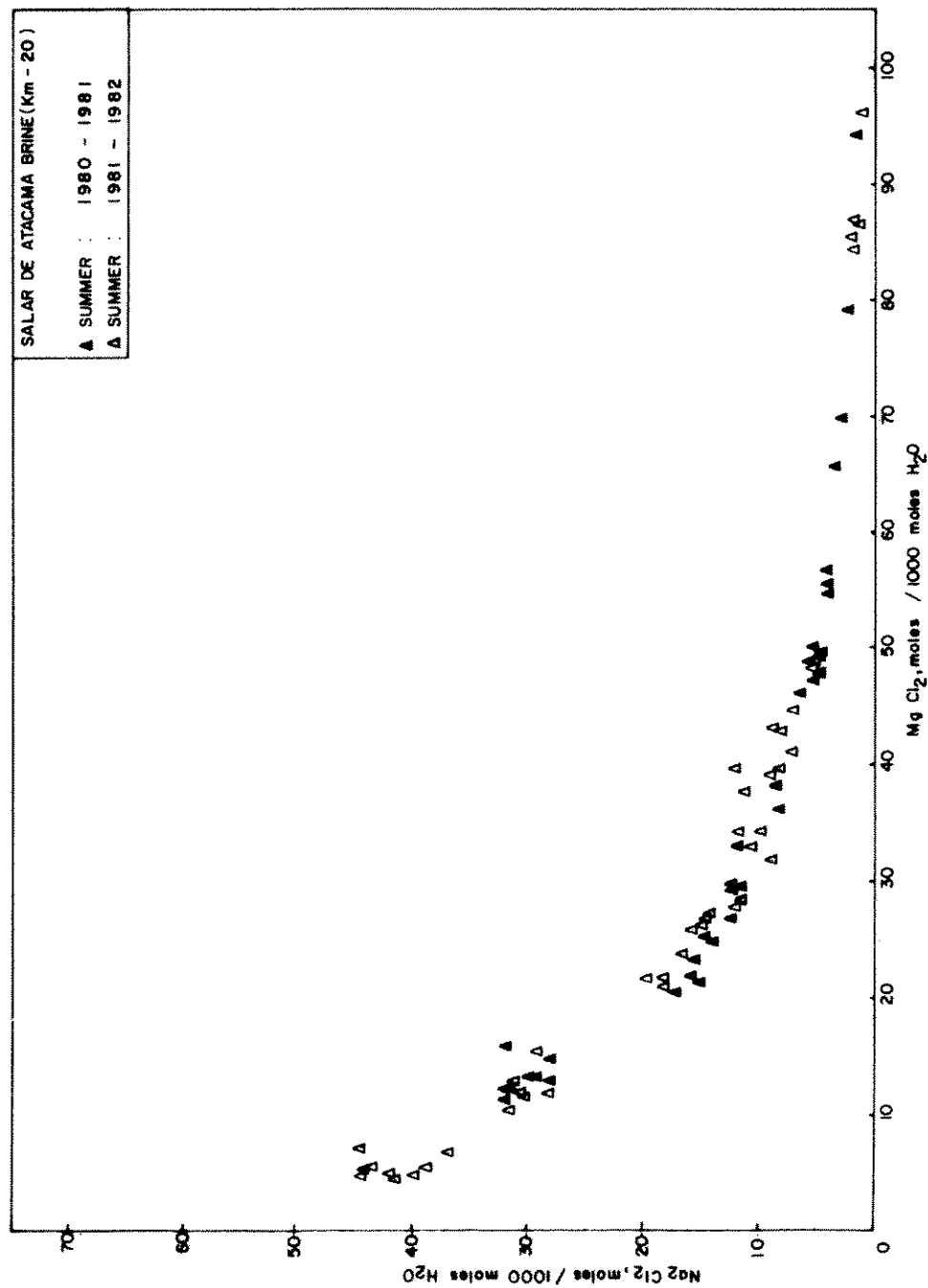


Figure 7. Sodium concentration of evaporating brine in summer

