GEOCHEMISTRY OF SALADO FORMATION BRINES RECOVERED
FROM THE WASTE ISOLATION PILOT PLANT (WIPP) REPOSITORY

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ABSTRACT

Intergranular brines recovered from the repository horizon of the Waste
Isolation Pilot Plant (WIPP) have major- and trace-element compositions that
reflect seawater evaporation and diagenetic processes. Brines obtained from
repository drill holes are heterogenous with respect to composition, but their
compositional fields are distinct from those obtained from fluid inclusions in
WIPP halite. The heterogeneity of brine compositions within the drill-hole
population indicates a lack of mixing and fluid homogenization within the salt
at the repository level. Compositional differences between intergranular
(drill hole) and intragranular (fluid inclusions) brines is attributed to
isolation of the latter from diagenetic fluids that were produced from
dehydration reactions involving gypsum and clay minerals.

Modeling of brine-rock equilibria indicates that equilibration with evaporite
minerals controls the concentrations of major elements in the brine.
Drill-hole brines are in equilibrium with the observed repository minerals
halite, anhydrite, magnesite, polyhalite and quartz. The equilibrium model
supports the derivation of drill-hole brines from near-field fluid, rather
than large-scale vertical migration of fluids from the overlying Rustler or
underlying Castile Formations.

INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) is a Department of Energy (DOE)
research and development facility designed to demonstrate the safe disposal of
radioactive waste generated from the defense activities of the United States.
The objective of the WIPP program is to demonstrate the safe handling and
disposal of transuranic (TRU) waste and to create a research facility for the
examination of technical issues related to the emplacement of TRU waste in
bedded salt deposits.

The WIPP facility is located in southeastern New Mexico on the
tectonically-stable, western margin of the Delaware basin shown in Fig. 1. To
isolate the waste from the environment, a repository horizon was excavated
about 650 meters below the surface in bedded salt deposits of the Permian

MASTER

Salado Formation in Fig. 1, an evaporite sequence consisting primarily of thick halite beds (> 90%) with interbeds of anhydrite and clay, and accessory minerals of magnesite, polyhalite and quartz (1). Anhydrite interbeds up to one meter thick are laterally continuous and several serve as marker beds in the underground excavations. Marker Bed 139 lies about one to two meters below the repository floor and anhydrite beds A and B lie, respectively, about five and two meters above the back of most drifts. The salt recovered from the repository excavations contains about 0.6 weight percent of intragranular fluid in the form of inclusions (1).

An extensive program of site characterization and validation has been conducted for over ten years, and results of these studies have been presented elsewhere (5,11,13). Additional site investigations are being conducted to investigate the origin, hydraulic characteristics, extent, and composition of brine occurrences in the underground workings. These studies have been organized and implemented under the Brine Sampling and Evaluation Program (BSEP). The BSEP monitors the inflow rates and compositions of the brine occurrences to evaluate if vertical fluid movement is occurring between the repository and the overlying Rustler Formation or underlying Castile Formation illustrated in Fig. 1, and to assist in assessing the long-term impacts of brine inflow on repository operations and performance during the waste-retrieval period and after closure of the facility (2,3). Of primary importance to demonstrating the safe disposal of transuranic waste in salt is: 1) the origin of the brine as a near-field (local redistribution of brine within the volume of rock disturbed by the excavation) or far-field fluid (flow through a large volume of undisturbed rock); 2) the accumulation of brine in the repository prior to repressurization and closure of the excavations; and 3) the solubility and migration of radionuclides in the accumulated brine. This paper addresses the origin and composition of the brines to evaluate vertical fluid movement and, therefore, the potential for transport of soluble radionuclides, and provides a chemical data base for future evaluation of waste/brine interactions and radionuclide solubility in the brine.

Fig. 1. Location Map of the WIPP Site and Stratigraphic
Cross Section Through the Site

SAMPLE COLLECTION AND ANALYTICAL METHODS

Drill holes used for brine observations and sample sites are located in the northern experimental area and the southern waste-panel area of the underground workings presented in Fig. 2. The drill holes are up to 15 meters in length and are placed into the floor (down), back (up), and ribs (horizontal) of the drifts. Presently, 15 drill holes (11 down, 2 up, and 2 horizontal) have brine inflow rates which allow recovery of a sufficient volume for analysis (> 300 ml) about every three months. Brine inflow rates vary significantly between holes less than a meter apart, which may result from the local effects of mined-induced changes in porosity and permeability. Sample collection has been carried out a minimum of four times per year since April 1987.

