DIAGENETIC POLYHALITE IN RECENT SALT
FROM BAJA CALIFORNIA

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ABSTRACT

Halite and gypsum now being deposited on extensive tidal flats at Laguna Ojo de Liebre, Baja California, are underlain by up to two meters of bedded evaporites. The porous evaporite sediments are permeated by bitterns whose stage of evaporation increases with distance from the lagoon. Beyond 4 to 8 km from the lagoon, gypsum crystals in the sediments have been altered to fine-grained polyhalite, by a bittern nearly in the potash-magnesia facies (concentration 60× sea water).

Although older polyhalite has occasionally been described as a primary precipitate, this modern occurrence confirms other geological and experimental evidence that polyhalite can replace calcium sulfate and that this can occur at an early diagenetic stage.

INTRODUCTION

Polyhalite, $K_2MgCa_2(SO_4)_4 \cdot 2H_2O$, is a common mineral in evaporite rocks of the potash-magnesia facies, but has not been described in evaporites forming from sea water at the present time. Although some polyhalite is considered to be a primary mineral crystallized directly from brine, most polyhalite is evidently a replacement of other sulfate minerals. The timing of this replacement is generally not known in the rocks, so this first discovery of polyhalite replacing Recent gypsum sediments may be useful in the interpretation of the earlier geological occurrences.

The polyhalite occurs in thin evaporites along the inner shore of Laguna Ojo de Liebre, about half way down the west coast of Baja California, Mexico. Field work was done in cooperation with F. B. Phleger and J. R. Bradshaw of the Scripps Institution of Oceanography. The courtesies extended by Mr. Charles McClaughry, Manager, Exportadora de Sal, Guerrero Negro, B.C.N., and by Mr. Francisco Muñoz, charter pilot at Tijuana, B.C.N., greatly facilitated the field work.

Material was first collected in May 1960, and in August 1961 we returned to core the evaporite sediments. Although study of this material is incomplete, the occurrence of polyhalite seems of sufficient interest to warrant a separate preliminary description.

SALT FLATS OF LAGUNA OJO DE LIEBRE

These salt deposits were first described in detail by Wittich (1916). Recently Phleger and Ewing (1962) described the general sedimentology and oceanography of the coastal lagoons in Baja California, with particular attention to Laguna Ojo de Liebre. Since then, the sediments of

the beaches and salt flats have been cored, and we will publish the details
when the new material has been thoroughly studied. Here I will only
outline those features of the deposits that are pertinent to the occurrence
of polyhalite.

Figure 1 shows Laguna Ojo de Liebre (also known as Scammon La-
goon) extending from the Pacific Ocean nearly 40 kilometers into the
coastal plain of Baja California. The detailed study by Phleger and
Ewing (1962) shows that the lagoon has a U-shaped tidal channel about
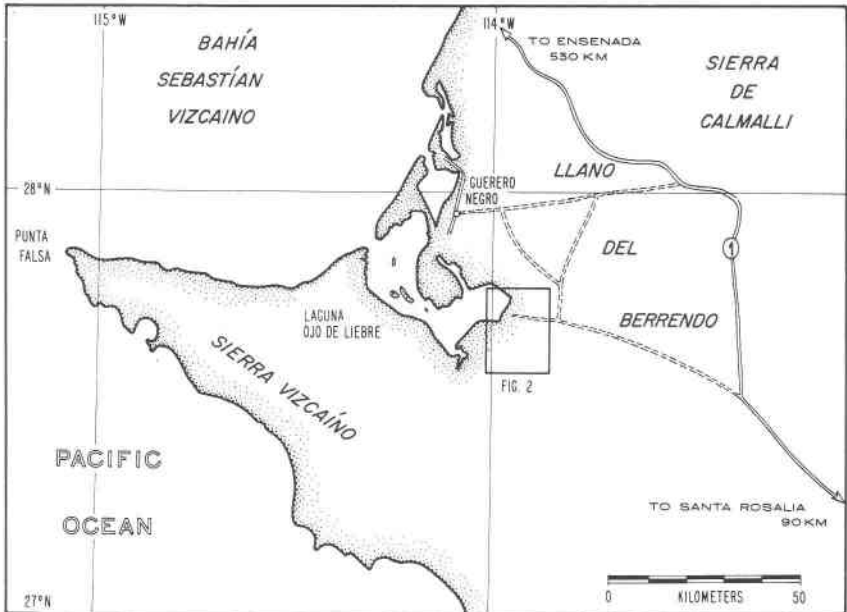

FIG. 1. Index map of part of Baja California.