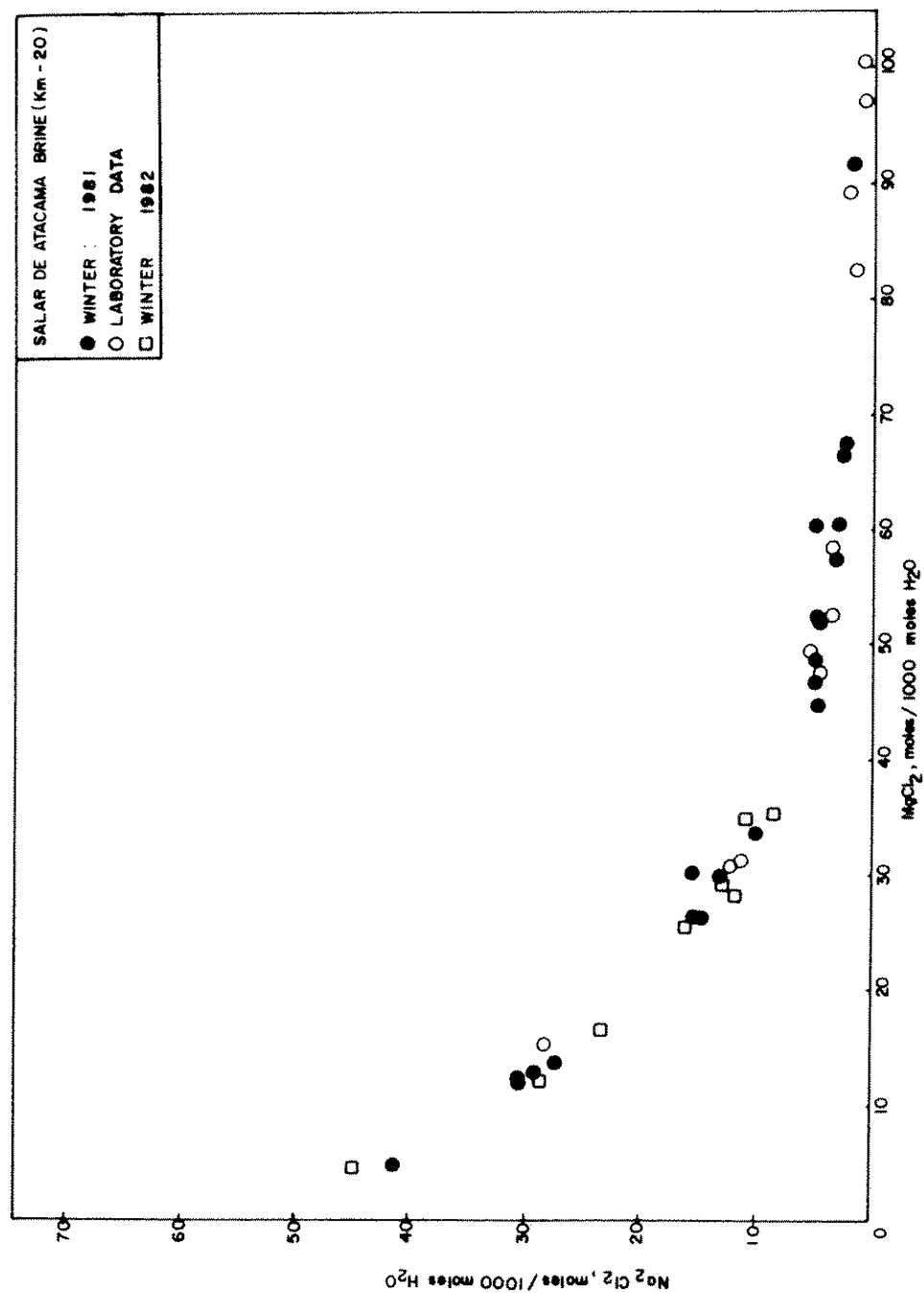
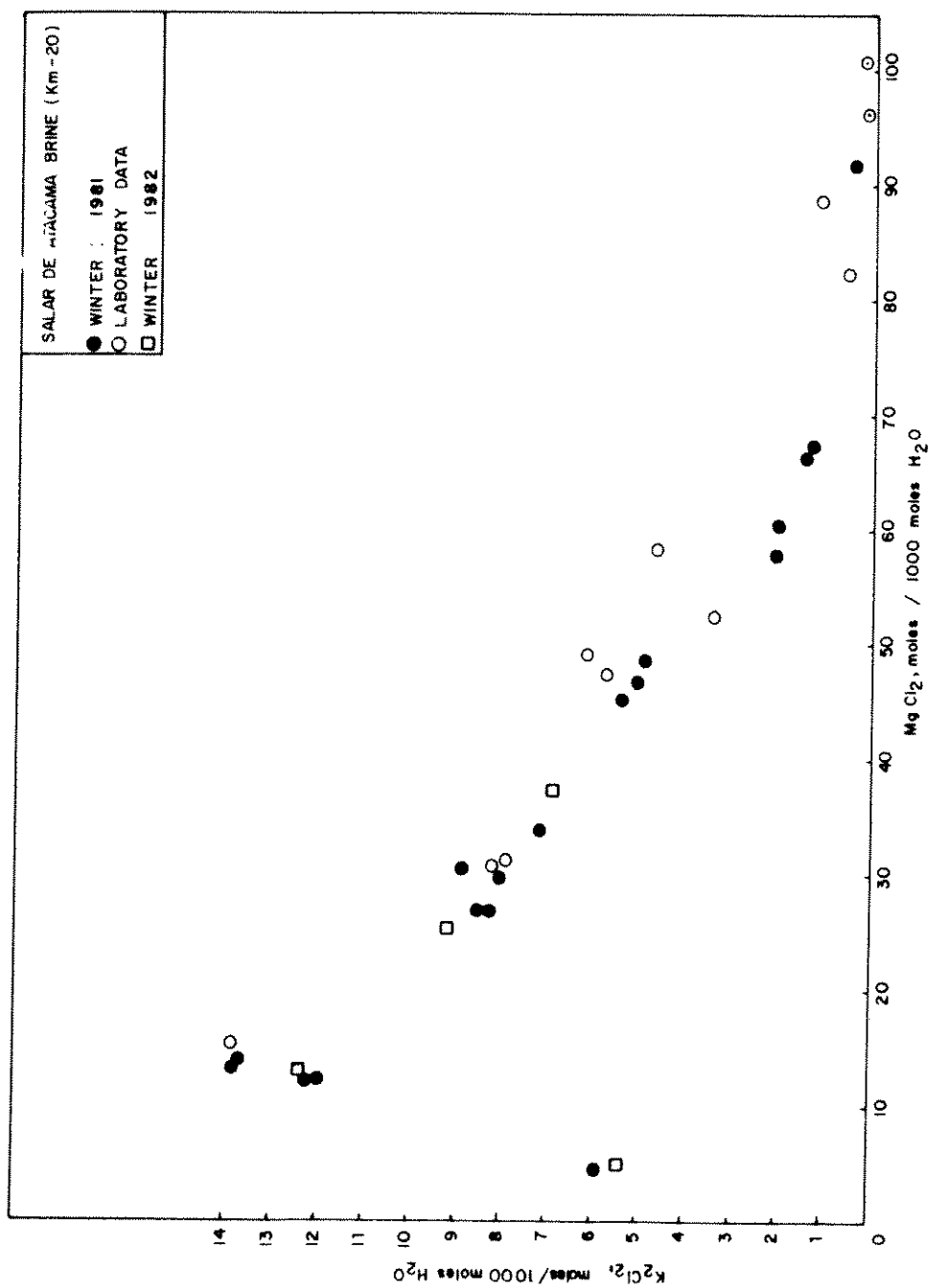


