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SAND90–0584 • UC–721
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Intergranular Fluid Compositions from the Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico

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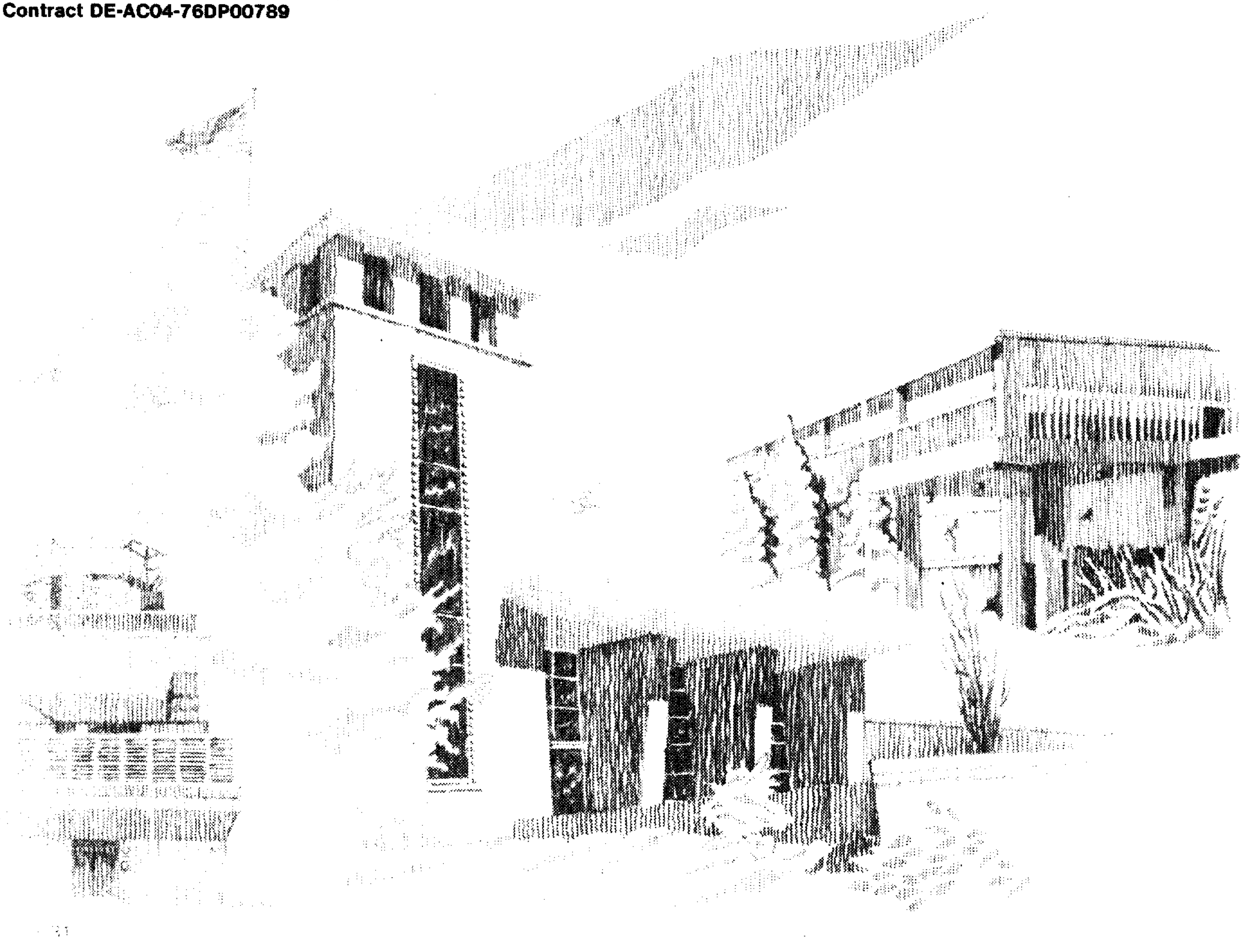
Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-76DP00789



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SAND90-0584
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Printed March 12, 1991

Intergranular Fluid Compositions from the Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico

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The objective of this study was to perform a systematic sampling of the intergranular brines that slowly "weep" from four of the main stratigraphic units exposed in the WIPP. This information was added to the data base on brine compositions used in performance assessment and also employed in characterizing Salado Formation hydrology at the repository horizon.

Concentrations of Na, K, Mg, Ca, Cl, SO_4, and Br were all highly variable. It was also established that this variability reflects neither post-excavation evaporation nor imprecision in the analytical techniques. Compositional variability on the length scale of a few tens of centimeters is as large as that found over several hundreds of meters. Stratigraphy did not appear to exert any control over weep brine compositions.

Programmatically relevant applications of these results are: a) a valid performance assessment must consider the possibility of a wide range of brines, rather than carry out evaluations using a single "best" average brine, and b) the Salado appears not to function as a continuous aquifer since brines originating millions of years ago have failed to homogenize though separated by only short distances.

Summary

An investigation of the origin and distribution of brine from the Waste Isolation Pilot Plant (WIPP), located in the lower Salado Formation, will contribute toward understanding the mechanisms by which brine migrates into the repository. Such knowledge, in turn, is important to an evaluation of this facility as a disposal site for transuranic waste.

The WIPP site is located at a subsurface depth of ~ 645 m in the thick, Permian evaporite section that makes up the lower part of the Salado Formation in the Delaware Basin of southeastern New Mexico. Brines occur in this formation either as fluid inclusions or in intergranular spaces. The possibility of this fluid migrating has recently been the focus of much attention due to the potential threat to the integrity of the repository in general and to waste packages in particular.

The chemistry of the fluid inclusions in lower Salado halite was discussed in previous work (Stein and Krumhansl, 1986, 1988). This report describes the results of a systematic study of the weep, or intergranular, fluids from the WIPP. The results published here include analyses of brines that were collected in such a manner as to provide systematic sampling of four lithologic units that are, for the most part, laterally continuous over the dimensions of the WIPP. These strata consist of clear, colorless halite with few visual impurities; polyhalite-rich halite; and two gray to reddish-brown, argillaceous halite beds. In addition, sampling was conducted in a manner that provided some understanding of the length scales over which compositional variability is observed (from the scale of a few tens of centimeters to over a thousand meters). Sample devices were installed in short (~25-cm) holes drilled normal to freshly-excavated faces. Three widely-spaced locations, each with newly-mined faces, were chosen as sampling sites in the repository. Each array consisted of 24 to 30 holes; in each array, 6

holes were drilled in each of the four or five primary horizontal, lithologic units (where visible). Spacing of the holes in each stratum ranged from 50 cm to 3 m. Sponge samplers were placed in these holes, which were then sealed and left for a period of approximately six weeks to two months. Upon retrieval, the samplers were extracted and the fluids were analyzed for major cations (Na, K, Ca, Mg) and anions (Cl, SO_4, Br).

This report also includes a detailed description of our analytical procedures, as well as a number of analyses of nine "unknown" brines that are part of an interlaboratory comparison of techniques and analytical accuracy. Our results indicate that these samples consist of three splits of three different brines. The accuracy of our technique was generally better than ±5%.

The most significant conclusion from this work is that the intergranular fluids are highly variable, and that this variability apparently reflects neither post-excavation evaporation nor imprecision in the analytical techniques. Rather, this variability may reflect inhomogeneities in both distribution and composition of intergranular brines in Salado halite that may be traced back to the time of deposition. Compositional variability on the length scale of a few tens of centimeters is as large as that observed over a few tens of meters, which is, in turn, as great as that found over several hundreds of meters. The compositional groups from each array are statistically distinct. Therefore, results presented here demonstrate that any "average brine composition" is an artificial construction assembled from brine compositions that are truly distinct, and hence unique from each other in origin. In fact, the only use of an average brine would be as a reference point for evaluation of the functional dependence of a process of concern with regard to significant variations in each brine component. Thus, the designation of any "single average brine" and its applications must be carefully defined and rigorously qualified.

The data base presented here is insufficient to address such questions as geographic trends of the observed variability. Is there any length scale over which the brines are statistically homogeneous? How will this information be coupled to the brine- and gas-migration modeling efforts? These and other questions raised by the observed compositional variability in intergranular brines are important in evaluating models that invoke the concept of a uniform, isotropic, homogeneous medium. However, answers to these questions are beyond the scope of this study.

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1 Introduction

1.1 Motivation

This work was undertaken in order to determine a) the compositional variability of intergranular brines (*i.e.*, the weeps, or wet areas on repository walls) at the WIPP, and b) the length scales (*i.e.*, spatial distribution) over which this variability occurs. A critical question in evaluating the observed variability of brines noted in the field was the effect of evaporation (before or during sample collection) on brine composition. This was addressed by a combined laboratory and field effort, in which a WIPP brine was carefully evaporated to dryness and the brine composition monitored. The salts formed were then compared with those formed under natural conditions in one of the underground rooms.

Another question to be addressed by this study was the extent to which observed variations in brine composition could be traced to noise in the analytic techniques. The issue of analytic variability, which also served as part of an interlaboratory comparison of techniques, consisted of a "blind test" using splits of brines of unknown compositions.

This work was also intended to form a data base for comparison with brines collected and analyzed during the Brine Sampling and Evaluation Program (BSEP), an effort coordinated by the International Technologies Corp. under contract to Westinghouse. A detailed description of the BSEP methods and results can be found elsewhere (Deal and Case, 1987; Deal *et al*, 1987). In summary, the purpose of the BSEP is to sample brines collecting in the holes in the floor of the WIPP and to measure brine quantities and recharge rates in these holes. Henceforth, any reference to any comparison between the results of the weep study presented here and the BSEP results and conclusions must note the difference in sampling techniques and the origin of the brines sampled. Samples collected by the technique described in this report, in which samplers penetrate less than 25 cm into the wall, yield compositional information from a *known stratigraphic horizon.* The brines collected from the bottom of a borehole are a composite of brines from all stratigraphic horizons intersected by that borehole as well as the interactions of these brines with the borehole surfaces and the bottom of the hole.

Further, an overall objective of these activities was to integrate the weep data with those from the BSEP to formulate a single, statistically-defensible, "standard WIPP brine" whose composition would be considered to be typical and representative of all brine expected to seep into the WIPP. This "standard WIPP brine" presumably will be used for all future testing, experimental, modeling, and performance-assessment purposes.

1.2 Previous Work

We began an initial investigation of weep sampling in 1984 (Stein and Krumhansl, 1986) in which we drilled a number of small (20–25 cm long) holes directly into weeps, or wet places on the repository walls. Small sponges were then inserted and the holes sealed to allow brine to accumulate. The brines recovered on the sponges were analyzed for Na, K, Ca, Mg, Li, B, Cl, SO_4, and Br. The primary objective of this early work was to determine a) if it was possible to obtain samples of the intergranular water, b) the degree of compositional variability in these brines, and c) whether the intergranular brine compositions obtained by this sampling procedure were similar to the fluid inclusion chemistry (Stein and Krumhansl, 1988).

At the time of this initial investigation, no attempt was made to select for the most recently-excavated faces, or to correlate fluid chemistry with the age (from time of excavation) of the faces from which the fluids were collected. Distribution of the samplers was erratic, without regard to lithology or stratigraphic units. In this preliminary effort, sample location was chosen by a visual examination of brine flow at the mined face, the abundance of salt efflorescences, and size and number of apparently active weeps in the general vicinity. In spite of the shortcomings of our early work, the technique produced useful information. The data obtained from the intergranular fluids were distinctly different, in major element composition, from the fluid inclusion compositions, though both brine populations (inclusions and intergranular fluids) were consistent with an origin in a mid-halite-facies evaporite environment. Independently-derived data, including isotopic analyses, (*e.g.*, Knauth and Beeunas, 1986), support this interpretation.

In addition, we observed that the data were variable from one weep to the next, even over very short distances (a few tens of cm); and the data showed a consistent, linear trend on a Na/Cl–K/Mg plot that was clearly different from the compositional trend obtained from the fluid inclusion analyses. Moreover, the compositions of the intergranular brines could not be obtained by mixing of the fluid inclusion populations. These early data and results are documented in Stein and Krumhansl, 1986, 1988.

Furthermore, the intergranular and fluid inclusion brine compositions were used to construct a diagenetic scenario to explain the origins of the observed major-element chemistry (Stein and Krumhansl, 1988). In brief summary, the most significant diagenetic reactions are:

1. the gypsum/anhydrite transition, which results in either the liberation or consumption of H_2O, *e.g.*,

$$CaSO_4 \cdot 2H_2O \rightleftharpoons CaSO_4 + 2H_2O \tag{1}$$

2. the formation of magnesite, $MgCO_3$, by reaction with biogenic $CaCO_3$:

$$CaCO_3 + Mg^{2+} \rightarrow MgCO_3 + Ca^{2+} \tag{2}$$

or by the decomposition of organic matter by sulfate-reducing microbiota:

$$2Mg^{2+} + 2CH_2O + CaSO_4 \rightarrow 2MgCO_3 + H_2S + 2H^+ + Ca^{2+} \tag{3}$$

3. the consumption of K and Mg during formation of polyhalite, $K_2Ca_2Mg(SO_4)_4{\cdot}2H_2O$, by interaction of an evaporite brine with either gypsum (Eq. 4) or anhydrite (Eq. 5):

$$2CaSO_4{\cdot}2H_2O + 2K^+ + Mg^{2+} + 2SO_4^{2-} \rightarrow K_2Ca_2Mg(SO_4)_4{\cdot}2H_2O + 2H_2O \tag{4}$$

$$2CaSO_4 + 2K^+ + Mg^{2+} + 2SO_4^{2-} + 2H_2O \rightarrow K_2Ca_2Mg(SO_4)_4{\cdot}2H_2O \tag{5}$$

4. the uptake of Mg by clays, which produces the observed suite of Mg-rich, randomly-stratified, mixed-layer clays (Bodine, 1978, 1983), and probably added K to the brine. It is also apparent from the observed mineralogy in argillaceous halite units in the WIPP that the diagenetic reactions involving the clay fraction also produce authigenic quartz and K-feldspar. A detailed interpretation of the diagenesis of silicate minerals in the lower Salado may be found in (Stein and Krumhansl, 1990).

In particular, intergranular (weep) fluids had greater access to clays than brines isolated as inclusions in halite. The compositional changes that occurred during silicate diagenesis may account for the systematic differences between weep and inclusion brines.

2 Technical Approach

2.1 Installation and Collection of Weep Brines

A detailed account of the sample array placement is discussed in Appendix 1, but briefly absorbent samplers were sealed in arrays of one-inch-diameter holes at three places in the mine. The samplers consisted of 1 x 1 x 15 cm strips of polyethylene sponge wrapped in two layers of Whatman #1 filter paper. The sponges were washed repeatedly in deionized water and then dried at 90°C prior to making up the samplers. The holes were drilled horizontally to a depth of about 20 cm and after the sampler was inserted, the hole was sealed with a #6 rubber stopper wrapped in Parafilm. Samplers were retrieved by prying out the stopper and extracting the sponge–filter paper assembly with forceps. The assembly was then placed in a sealed, labelled, polyethylene bottle (one sample per bottle) and transported to Sandia, Albuquerque, for analysis.

One of the primary objectives in the geographic placement of arrays in the mine was to maximize the horizontal distances between them, in order to examine the spatial variability of compositions from each array on a length scale of several hundreds of meters. The first array was located approximately 20 m from the corner of the Room Q entryway, approximately midway between the next two. The second array was located at the south end of the repository across from Room 1, and the third array was installed at the north end of the repository, in an instrument alcove designated L-4.

The second primary objective in selecting the array locations was to place the samplers in the most recently excavated drifts in order to minimize the effects of mixing along microcracks and of evaporation that might occur at older faces. It has also been noted that, as mined faces age, weep flow decreases and ultimately ceases completely. Our intention was to sample brine flow at the earliest and highest flow rate.

The first array, located in the access drift to Room Q (S-90), was drilled on 7 March 1989; the entryway to Room Q was excavated 1/89. The second array, located in the north rib of S1600 drift across from Room 1, was drilled on 29 March 1989. This face was excavated during June, 1988. The third array, in the east rib of Room L-4, was drilled on 6 April 1989; the face in which these samplers were installed was excavated during 3/89.

2.2 Collection of Weep Salts

Samples of weep salts for this study were scraped from the walls in rooms J and B. All Room J material was obtained from a single restricted area, adjacent to the wall telephone, which contained many completely dried weeps. Coordinates following each sample number (Table 1) refer to vertical and horizontal distances (in inches), respectively, of the weeps relative to the telephone. More diverse localities were sampled in room B:

- #1 through #4 are from the walls of a large heater hole;
  - #1 West side nine feet below grade,
  - #2 West side 11.5 feet below grade,
  - #3 Ten feet below grade,
  - #4 East Side 8.5 feet below grade, highest efflorescence in hole.
- #5 and #6 are normal weeps from the wall and floor of room B.

Thus, samples #1 through #4 are relatively young weeps, as compared to the old essentially dry materials sampled in #5 and #6 (and all the materials from room J).

2.3 Evaporation Experiment

To complement the field study, a laboratory experiment was undertaken where a "typical" WIPP brine was evaporated and brine samples taken for analysis at various stages. The brine used for this experiment was collected by S. J. Finley from a floor hole (QPB-02) in the Room Q entryway.

The experiment was carried out at room temperature (~25°C) from July 1, 1989 to Jan. 30, 1990. Samples were withdrawn at regular intervals, weighed, and diluted for final analysis in the same manner as the natural weep fluids.

3 Analytical Work

3.1 Methodology and Instrumentation

On completion of this study, five groups of samples had been analysed: Weeps-I, Weeps-II, Weeps-III, samples from the interlab comparison study, and samples from the brine evaporation experiment. In all, this amounted to a total of 103 samples. Three instruments were used in the analysis of these fluids; a Buchler chloridometer (for Cl), a Dionex 2000i ion chromatograph (for SO_4, Br), and a Spectraspan IIIB emission spectrograph (for Na, Mg, Ca, K, Li, B).

3.1.1 Processing Free Brine Samples

The interlab comparison and evaporation experiment source materials were free brine, so preparation of these dilutions was simply a matter of pipetting an appropriate weighed amount of brine into a weighed amount of deionized water. All brine dilutions were based on weight, and house deionized water was used in diluting the brines.

3.1.2 Processing Weep Samples

The weep samples arrived as brines absorbed onto samplers consisting of strips of polyethylene sponge, ~1 x 1 x 15 cm, wrapped in two layers of Whatman #1 filter paper. The first step in processing these samples was to discard the outer paper layer as it was inevitably contaminated with powdered salt. In many cases, the sponge weight was unchanged at the end of the experiment. This left the inner layer of filter paper as a source of brine. In point of fact, a number of dry holes were encountered in the 1984 weep sampling exercise reported in Stein and Krumhansl (1986). This suggested that a material with better sorptive properties than a sponge might improve the success of such a sampling program. Thus, past experience was the reason for including a second, preweighed piece of filter paper, along with the sponge.

To extract the brine, each damp piece of filter paper was weighed and then placed in a sealed polyethylene bottle with enough house deionized water so that the total volume of fluid would be increased about ten-fold over that actually on the filter paper. Samples were allowed to stand for several days and repeatedly shaken during this period to assure that the free liquid had a chance to homogenize with the brine on the filter paper.

3.1.3 Analytic Instrumentation

Of the various analytic techniques used, that employed for chloride was the least subject to random variations. It is a standardless ampierometric technique based on titrating chloride by precipitating silver chloride. The principal interferences, thus, are salts of other anions that form insoluble silver salts. Of these, only bromide occurs commonly in WIPP brines, and its concentration is trivial compared to that of chloride. In practice, the technique involved pipetting a weighed amount of 1 to 10 (by weight) diluted brine (about 0.1 cc) into 4 ml of standard matrix solution supplied by the manufacturer. Three or four repeat measurements were typically made on each sample. Relative error was typically less than one percent.

Sulfate and bromide were determined by ion chromatography. Standards for this procedure were obtained by dissolving weighed amounts of pre-dried sodium salts in a weighed amount of deionized water (Table 2). A five point calibration curve was used for sulfate. For bromide, a four point calibration curve was used because with standard #5 the large amount of chloride interfers with the nearby bromide peak. To obtain a calibration curve, each standard was run three times and the results averaged. Dilution ratios of 1/1000 and 1/5000 (by weight) were used to determine bromide and sulfate respectively. The samples were analyzed as a batch at the time each group was received.

Both fluoride and nitrate were readily detected in the least concentrated standard used in calibrating the ion chromatograph (#1, Table 2). Since fluoride and nitrate peaks were generally absent from the weep samples, it follows that these brines contain less than 30 ppm of these components. Chloride was not determined by ion chromatography because a dilution factor of 1/50,000 would be required to keep the instrument from overranging. Such a large dilution would introduce large errors into the analysis and would be difficult to carry out for the many samples involved.