50 ft deep, bordered by a very shallow shelf. Surface temperatures of up
to 25° C. combined with a light but steady northwest wind, lead to an
evaporation rate of nearly two meters per year. Consequently, the sa-
linity increases to about 45°/$_{oo}$ (parts per thousand by weight) by the
time the water has reached the head of the lagoon (Phleger and Ewing,
1962). However, the lagoon is locally mixed, with no salinity layering.
At the upper end of the lagoon, the lagoon shallows are bordered by a
low sand beach, cut in a few places where tidal channels flood and drain
the flats behind the beach (Figs. 2, 3). The flats are covered intermit-
tently with a few inches of brine with salinity over 70°/$_{oo}$, driven shore-
ward by wind as well as tide. It supports a considerable growth of both

algae and salt grass, and in the landward part of this zone gypsum is crystallizing. Beyond this, the flats are white with both salt and gypsum crystals, and are apparently covered with brine only at irregular intervals, probably driven by high winds or storm tides.
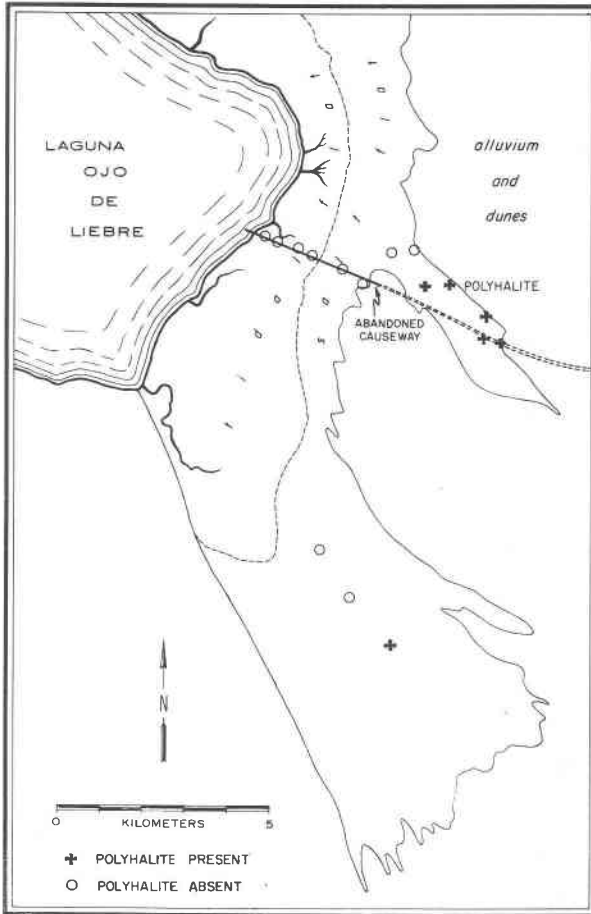

Fig. 2. Polyhalite at Laguna Ojo de Liebre.

The flats are underlain by thinly bedded sediments to a depth of 1–2 meters, mainly gypsum and detrital (quartz and calcite) sands alternating with dark mats of algae and grass. These beds lie on massive and compact gray-green silts and sands that possibly represent an earlier beach deposit. A wide variety of earlier strand lines have been noted along this coast (Wittich, 1912), and 15 km east of the salt flats wells

have penetrated 50 m or more of Pleistocene and Recent sands (Mina, 1957). Beneath the salt flats halite is in the upper part of the bedded sediments, only a centimeter or two thick at the outer edge of the flats, increasing to 1.3 m in the centers of the two "bays" that extend eastward and southeastward from the main flat (Figs. 2, 3). Gypsum is wide-spread: mixed with the halite, as separate layers, as large crystals in the underlying detrital silts, and as windblown surface sand.