Fig. 2.   Schematic Plan of the WIPP Repository Showing Brine Samples

Brine samples are recovered from down holes with a vacuum-assisted bailer and hand-operated rotary suction pump. After bailing or pumping, the down holes are plugged just below the collar with a piece of plastic foam and covered with a metal lid to prevent the introduction of foreign solids into the hole and reduce moisture loss by evaporation. Up holes are sampled by continuous, gravity-driven collection devices and several techniques are used to seal the interface between the collar and collection device. However, none of the techniques completely control the evaporation of brine in up holes, because the brine must flow down the sides of the hole to the collection device, resulting in a greater moist surface area being exposed to the underground atmosphere, relative to downholes. Lysimeters are used to recover brine from the horizontal holes, but recovered volumes have been small and few analyses are available.

Collected samples are sent to the United Nuclear Corporation Geotech Laboratory (UNC Geotech) in Grand Junction, Colorado and the International Technology Corporation Export Laboratory in Export, Pennsylvania. When sample volumes are insufficient to produce more than one split (i.e., < 300 ml), the single split was sent to UNC Geotech for analysis. The analytical methods of each laboratory are summarized in Table I.

Table I.   Analytical Methods used in the Analysis of WIPP Brines

The accuracy and precision of the analytical methods is evaluated by running spiked and duplicate samples, respectively. For UNC Geotech, the accuracy of I, SO_4-2 and Al is better than 10%, and all other parameters are better than 5%. Precision is better than 5% on all parameters except total inorganic carbon (TIC; better than 10%) and phosphate (PO4; better than 20%). IT-Export reported an accuracy of better than 5% for all parameters except Br, B, K, Mg, Si and Sr (better than 10%), and NH4, NO3 and Na (better than 15%). The precision of most parameters is better than 5%, but up to 10% for Br, SO_4-2 and Si, 15% for NH4+, and 20% for TIC and B. In addition to the analytical uncertainty, there is an uncertainty introduced into the analytical result by the dilution factor required for each parameter prior to analysis. The uncertainty associated with the dilution of the sample is probably less than 5%, but may be greater for trace elements that are near the detection limit of the analytical technique.

ANALYTICAL RESULTS

Tables II and III summarize the analytical results for UNC Geotech and IT-Export, respectively. The presented results are mean values obtained from all analyses over the period of April 1987 to December 1988, for holes with multiple sample rounds. Drill holes represented in Table II but not Table III indicate that these holes produced very little brine, and the volume collected was always sent to UNC Geotech.

Table II. Mean Physical and Chemical Parameters

Table III. Physical and Chemical Parameters of WIPP Brines

Brines recovered from the WIPP repository horizon (referred to as WIPP brines) have specific-gravity (SG) values greater than 1.2 g/ml, total dissolved solids (TDS) in excess of 330 g/l, pH near 6, and titration-alkalinity (TA) values greater than 800 mg/l (expressed as equivalent HCO_3-; Tables II and III). With the exception of TDS values, the interlaboratory values for these parameters are in good agreement. IT-Export reports TDS values that are 30 to 50 g/l less than those reported by UNC Geotech (cf, A1X02 in Tables II and III). This difference arises from IT-Export drying the precipitates at 180°C, which results in dehydration of complex salts (e.g., $MgCl_2:6H_2O$), versus 105°C for UNC Geotech.

For the remaining chemical parameters, interlaboratory results are in good agreement with the following exceptions: relative to UNC Geotech, IT-Export results for Cl, NO_3- and Si are lower, and Fe and K are higher. The differences are attributed to the different analytical techniques presented in Table I and procedures used by the laboratories on these analyses. Overall analytical quality, as judged by low charge imbalance (i.e., between -5 and 5 percent) is superior for the UNC Geotech laboratory.