Cation analyses used a more complicated procedure because of the care needed to obtain a high degree of precision from the Spectraspan. The Spectraspan can operate in the single element or multi-element mode. However, in using the multi-element cassette, there is a significant loss of sensitivity. For sodium, magnesium and potassium this is not a problem. Calcium, however, was near its detection limit. Therefore, as a check all the samples were rerun for calcium in the single element mode. Lithium and boron are not on the multi-element cassette so they also were analyzed in the single channel mode.

Samples were diluted to between 1/300 to 1/600 for the Spectraspan analyses, and then run against standards prepared by weighed dilutions of commercially prepared 1000 ppm solutions of the various elements. As each batch of samples was received, it was analyzed and then archived. Then, after all the samples were assembled, a single day-long run (for Na, Mg, K, and Ca using the multichannel cassette) was carried out. This was done so that one data set would exist with minimal differences arising from the day to day changes in instrumental parameters, and from the use of different standards. In Tables 3.1–3.3, the left column for Ca, Mg, K and Na refers to the data obtained during this exercise. The middle Ca column and right column for Mg, Na, and K were data obtained when each group of samples was analyzed as an individual batch. The right Ca column contains Ca values obtained by operating the Spectraspan in the single-channel mode.

Finally, a correction for instrument drift is required because plasma temperature and optimal slit positions shift as the electrodes burn and the optical bench slowly warms. When the weeps were first analyzed in 1984, drift correction was not done in a rigorous manner. The basic procedure used then was to note that the high standard had drifted by the end of a run, assume the drift was linear over time, and correct the sample reading by the percentage change presumed to have occurred at the time the sample was run. Since then, this process has been formalized into an algorithm. Drift between standards is still assumed to be linear. However, now the drift of each standard is calibrated separately. Then, a new calibration curve is constructed that is specific to the relative positions in the analytic sequence of each sample and the various standards. This automated correction procedure was used to remove drift from the Spectraspan analyses reported here.

3.2 Internal Standard Corrections

With the multi-element cassette it is further possible to make internal standard corrections for the principal cations in the brines. This follows from the fact that weep brines carry essentially none of certain other elements on the cassette (*e.g.*, Ti, Ta, Fe, Al, Cs, Sr, Pr, U, W, Au, P, Si). Thus, if these are mixed with both samples and standards in exactly the same amount, fluctuations in the apparent concentrations of these elements may be used to correct analyses of the various brine components. The mixing operation was accomplished by using a two channel peristaltic pump to feed the nebulizer. One side accessed standards or samples, while the other side continuously fed from a large reservoir containing the internal standard elements and matrixing agents. Such corrections also require that the covariance of various element pairs be assessed. Experience indicates several regularities: Fe typically is a good predictor for Ca, Al does well at mimicking Mg, and Cs usually – though not always – will show if there are problems with a K or Na analysis. Because this technique was unavailable when the original weep samples were analyzed, data will be reported both with and without internal standard corrections.

3.3 X-ray Diffraction

Sample mineralogy of the solid weep salts collected in Rooms J and B was characterized by x-ray diffraction. The x-ray diffraction patterns are shown in Figure 1. In all cases halite was the predominant constituent, mixed with minor amounts of bittern salts. Identification of the bittern salts was complicated by their small concentration in the sample, and because orientation effects sometimes reduced the intensity of stronger peaks, while accentuating the intensity of weaker ones.

4 Results

4.1 Weep fluid chemistry

The weep sampling strategy was successful in that only one completely dry hole was encountered, and evidence of drying from a leaky seal (as indicated by dried salts on the samplers) was seen in only two other cases. The brines obtained in this manner were typical of other fluids obtained from the WIPP, in that in addition to Na and Cl, significant concentrations of Mg, SO_4, K, Br, B, and Li were detected. The brine data are presented in Tables 3.1–3.3.

Further, it was established that the brines were indeed a heterogeneous population of fluids. In our previous work (Stein and Krumhansl, 1986), we chose to represent these brine compositions using element ratios. Accordingly, the use of element ratios was continued in this study (Figs. 2–7) and, in addition, was supplemented with the use of three-component, Na-K_2-Mg plots (Figs. 8–10).

Though groupings characteristic of each sample site are discernable in these plots, there was much scatter so that the clusters showed considerable overlap (for example, in Fig. 2). Moreover, it was not possible to define trends which could be related to the individual strata which were sampled (Fig. 11). Finally, given the great age of the sediments, one might theorize that fluids residing in close proximity to each other would have homogenized. However, it did not prove possible to identify a characteristic length scale over which sample compositions were uniform. That is, there seemed to be as much variability between two closely spaced samples as between any two samples from different arrays.

4.2 Weep salt mineralogy

As predicted from the bulk weep fluid compositions, the principal weep salt is halite (NaCl), and other salts were detectable only in trace amounts. In spite of difficulties in identifying the bittern salt minerals, some systematic associations were apparent. Where sylvite (KCl) was readily discernable, the other bittern salts were either undetectable, or present only in trivial amounts. Carnallite ($KMgCl_3 \cdot 6H_2O$) was the other bittern salt commonly observed. In samples richest in carnallite, partial patterns for bischofite ($MgCl_2 \cdot 6H_2O$) and/or kainite ($4[K_4Mg_4Cl_4(SO_4)_4 \cdot 11H_2O]$) were also sometimes barely discernable.

The chemical analyses obtained for the weep salt samples (Table 1) demonstrated that even samples from the restricted area in room J did not have a uniform composition. Further, the weep salts clearly do not represent naturally occurring mine brines (*e.g.*, a floor hole brine) evaporated completely to dryness, as discussed in the following section. The weep brines are typically richer in halite, the K/Mg ratio is generally greater than that of a floor hole brine, and sulfate is depleted relative to potassium.

4.3 Brine evaporation experiment

The nature of the chemical trends typical of brine evaporation are clearly illustrated using the data from the brine evaporation experiment (Table 4). These data, indicative of chemical changes occurring during this process, are shown on a Jānecke diagram (Figure 12, from Braitsch, 1985). Such a plot monitors variations in sulfate, potassium and magnesium while assuming saturation with halite. Initial evaporation did little to change the K/Mg ratio (Figure 12, point "A"). Though halite precipitated, the brine was apparently unsaturated with any of the bittern salts. Such a finding is consistent with the field observation that at this level in the Salado the bittern salts are generally absent. It also explains why halite is the first, and principal, mineral deposited as weep salts accumulate in the mine.

In the following discussion of evaporite paragenesis, we note that all mineralogy is inferred from the Jãnecke diagram (from Braitsch, 1971); time and sample volume did not permit identification of individual phases by x-ray diffraction. We do, however, note that the solution composition, plotted as K/Mg vs. Na/Cl in Figure 13, follows an evaporation path that is consistent with the expected mineralogy shown on the Jãnecke diagram in Figure 12.

Sylvite precipitation started after slightly more than 25 percent of the weight of the brine was lost to evaporation. As shown in Figure 12, this process should result in brines whose compositions lie along a line joining the 100% K corner of the triangle and the initial composition of the brine. V1 represents the actual evaporation path and V2 represents the theoretical vector. That they are not quite identical suggests a trace of some sulfate containing mineral was also precipitating at this time. Alternatively, in going from B to C the brine may have taken the theoretically predicted path, followed by a short interval where the sylvite-epsomite boundary was followed. In either case, it is evident that during most of the transition between B and C, sylvite and halite would be the principal phases precipitated. It is likely that the weep salts containing both sylvite and halite noted earlier formed during this stage of evaporation.

Sylvite is not a stable phase beyond point C so further concentration of the brine first resulted in conversion of sylvite to carnallite. This continued until all the sylvite accessible to the solution was used up. After this, the brine composition could continue toward point D. Initially the path followed was the boundary between carnallite and hexahydrite, precipitating a mixture of both minerals. At some point, however, the path deviated into a field where only magnesium sulfate precipitated. This would require a brine so depleted in potassium that carnallite could no longer form, and that the carnallite already deposited be isolated from the solution (possibly by a coating of magnesium sulfate). At this point the brine was effectively a magnesium-chloride-sulfate solution. Further evaporation then finally resulted in precipitation of magnesium chloride as well as magnesium sulfate (point E). The traces of carnallite, bischoffite and kainite noted earlier in some weep salts probably formed during the last stage before fluid flow to the weep ceased.

To summarize, a newly formed weep will consist of mostly halite, and a little sylvite. As the mine ages, further sylvite should be replaced by carnallite. Eventually small amounts of the various magnesium sulfate- hydrates may also form. All of these stages are, in fact, found in existing weep salts, giving fair degree of confidence in the general validity of this model. In addition, it has been found that as evaporation occurs, the fluid compositions follow well-defined compositional trends. Thus, it should be possible to show whether any pair of fluids are related by simple evaporation. For comparison with the weep data in Figures 2–7, element-ratio plots of the brine evaporation experiment data are shown in Figures 13–18. Also, for comparison with the weep data (Figures 8–10), the Na-Mg-K_2 composition of the brine evaporation experiment is shown in Figure 19.

4.4 Interlab comparison results

Triplicate splits of three unknown brines simulating those from WIPP were given to us for comparison to analyses from other laboratories. In addition to supporting the objectives of the interlab comparison, the data from these samples also demonstrates the precision of the analytic techniques. These results are important since any assessment of brine uniformity (or a lack thereof) can only be made in reference to the precision of the analytic techniques used.

Analytic results are presented in Table 5 (anions) and Tables 6.1–6.4 (cations). In these tables, "Big Run" refers to the comprehensive run involving all the samples, while "Batch 1, 2, etc." refers to analyses which were made as an isolated batch.

From the replicate analyses it is evident that chloride and boron results are meaningful to three places, while those for sulfate and bromide are good to two places. Fluoride is only good to one place, but since it is unreported for the weeps this is of no further concern in this study. Lithium was not encountered in any of the interlab comparison test samples so that we could not assess the analytic variability for this element. Sodium, magnesium and potassium are also good to two places, with an error of plus or minus 1 ppt. Interpreting the calcium data requires more imagination. If the multichannel cassette was used, then only one place reporting is warranted. However, with the single channel cassette (Batch 3, Table 6.1), two place accuracy is indicated. Further, calcium obtained with the multi-channel cassette appears to fall systematically below the single channel analyses. Assuming the latter to be "correct," then a liberal policy of rounding upward is likely to bias the multichannel calcium numbers in the appropriate direction.

5 Discussion

5.1 *In situ* effects of evaporation on natural weep fluid compositions

Since weep salts occur ubiquitously in the mine workings, it is natural to speculate that the brines might have originated from a common source. This brine may have been subsequently modified to various degrees by the precipitation of various salts during evaporation (see, for example, Braitsch, 1971). Alternatively, the present brines may have attained their compositions through interactions with previously-precipitated weep salts. The salts deposited during evaporation are also of programmatic concern in their own right because (a) they will come in contact with waste packaging materials, and (b) because salt deposition influences the mechanism(s) and composition(s) of brines accumulating in the mine. For these reasons the following discussion considers the origin of these salts in the larger context of whether such processes could have also affected the compositions of the weep fluids collected in the three arrays sampled during this study.

The field evidence suggests strongly that at least some brines undergo considerable differentiation as they approached the mine wall. Because most weep fluids lie in the sylvite (+ halite) field (Figure 12), their evaporation histories should all be broadly similar. Results from the drying experiment were, therefore, replotted on diagrams such as those used earlier in this report (Figure 13). In the early stages of evaporation, the path followed went directly downward – *e.g.*, on the Na/Cl–K/Mg plot – and only halite precipitates. It then deviates slightly to the left as sylvite precipitation starts. This trend contrasts sharply with the pattern observed for natural conditions. Instead of points scattered along a vertical trend, the weep brine data typically plot with more scatter in the horizontal (K/Mg) direction. The same dissimilarity between the patterns formed by the weep fluids and those found during the evaporation experiment were also noted for the other dissolved components in the brine (Figures 14–19). Thus, brines collected during this study are not related to each other by evaporation, and were not derived from a single common source brine by this mechanism. Moreover, the results of replicate analyses of the brines and the interlab comparison results demonstrate that the error in the brine analyses is considerably smaller than the actual scatter in the various analyses of fluids from different sources. Instead, diagenetic reactions (Section

1.2) probably account for the lack of homogeneity. Because these reactions are slow even by geologic standards, individual brine reservoirs must have remained isolated from each other for tens or even hundreds of millions of years.

5.2 Programmatic applications

The primary objective of this work was to obtain data on the local variability of weep fluids and salts found in the mine. Toward this end, a collection procedure was devised which assured that only fluids from a small body of adjacent rock would be absorbed on any given sampler. This effort produced a data base that is unique in two respects: a) multiple, closely-spaced samples were obtained at each of three localities in the mine, and b) samplers were placed in individual stratigraphic units. With the exception of data reported by Stein and Krumhansl (1986), the remainder of the available information on WIPP brine compositions pertains to samples from widely-separated, relatively long drill holes, most of which penetrate several stratigraphic units (Deal and Case, 1987; Deal *et al*, 1987). Because of the differences in approach to sampling intergranular fluids, our data (this work) support several new conclusions of programmatic relevance.

One conclusion of programmatic relevance concerns fluid accumulation mechanisms in the mine. Preceding discussions showed that weep salts are systematically depleted in both magnesium and sulfate relative to the brines from which they originated and secondly, that initial evaporation of a weep brine precipitates salts rich in potassium, magnesium, and chloride, while leaving a brine rich in magnesium and sulfate. It has also been found that a zone of microcracking develops adjacent to a drift when it is excavated and then penetrates deeper into the walls as closure of the drift progresses. As the network of cracks becomes more voluminous, it may accommodate all the brine moving toward the mined face, at which time weep growth appears to stop. However, evaporation into the wall rock, away from the face, will continue precipitating the same salts as found in surface weeps and leaving behind the same residual, Mg-rich brine. Eventually this residual fluid may become the predominant interstitial brine near the mine workings; however, to date, no brine having this distinctive Mg-enriched chemistry has actually been recovered from the mine. Later, when the mine approaches final closure, it could be squeezed into the mine, supplying brines richer in magnesium than any fluid sampled to date. Thus, in addition to the observed brine compositions, any test plans must consider the potential occurrence of residual brines high in Mg.

The data shown in Figures 2–11 also suggest that the weep brines are variable over a length scale of tens of centimeters to a few meters. Although a rigorous statistical analysis of these data was not carried out, the plots shown in these figures suggest significant heterogeneity in the chemistry of these weep brines. The different lithologies, indicated as layers A, B, C, D, or E in Figure 11, apparently exert no control on weep chemical composition. However, in contrast to the apparent uniform heterogeneity of the individual arrays, the plots shown in Figures 2–7 suggest a slight differentiation between data for the three different arrays. This observation indicates that, over long length scales (*i.e.*, several thousand meters), the intergranular brine compositions are significantly distinct. Regional trends in brine compositions cannot be detected on this small data base.

We propose a model of more or less isolated brine pockets as an explanation for the observed weep brine compositions. The best way of explaining the origin of brines containing the observed distribution of major and minor elements is, of course, to assume that they ultimately were derived from seawater. Therefore, at some point in time, their compositions were uniform and homogeneous. The first differentiation process would have been local differences in the intensity of evaporation. Sporadic incursions of fresh water into the Delaware Basin, recrystallization of the host salt, and topographic variations also contributed to further early variability in the weep brines. With increasing time and burial diagenesis, these compositions were further modified according to a suite of diagenetic reactions that are also consistent with the observed mineralogy (Stein, 1985). Clearly, evaporation cannot wholly account for the observed differences. Thus, the diverse compositions of the various WIPP brines are the result of prolonged isolation and processes that operated, cumulatively, on a time scale of hundreds of millions of years. Evidence for the existence of numerous effectively isolated pockets has implications for any model of brine flow into the repository or for the migration of dissolved gases or radionuclides away from it.

Finally, from brine to brine, the concentrations of the elements presented here vary by factors ranging from close to 1 (for B), to 2 or 3 (for Na and Mg). Results of the "blind testing" indicate that these are real differences that do not originate as noise in the analytic procedures. Error arising from analytical imprecision appears to be much smaller than that arising from the individual samplers. Therefore, it seems that a best "standard WIPP brine" cannot be defined unequivocally.

6 Conclusions

In general, all of the brine compositions observed in this study fall in approximately the same range of major and minor element concentrations as were observed several years ago. Within this range, the mean compositions of each array indicate fluid populations that are distinct over distances of several thousand meters. Moreover, upon examination of the data within each of the arrays, the degree of compositional variability within each stratigraphic unit is approximately the same as the variability between the units. In summary, the intergranular brines show compositional heterogeneity over all the length scales examined in this study.

At this time, there is insufficient data to define regional geographic trends. This study has also shown that the observed variations in WIPP brine compositions are real and cannot be explained by either artifacts of sampling or analytical procedures, or by the effects of post-excavation evaporation. Rather, a variety of diagenetic processes, operating to varying degrees over millions of years, produced discrete, isolated, compositionally-distinct, brine reservoirs. Since presently no single brine serves as a source for the weep fluids, it follows that the concept of an "average WIPP brine" must be defined very specifically and any applications must be qualified accordingly.

7 Acknowledgements

We thank A. Rutledge and T. Burford for their help in installation of the arrays and collection of the samplers. The manuscript was reviewed by R. T. Cygan and L. H. Brush, whose helpful comments we also acknowledge.

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Figures

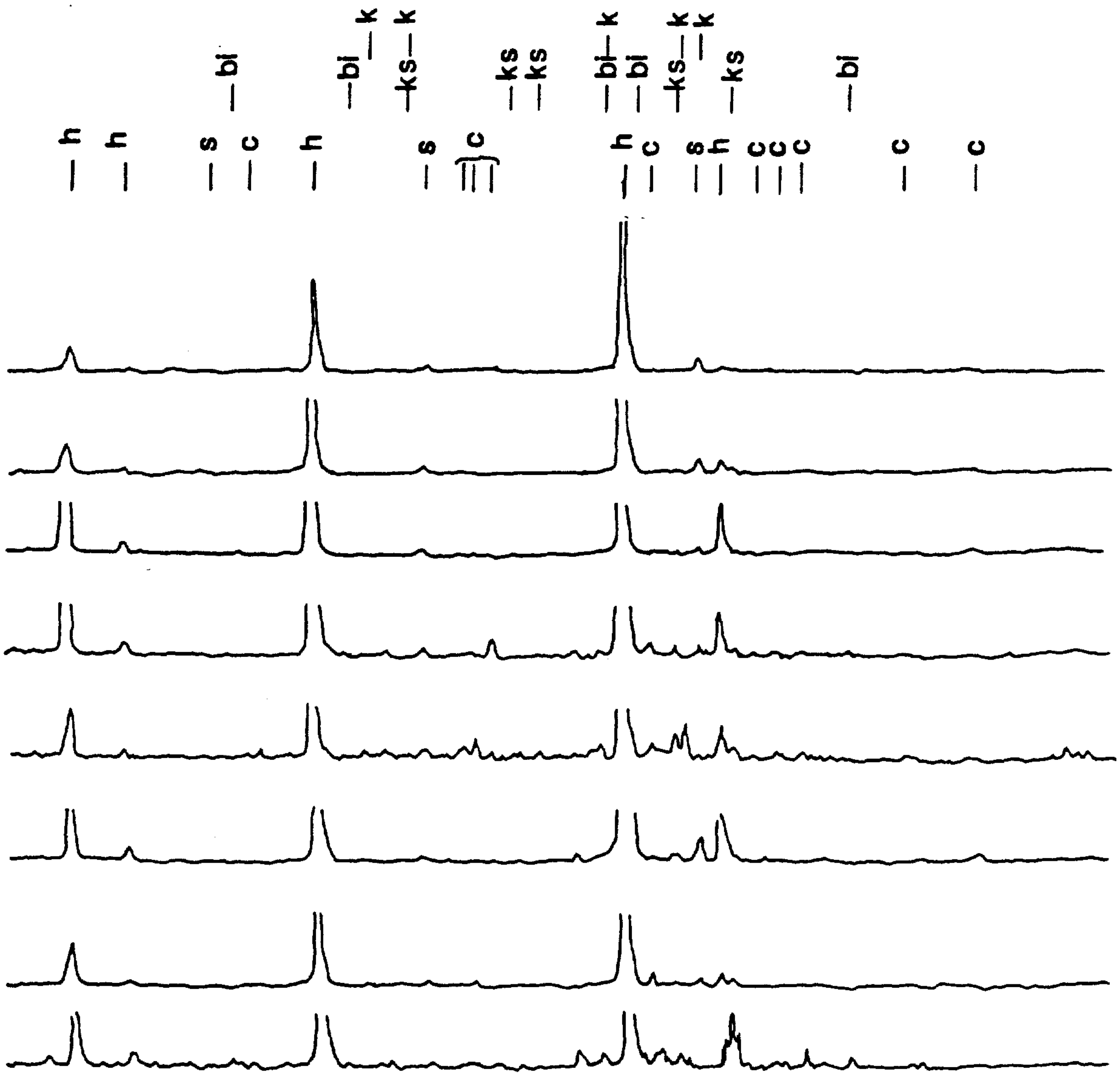


Figure 1: X-ray diffraction patterns of weep salts. Across the top of the figure, peak positions are noted for the following salts: halite, **h**; sylvite, **s**; kainite, **k**; bischofite, **bi**; carnallite, **c**; and kieserite, **ks**. Locations relative to a reference point described in the text are listed to the right and correspond to analyses found in Table 1.