Brine lies only a few cm below the surface of the salt flats. It is not only saturated with sodium chloride, but shows the high potassium,
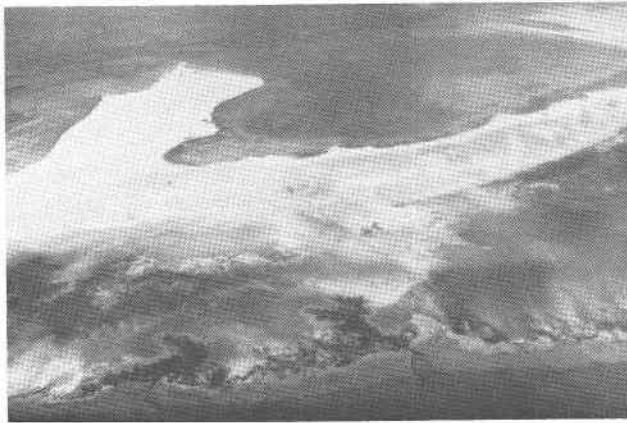

FIG. 3. Salt flats viewed eastward from above the lagoon, with tidal rivers cutting through the beach ridge into the lagoon in the foreground. Tidal flats are darkened by algae and grass. The remains of a causeway and loading dock runs for 3 kilometers across the flats. The thickest deposits of salt, permeated with highly evaporated brines, fill the white "bays" in the background.

magnesium, and bromide indicative of a high degree of evaporation (Table 1). A low rainfall of only 3 cm per year has never resulted in any surface runoff within the memory of local inhabitants. Consequently, the brine has not been diluted by fresh water in recent times. However, Phleger and Ewing (1962) believe that the detritus on the beach and the lagoon had their ultimate origin in floods from the coastal plain in a wet cycle several hundred years ago. The detrital components of the evaporite sediments, principally composed of quartz, hornblende, biotite and plagioclase, probably represents a reworking by tidal currents of these older sediments. The evaporites must be more recent than the wet cycle. Wittich (1916) emphasizes the importance of shoreline emergence in the formation of the evaporites, but he also points out that much of the salt may even have been reformed in the few years since a large but uncertain amount was mined during the last half of the nineteenth century.

Phleger and Ewing (1962) suggest a mechanism for supply of the partially concentrated lagoon water onto the tidal flats, by an asymmetric tidal flow. I should also like to suggest the importance of the on-shore wind, which can be seen to drive a surface layer of brine landward, even as the ebbing tide is flowing outward in the lower part of the brine.

In summary, the present evaporite regine on the tidal flats seems to

TABLE 1. BRINES FROM LAGUNA OJO DE LIEBRE, B.C.S., MEXICO

	1	2	3	4
Na	10.77	13.6	42.5	47.4
K	0.39	0.45	1.05	11.2
Mg	1.33	1.82_6	n.d.	47.3
Ca	0.42	0.52_8	n.d.	0.1
Cl	19.8	26.4_8	61.0	183.1
Br	0.066	0.088	0.188	2.44
SO$_4$	2.76	n.d.	n.d.	n.d.
Total Solids	35.54	42.97	—	291.5
K/Cl	0.020	0.017	0.017	0.061
Mg/Cl	0.067	0.069	—	0.258
Br/Cl	0.0033	0.0033	0.0031	0.0133
Mg/K	3.4	4.1	—	4.2
Br/K	0.17	0.19	0.18	0.22

1. Normal sea water (Harvey, 1955, p. 4).
2. CRC 17,008-3. From lagoon shallows near beach.[1]
3. CRC 17,008-7. Tidal flat, with gypsum and algae mats, 1 km east of beach.[1]
4. CRC 17,008-20. Brine under surface of salt flat, 4 km east of beach.[1]

[1] Analyses for K and Na by Smith-Emery Company, for all other elements by Gale Baker.

have resulted from a fortuitous combination of low runoff and high evaporation.