In order of decreasing concentration, the major constituents (> 100 mg/l) in WIPP brines are: Cl, Na, Mg, K, SO_4-2, Br, B, Ca and NH_4+ shown in Tables II and III. The five most abundant elements have been plotted as mass ratios in Fig. 3. Most WIPP brines have Na/Cl mass ratios similar to those found in seawater in equilibrium with modern evaporites in Peru (10) and slightly greater than fluid inclusions recovered from WIPP halite (1), but K/Mg mass ratios are comparatively greater as presented in Fig. 3. The presence of authigenic magnesite in argillaceous halite recovered from the repository (1) suggests that the greater K/Mg mass ratios of these brines could result from diagenetic formation of magnesite or exchange of Ca, Na or K with Mg in clay minerals, which would deplete Mg relative to K and shift the ratio to the right in Fig. 3. However, the brines obtained from up holes have Na/Cl and K/Mg mass ratios that are lower than down hole samples, possibly due to evaporation of brine producing halite precipitates around the collar of up-hole sampling devices, which depletes Na and K. The depletion of K in up-hole brines is probably due to limited solid solution of sylvite in the halite structure, and/or precipitation of polyhalite.

Fig. 3. Major-Element Mass Ratios for WIPP Brines

In contrast, many fluid inclusions in WIPP halite have Na/Cl and K/Mg ratios that are less than the fields defined for seawater in equilibrium with modern evaporites and WIPP brines in Fig. 3. The difference in composition between fluid inclusions and drill hole brines appears to be related to the origin of the former as intragranular fluid and the latter as intergranular fluid.

Intergranular fluids may represent a mixture of initial evaporated seawater, fluid released and modified during clay diagenesis, and fluid released from the gypsum-anhydrite transition. Whereas the halite fluid inclusions may have been isolated from fluids produced by the diagenesis of clay minerals and gypsum. However, the fluid inclusions have relatively low K/Mg ratios that have been attributed to the formation of polyhalite (1). An early diagenetic event is supported by age dates greater than 200 Ma on polyhalite from the Salado Formation (4), and intergranular fluids may have evolved independently after this event.

Fig. 3 illustrates the sympathetic variation of Mg/K with SO_4-2/Ca. This linear relationship is due to partial evaporation of brine from the up holes prior to collection. As noted above, K can be depleted by limited solid solution of sylvite in the halite structure or precipitation of polyhalite during evaporation of the brine. Lower Ca concentrations in up holes, relative to down holes, indicates the solubility product of anhydrite may also be exceeded in the evaporating brine, which has the net effect of increasing the SO_4-2/Ca ratio because SO_4-2 concentrations in the brines are one to two orders of magnitude greater than Ca concentrations. Therefore, Mg/K and SO_4-2/Ca ratios increase with increasing evaporation because K and Ca are concentrated in the brines less than Mg and SO_4-2. An exception to this observation is brine recovered from the GSEEP hole in Fig. 3, a down hole that produces brine with high SO_4-2/Ca and low Mg/K ratios relative to, respectively, samples obtained from down holes and up holes. The origin of the relatively high SO_4-2/Ca ratio in GSEEP brine has not been completely resolved at this time, except that it is not due to recent evaporation (note Mg/K ratio in Fig. 3) and could be affected by the proximity of the bottom of the GSEEP hole to a fractured anhydrite bed (Marker Bed 139).

The HCO_3- concentration in the brines, which is established by the analysis for total inorganic carbon (TIC), is not a major constituent (i.e., TIC values < 95 mg/l), despite the high values for TA (Tables II and III). This observation indicates weak acids other than HCO_3- are protonated during the alkalinity titration. Several samples were analyzed for organic acids to determine their contribution (if any) to the TA values. Results for these analyses are given in Table IV, and indicate that organic acids do not contribute significantly to the TA values. Examination of Tables II and III reveals that only B is present in sufficient concentration (> 1400 mg/l) to account for the majority of the alkalinity displayed by these samples. Accordingly, an experiment was conducted with a WIPP brine to determine the response of the measured titration alkalinity to the addition of $Na_2B_4O_7$. A brine diluted 1:1 with distilled water was used in this experiment to avoid precipitation of NaCl upon addition of $Na_2B_4O_7$. Results are presented as titration curves in Fig. 4.