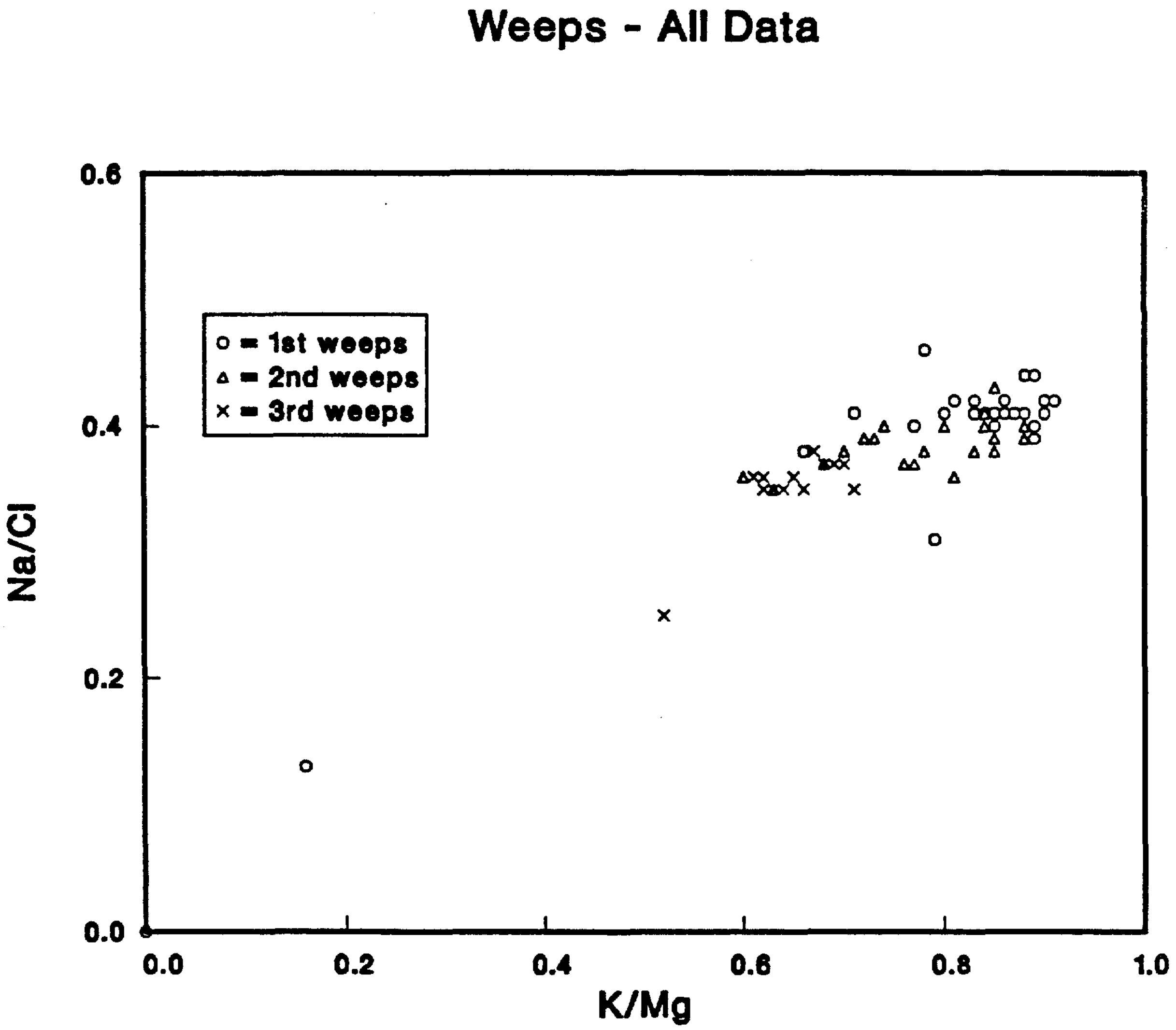


Figure 2: Figures 2–11 were constructed from the data contained in Tables 3.1–3.3 and are plotted as weight ratios. For example, the units for the axis labeled K/Mg are ppt/ppt, while the units for the axis labeled Li/Cl are ppm/ppt. For Ca, the single channel analyses were used; for Na, K, and Mg, "Big Run" data were used.

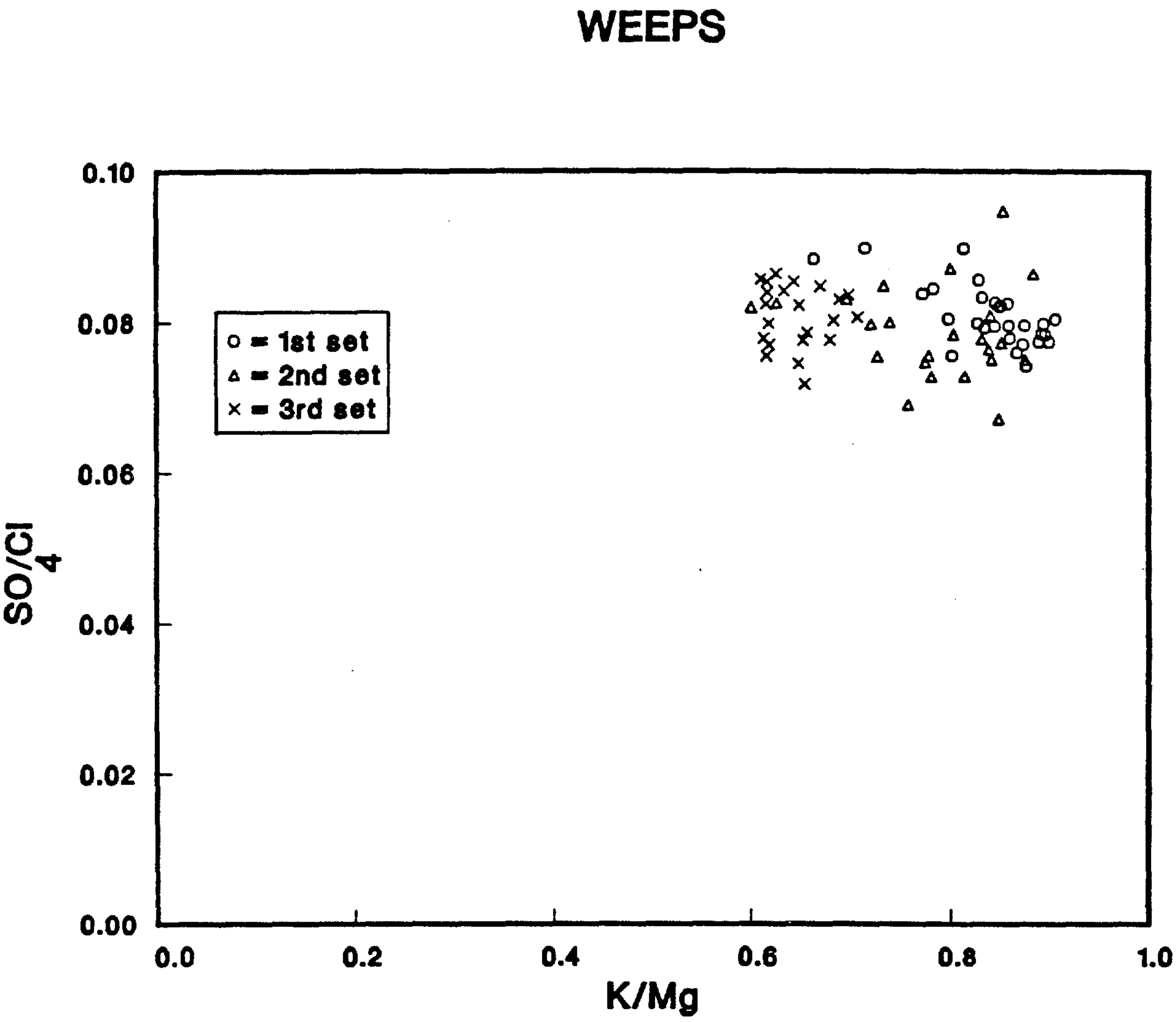


Figure 3: Weeps (all data) plotted as SO_4/Cl vs. K/Mg.

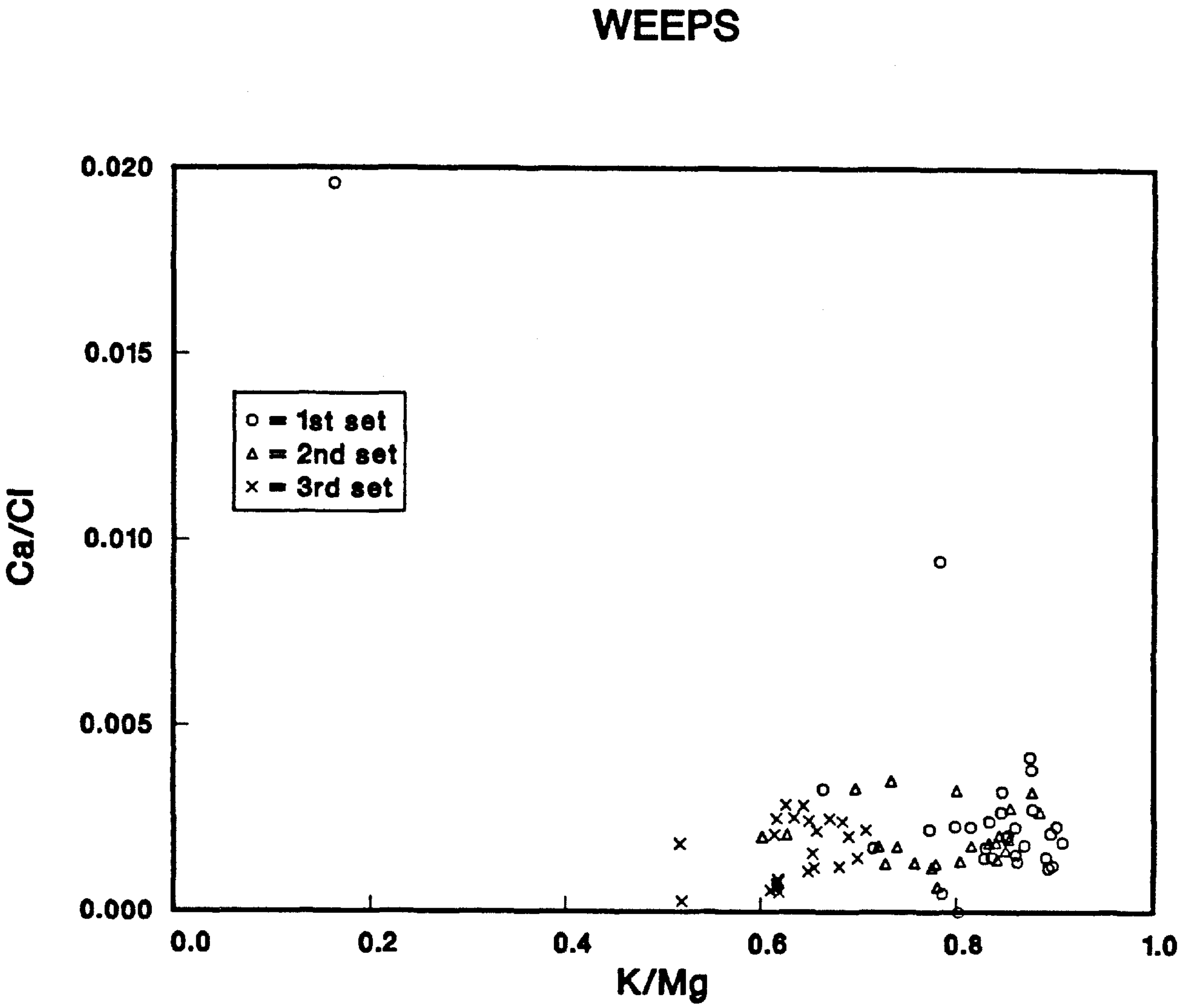


Figure 4: Weeps (all data) plotted as Ca/Cl vs. K/Mg.

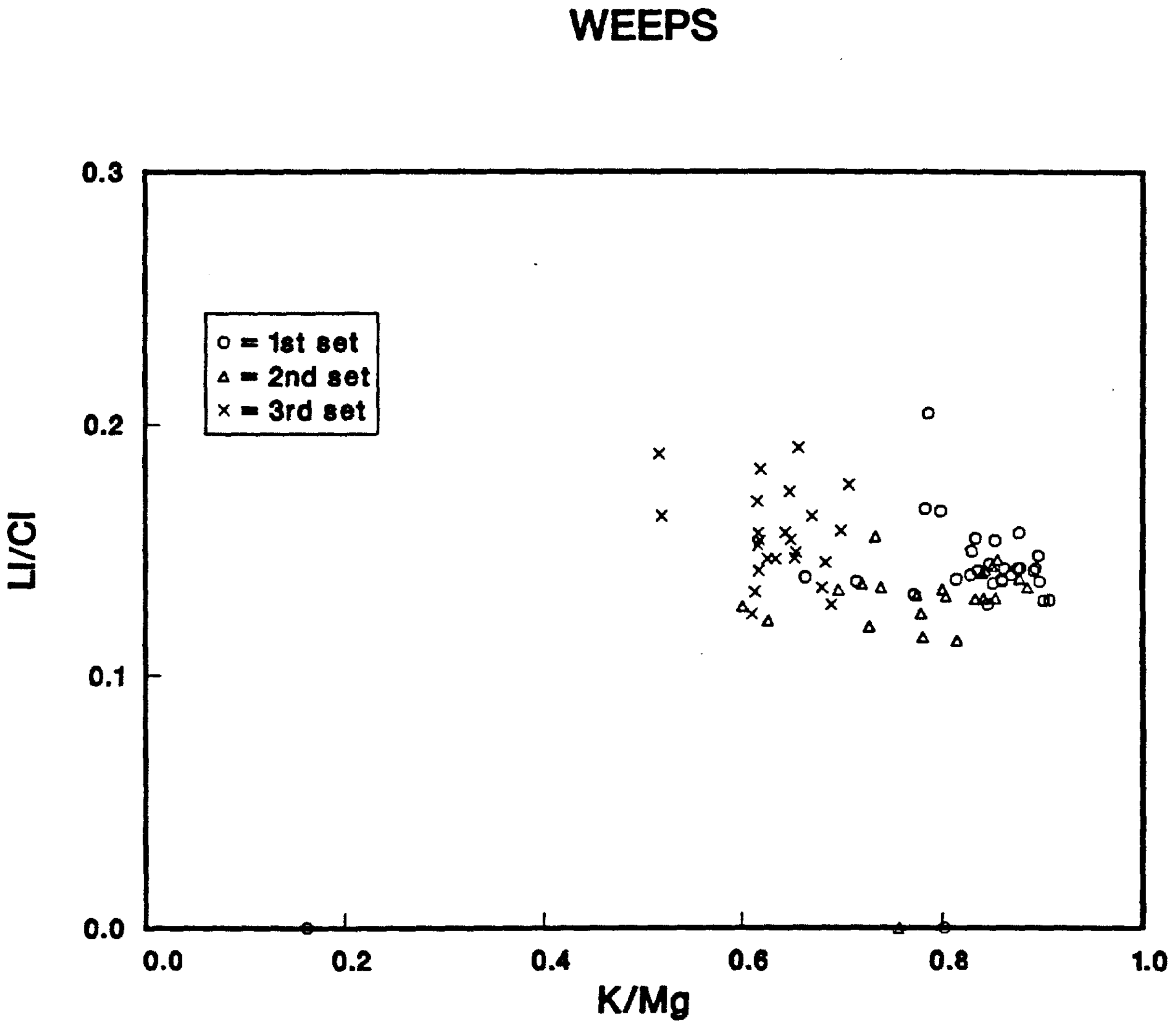


Figure 5: Weeps (all data) plotted as Li/Cl vs. K/Mg.

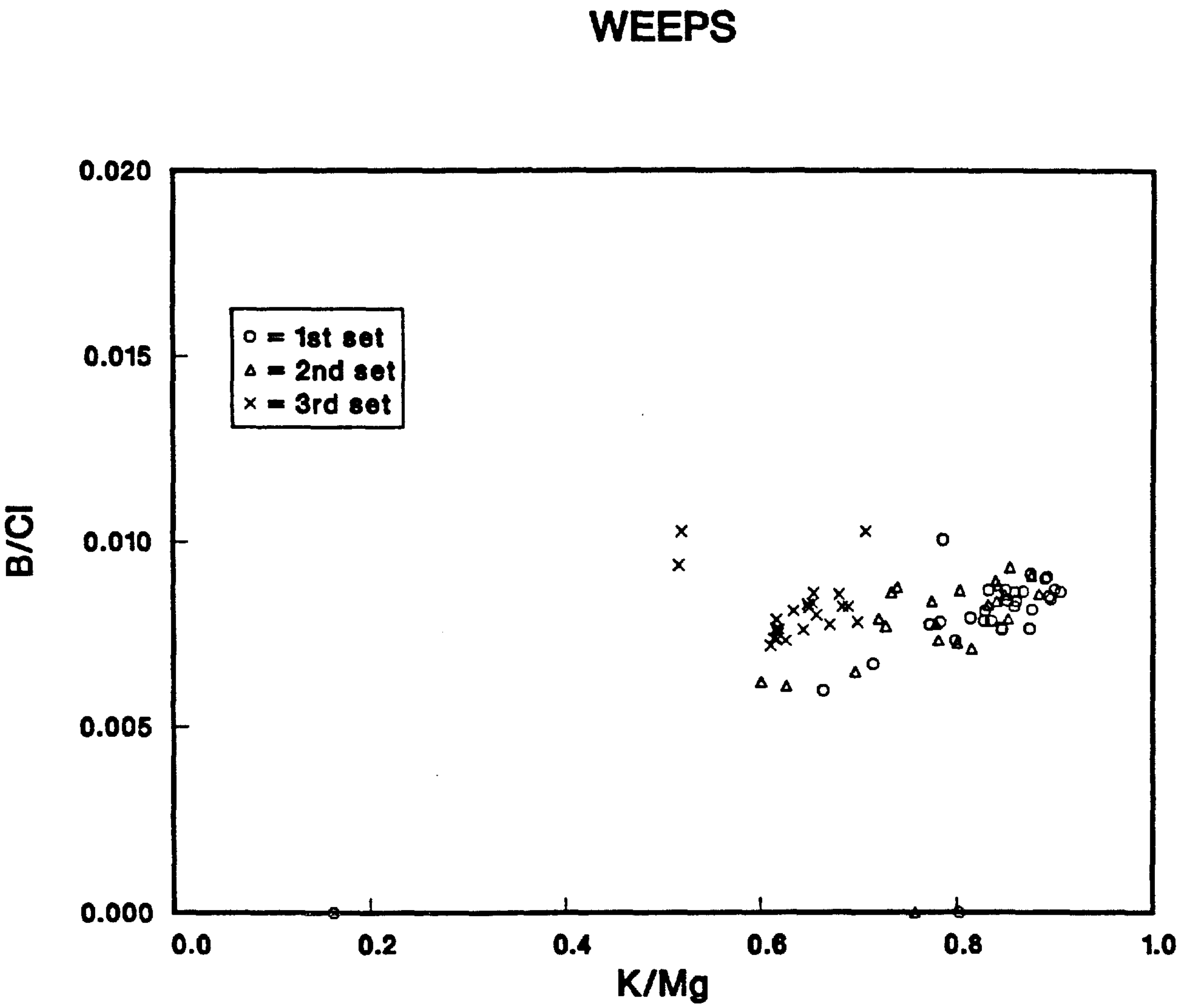


Figure 6: Weeps (all data) plotted as B/Cl vs. K/Mg.