Figure 8. Sodium concentration of evaporating brine in winter



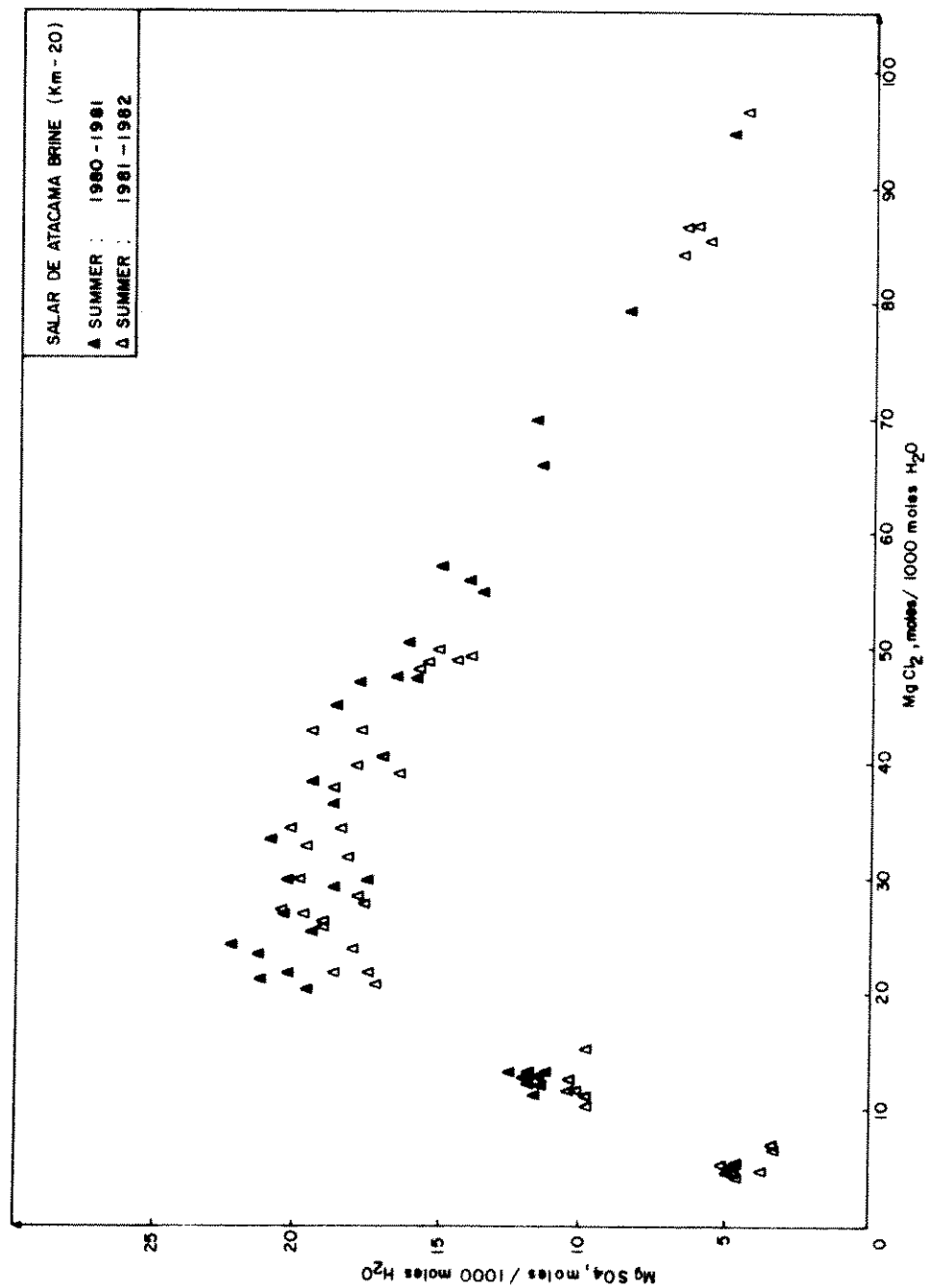


Figure 11. Sulfate concentration of evaporating brine in summer

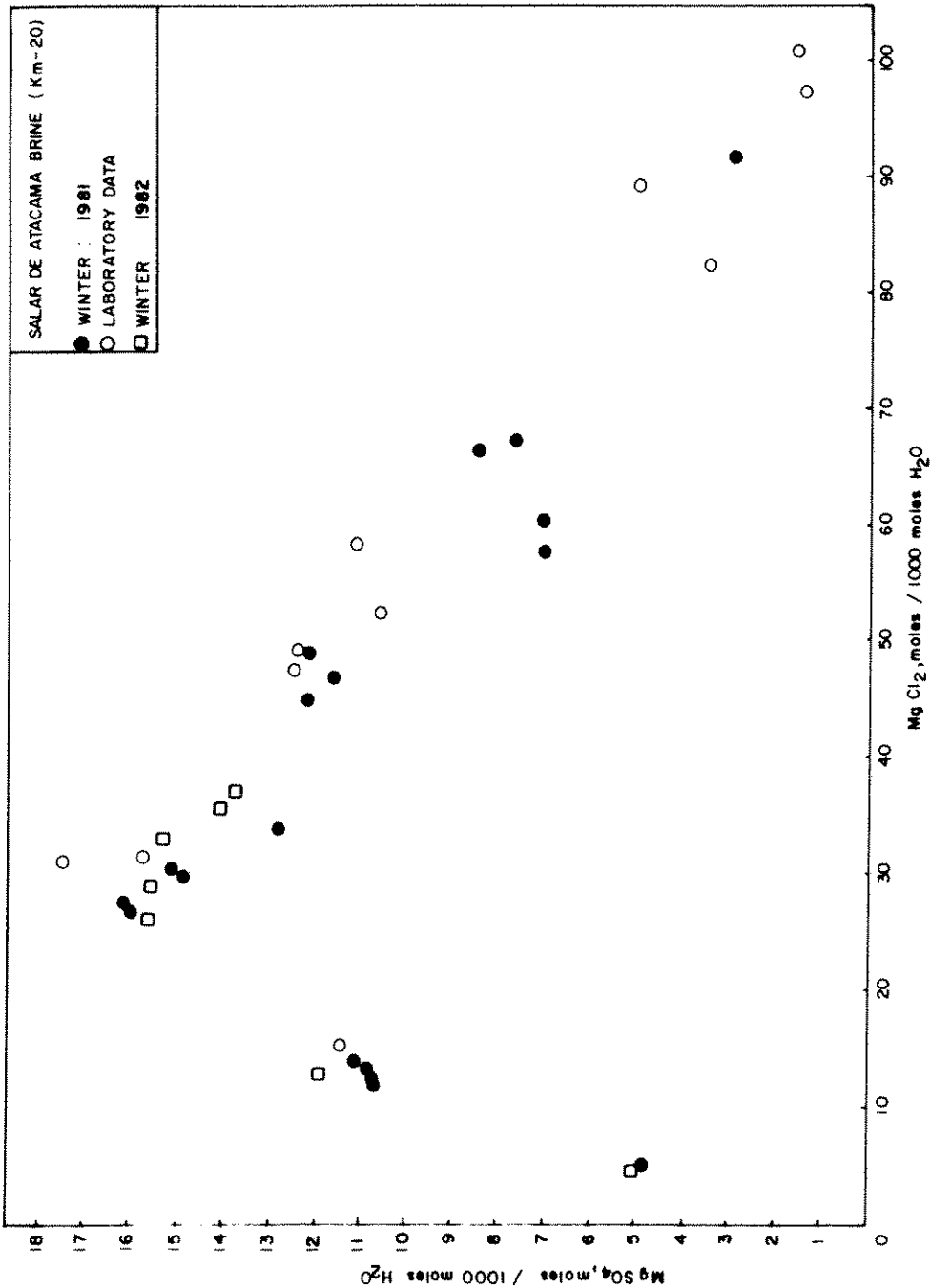


Figure 12. Sulfate concentration of evaporating brine in winter

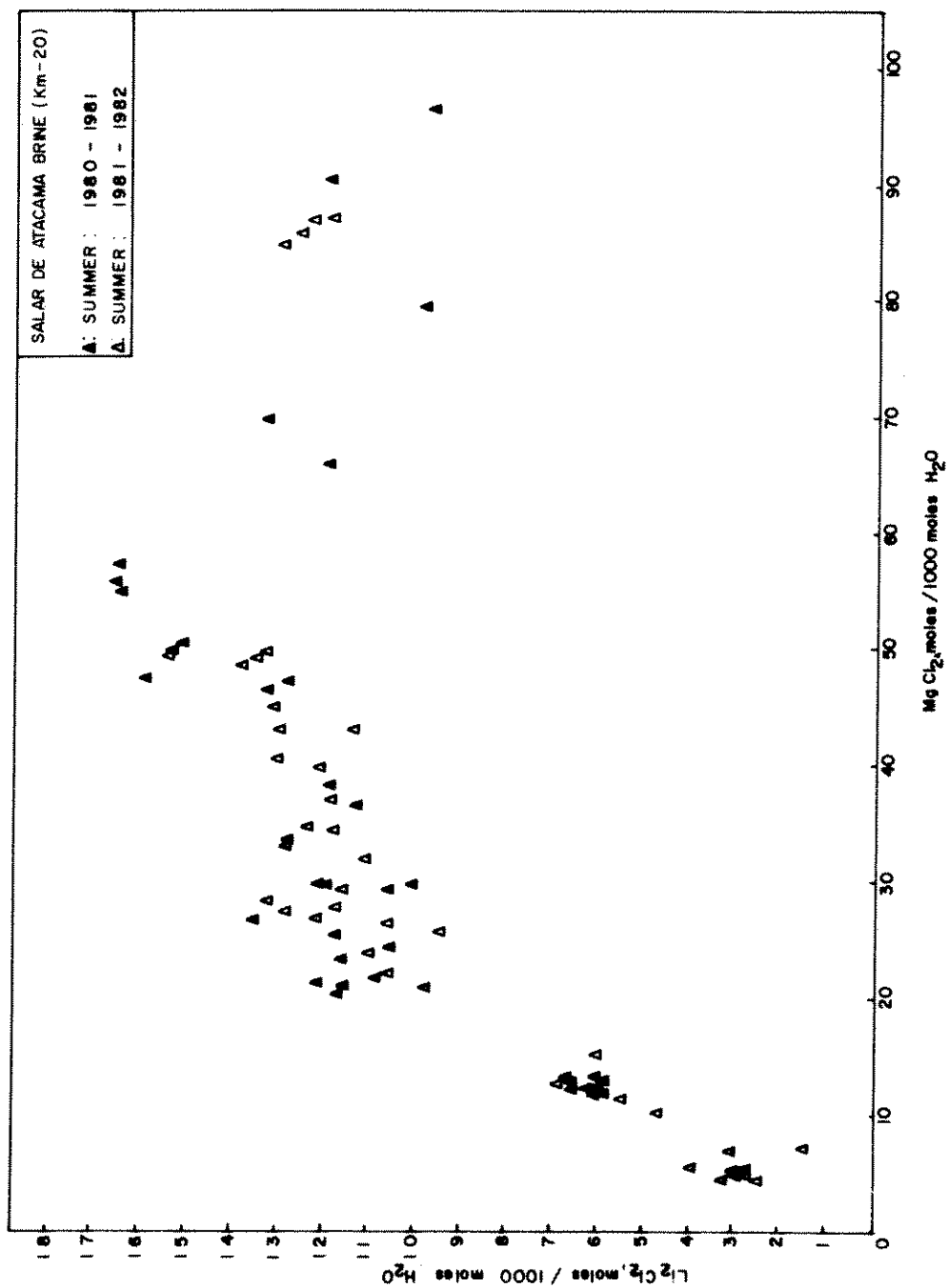


Figure 13. Lithium concentration of evaporating brine in summer

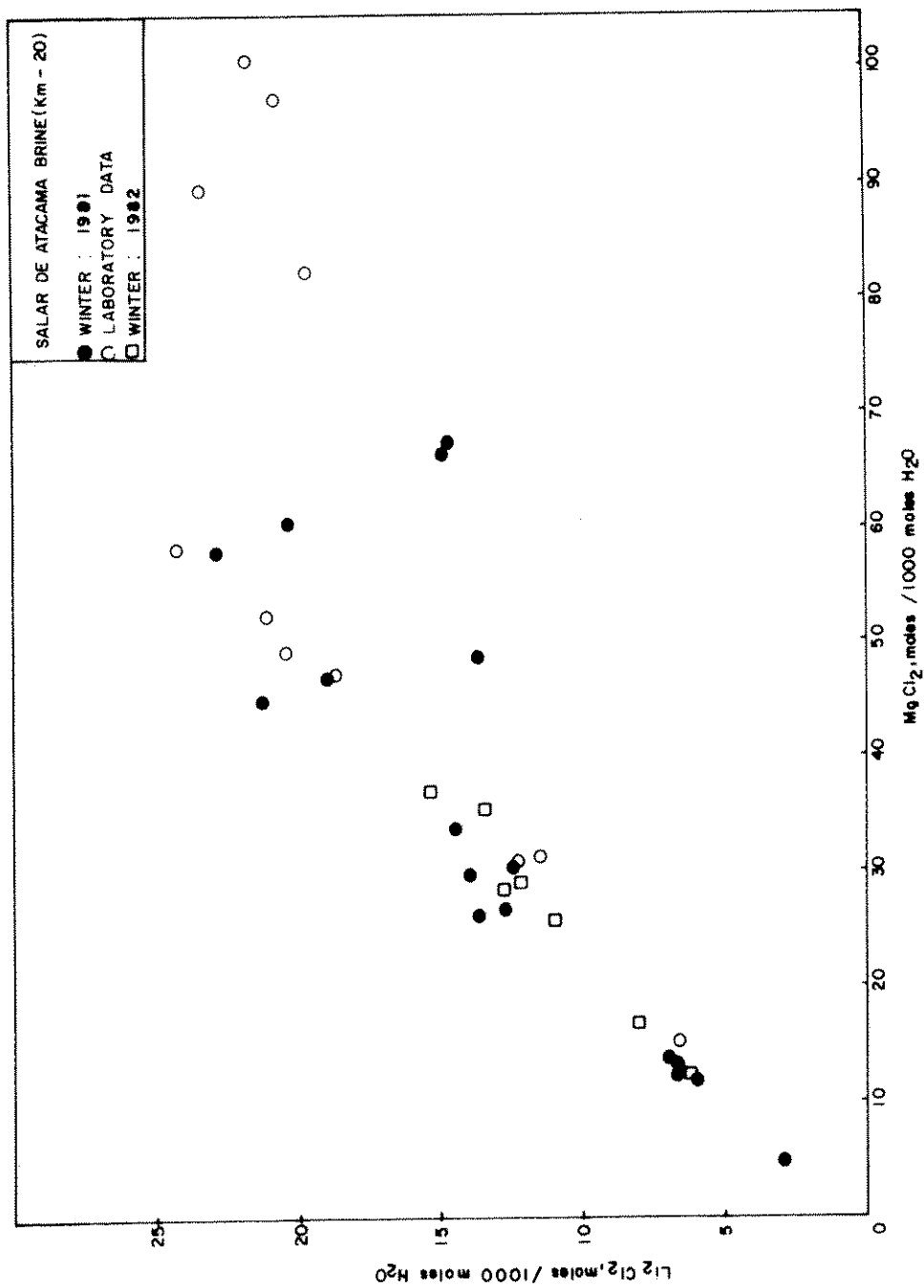


Figure 14. Lithium concentration of evaporating brine in winter

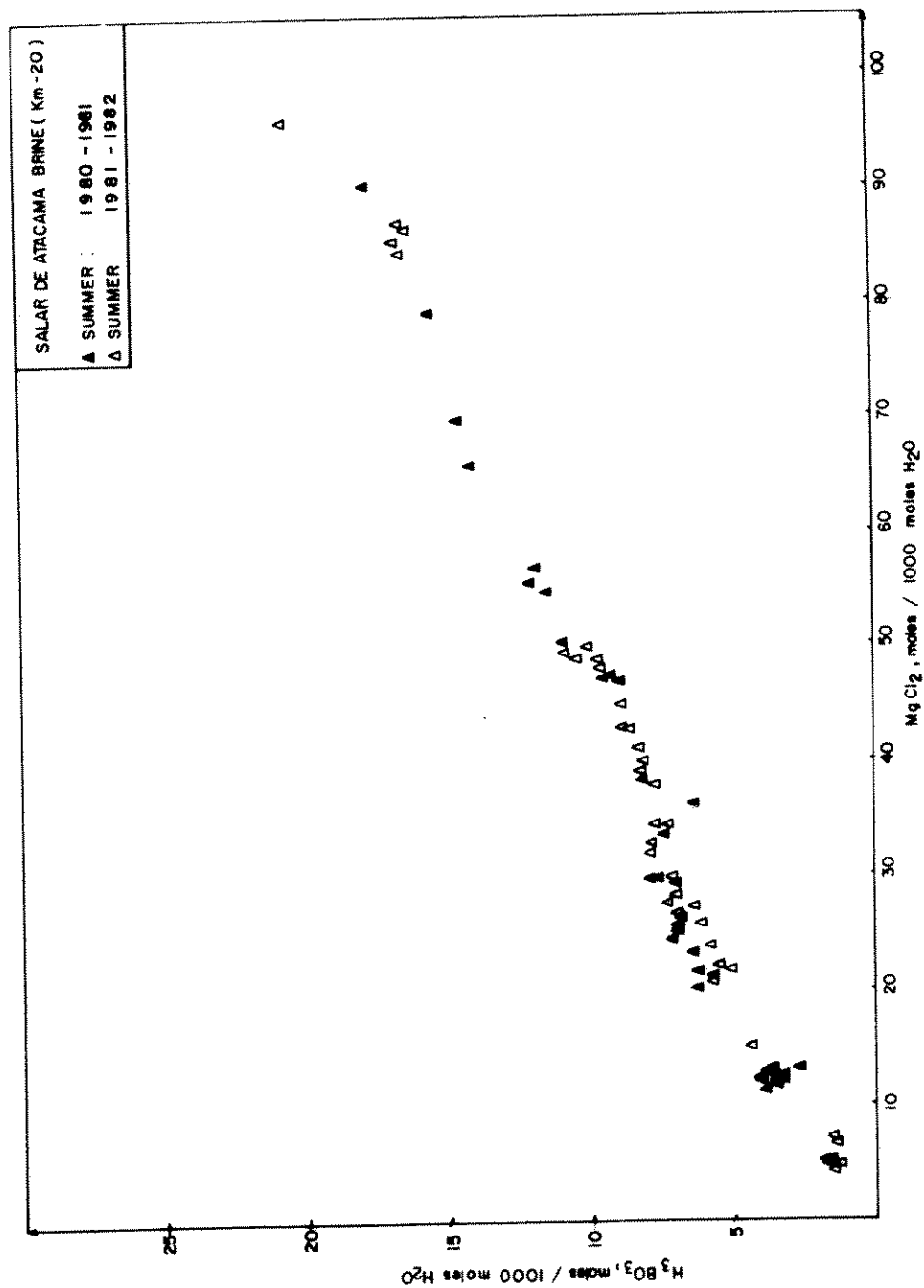


Figure 15. Boric acid concentration of evaporating brine in summer