Fig. 4. Results of the Titration Alkalinity Test for Brine
Spiked with Sodium Tetraborate

The undiluted WIPP brine contained 2070 mg B/l and was titrated to an endpoint pH of 2, with a corresponding alkalinity value (read directly from the x-axis

by dropping a vertical line from the inflection point on the titration curve) of about 1100 mg/l, expressed as bicarbonate in Fig. 4. Diluting the brine 1:1 with distilled water increased the initial pH by one unit (i.e., lowered the hydrogen activity), and decreased the boron and alkalinity values by one-half their undiluted values. Addition of 500 mg B/l (i.e., 11.56 millimoles of $Na_2B_4O_7$ per liter) to the diluted brine raised the total B to 1535 mg/l, and increased the initial pH and alkalinity to about 7.3 and 2100 mg/l, respectively. An increase in the initial pH was attributed to the formation of HB_4O_7- after dissociation of the added $Na_2B_4O_7$, and the increase in alkalinity results from the protonation of HB_4O_7- to $H_2B_4O_7o$ during the titration. This latter step was repeated a second time and a further increase in alkalinity was observed in Fig. 4. The experimental results indicate that the presence of HB_4O_7- in the brine can account for the high alkalinity values. However, the diluted brine with an added 1000 mg B/l contains less B than the undiluted brine (2035 versus 2070 mg B/l), yet the undiluted brine has only one-third the alkalinity of the diluted and spiked sample in Fig.4. This observation indicates the dominant B specie in each of these solutions is different.

To investigate the B speciation of these two samples, the initial solutions in Fig. 4 have been plotted with the stability fields for B species in the system $B-H_2O$ at 25°C in Fig. 4. Fig. 4 suggests that the undiluted sample has most of its B partitioned into the H_3BO_3o specie, while the diluted and B-spiked sample containing a similar amount of B has most of its B partitioned into the HB_4O_7- specie. The undiluted brine has a lower TA value because relatively more B is present as the H_3BO_3o specie, which cannot be further protonated during the titration. However, regardless of which B specie is dominant in the solutions, the conclusion reached from the experimental titrations and Fig. 4 is that high TA values in WIPP brines are largely due to the presence of the HB_4O_7-specie.

Analytical results for trace constituents (< 20 mg/l) in the brines are available for (in approximate decreasing abundance): I, F, Sr, Mn, Si, Fe, Al, Ba, and As shown in Table II and III. In this suite of trace elements, F, Sr, and Mn have reported concentration values for a given drill hole that are similar for both analytical groups in Tables II and III, indicating they may be the most reliable trace elements for identifying chemical processes associated with the origin of the brines. Results for I, Si, Fe, Al, Ba, and As are tenuous because of poor interlaboratory agreement (cf, Si values in Tables II and III), higher detection limits as a result of dilution factors (e.g., Al in Table III), and possible iron contamination from instruments placed in sampled drill holes (e.g., A2X01 in Table II).

In Fig. 5, Mn and Sr have been plotted against Br to illustrate the processes which control these trace-element concentrations in the brines. Down holes have concentrations of Br that are less than 1600 mg/l (except L1X00), Mn less than 2 mg/l and Sr less than 3 mg/l, whereas up holes have concentrations of Br that are greater than 1900 mg/l, Mn greater than 4 mg/l and Sr greater than 5 mg/l. As previously noted in Fig. 3, halite occurs around the collar of up holes, suggesting that brine samples recovered from these drill holes have experienced some evaporative modification. This process is evident from the linear trend exhibited by up holes for Mn versus Br in Fig. 5. However, the

Sr concentrations of up-hole brines do not lie along a linear trend when plotted against Br in Fig. 5, suggesting mineral solubility controls Sr levels in these brines. The probable minerals controlling Sr concentrations are celestite, anhydrite, and/or gypsum. The relatively high Br concentration in brine recovered from down hole L1X00 may reflect spatial heterogeneity in the brines.

Fig. 5. Selected Trace Elements versus Br for WIPP Brines

A comparison of the WIPP brine analyses in Tables II and III with analyses obtained on waters in the overlying Rustler Formation (7) and the underlying Castile Formation (9) indicates each stratigraphic horizon contains unique fluid compositions. For instance, the low concentrations of B and Br (< 30 mg/l) in waters of the Rustler Formation (7) are one to two orders of magnitude less than WIPP brines, and contamination would easily be detected by lower B and Br concentrations in the WIPP brines. Similar fingerprinting techniques can be applied to rule out contamination of WIPP brines by brine present in the underlying Castile Formation. The comparison of analytical results on waters from the three formations indicates the brines recovered from the Salado Formation are near-field fluids, which have not undergone large-scale vertical migration. Furthermore, analyses on brines recovered from the GSEEP and L1X00 down holes indicate WIPP brines are not uniform in composition, which implies small-scale vertical migration and fluid mixing may also be limited.