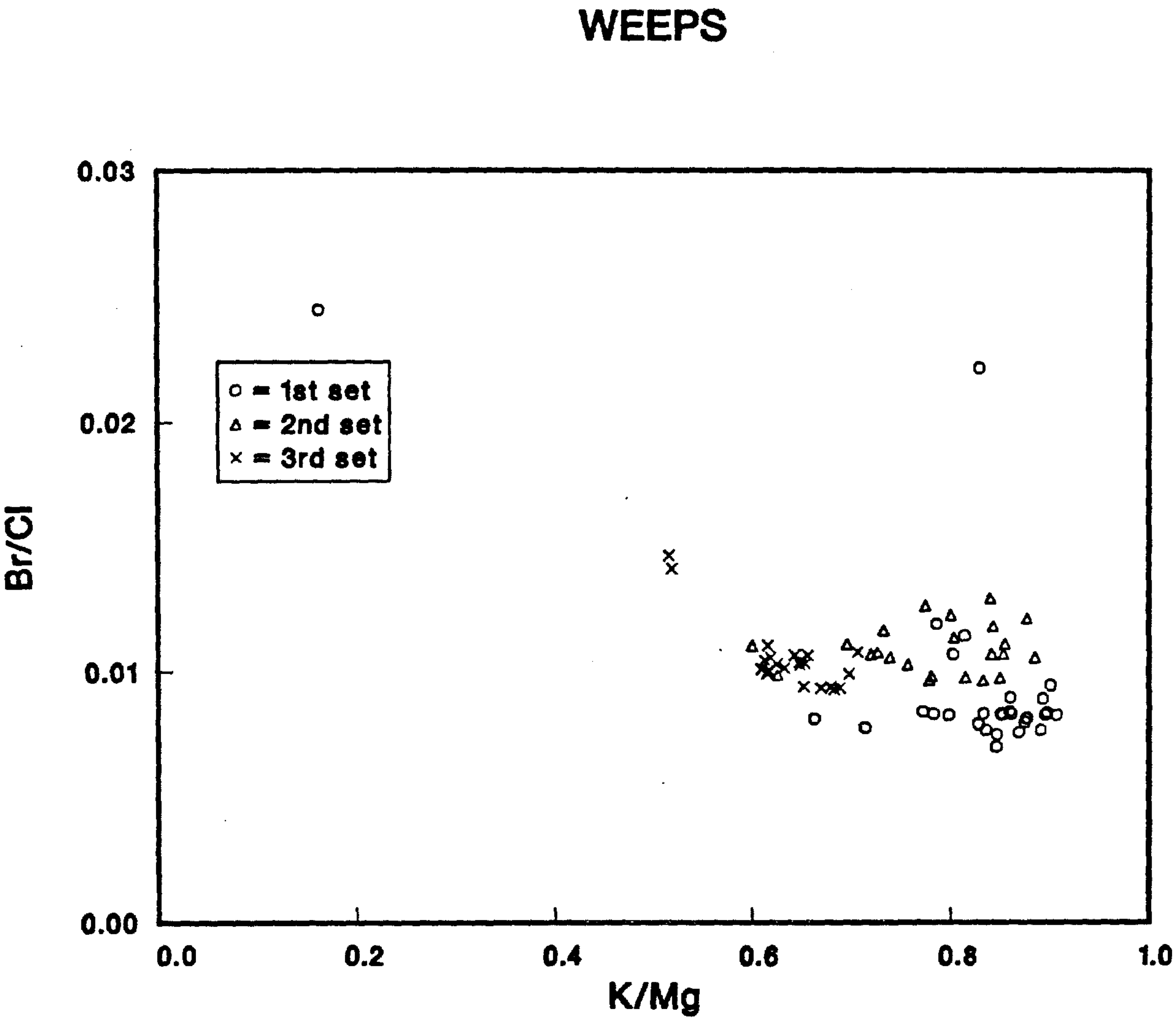


Figure 7: Weeps (all data) plotted as Br/Cl vs. K/Mg.

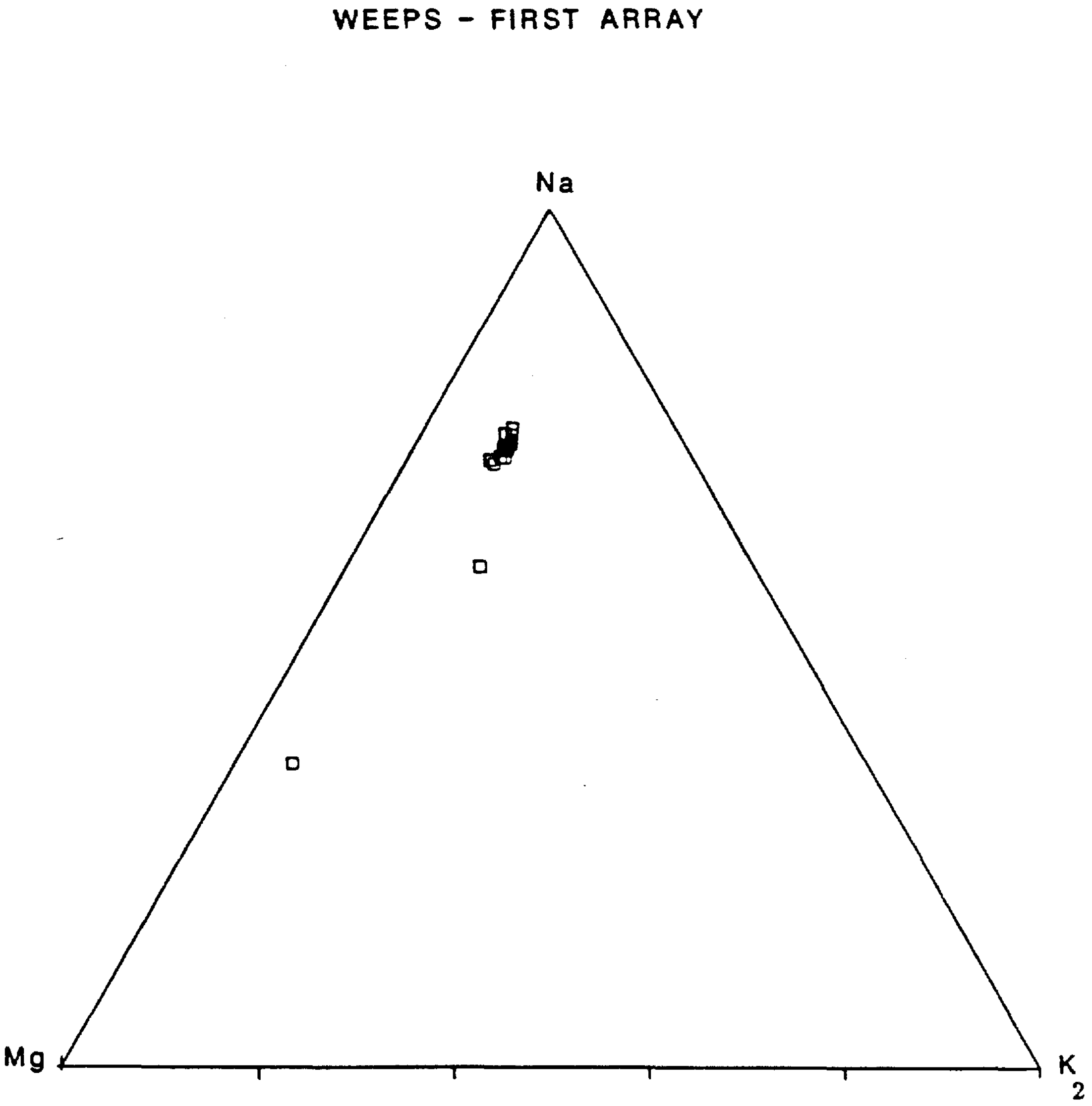


Figure 8: Triangular plot of weep array #1: Na–K_2–Mg.

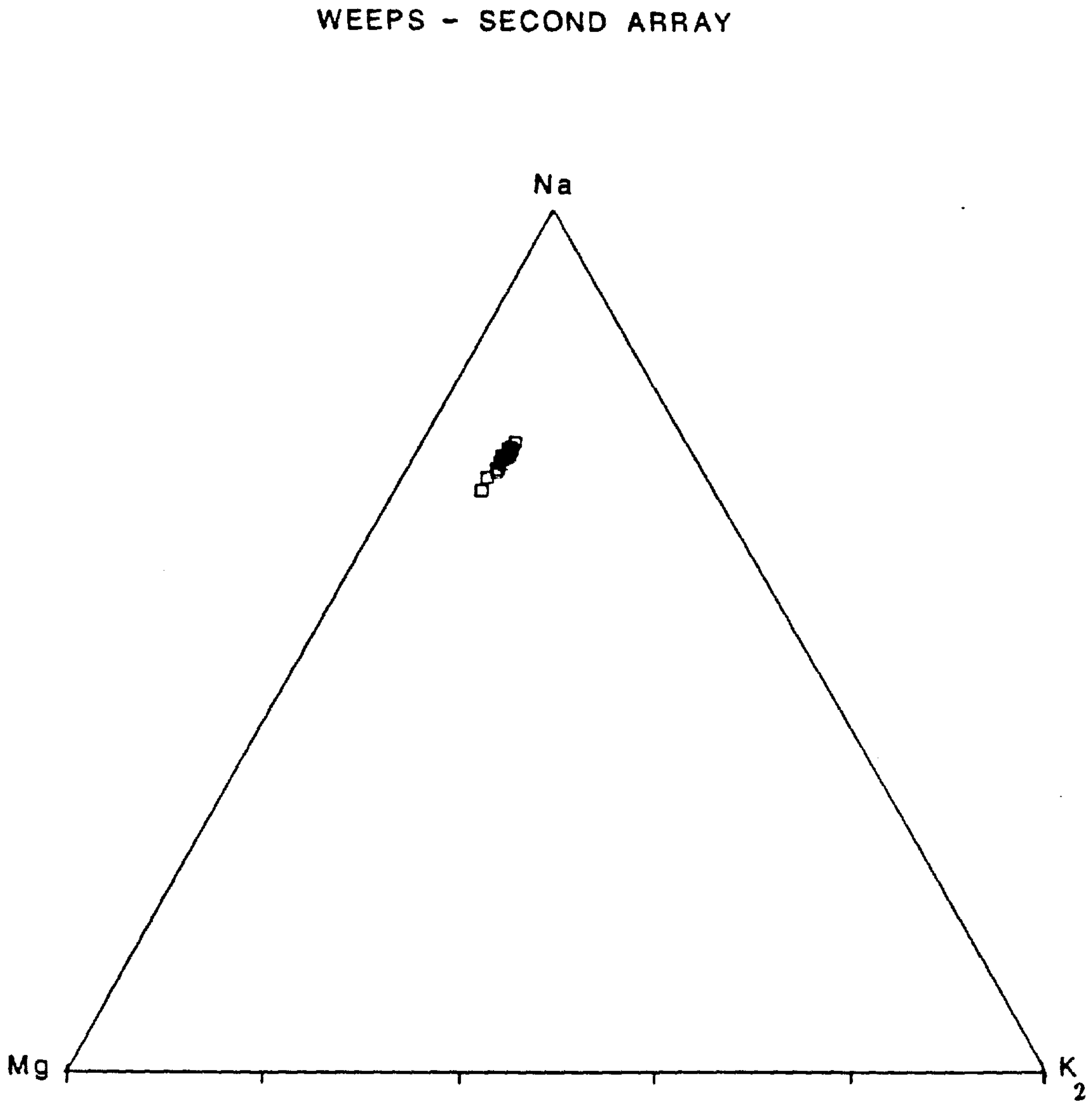


Figure 9: Triangular plot of weep array #2: Na–K_2–Mg.

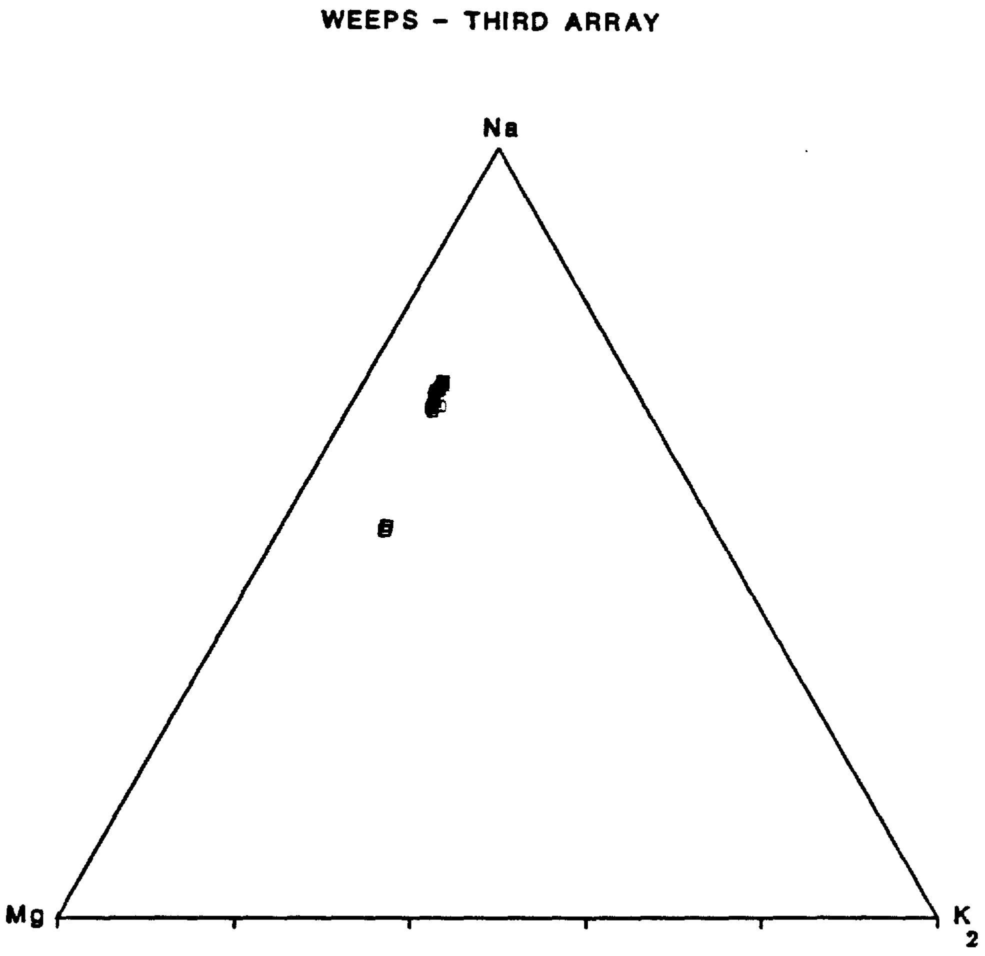


Figure 10: Triangular plot of weep array #3: Na–K_2–Mg.

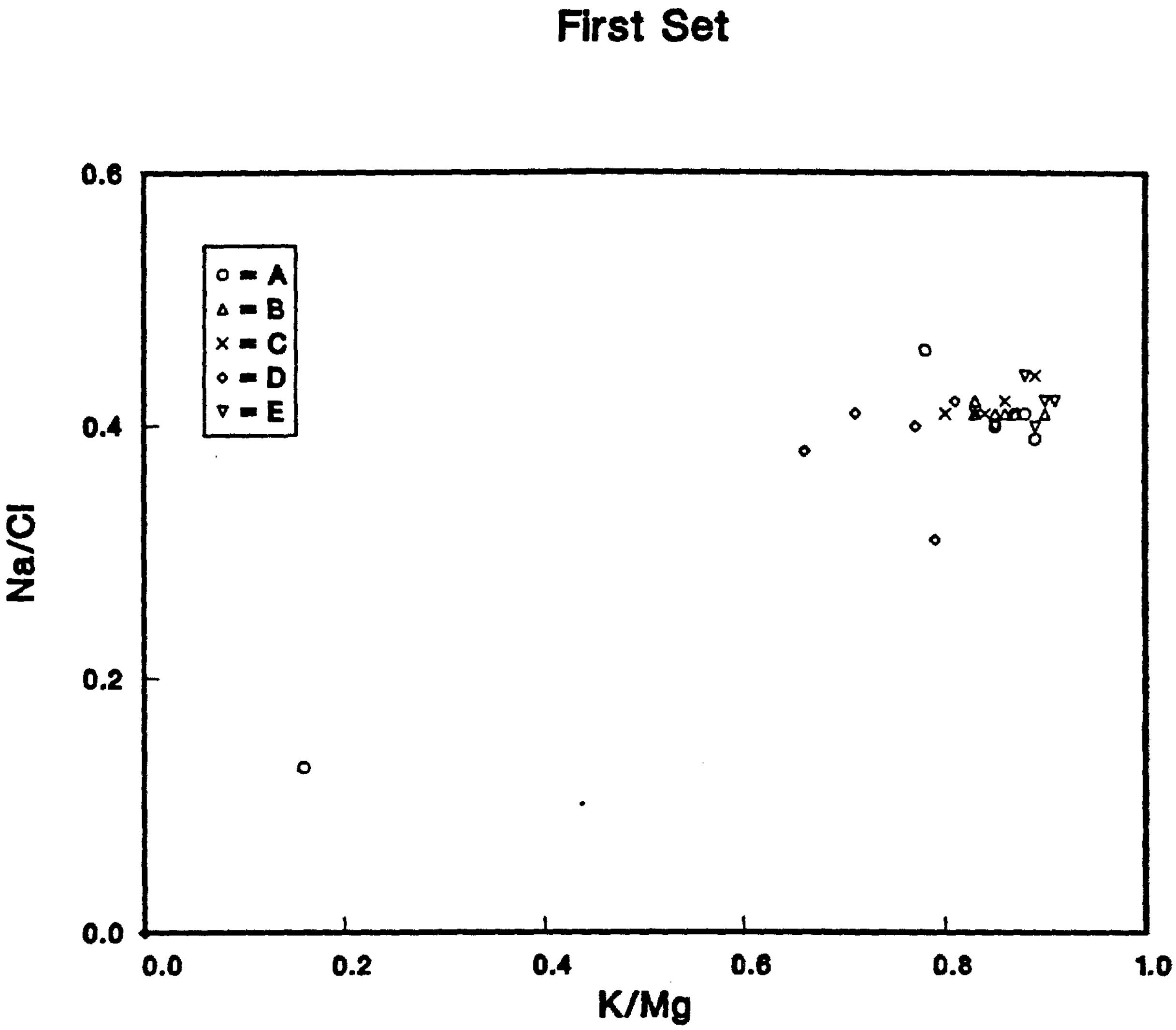
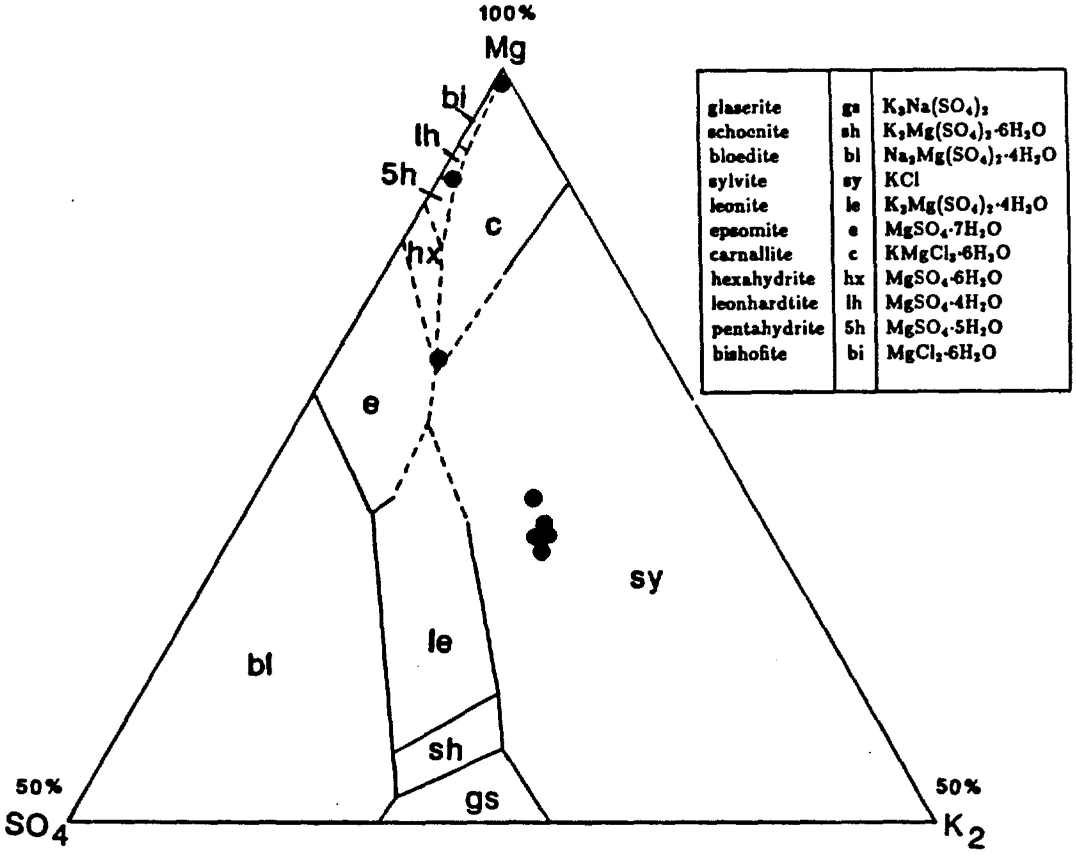


Figure 11: Weep array #1 showing lack of correlation with stratigraphy; Na/Cl vs. K/Mg. Unit A is the lowest stratigraphic unit exposed throughout the mine and is typically within one meter of the floor. Unit D is typically within 0.6 meters of the ceiling.



glaserite	gs	$K_3Na(SO_4)_2$
schoenite	sh	$K_2Mg(SO_4)_2 \cdot 6H_2O$
bloedite	bl	$Na_2Mg(SO_4)_2 \cdot 4H_2O$
sylvite	sy	KCl
leonite	le	$K_2Mg(SO_4)_2 \cdot 4H_2O$
epsomite	e	$MgSO_4 \cdot 7H_2O$
carnallite	c	$KMgCl_3 \cdot 6H_2O$
hexahydrite	hx	$MgSO_4 \cdot 6H_2O$
leonhardtite	lh	$MgSO_4 \cdot 4H_2O$
pentahydrite	5h	$MgSO_4 \cdot 5H_2O$
bishofite	bi	$MgCl_2 \cdot 6H_2O$

Figure 12: Jänecke diagram (from Braitsch, 1971) showing data from brine evaporation experiment plotted as Mg–K_2–SO_4. Phases shown are glaserite, gs; schoenite, sh; bloedite, bl; sylvite, sy; leonite, le; epsomite, e; carnallite, c; hexahydrite, hx; leonhardtite, lh; pentahydrite, 5h; and bishofite, bi.