POLYHALITE

Figure 2 shows where the polyhalite was found, in two large embayments on the salt flats, 4–8 km from the edge of the lagoon. The polyhalite occurs as a 1 cm thick layer of white hardpan underlying about 5 cm of coarse halite-gypsum sand, interbedded with some organic material (Fig. 4). At the northwesternmost locality (Fig. 2) coring showed scattered polyhalite to a depth 1.2 meters in halite and gypsum-rich silts. This may be the "dünnen Calichebändern" identified by Wittich (1916, p. 26, 28) as calcite.

An *x*-ray diffraction pattern of the white hardpan material showed

many lines of polyhalite coincident with the new standard pattern (XRDF 10–355) for polyhalite. A minor amount of polyhalite was also seen in x-ray diffraction patterns of an underlying black sand.

A thin section of the hardpan confirmed the presence of polyhalite.

FIG. 4. Evaporite sediments in the polyhalite area. Brine, which normally levels near the top of the pit, was scooped out to display the sedimentary structure. White layers are halite and gypsum, dark layers are mainly decomposed grass, and the dead white layer near the bottom of the pit is polyhalite.

As shown in Fig. 5, the outlines of gypsum crystals are easily seen in plain polarized light. However, examination under crossed polarizers shows that only a small central part of each crystal is really gypsum. This remaining gypsum is surrounded by a narrow band of radially oriented, fibrous polyhalite, and the remainder of the crystal is an aggregate of 0.005 mm crystals of polyhalite. Polyhalite also occurs between evident gypsum pseudomorphs, where it may represent either a cement or replacement of a gypsum cement.

The extremely fine size of the polyhalite crystals precluded detailed optical measurements, but the average refractive index is normal for the

mineral. The fibrous polyhalite rims on the gypsum are length-slow. The individual polyhalite crystals have a very irregular extinction, with a suggestion of spherulitic structure. Gypsum crystals in all stages of replacements are found in this layer, although most are nearly completely replaced by polyhalite. The texture is very similar to the mosaic and fibrous polyhalite crystals described from evaporite rocks of various ages and localities (Braitsch, 1961; Celet, 1953; Ladame, 1942; Schaller and Henderson, 1932; Stewart, 1949).

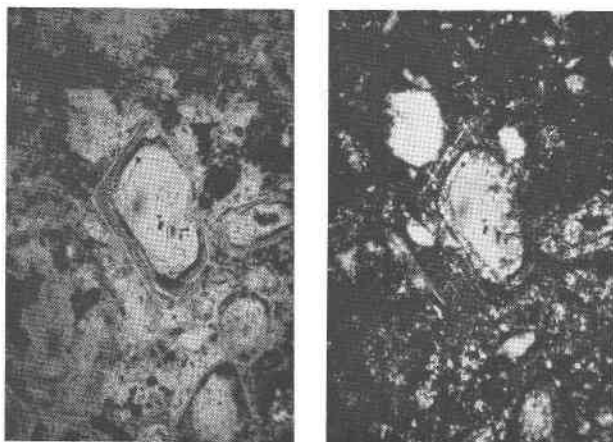Some crystals are not only replaced by polyhalite, but have rims of an

FIG. 5. Photomicrographs of polyhalite replacing euhedral gypsum crystals; interstitial material is also polyhalite. $\times 40$, plane polarized light on left, crossed polarizers on right.

opaque white mineral that also appears as a cement between the grains along with polyhalite. At high magnification this material is found to be composed of very small (less than 0.1μ) equant grains of high refractive index and high birefringence, but it has not been identified.

The occasional detrital grains of plagioclase, hornblende, and biotite are unaltered.

Brine and Crystal Equilibria

The question arises as to why calcium sulfate was deposited first as gypsum and then altered to polyhalite. Can it be explained on the basis of equilibrium with a brine of changing composition, or does one have to assume that the gypsum was crystallized metastably and then converted to a more stable polyhalite?