MODELING ROCK/BRINE EQUILIBRIA

An objective of the WIPP Brine Sampling and Evaluation Program is the characterization of rock/brine equilibria. As partial fulfillment of this objective, aqueous-speciation and mineral-solubility modeling was carried out with the EQ3NR geochemical code using the Pitzer option (12,6). Computer runs utilized the Pitzer and Harvie-Moeller-Weare (HMW) data bases for ion-interaction parameters, because all of the available analyses are not incorporated into a single data base. Input files for the Pitzer runs contained the analyses Br, Ca, Cl, F, I, K, Mg, Mn, Na, NH4+, NO3-, pH, SO4-2, and Sr. Eh was estimated by the NH4+/NO3- couple, which yielded a bounding upper limit of about 400 mV. The trace elements Al, Fe and Si were not entered into the input file for Pitzer runs for reasons discussed in the section on analytical results. For the HMW data base, the input files contained analytical results for Ca, Cl, HCO3- (as converted total inorganic carbon; detection limit values entered for IT-Export analyses), K, Mg, Na, pH, and SO4-2. Eh was entered as 400 mV, based on the results generated from the Pitzer data base with the NH4+/NO3- couple.

Solubility results generated from the EQ3NR runs are given in Tables V and VI. Minerals are listed with their saturation index (SI), which is the log of its ion-activity product divided by its solubility product [SI=log(IAP/Ksp)]. In general, undersaturation, saturation and supersaturation of a mineral are indicated by, respectively, negative, zero and positive SI values. However, the precision of the thermodynamic data base is probably less than +/- 0.4 SI

units (12), indicating most minerals are considered to be saturated when their SI values lie between about -0.4 and 0.4. SI values for minerals in Tables V and VI were obtained from runs which used the HMW ion-interaction parameters, except for the minerals barite, celestite and fluorite. The SI values for the latter three minerals were obtained with the Pitzer ion-interaction parameters because Ba, Sr and F interaction parameters are not available in the HMW data base.

Table V. Saturation Indices (SI) Based on EQ3NR Modeling
Results for Brines in Table II

Fig. 6. Saturation Fields for (a) Halite, (b) Anhydrite
(c) Magnesite, and (d) Celestite Based on Solubility Calculations
With EQ3NR Code

The modeling results in Tables V and IV indicate that the compositions of WIPP brines reflect equilibration with evaporite salts. Saturation indices (SI) derived from EQ3NR runs with the UNC Geotech analyses in Table V reveal that all WIPP brines are saturated with respect to anhydrite, barite, fluorite, glauberite, gypsum and halite, and most brines are saturated with respect to dolomite and magnesite. SI values for celestite, polyhalite, and syngenite are saturated for brines recovered from, respectively A1X02, DHP401, and GSEEP; A1X02, DHP401, GSEEP, and L1X00; and L1X00. For EQ3NR runs based on the IT-Export analytical results in Table VI, SI values indicate all brines are saturated with respect to anhydrite, fluorite and halite, most with respect to glauberite and gypsum, and A1X02 and GSEEP brines are saturated with respect to celestite. The saturation fields for halite, anhydrite, magnesite (evaluated at pH = 6), and celestite have been plotted in Fig. 6.

Table IV. Analytical Results (mgCl) for Total Organic Carbon (TOC),
Alcohol, Phenol, and Monocarboxylic Acids

Table VI. Saturation Indices (SI) Based on EQ3NR Modeling
Results for Brines in Table III

Modeling results reported in Tables V and VI agree with the observed mineralogy present at the WIPP repository horizon. At this level, Salado Formation mineralogy consists primarily of halite with thin horizons of anhydrite and trace amounts of quartz, polyhalite, gypsum, magnesite and clay minerals (1). Barite, celestite, dolomite, glauberite and syngenite have not been identified in the dominantly halitic samples studied to date (1). Although barite and celestite may be present in the anhydrite interbeds, glauberite and syngenite are not as likely to be found in the anhydrite because the high Mg concentrations in the intergranular brines would favor the formation of polyhalite.

Failure to achieve a perfect match between the observed phases and those calculated to be saturated in the brine probably reflects the need for obtaining data on crystal growth and dissolution kinetics to incorporate in low-temperature solution models. Additionally, a complete set of ion-interaction parameters for all major and minor seawater species, and thorough mineralogic investigations of additional repository samples, would allow a more complete analysis of the speciation and solubility properties of WIPP brines.