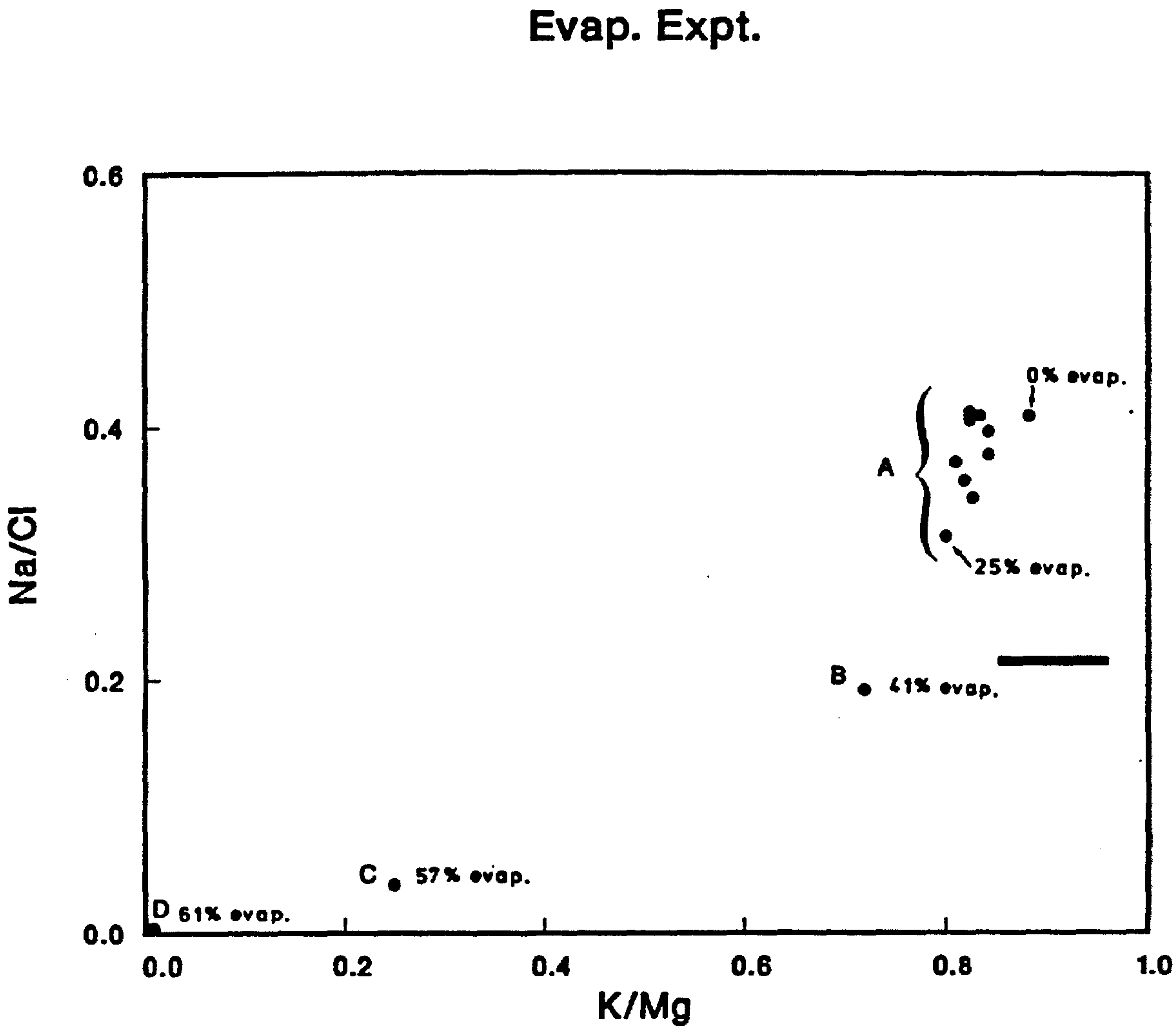


Figure 13: Brine evaporation experiment plotted as Na/Cl vs. K/Mg.

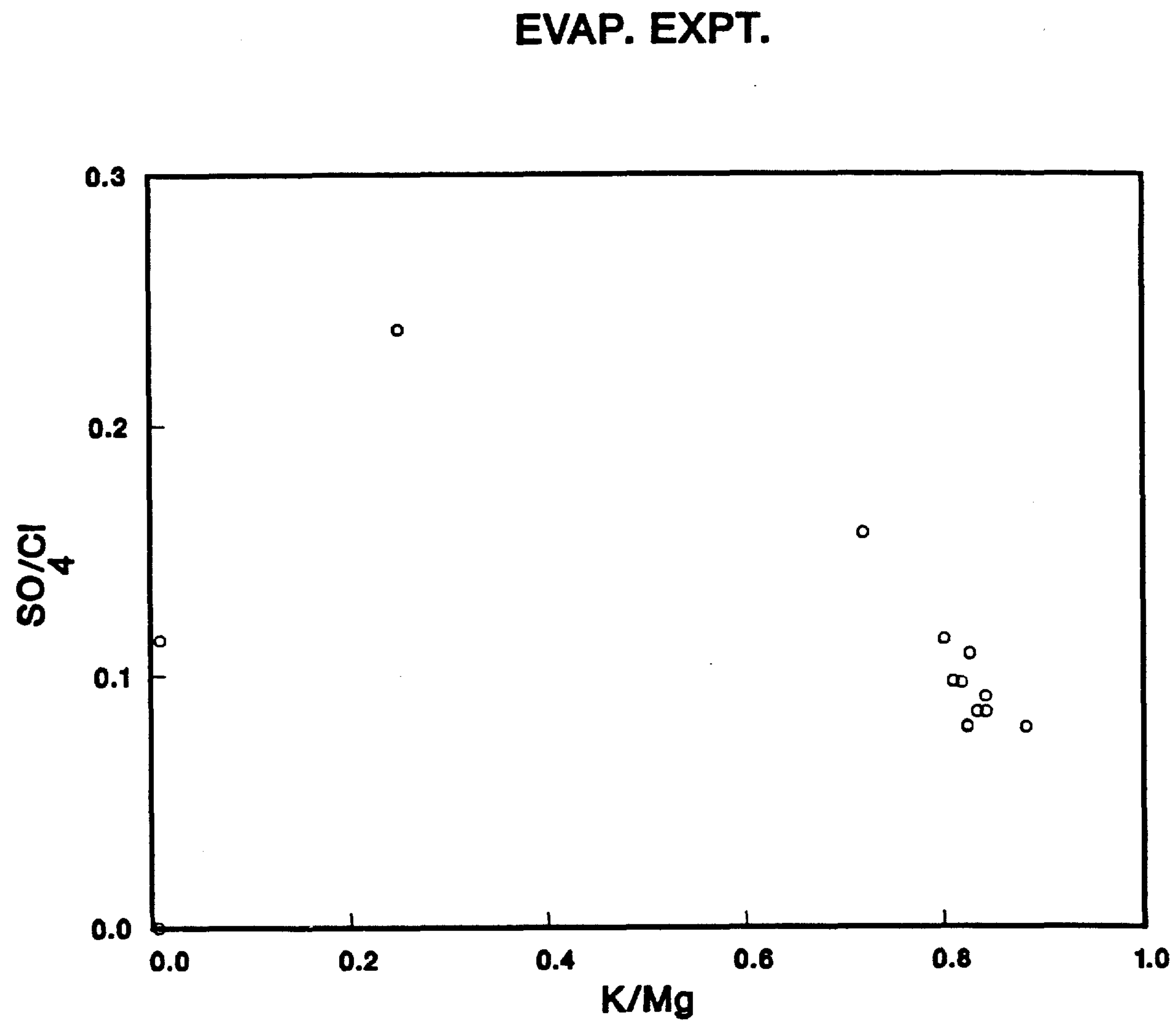


Figure 14: Brine evaporation experiment plotted as SO_4/Cl vs. K/Mg.

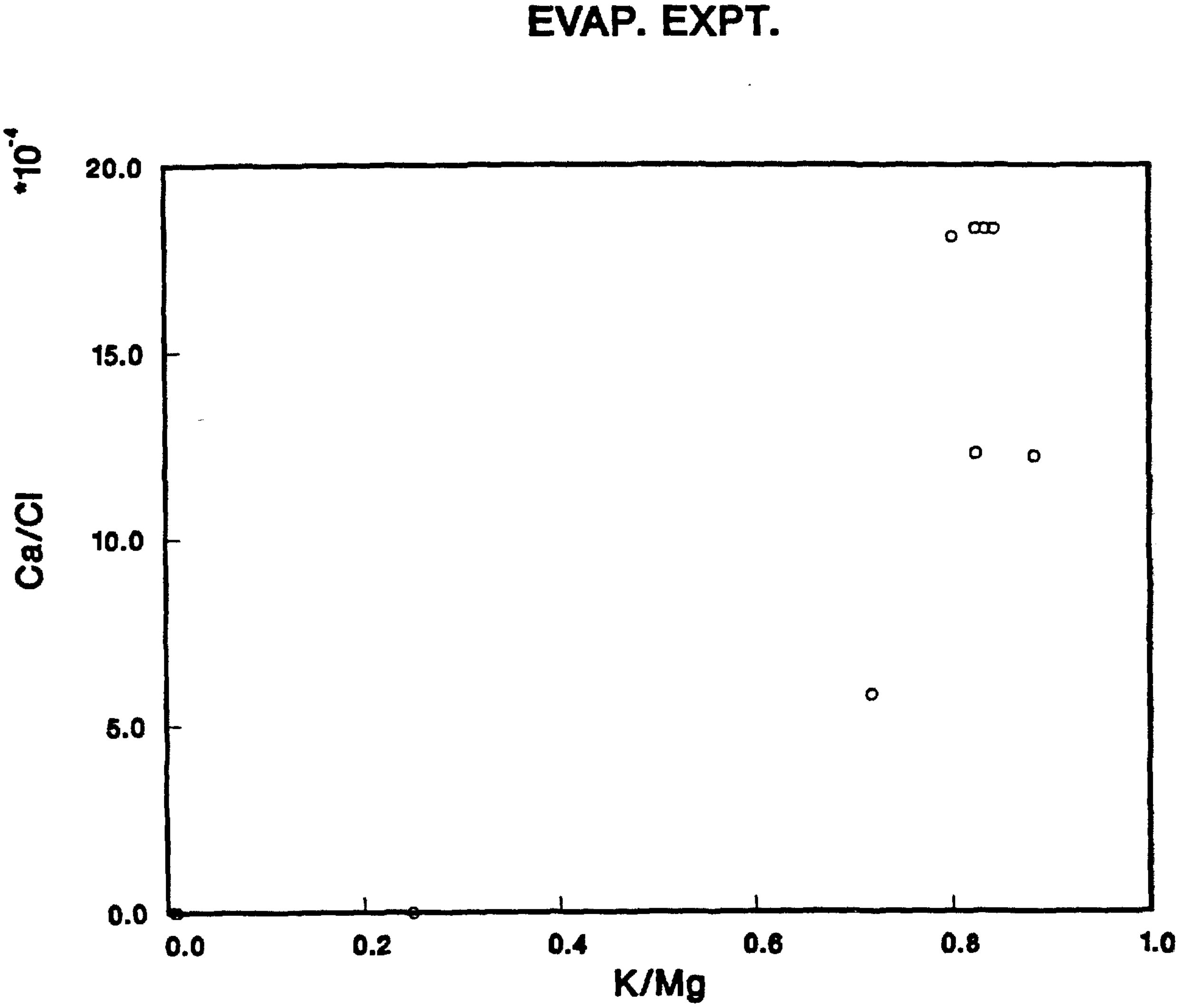


Figure 15: Brine evaporation experiment plotted as Ca/Cl vs. K/Mg.

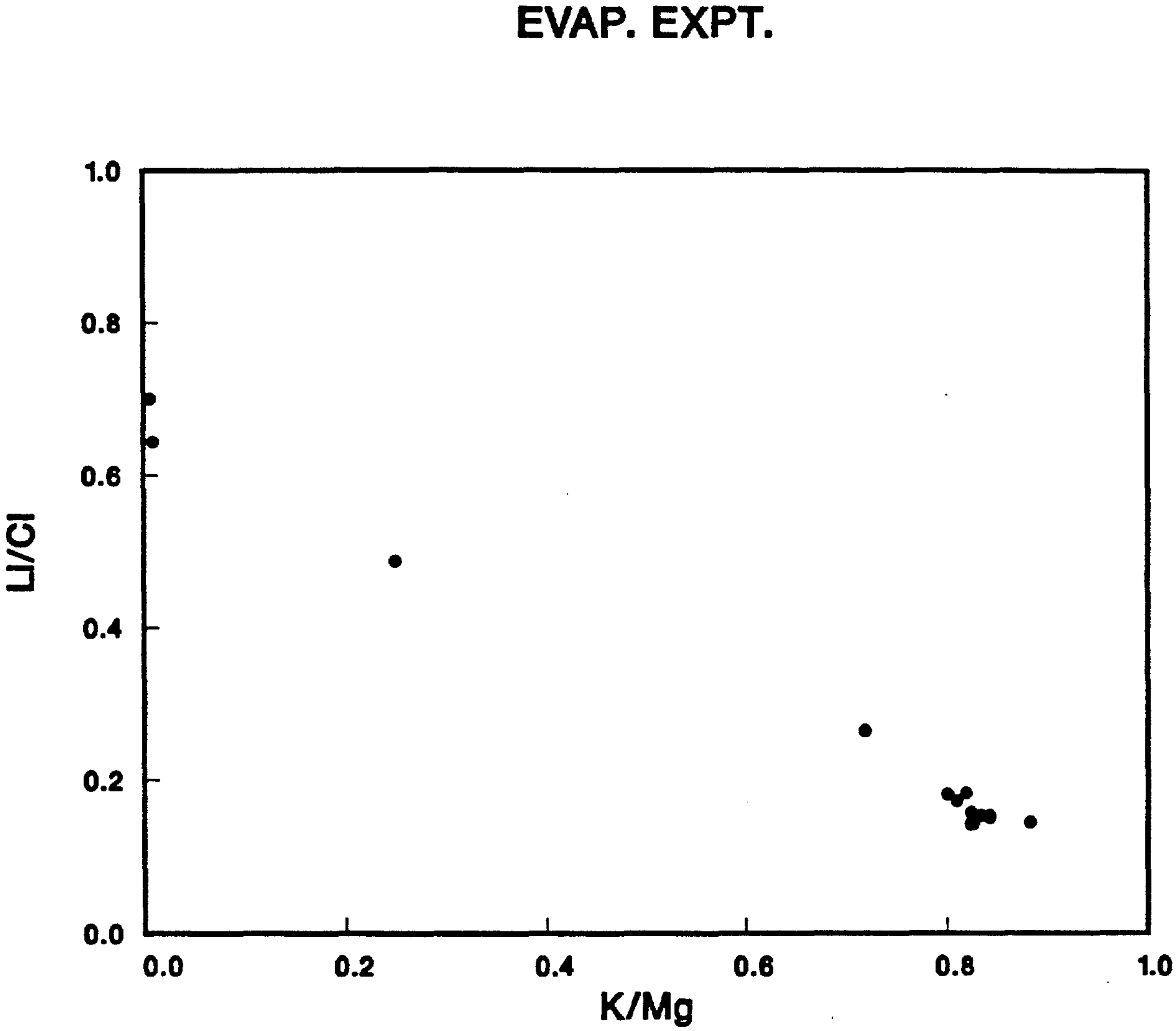


Figure 16: Brine evaporation experiment plotted as Li/Cl vs. K/Mg.

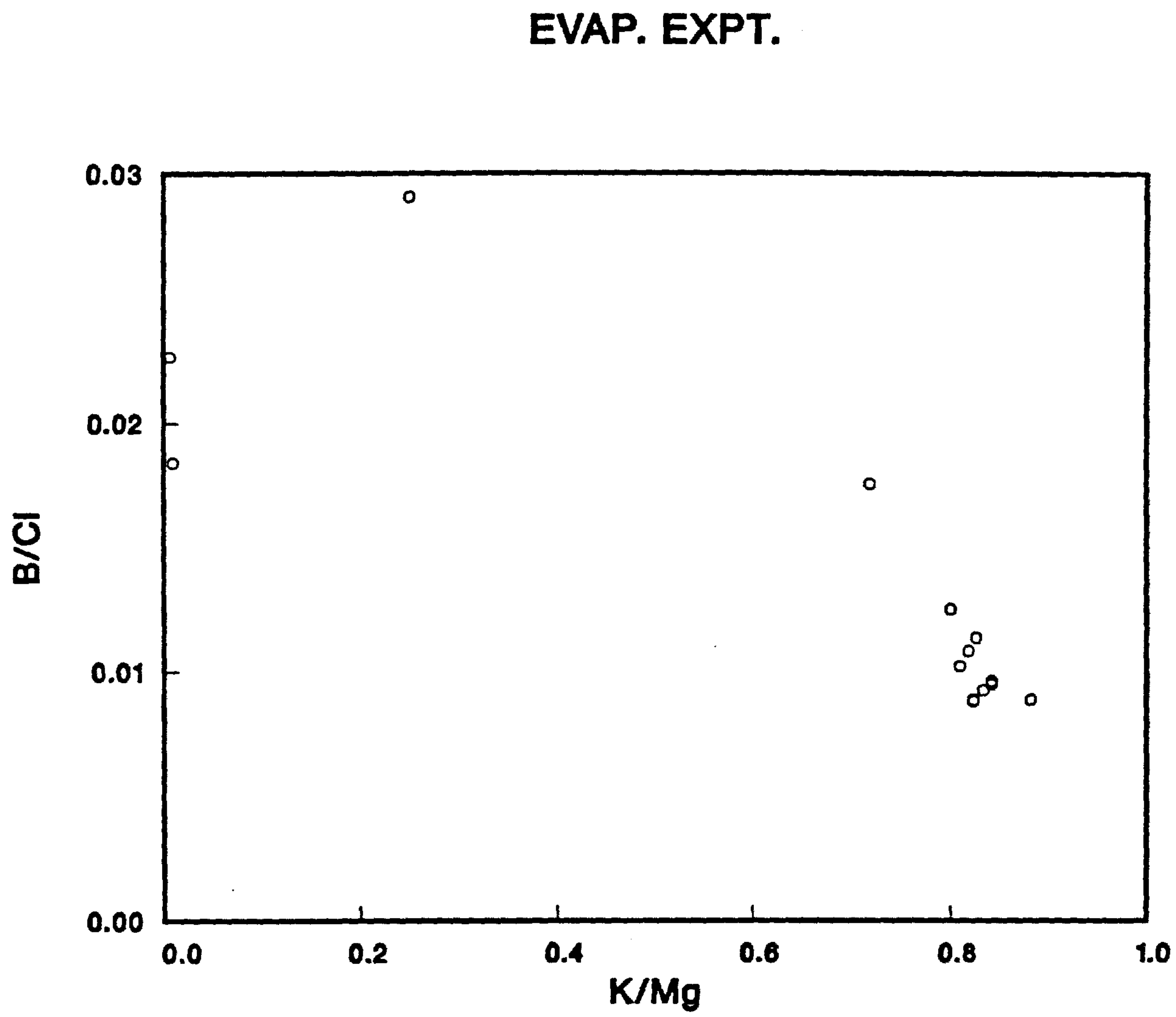


Figure 17: Brine evaporation experiment plotted as B/Cl vs. K/Mg.