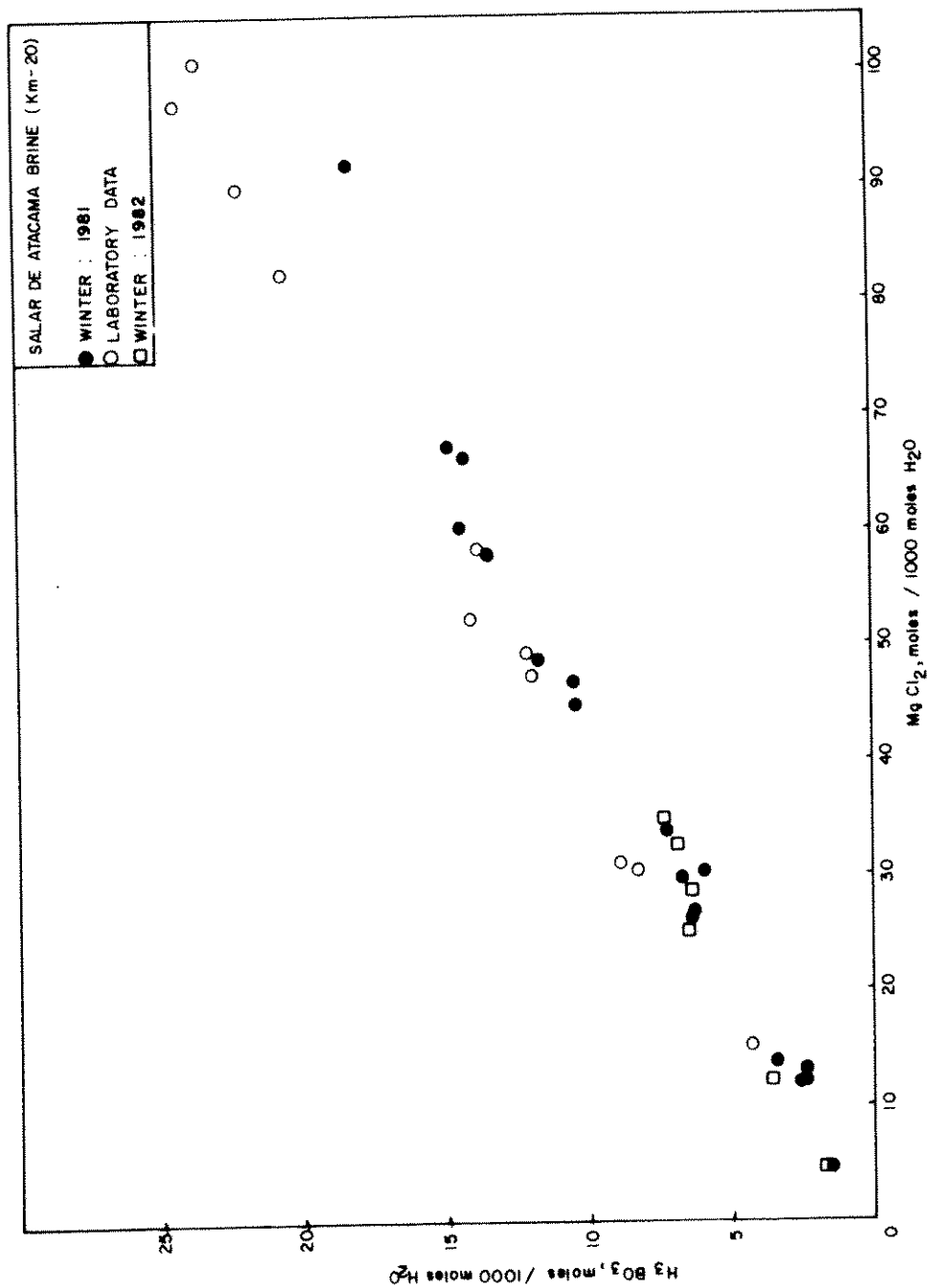


Figure 16. Boric acid concentration of evaporating brine in winter

sium exist, it is possible to represent these brines on the diagram of the reciprocal salt pairs Li_2 , Mg/SO_4 , Cl_2 (Figure 17), assuming the boric acid to be an inert. This representation was successfully used to design a salting-out process to recover $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ from high concentrated brines.

Material balances were also made, using the brine data expressed in moles per 1000 moles of water. Yield data vs MgCl_2 were plotted in Figures 18 and 19, for summer and winter experiments, respectively.

CONCLUSION

It is possible to design a solar evaporation process to selectively crystallize different salts in a sequence of

ponds in order to recover potassium and lithium. Potash can be produced as KCl and K_2SO_4 , being sylvinit the raw material for the first, and schoenite and kainite for K_2SO_4 . Lithium can be obtained from $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and KLiSO_4 salts, and also from the final more concentrated brines (10 — 14 g/l of Li).

Research work has shown that changes in brine temperature changes the nature of the crystallized salts due to the presence of lithium. In general terms it appears that if the brine is evaporated in summer (temperatures over 20°C), considerable lithium crystallizes early in the field of the double sulfate salts, as KLiSO_4 ; no schoenite appears, kainite has a normal field, and carnallite is crystallized at the end (over 52 moles $\text{MgCl}_2/1000$ moles H_2O) with large quantities of lithium sulfate monohydrate. On the other hand, in winter, lithium does not crys-