CONCLUSIONS

The composition and origin of Salado Formation brine recovered from the WIPP repository horizon has been investigated to evaluate the vertical migration of fluids from the overlying Rustler Formation and underlying Castile Formation, and to provide a chemical data base for future evaluation of waste/brine interactions and radionuclide solubilities in the brine.

Major-element compositions of WIPP brines suggest an origin from evaporated seawater modified by diagenetic reactions involving clay minerals, gypsum, magnesite, and polyhalite. The major-element compositions of brines recovered from down holes are distinct from fluid inclusion in WIPP halite. This observation indicates that the brine recovered in drill holes is largely intergranular fluid, and not intragranular fluid released by migration of fluid inclusions to grain boundaries by stress relief. Relatively high alkalinity in the brines is attributed to the $HB4O7^-$ specie.

Brines recovered from up holes have been modified by evaporation during the sample collection process. Variation in the composition of brines recovered from down holes suggests spatial heterogeneity exists, which implies mixing and fluid homogenization is limited within the Salado Formation at the WIPP repository horizon. The heterogeneity of down-hole brines cannot be linked to large-scale vertical migration of waters from the overlying Rustler Formation or underlying Castile Formation, because each of these formational waters are chemically distinct from WIPP brines.

Rock-brine equilibria was evaluated using the brine analyses and the speciation-solubility code EQ3NR. The modeling results indicated all WIPP brines are saturated with respect to anhydrite, barite, fluorite, glauberite, gypsum and halite, and several brines were calculated to be saturated with respect to celestite, dolomite, magnesite and polyhalite. Model results agree with the observed mineralogy at the WIPP repository, and support the contention that WIPP brines are intergranular fluids which have equilibrated with evaporite salts.

Finally, the analytical results and solubility calculations presented in this study argue for derivation of WIPP brines from near-field, intergranular fluids. Although the data presented here does not unequivocally rule out large-scale brine migration, the time scale required for migration of the fluid through the halite in the Salado Formation would have to be greater than that required for diagenetic reactions which produced magnesite, polyhalite and quartz. Excluding human intrusion scenarios, the time constraints on fluid migration through halite after the repository is sealed and repressurized suggest that soluble radionuclides will be constrained to the

near-field environment of the waste for time periods sufficient to meet regulatory guidelines.

DISCLAIMER

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Table I.   ANALYTICAL METHODS USED IN
THE ANALYSIS OF WIPP BRINES

Parameter Measured	UNC Geotech	IT-Export
SG[a]	gravimetry	gravimetry
TDS[b]	gravimetry	gravimetry
pH	electrometer	electrometer
Alkalinity	titration	titration
Br	IC[c]	SP[d]
Cl	titration	titration
F	IC[c]	potentiometry
I	IC[c]	titration
NH_4^+	SP[d]	titration
NO_3^-	IC[c]	IFI[e]
PO_4^{-3}	IC[c]	ND[f]
SO_4^{-2}	IC[c]	SP[d]
TIC[g]	titration	titration
Al	AAS[h]	ICAP[i]
As	AAS[j]	AAS[h]
B	ICAP[i]	ICAP[i]
Ba	ICAP[i]	ICAP[i]
Ca	ICAP[i]	ICAP[i]
Fe	ICAP[j]	ICAP[i]
K	AAS[k]	ICAP[i]
Mg	ICAP[i]	ICAP[i]
Mn	ICAP[i]	ICAP[i]
Na	AAS[k]	ICAP[i]
Si	ICAP[i]	IFI[e]
Sr	ICAP[i]	AAS[k]

[a]Specific gravity
[b]Total dissolved solids
[c]Ion chromatography
[d]Spectrophotometry
[e]Ion flow injection
[f]Parameter was not determined
[g]Total inorganic carbon
[h]Atomic absorption, furnace
[i]Inductively-coupled Ar plasma
[j]Atomic absorption, flameless
[k]Atomic absorption, flame

Table II. MEAN PHYSICAL AND CHEMICAL PARAMETERS FOR WIPP BRINES;
UNC GEOTECH RESULTS

(All chemical parameters in mg/1, except pH.
Letter after drill-hole ID indicates up (u) or down (d).)