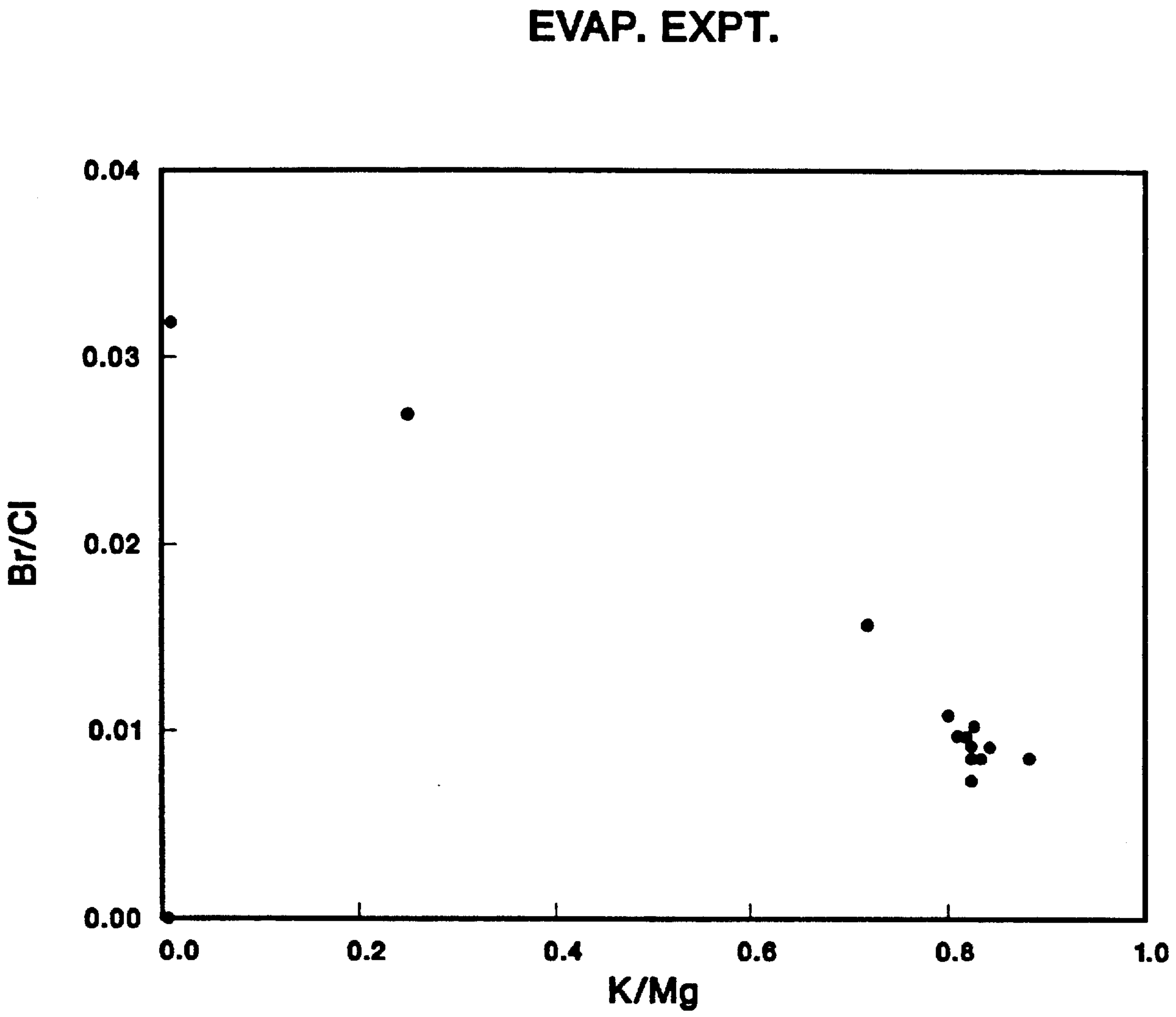


Figure 18: Brine evaporation experiment plotted as Br/Cl vs. K/Mg.

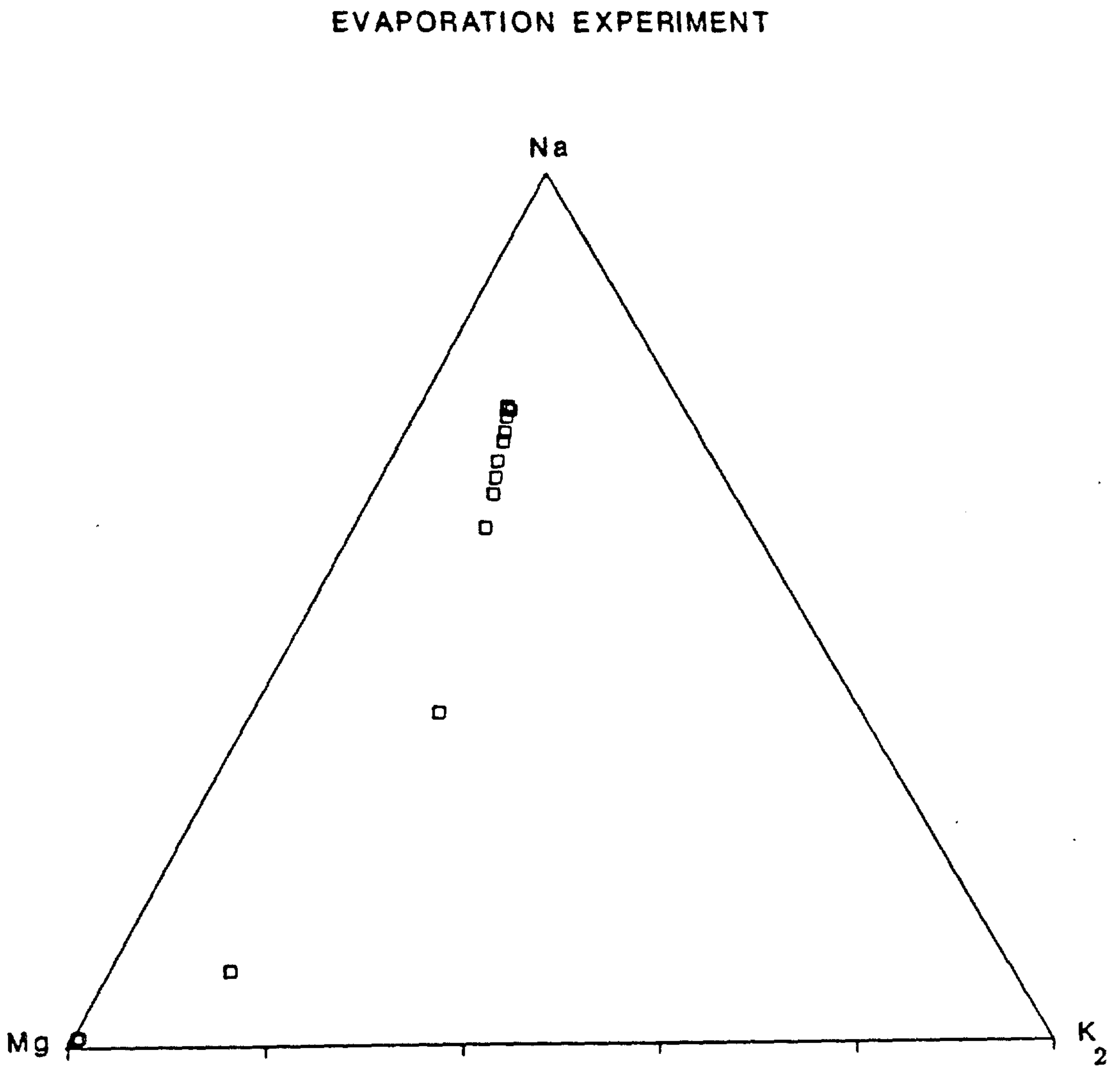


Figure 19: Triangular plot of data from brine evaporation experiment: Na–K_2–Mg.

Tables

Sample Designation	Na	Mg	K	Ca	Cl	Br	SO_4	Na/Cl	K/Mg	Charge Balance	Mass Balance
J-0/23	35.5	.1654	3.313	.1113	60.13	0.0596	0.9190	0.587	20.03	0.955	0.986
J-36/19	34.80	1.360	2.847	.170	58.18	0.093	2.555	0.598	2.093	1.007	0.950
J-6/6.5	33.50	1.588	4.676	0.451	56.78	0.127	2.887	0.590	2.945	1.0399	0.959
J-10/12	27.60	1.57	4.90	0.246	49.40	0.451	15.8	0.558	3.12	0.848	1.13
J-11/13	31.39	1.59	5.41	0.148	57.44	0.092	3.92	0.546	3.40	0.964	1.03
J-32/24	30.57	1.26	6.98	0.163	55.45	0.071	5.50	0.551	5.54	0.965	0.997
J-12/13	35.56	.978	2.17	.096	59.17	0.073	1.95	0.551	5.51	0.986	1.044
J-14/15.5	16.97	1.26	9.26	0.056	64.26	0.231	7.99	0.263	7.34	0.545	.817
J-15/6.5	35.94	0.910	2.93	0.176	58.30	0.090	1.64	0.616	3.22	1.03	1.01
J-19/9.5	35.73	0.253	2.06	0.114	60.00	0.050	1.79	0.595	8.13	0.944	0.937
J-22/-4	36.85	0.662	1.58	0.213	59.05	0.052	1.57	0.624	2.39	1.01	0.968
J-18.5/13	26.07	2.41	11.2	0.104	56.38	0.212	3.60	.462	4.64	0.974	0.960
J-2.25/9	27.26	2.24	9.44	0.143	54.97	0.146	5.80	0.495	4.20	0.967	0.907
J-7.8/8.5	35.34	2.17	6.60	0.099	54.17	0.156	1.45	0.515	3.05	1.00	0.992
J-5/8	34.99	1.06	4.38	0.259	56.63	0.078	2.60	0.618	4.15	1.05	0.978
B-1	33.46	3.21	2.10	0.043	58.41	0.191	2.57	0.573	0.654	1.04	0.936
B-2	31.07	4.27	2.15	0.051	56.35	0.179	5.92	0.552	0.503	1.03	0.970
B-3	31.75	2.99	2.84	0.151	57.25	0.211	4.81	0.555	0.949	0.994	0.936
B-4	34.41	1.114	1.629	0.1109	61.10	0.120	1.517	0.587	20.03	0.931	1.027
B-5	31.80	2.59	3.17	0.161	58.80	0.113	3.37	0.541	1.224	0.974	0.951
B-6	12.67	7.52	12.6	0.014	47.53	0.291	19.4	0.266	1.67	0.854	0.845

Table 1: Salt compositions from Rooms J and B. Data are in weight percent.

Sample	F (ppm)	Cl (ppm)	NO_3 (ppm)	Br (ppm)	SO_4 (ppm)
1	0.33	0.31	0.35	0.38	0.34
2	0.65	0.62	0.69	0.76	0.68
3	1.31	1.24	1.39	1.51	1.37
4	3.27	3.09	3.48	3.78	3.42
5	6.54	6.18	6.96	7.57	6.84

Table 2: Ion chromatograph analyses of anion standards (expressed as parts per million).

Sample	Ca			B	Li	Mg		K		Na		Cl	SO_4	Br
21A1	2.8	2.9	0	0	0	32.0	38.7	5.2	6.3	18.1	20.9	143	20.2	3.5
26A2	1.7	1.6	1.7	1.41	30	20.7	20.0	16.2	16.2	82.1	84.2	180	15.2	1.5
27A3	0.73	0.70	0.69	1.34	25	17.5	16.9	15.3	15.6	71.8	77.3	175	13.5	1.4
28A4	0.66	0.56	0.61	1.57	27	18.5	18.2	16.2	16.8	71.3	78.2	172	13.7	1.4
29A5	0.56	0.58	0.58	1.32	25	18.2	18.1	15.4	15.6	68.9	75.3	173	14.3	1.3
30A6	0.36	0.44	0.46	1.44	25	17.1	17.2	15.3	15.8	66.7	72.2	169	13.5	1.4
3B1	0.31	0.35	0.37	1.48	24	18.2	17.3	15.8	15.9	70.3	73.1	171	13.0	1.3
16B2	0.21	0.31	0.33	1.41	23	17.4	16.9	15.6	15.1	69.0	72.4	167	13.1	1.4
19B3	0.38	0.40	0.44	1.37	23	17.7	16.9	15.2	14.5	67.7	69.2	166	13.7	1.4
20B4	0.29	0.39	0.44	1.36	25	18.7	17.1	15.5	13.9	70.3	67.7	167	14.3	3.7
24B5	0.24	0.28	0.32	1.29	23	18.0	17.0	14.9	14.2	67.1	67.6	164	13.1	1.3
22B6	0.35	0.44	0.47	1.42	26	18.9	17.6	16.1	14.8	69.8	68.5	169	13.9	1.4
2C1	0.41	0.46	0.46	1.46	26	19.7	18.3	16.4	16.0	69.4	69.9	168	14.0	1.4
4C2	0.26	0.28	0.31	1.44	23	18.5	17.4	15.9	15.5	69.4	71.5	167	13.3	1.5
14C3	0.20	0.35	0.38	1.52	24	18.6	17.7	16.6	15.8	73.4	74.1	168	13.2	1.5
15C4	0.23	0.37	0.40	1.41	24	18.7	17.8	16.1	15.2	71.3	71.8	168	13.1	1.4
25C5	0.39	0.45	0.50	1.24	28	18.8	18.2	15.0	14.4	69.3	70.8	169	13.6	1.4
23C6	0.25	0.32	0.38	1.33	24	18.8	16.8	15.7	13.8	69.2	65.5	169	13.4	1.3
5D1	0.09	0.23	0.24	1.77	36	28.0	26.7	22.0	21.2	55.2	55.1	176	18.5	2.1
6D2	0.0	0.31	0.0	0.0	0.0	0.0	18.7	0.0	15.0	0.0	68.4	168	12.7	1.8
1D3	0.38	0.40	0.42	1.32	23	18.8	17.6	15.3	14.8	69.4	70.0	166	14.9	1.9
9D4	0.37	0.40	0.41	1.29	22	19.3	18.7	14.9	15.2	66.6	72.4	166	13.9	1.4
7D5	0.29	0.42	0.44	1.12	23	21.0	20.2	15.0	14.7	68.1	69.7	167	15.0	1.3
8D6	0.57	0.64	0.67	1.03	24	20.2	21.2	13.4	14.1	65.4	68.9	172	15.2	1.4
18E1	0.25	0.30	0.33	1.52	24	17.3	17.0	15.4	15.2	68.1	72.0	169	13.1	1.3
17E2	0.34	0.42	0.46	1.46	23	18.0	17.8	15.3	15.4	67.6	72.0	168	13.8	1.4
13E3	0.32	0.38	0.42	1.46	22	18.2	17.2	16.5	15.9	71.5	73.1	169	13.6	1.4
12E4	0.39	0.47	0.47	1.47	22	18.1	17.4	16.3	16.1	71.4	74.3	169	13.1	1.6
11E5	0.46	0.51	0.53	1.31	22	18.1	18.1	15.3	16.3	67.7	74.8	171	13.6	1.2
10E6	0.68	0.74	0.75	2.00	35	25.2	26.1	22.1	23.6	107.3	115.7	245	18.2	2.0

Table **3.1:** Weeps: Array #1 (parts per thousand).

Sample	Ca			B	Li	Mg		K		Na		Cl	SO_4	Br
53AA1	0.32	0.31	0.32	1.52	24	18.7	18.3	15.7	15.7	68.3	69.2	170	13.0	2.2
55AA2	0.29	0.27	0.29	1.49	25	17.9	17.8	15.2	15.2	66.1	67.6	174	11.7	1.7
56AA3	0.35	0.34	0.33	1.49	24	18.4	18.3	15.5	15.7	68.7	70.9	169	12.7	2.0
57AA4	0.48	0.42	0.41	1.59	25	19.2	19.6	16.4	17.2	72.9	77.9	171	16.2	1.9
58AA5	1.0	0.92	1.0	2.44	44	34.8	35.2	25.5	27.0	111.2	117.9	283	24.0	3.3
59AA6	0.56	0.49	0.57	1.57	24	17.8	17.6	15.6	15.7	67.3	67.5	173	13.0	2.1
75BB1	0.22	0.22	0.26	1.29	20	19.4	19.3	14.1	14.3	64.3	65.8	167	12.6	1.8
74BB2	0.30	0.28	0.32	1.49	23	19.9	19.8	14.7	15.0	68.8	70.7	170	13.6	1.8
77BB3	0.30	0.30	0.33	1.33	23	20.7	20.1	14.9	14.8	64.7	65.5	168	13.4	1.8
80BB4	0.35	0.42	0.47	1.07	22	22.8	22.4	13.7	13.5	61.4	62.2	172	14.1	1.9
79BB5	0.12	0.23	0.26	1.27	20	18.7	18.8	14.6	14.6	65.4	67.3	173	12.6	1.7
61BB6	0.22	0.21	0.0	0.0	0.0	18.1	18.1	13.7	13.9	61.6	64.2	165	11.4	1.7
78CC1	0.23	0.28	0.31	1.37	22	19.4	19.4	15.1	15.2	67.1	69.1	176	13.3	1.7
76CC2	0.24	0.29	0.33	1.41	22	18.2	18.5	15.3	15.7	69.0	72.4	168	13.6	1.8
74CC3	0.33	0.29	0.30	1.33	22	18.3	18.1	15.6	15.8	66.3	68.9	168	13.0	1.8
68CC4	0.33	0.32	0.37	1.46	23	17.9	17.5	14.9	14.6	67.3	67.3	176	13.7	1.7
62CC5	0.33	0.31	0.25	1.31	21	18.9	18.4	15.4	15.1	66.5	67.4	184	13.4	1.8
63CC6	0.46	0.55	0.60	1.46	23	17.3	18.0	15.3	15.8	68.7	73.0	170	14.7	1.8
69DD2	0.23	0.27	0.29	1.45	22	18.8	17.7	15.1	14.4	66.0	65.2	167	13.1	1.9
72DD3	0.57	0.54	0.58	1.11	23	20.4	20.5	14.2	14.3	64.3	66.8	171	14.2	1.9
65DD4	0.21	0.28	0.31	1.46	23	19.5	20.0	15.1	15.6	65.0	67.8	174	13.0	2.2
64DD5	0.36	0.47	0.51	1.05	21	20.6	20.5	12.9	12.9	60.0	61.7	172	14.2	1.7
66DD6	0.56	0.62	0.67	1.24	23	18.5	18.9	14.8	15.1	68.3	70.7	171	14.9	2.1

Table **3.2**: Weeps: Array #2 (parts per thousand).