Considerable information is available on the equilibrium relations of calcium sulfate minerals in the sea water system. Although at 25° C.

gypsum is the stable crystal in equilibirum with sea water concentrated by a factor of up to $5.5\times$, anhydrite is the stable mineral at higher sea salt concentrations, at least up to $11.5\times$, where halite starts to precipitate (*e.g.*, D'Ans *et al.*, 1955). On the other hand, laboratory experiments and field observations indicate that the crystal actually growing from these brines is usually metastable gypsum, even along with halite.

The experiments by Van't Hoff and D'Ans (D'Ans, 1933, see also, Autenreith, 1958; Braitsch, 1962) show that polyhalite is the form of calcium sulfate at equilibrium by the time the sea salt is concentrated enough to precipitate potash-magnesia salts at about $63\times$. In a much-quoted calculation, Janecke (1912) placed the transition anhydrite-polyhalite at about $22\times$ sea salt concentration but there seems to be no good data on which to base such a calculation. However, it is still rather certain that the transition takes place somewhere in the halite facies. After the simple evaporation of sea water to this stage of evaporation, there is not much sulfate available to form polyhalite, it all having been precipitated previously as gypsum or anhydrite. However, if additional sea water or sulfatic meteoric water is added to the system, sulfate should precipitate. Experiments by Lepeshkov and Novikova (1958) indicate that, unlike anhydrite, polyhalite is easily crystallized when such an addition of sulfate is made to the concentrated sea water. There is, therefore, less chance for the metastable crystallization of gypsum from these highly concentrated brines.

This suggests that at Laguna Ojo de Liebre the brine has become much more concentrated since the original crystallization of the gypsum, leading finally to replacement by polyhalite. The conversion of gypsum or other sulfates into polyhalite, within the stability range of the latter mineral, has been shown experimentally by Van't Hoff (1912).

It is interesting to note that no trace of anhydrite was found in any sediments at Laguna Ojo de Liebre, despite a diligent search for it.

Evidence for a change in concentration of the brine since crystallization of the main part of the evaporite is also shown by studies of bromide geochemistry. The pioneering studies of D'Ans and Kuhn (1940) and much subsequent work in Germany, the Soviet Union, and elsewhere, have proved that the bromide in solid solution in halite is a direct measure of the stage of sea salt concentration in the brine from which the halite crystallized. The distribution coefficient for bromide between crystal and brine, based on measurement of both artificial and natural solutions, is such that the first halite crystals to grow from the present-day sea water should have a bromide content of about 70 ppm. As evaporation proceeds, with or without additions of new sea water, the major part of the bromide, rejected from crystallization with the salt,

builds up in concentration. Consequently, the bromide content of new salt crystals is higher; and at the point where potash-magnesia minerals begin to crystallize it is about 250 ppm. At Laguna Ojo de Liebre, samples of halite near the polyhalite locality analyzed 51 and 92 ppm. Brine that flowed from the salt into the hole from which these samples were taken gave the analysis shown in Table 1, column 4. Not only the bromide, but also the magnesium and potassium contents of the brine (relative to chloride) indicate a sea salt concentration of $60\times$, nearly to the potash-magnesia facies. A brine of this composition should be in equilibrium with halite containing about 270 ppm Br.

In a series of publications, Valiashko (1951; 1959) has emphasized the change of physical conditions that occurs when an evaporite is far enough along in its course of crystallization to form a solid but porous crystalline body. He suggests that the process stabilizes at this point, with little further evaporation, awaiting tectonic or other changes. Valiashko has calculated that such a stage is reached with about 50 per cent porosity, near the beginning of the potash-magnesia facies, and I suggest that loss of brine by reflux (Scruton, 1953) may bring on consolidation of the evaporites at an earlier stage. Also evaporation may still be important from this aggregate, with the assistance of capillary movement of brine upward through the pores. This may result in a higher stage of evaporation of the brine, with the deposition of only a small quantity of late-stage halite around the pores. At Laguna Ojo de Liebre, the occurrence of polyhalite in a band cementing the loose sediments just under the surface of the salt flat suggests such a caliche-type deposit. The high-Br halite that should be associated with the brine might be present in only a small amount that was overlooked in our sampling.