	A1X01-d	A1X02-u	A2X01-d	A3X01-d	BX01-d	DH36-d	DH38-d
SG[a] g/ml	1.23	1.23	1.22	1.22	1.22	1.22	1.23
TDS[b] g/1	373	395	402	380	384	377	369
pH	6.3	5.6	5.9	6.2	6.1	6.0	6.2
ALK[c]	965	839	1005	932	845	831	889
Br	1450	1950	1460	1390	1420	1450	1580
Cl	193000	199000	196000	192000	195000	195000	194000
F	6.2	6.4	7.4	6.9	7.4	5.4	6.3
I	12.8	12.2	13.5	13.7	14.1	15.7	15.2
NH_4^+	145	152	158	149	150	164	165
NO_3^-	2	5	3	1	10	4	5
PO_4^{-3}	< 1	< 1	< 1	< 1	< 1	< 1	< 1
SO_4^{-2}	18100	21700	17200	17000	17400	16300	16200
TIC[d]	11	6	60	60	30	60	23
Al	0.137	0.109	0.385	0.561	0.483	0.452	0.413
As	0.006	0.002	0.001	0.002	0.002	0.012	0.004
B	1470	1510	1420	1420	1550	1490	..480
Ba	0.026	0.039	0.074	0.035	0.029	0.028	0.026
Ca	301	294	333	312	298	340	336
Fe	0.73	0.31	15.6	1.62	2.22	0.35	0.38
K	16200	15100	16200	15800	16500	18200	18200
Mg	23200	33000	23000	22800	22900	18300	18000
Mn	1.39	4.69	1.81	1.55	1.39	1.01	1.00
Na	79500	64500	79400	78800	80800	87200	85800
Si	2.27	1.22	2.95	2.76	2.50	3.28	2.71
Sr	1.68	5.89	1.03	2.52	2.11	1.40	0.89

Table II (continued)

	DH42-d	DH42A-d	DHP401-u	GSEEP-d	L1X00-d	NG252-d
SG^a g/ml	1.22	1.23	1.25	1.23	1.23	1.22
TDS^b g/l	368	373	389	385	392	376
pH	6.4	6.2	6.0	6.2	5.9	6.1
ALK^c	1044	856	1152	952	1253	818
Br	1340	1520	2410	1470	1850	1410
Cl	193000	195000	202000	187000	197000	194000
F	5.3	5.9	10.9	4.9	6.8	6.2
I	15.9	15.5	14.3	17.9	15.0	13.5
NH_4^+	165	171	198	198	205	149
NO_3^-	6	5	21	5	4	5
FO_4^{-3}	< 1	< 1	< 1	< 1	< 1	< 1
SO_4^{-2}	16000	16100	27900	31800	21600	16600
TIC^d	95	7	3	3	8	7
Al	0.685	0.184	0.033	0.235	0.989	0.165
As	0.007	0.004	0.007	0.003	0.002	0.002
B	1470	1430	1790	1780	1880	1450
Ba	0.057	0.020	0.050	0.015	0.024	0.026
Ca	381	337	270	281	340	310
Fe	1.14	0.25	2.48	0.38	0.74	10.3
K	18200	18500	15800	15400	22700	17000
Hg	17500	17700	44300	16200	26800	20300
Mn	1.14	1.00	7.99	0.67	1.34	1.16
Na	87200	86500	50800	94700	71800	82700
Si	5.14	2.65	1.77	1.74	5.10	1.74
Sr	1.08	0.87	5.25	2.67	1.61	1.68

^{a}Specific gravity
^{b}Total dissolved solids
^{c}Titration alkalinity expressed as HCO_3^-
^{d}Total inorganic carbon expressed as HCO_3^-

Table III. PHYSICAL AND CHEMICAL PARAMETERS OF WIPP BRINES;
IT-EXPORT ANALYTICAL RESULTS

(All chemical parameters in mg/l, except pH).
Letter after drill-hole ID indicates up (u) or down (d).)