Sample	Ca			B	Li	Mg		K		Na		Cl	SO_4	Br
49A1	0.43	0.52	0.59	1.44	27	22.5	22.7	14.6	14.6	63.0	62.3	175	14.4	1.8
50A2	0.43	0.48	0.54	1.31	29	21.6	22.1	13.3	13.8	60.3	61.9	171	14.1	1.7
51A3	0.27	0.42	0.43	1.42	25	21.3	21.8	13.9	14.0	61.8	61.7	170	13.2	1.6
52A4	0.19	0.33	0.33	1.44	30	21.3	22.0	13.8	14.1	61.8	61.7	173	12.9	1.8
47A5	0.21	0.33	0.32	1.50	26	21.1	21.6	13.8	14.0	62.4	63.0	174	12.5	1.8
45A6	0.45	0.54	0.61	1.44	26	23.2	23.3	14.7	14.7	62.5	61.7	177	14.9	1.8
37B1	0.05	0.20	0.22	1.82	29	34.1	32.1	17.7	16.2	44.3	44.6	177	17.8	2.5
38B2	0.53	0.76	0.80	1.35	27	24.3	25.1	15.2	14.9	63.8	64.4	184	15.9	1.9
41B3	0.39	0.66	0.65	1.43	34	23.3	23.9	15.3	14.9	61.6	61.6	178	14.0	1.9
43B4	0.35	0.53	0.52	1.79	36	37.0	35.3	19.1	17.8	46.8	48.5	191	20.8	2.8
42B5	0.51	0.64	0.72	1.36	28	24.4	24.1	15.7	15.4	62.2	61.5	178	15.2	1.9
46B6	0.13	0.25	0.27	1.36	27	23.2	23.2	14.3	14.2	59.6	59.3	172	13.0	1.9
31C1	0.14	0.31	0.28	1.27	26	22.0	22.4	13.6	13.7	60.1	60.3	169	13.5	1.7
32C2	0.10	0.27	0.26	1.21	21	21.8	22.0	13.3	13.3	59.8	59.8	168	14.4	1.7
33C3	0.11	0.26	0.26	1.26	26	21.9	21.5	13.5	13.5	62.2	62.1	171	14.6	1.7
34C4	0.15	0.27	0.28	1.28	24	22.2	22.1	13.7	13.8	60.2	59.9	169	14.2	1.7
36C5	0.36	0.53	0.58	1.27	23	22.5	22.1	13.8	13.4	62.7	60.8	172	13.4	1.8
40C6	0.09	0.26	0.25	1.30	31	22.3	22.4	13.8	13.6	60.9	59.8	170	13.1	1.8
44D1	0.21	0.32	0.33	1.46	23	20.6	20.8	14.0	14.1	63.0	63.5	170	13.2	1.6
48D2	0.43	0.54	0.55	1.33	28	20.9	21.0	14.0	14.1	64.5	64.2	171	14.5	1.6
35D3	0.35	0.55	0.54	1.41	22	20.9	20.9	14.4	14.2	63.6	63.3	171	14.2	1.6
39D4	0.25	0.55	0.51	1.34	27	21.2	21.8	14.8	14.7	63.1	63.1	171	14.3	1.7
60D5	0.39	0.57	0.51	1.81	31	22.5	23.0	15.9	15.9	60.8	62.2	176	14.2	1.9
54D6	0.42	0.60	0.57	1.42	25	20.5	20.9	14.0	14.1	63.7	64.0	172	13.8	1.6

Table **3.3**: Weeps: Array #3 (parts per thousand).

Sample #	% Evap.	Na	Cl	Mg	K	Li	B	SO_4	Br	Ca	K/Mg	Na/Cl
1	0.0	67	163	17	14	23.5	1.45	13	1.2	0.30	0.86	0.41
2	1.1	66	163	17	14	23.2	1.44	13	1.5	0.30	0.86	0.40
3	2.0	67	164	17	14	25.9	1.45	13	1.4	0.30	0.84	0.41
4	2.9	67	164	17	15	23.7	1.46	13	1.4	0.31	0.84	0.41
5	4.3	67	164	18	15	25.2	1.52	14	1.4	0.32	0.84	0.41
6	9.6	65	164	19	16	24.7	1.56	14	1.5	0.34	0.84	0.40
7	9.7	62	164	19	16	25.2	1.58	15	1.5	0.33	0.84	0.38
8	14.1	61	164	21	17	28.3	1.68	16	1.6	0.36	0.82	0.37
9	16.7	59	165	22	18	30.1	1.79	16	1.6	0.37	0.83	0.36
10	20.0	57	166	23	19	23.7	1.89	18	1.7	0.30	0.82	0.34
11	24.9	52	166	25	20	30.1	2.08	19	1.8	0.27	0.82	0.32
12	40.7	33	172	39	28	45.5	3.02	27	2.7	0.16	0.72	0.19
13	57.0	7.4	193	69	18	98.3	5.61	47	5.2	0.04	0.26	0.038
14	61.6	1.5	245	107	0.6	127	4.51	29	7.8	0.03	0.006	0.006
15	65.8	1.2	248	89	0.5	172	5.62	211	79	0.02	0.006	0.005
16	66.0	1.3	245	91	0.5	199	6.35	285	100	0.02	0.006	0.005

Table 4: Evaporation experiment brine compositions (parts per thousand).

Sample	Batch 1 Cl (ppt)	Batch 1 SO_4 (ppt)	Batch 1 Br (ppt)	Batch 1 F (ppm)	Batch 1 B* (ppm)
LB1	138	2.7	0.44	49	168
LB3	137	2.7	0.44	45	172
LB6	137	2.7	0.44	50	166
LB2	94	1.9	0.35	83	108
LB7	94	1.9	0.35	107	104
LB9	94	1.9	0.34	74	106
LB4	103	2.2	0.36	77	125
LB5	103	2.2	0.37	81	125
LB8	103	2.1	0.38	79	123

*** expressed as ppm boron though the probable chemical species is borate**

Table 5: Ion chromatograph analyses of anions in "unknowns": F and B expressed as parts per million; Cl, SO_4, and Br as parts per thousand.

Table 6.1. "Unknowns": Calcium (in parts per thousand)

Sample	Big Run		Batch 1		Batch 2		Batch 3
LB1	0.28	0.21	0.46	0.44	0.36	0.39	0.41
LB3	0.30	0.22	0.30	0.31	0.35	0.37	0.42
LB6	0.23	0.18	0.21	0.24	0.34	0.36	0.41
LB2	0.19	0.14	0.25	0.25	0.22	0.24	0.29
LB7	0.17	0.12	0.18	0.18	0.27	0.29	0.29
LB9	0.26	0.18	0.22	0.22	0.22	0.23	0.29
LB4	0.24	0.18	0.05	0.06	0.26	0.29	0.33
LB5	0.21	0.16	0.24	0.23	0.27	0.28	0.33
LB8	0.28	0.20	0.19	0.19	0.32	0.32	0.33

Table 6.2. "Unknowns": Sodium (in parts per thousand)

Sample	Big Run		Batch 1		Batch 2	
LB1	29	30	29	30	31	30
LB3	28	30	28	29	31	30
LB6	27	30	29	29	29	30
LB2	19	19	19	19	21	20
LB7	17	18	19	19	20	20
LB9	19	19	19	20	19	20
LB4	22	23	23	22	23	23
LB5	22	23	22	21	22	23
LB8	22	22	22	23	22	22

Table 6.3. "Unknowns": Magnesium (in parts per thousand)

Sample	Big Run		Batch 1		Batch 2	
LB1	24	26	26	27	24	23
LB3	24	27	25	27	24	23
LB6	24	26	25	27	23	24
LB2	17	18	18	18	17	17
LB7	16	17	17	18	17	18
LB9	17	18	18	18	17	17
LB4	18	19	18	19	18	18
LB5	18	19	18	19	17	18
LB8	18	19	18	19	18	18

Table 6.4. "Unknowns": Potassium (in parts per thousand)

Sample	Big Run		Batch 1		Batch 2	
LB1	21	22	20	21	22	22
LB3	21	22	20	21	22	22
LB6	21	22	21	21	21	22
LB2	14	15	14	14	15	15
LB7	13	14	14	14	14	15
LB9	14	14	14	15	14	14
LB4	16	17	17	16	17	17
LB5	16	17	16	16	16	17
LB8	16	17	16	16	16	17

APPENDIX I

Location and Installation of Sampling Arrays for Additional Characterization of Intergranular Brines from the Salado Formation.

Introduction

The installation of brine sampling arrays was completed April 6, 1989. The array design for additional characterization of intergranular Salado Fm. brines was provided by J. L. Krumhansl and C. L. Stein, 6233, and was based on their earlier work on brine weeps in the WIPP facility (fig. 1). The array design (hole spacing pattern) was changed after the first array was installed, so its design is not identical to that used in the second and third arrays (figs. 4, 6, and 8).

Stratigraphy

Seven map units are defined for the WIPP repository horizon (table 1; DOE, 1987). Locally, units# 1 and 2 are replaced by syndepositional dissolution and reprecipitation of unit# 3, and unit# 4 and 5 have been displaced as a result of channel cutting of subaerial mudflats. In the area of the first panel the strata exhibit a slight eastward dip. The stratigraphy and sampler locations for each of the brine sampling arrays are shown in Figure 2.

Methods

Using a Ramset 340-2 Dyna-Drill and a 2.5 cm bit, the brine sampling holes were drilled to a depth of approximately 20 cm. The cuttings were removed from the sample holes by scraping the sides of the holes with a bottle brush and then blowing the hole out with compressed air. Each of the samplers provided had to be modified prior to installation to decrease their diameter. This was accomplished by tightening the cable tie used to secure the filter paper to the sponge. Finally, the holes were sealed with Parafilm and #6 rubber stoppers.

Installation

On March 7, 1989 the first array was installed in the access drift to Room-Q (S-90) approximately 15 m west of the room-Q instrument alcove (fig. 3). The array consists of 30 sampling holes arranged in 5 rows of 6 columns (fig. 4). The lithology associated with the sampling holes is as follows:

1. Row 1 - clay "F"
2. Row 2 - map unit# 4 - argillaceous halite
3. Row 3 - map unit# 2 - argillaceous halite
4. Row 4 - map unit# 1 - halite
5. Row 5 - map unit# 0 - halite

Personnel mapping the stratigraphy in S-90 sprayed map units 1 and 2 with fresh water to remove the salt dust accumulation, a result of nearby mining activities. It is likely that this moisture was wicked into the microfractures of the Disturbed Rock Zone (DRZ), and as a result, data from brine samples from row 3 of the first array should be considered compromised.

On March 29, 1989 the second array was installed in north rib of S-1600 drift opposite Room 1, Panel 1 (fig. 5). The array consists of 24 sampling holes arranged in 4 rows of 6 holes (fig. 6). The lithology associated with the sampling holes is as follows:

1. Row 1 - map unit# 6 - halite
2. Row 2 - map unit# 5 - halite
3. Row 3 - map unit# 1 - halite
4. Row 4 - map unit# 0 - halite

On April 6, 1989 the third array was installed in the east rib of Room L-4 approximately 10m from the face (fig. 7). The array consists of 24 sampling holes arranged in 4 rows of 6 holes (fig. 8). The lithology associated with the sampling holes is as follows:

1. Row 1 - map unit# 5 - halite
2. Row 2 - map unit# 4 - argillaceous halite
3. Row 3 - map unit# 3 - halite
4. Row 4 - map unit# 0 - halite

It should be noted that the sample holes were numbered in the order they were drilled, and not in some random fashion as it might appear. In figures 2, 4, and 6 the numbers below each of the sampling holes are the hole number and the sampler number separated by a slash (i.e.: hole #/sampler #).

References

DOE, 1987, Geotechnical Field Data and Analysis Report: DOE-WIPP 87-017.

Table 1: Stratigraphy of WIPP Repository Horizon (DOE, 1987)

Stratigraphic Unit	Description
map unit# 6	Clear, some moderate reddish orange, coarsely crystalline, some fine to medium locally. <1/2% gray clay and polyhalite. Contact with lower unit gradational and/or diffuse.
map unit# 5	Clear coarsely crystalline. <1/2% gray clay. Contact with lower unit usually sharp with clay F.
map unit# 4	Clear to moderate brown and moderate reddish brown, coarsely crystalline. <1% polyhalite. <1 to 5% argillaceous material; predominantly brown, some gray, locally. Intercrystalline and discontinuous breaks and partings common in upper part of unit. Decreasing argillaceous contact downward. Contact with lower is usually sharp.
map unit# 3	Clear to moderate reddish orange, coarsely crystalline. ≤1% dispersed polyhalite and polyhalite blebs. Locally polyhalitic. Scattered gray clay locally. Contact with lower unit is usually sharp.
map unit# 2	Moderate reddish brown to medium gray, medium to coarsely crystalline. <1 to 3% argillaceous material. Contact with lower unit is usually sharp.
map unit# 1	Light reddish orange to moderate reddish orange, medium to coarsely crystalline. ≤1% dispersed polyhalite. Contact with lower unit is sharp.
map unit# 0	Clear to moderate reddish orange/brown, moderate brown and grayish brown. Medium to coarsely crystalline. <1 to 5% argillaceous material. Predominantly brown, some gray, intercrystalline argillaceous material and discontinuous breaks and partings. Upper two feet of unit is argillaceous halite decreasing in argillaceous material content downward. None to <1% polyhalite. Contact with lower unit is gradational based on polyhalite content.

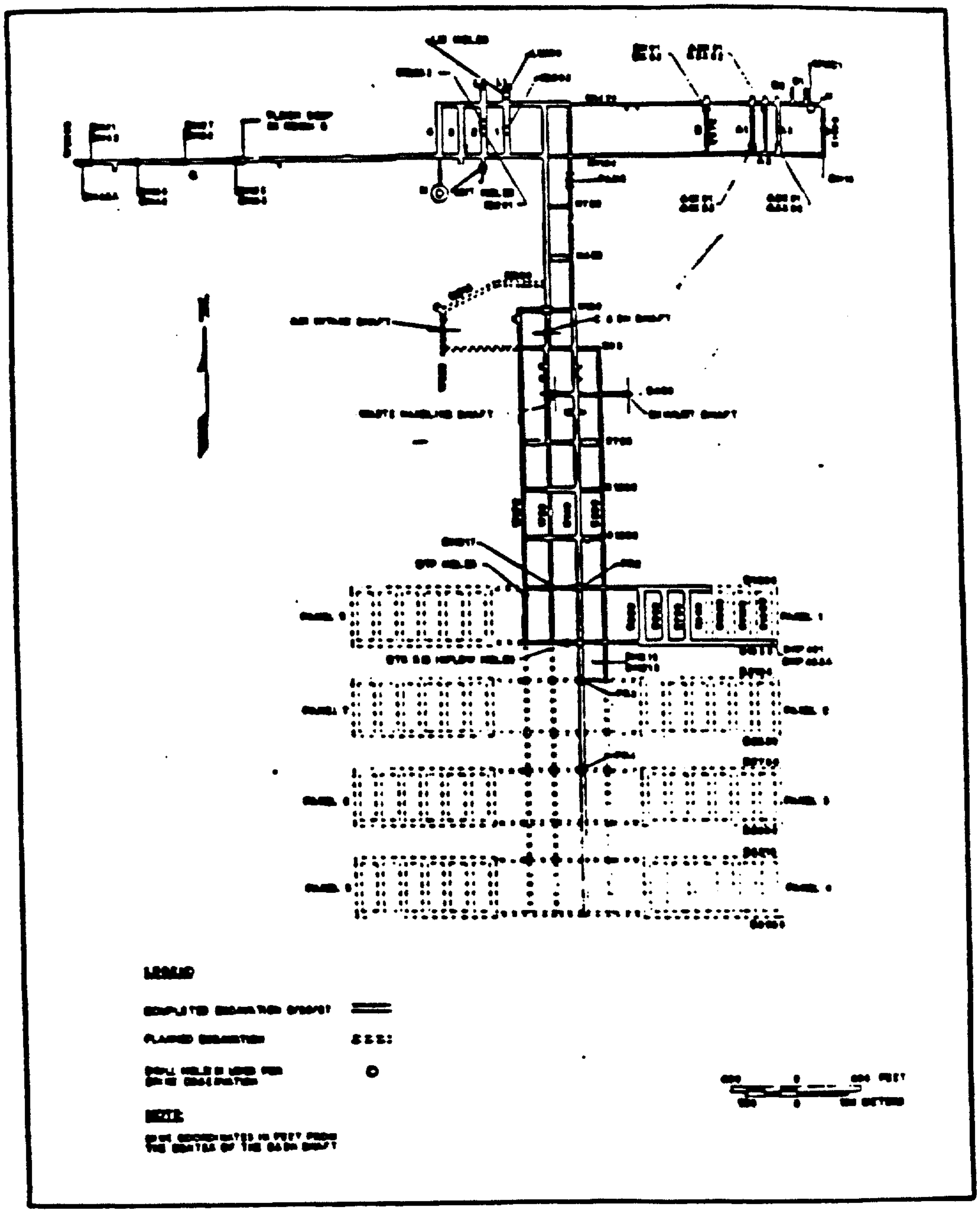


FIGURE 1

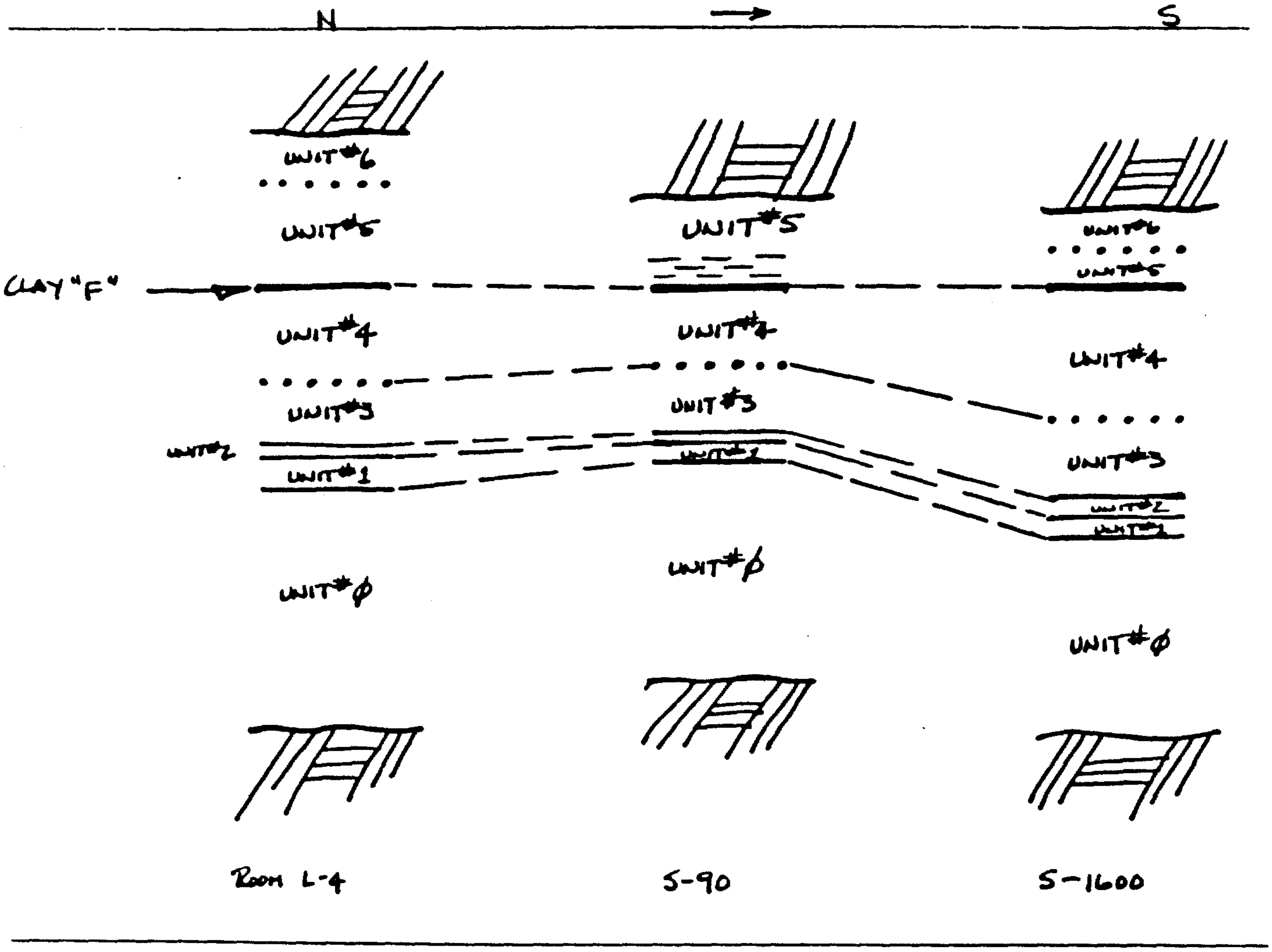

N
S
UNIT #6
UNIT #5
CLAY "F"
UNIT #4
UNIT #3
UNIT #2
UNIT #1
UNIT #0
Room L-4
UNIT #5
UNIT #4
UNIT #3
UNIT #2
UNIT #0
S-90
UNIT #6
UNIT #5
UNIT #4
UNIT #3
UNIT #2
UNIT #1
UNIT #0
S-1600