Similar apparent disequilibria of bromide between crystal and brine have been found by analyses of brine inclusions in halite, of Permian age from Kansas and Silurian age from Ontario. These may have a similar origin (Holser, 1962).

GEOLOGICAL SIGNIFICANCE

Much of the polyhalite in the geological section has long been recognized as a replacement of gypsum or anhydrite, because of pseudomorphic or other replacement textures. The early experiments of Van't Hoff supported the feasibility of the replacement reaction. The replacement origin has been well documented in many occurrences, from the Permian of New Mexico (Schaller and Henderson, 1932), England (Stewart, 1949), and Germany (Schulze, 1960), and in the Miocene of Ukrainian SSSR (YArzhemskii, 1949). In all of these localities the rocks have been deeply buried since deposition, so that calcium sulfate is also present as

anhydrite rather than gypsum. Pseudomorphs after early gypsum are common, having been replaced by anhydrite, halite or polyhalite. Polyhalite has also been found in lake beds in Central Asia, of Tertiary (Voronova, 1954) and Pleistocene (Norin, 1942) age, but details are lacking.

That the replacement of gypsum or anhydrite by polyhalite may have been diagenetic was suggested by Stewart (1949), Schaller and Henderson (1932), and Schulze (1960), as well as in the reviews by Lotze (1957), and Borchert (1959). However, all of these writers, except Schulze, still have some doubt as to whether the replacement by polyhalite may have taken place at a later time, after consolidation. Polyhalite diagenetically replacing gypsum at Laguna del Ojo de Liebre lends credence to a diagenetic origin for polyhalite in these earlier rocks. It also minimizes the necessity for an intermediate stage of anhydrite or bassanite, which was suggested by Dunham (1949), Schaller and Henderson (1932) and Braitsch (1962), without any direct evidence for either mineral. Such an intermediate stage, for which Stewart has considerable evidence in other transformations, is apparently not always necessary.

The relations between brines and evaporites at Laguna del Ojo de Liebre also suggest that some alterations to polyhalite, and perhaps other replacements, may be caused by a very localized change in brine composition, similar to caliche formation, without requiring the development of an extensive body of concentrated brine. Therefore, an occurrence of polyhalite in evaporite rocks has less significance as a lead to possible near deposits of soluble potash minerals, than might otherwise have been supposed.

REFERENCES

D'ANS, JEAN (1933) *Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen*. Berlin, Verlagsgesellschaft für Ackerbau M.B.H., 2 vol.

———— AND ROBERT KUHN (1940) Über den Bromgehalt von Salzgestein der Kalisalzlägerstatten. *Kali*, **34**, 43–46; 59–64; 77–83.

———— *et al*. (1955) Untersuchungen über die Calcium-sulfate. *Kali und Steinsalze*, **1** (9), 17–38.

AUTENREITH, HANS (1958) Untersuchungen im Sechs-Komponenten-System K·, Na·, Mg··, Ca··, SO₄″, (Cl′), H₂O mit Schlussfolgerungen für die Verarbeitung der Kalisalze. *Kali und Steinsalz*, **2** (6), 181–200.

BORCHERT, HERMANN (1959) *Ozeane Salzlägerstatten*. Berlin, Gebrüder Borntraeger.

BRAITSCH, OTTO (1961) Zur Kristallographie von Polyhalit. *Beitr. Mineral. Petrog.* **8**, p. 84–91.

———— (1962) *Enstehung und Stoffbestand der Salzlägerstatten*. Springer Verlag, Berlin.

CELET, P. (1953) Etude petrographique de la polyhalite du Keuper salifère du Jura. *Soc. Geol. Nord., Ann.* **73**, 171–181.