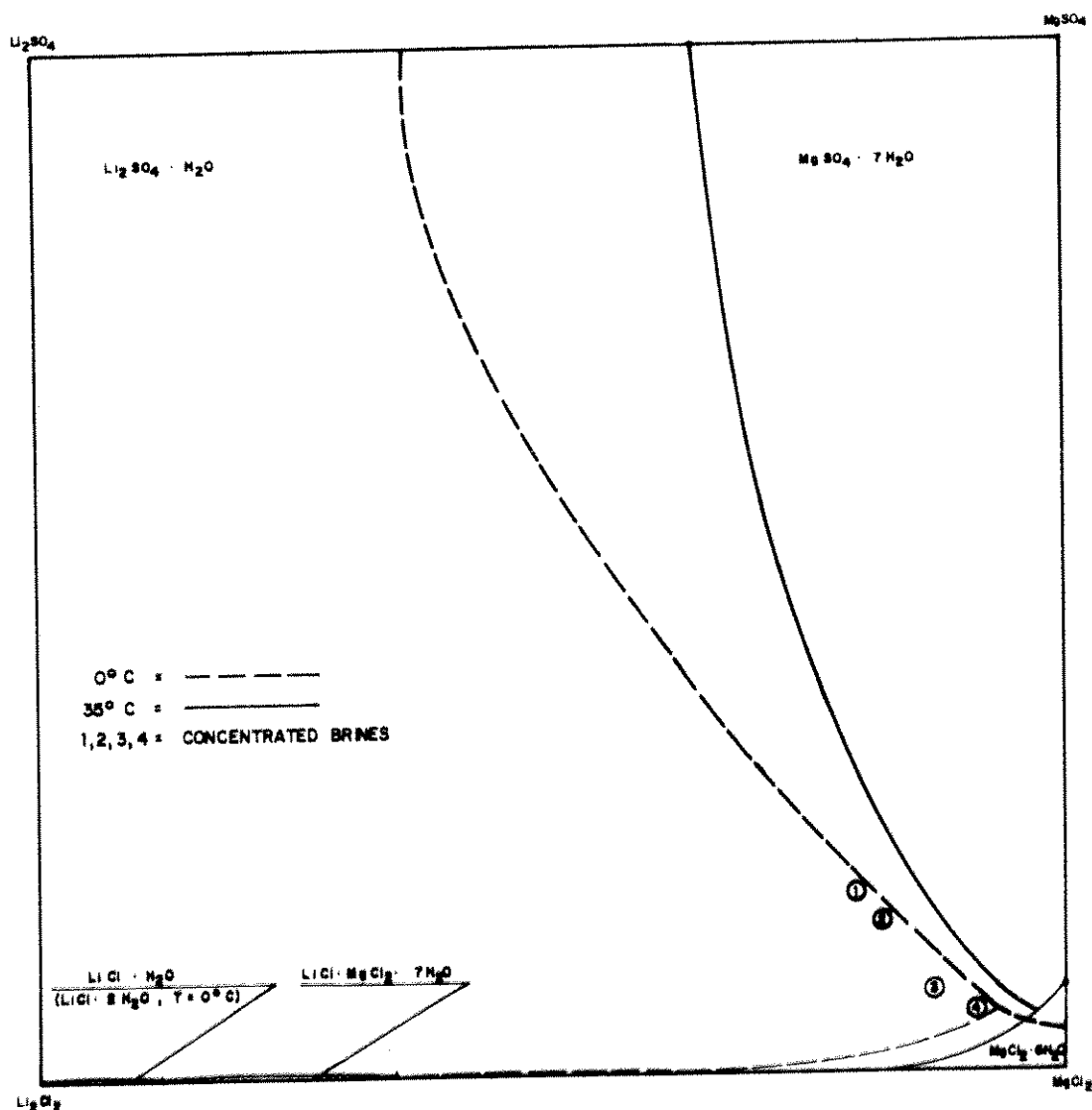


Figure 17. Evaporating brine on a diagram for the system of salt pairs $(\text{Li}_2, \text{Mg})/\text{SO}_4, \text{Cl}_2$.

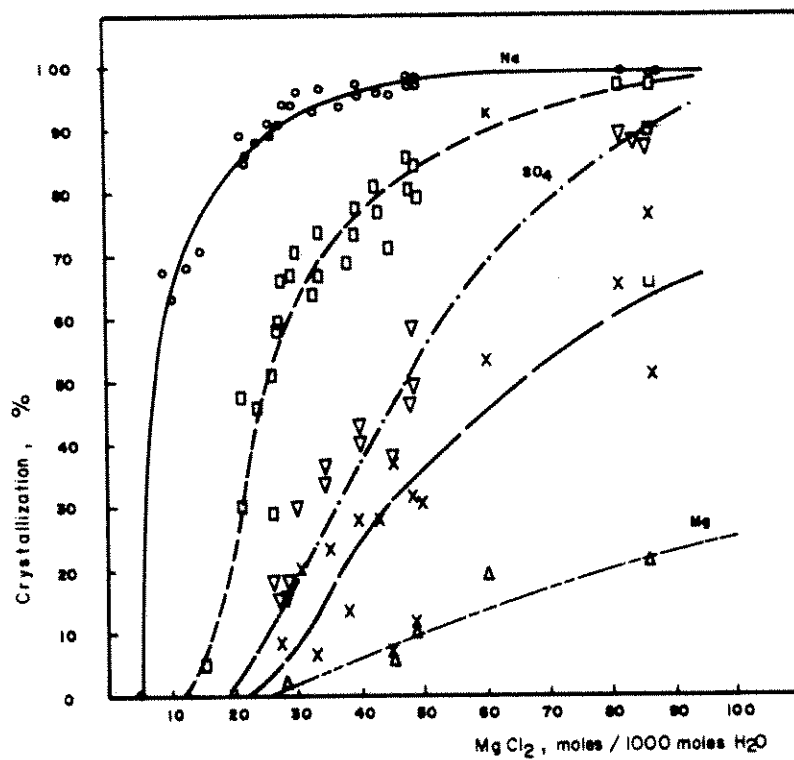


Figure 18. Recovery of salts from evaporating brine in summer

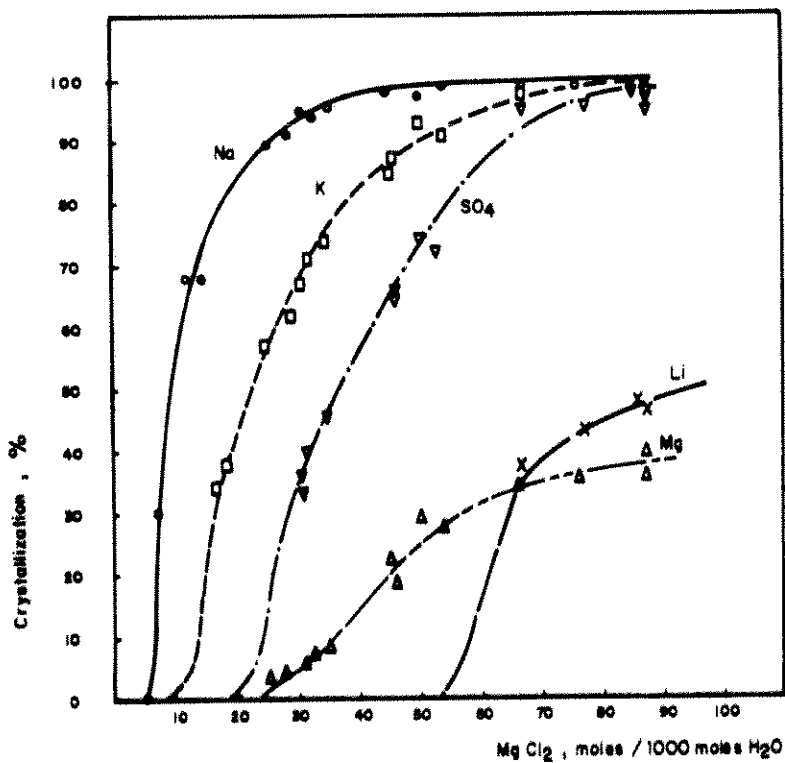


Figure 19. Recovery of salts from evaporating brine in winter

tallize until the final carnallite field, and schoenite crystallizes at the end of the sylvinite stage of evaporation.

The brine does not follow exactly the standard phase diagram for the quinary system. The Janecke diagram serves only as a rough guide to the crystallization path because it does not consider the presence of lithium salts, and because the evaporation in the Salar is not isothermal.

The Autenrieth type diagrams proved to be a useful representation for the brines in the concentration process, showing very clearly the different behavior in winter and summer (Figures 18 & 19).

More experimental work with these brines is being conducted on the Salar and in our laboratory to gather more information on the phase chemistry of the Salar de Atacama brines, and to define the best evaporation sequence.

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