FIGURE 2

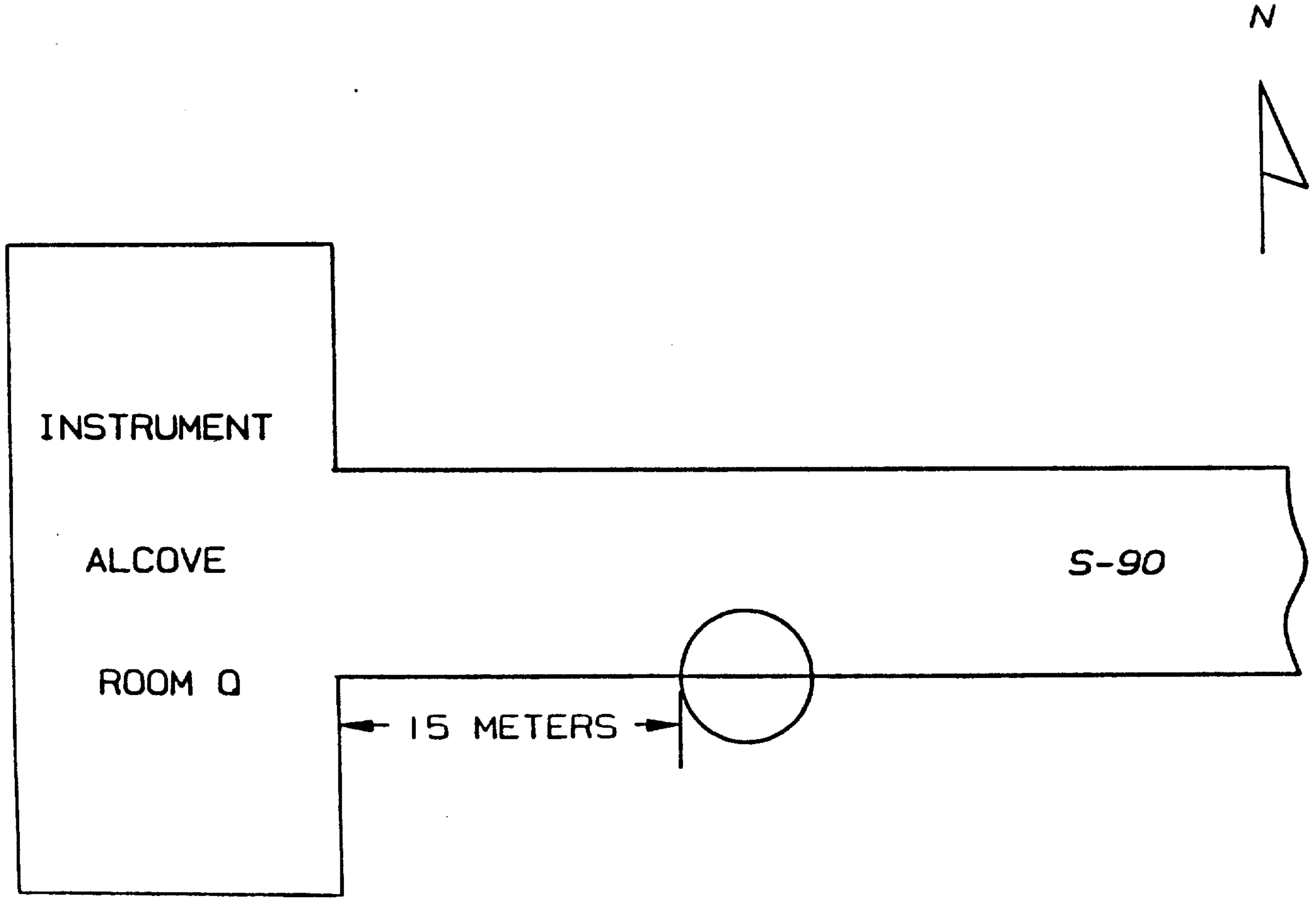


FIG.3

LOCATION OF BRINE SAMPLING ARRAY #1

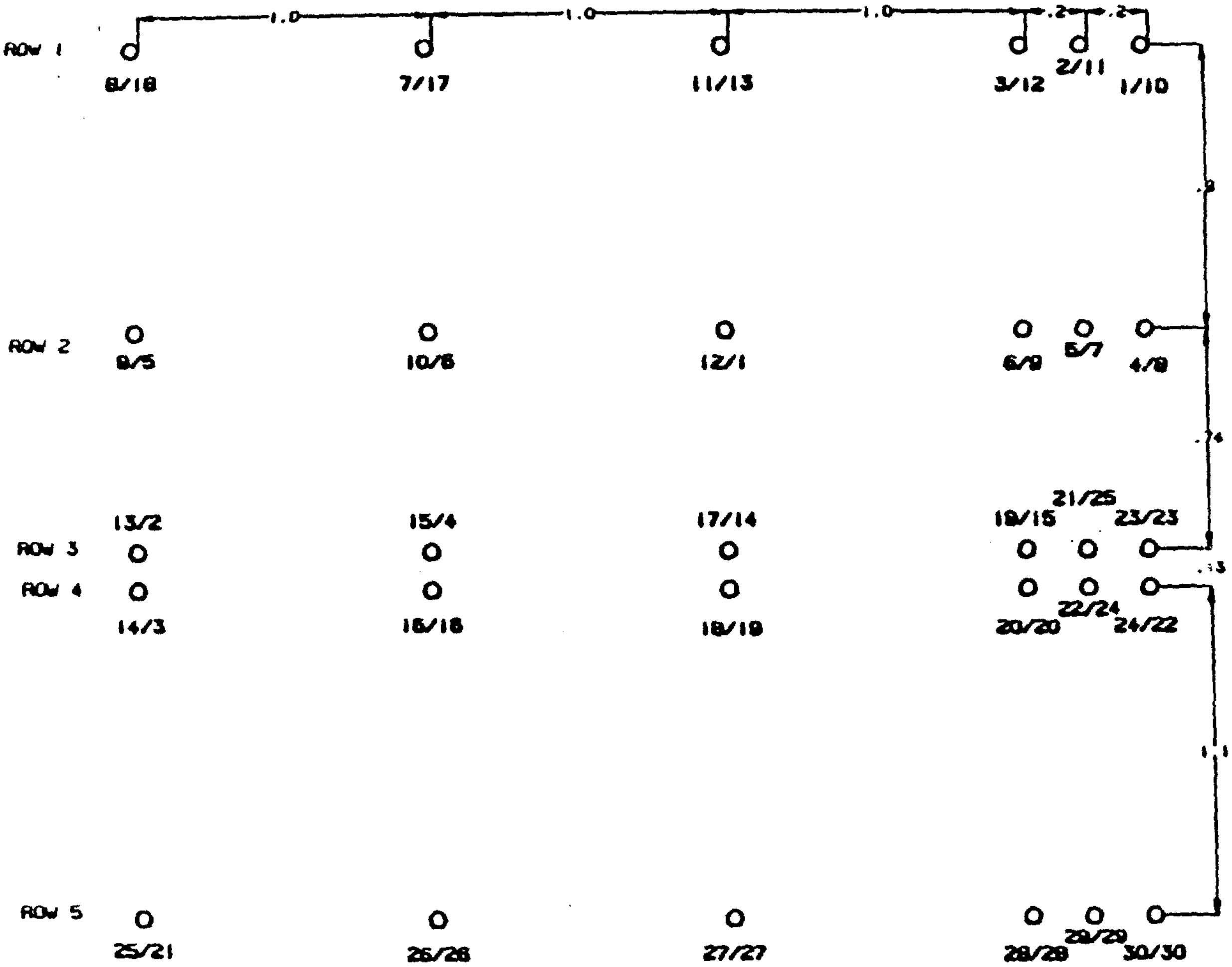


FIG. 4
BRINE SAMPLING ARRAY #1
DRILLED 3/07/89

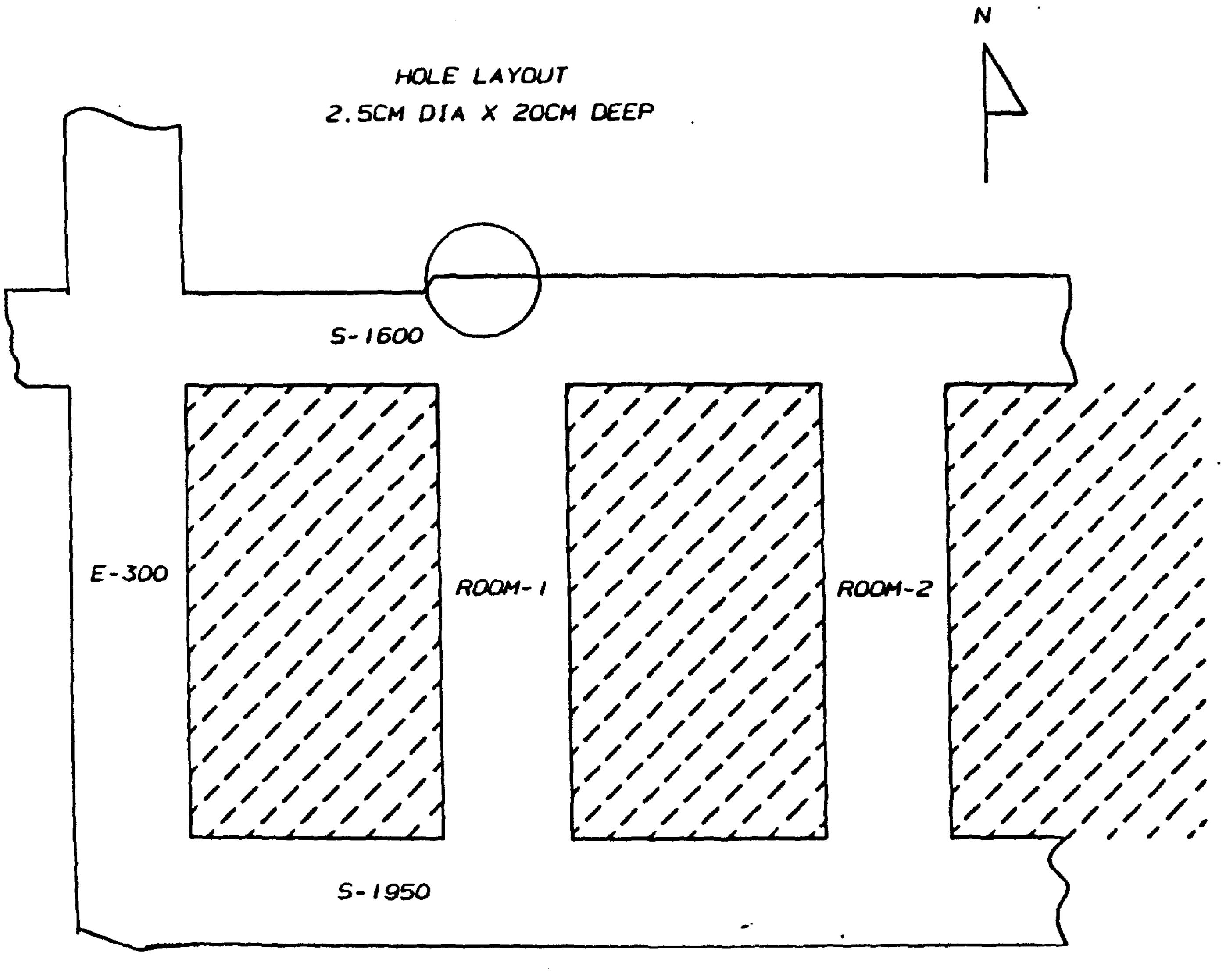
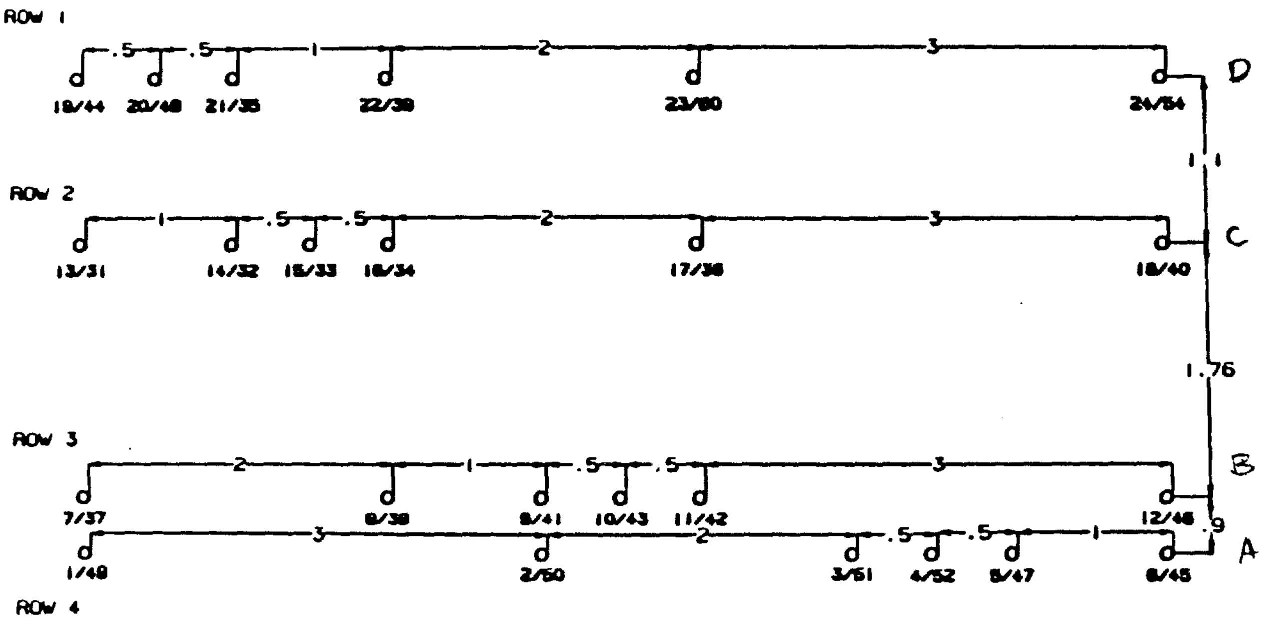


FIG. 5
LOCATION OF BRINE SAMPLING ARRAY #2



NOTE: ALL DIMENSIONS IN METERS

FIG. 6

BRINE SAMPLING ARRAY #2

DRILLED 3/29/89

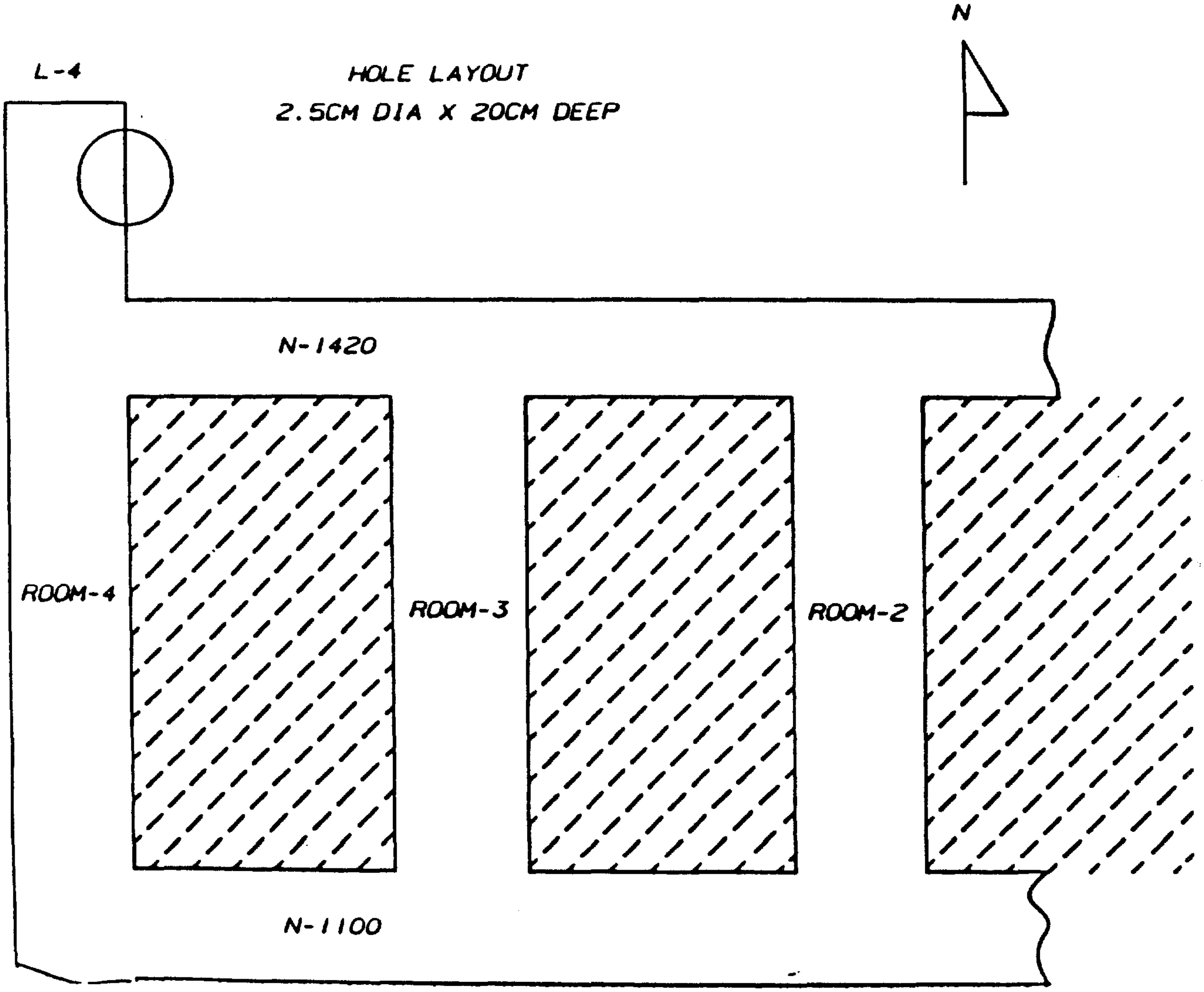
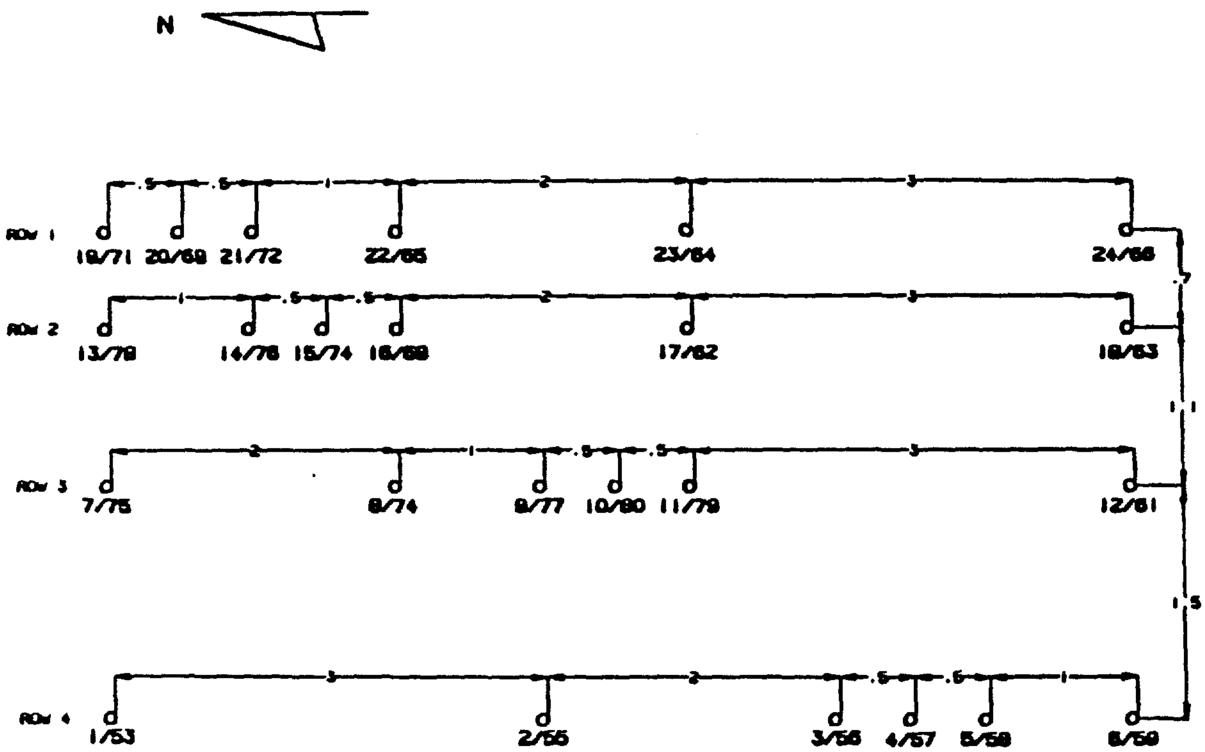


FIG. 7
LOCATION OF BRINE SAMPLING ARRAY #2



NOTE: ALL DIMENSIONS IN METERS

FIG. 8
BRINE SAMPLING ARRAY #3
WIPP WEEP HOLES DRILLED 4/05/89

Distrubution:

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C. Stein, 6233
S. Y. Pickering, 6330
D. R. Anderson, 6334
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