DUNHAM, K. C. (1948) A contribution to the petrology of the Permian evaporite deposits of northeastern England: *Yorkshire Geol. Soc. Proc.* **27**, 217–227.

HARVEY, H. W. (1955) *The Chemistry and Fertility of Sea Waters.* Cambridge, University Press.

HOLSER, W. T. (1963) Chemistry of brine inclusions in Permian salt from Hutchinson, Kansas. *Symposium on Salt, 1st, Cleveland, Ohio, May 1962, Northern Ohio Geol. Soc., Cleveland,* 86–95.

JÄNECKE, E. (1912) Eine graphische Darstellung der Gewichtsverhältnisse bei den ozeanischen Salzablagerungen. *Kali* **6,** 647.

LADAME, GEORGES (1942) Le gisement potassifère de Mamane en Iran. *Schweiz. Mineral. Petrog. Mitt.* **22,** 242–247.

LEPESHKOV, I. N. AND L. V. NOVIDOVA (1958) Formation of primary polyhalite. *Zhur. Neorgan. Khimii.* **3,** 1261–1264 (Calresearch Trans.).

LOTZE, FRANZ (1957) *Steinsalz und Kalisalze.* Berlin, Gebrüder Borntraeger, v. 1, 2nd ed.

NORIN, ERIC (1942) Two salt basins in Central Asia. *Lunds Univ. Geol.-Mineral. Inst., Medd.* **97.**

PHLEGER, F. B. AND G. C. EWING (1962) Sedimentology and oceanography of coastal lagoons in Baja California. *Geol. Soc. Am. Bull.* **73,** 145–182.

MINA U., FREDERICO (1957) Bosquejo geologico del territorio sur de la Baja California. *Assoc. Mex. Geol. Petrol., Bol.* **9,** 139–269.

SCHALLER, W. T. AND E. P. HENDERSON (1932) Mineralogy of drill cores from the potash field of New Mexico and Texas. *U. S. Geol. Survey Bull.* **833.**

SCHULZE, Günter (1960) Beitrag zur Genese des Polyhalites im deutschen Zechsteinsalinar. *Zeit. angew. Geol.* **7,** 310–317.

SCRUTON, P. C. (1953) Deposition of evaporites. *Am. Assoc. Petrol. Geol. Bull.* **37,** 2498–2512.

STEWART, F. H. (1949) Petrology of the evaporites of the Eskdale no. 2 boring, east Yorkshire, Part I: *Mineral. Mag.* **28,** 621–675.

VALIASHKO, M. G. (1951) Volume relations of liquid and solid phases in evaporating sea water. *Akad. Nauk S S S R, Dokl.,* **77,** 1055–1058 (SLA Transl. 61–13083).

——— (1956) Geochemistry of deposits of potassium salts. *In, Voprosy Geologii Agronomicheskikh Rud, Moskva, Izdat. Akad. Nauk S S S R,* 182–207 (Calresearch Transl.).

——— (1959) Die wichtigsten geochemischen Parameter für die Bildung der Kalisalzlägerstatten. *Frieberger Forschungshefte* **A123,** 197–235.

VAN'T HOFF, J. H. (1912) *Untersuchungen über die Bildunsverhältnisse der Ozeanischen Salzablagerungen.* Leipzig.

VORONOVA, M. L. (1954) Discovery of polyhalite and kainite in sulfate salts of Uzun-Su. *Akad. Nauk S S S R, Dokl.* **99,** 449–450, [*Chem. Abs.* **49,** 7453g].

WITTICH, E. (1912) Über Meeresschwankungen am der Küste von Kalifornien. *Deutsche geol. Gesell., Monatsber.* **64,** 505–512.

——— (1912) Die Salzlager am Ojo de Liebre au der Westküste von Nieder-Kalifornien. *Zent. Mineral.* 25–32.

YARZHEMSKII, YA. YA. (1949) Polyhalite in potassium salt deposits: *Akad. Nauk S S S R, Dokl.* **66,** 1157–1160 (*Mineral. Abs.* **11,** 59).