	A1X02-u	BX01-d	DH36-d	DH38-d	DH42A-d	GSEEP-d	NG252-d
SG[a] g/ml	1.23	1.22	1.21	1.21	1.21	1.22	1.21
TDS[b] g/l	343	342	348	330	342	350	338
pH	5.7	6.0	6.0	6.1	6.1	6.0	6.1
ALK[c]	693	807	802	847	834	925	802
Br	2000	1400	1400	1500	1290	1370	1280
Cl	191000	183000	182000	176000	180000	173000	179000
F	7	8	5	5	5	5	6
I	< 20	< 20	22	< 20	21	21	< 20
NH_4^+	143	136	152	146	170	182	131
NO_3^-	< 0.18	0.31	3.10	0.18	1.28	0.26	0.13
SO_4^{-2}	21000	17000	16000	16400	15200	33100	16100
TIC[d]	< 5	5	5	5	5	< 5	< 5
Al	< 10	< 10	< 10	< 10	< 10	< 10	< 10
As	0.009	0.020	0.017	0.006	0.020	0.014	0.017
B	1600	1480	1530	1550	1580	1860	1480
Ba	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Ca	265	262	322	330	330	260	298
Fe	3	3	2	2	2	2	4
K	16100	17400	19500	20100	20800	16900	18200
Mg	32500	22100	18500	18400	18200	16400	20100
Mn	5.1	1.5	1.1	1.1	1.2	0.8	1.2
Na	67500	80800	85000	88400	87400	98700	82300
Si	0.4	0.5	0.7	0.7	0.8	0.4	0.5
Sr	6.9	2.8	1.6	1.1	1.0	3.1	1.9

[a]Specific gravity
[b]Total dissolved solids
[c]Titration alkalinity expressed as HCO_3^-
[d]Total inorganic carbon expressed as HCO_3^-

Table IV.   ANALYTICAL RESULTS (mg/l) FOR TOTAL ORGANIC CARBON (TOC),
ALCOHOL, PHENOL, AND MONOCARBOXYLIC ACIDS

	A1X02-u	BX01-d	DH36-d	DH38-d	DH42A-d	GSEEP-d	NG252-d
TOC	6.6	22.4	4.1	12.7	15.7	7.1	2.5
methanol	< 5	< 5	< 5	< 5	< 5	< 5	< 5
ethanol	< 5	< 5	< 5	< 5	< 5	< 5	< 5
2-propanol	< 5	< 5	< 5	< 5	< 5	< 5	< 5
1-propanol	< 5	< 5	< 5	< 5	< 5	< 5	< 5
phenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1
ACIDS							
acetic	< 5	< 5	< 5	< 5	< 5	< 5	< 5
propionic	< 5	< 5	< 5	< 5	< 5	< 5	< 5
isobutyric	< 5	< 5	< 5	< 5	< 5	< 5	< 5
butyric	< 5	< 5	< 5	< 5	< 5	< 5	< 5
isovaleric	< 5	< 5	< 5	< 5	< 5	< 5	< 5
valeric	< 5	< 5	< 5	< 5	< 5	< 5	< 5

Analyses performed by Battelle, Columbus Division

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Table V. SATURATION INDICES (SI)[a] BASED ON EQ3NR MODELING RESULTS
FOR BRINES IN TABLE II

Letters following the SI number indicate undersaturation (us), saturation (s)
or supersaturation (ss). Only minerals with SI > -1 are listed.

	A1X01-d	A1X02-u	A2X01-d	A3X01-d	BX01-d	DH36-d	DH38-d
anhydrite	-0.096s	0.078s	0.041s	-0.071s	-0.055s	-0.051s	-0.106s
barite[b]	0.430ss	0.750ss	0.945ss	0.564ss	0.505ss	0.477ss	0.382ss
bassanite	-0.797us	-0.631us	-0.666us	-0.773us	-0.760us	-0.753us	-0.804us
celestite[b]	-0.649us	0.048s	-0.765us	-0.460us	-0.501us	-0.714us	-0.959us
dolomite	-0.085s	-2.171us	0.692ss	1.239ss	0.427ss	0.757ss	0.315s
fluorite[b]	1.138ss	1.129ss	1.486ss	1.295ss	1.373ss	1.212ss	1.285ss
glauberite	-0.137s	0.041s	0.073s	-0.113s	-0.047s	-0.042s	-0.160s
gypsum	-0.226s	-0.087s	-0.113s	-0.206s	-0.200s	-0.186s	-0.227s
halite	-0.033s	0.024s	0.058s	-0.013s	0.026s	0.008s	-0.047s
magnesite	0.001s	-0.936us	0.375ss	0.653ss	0.261s	0.341s	0.114s
polyhalite	-0.788us	-0.072s	-0.404us	-0.763us	-0.648us	-0.737us	-0.920us
sylvite	-0.705us	-0.642us	-0.638us	-0.696us	-0.658us	-0.647us	-0.682us
syngenite	-0.826us	-0.652us	-0.675us	-0.828us	-0.768us	-0.699us	-0.770us
thenardite	-0.899us	-0.894us	-0.825us	-0.900us	-0.849us	-0.849us	-0.912us

Table V (continued)

	DH42-d	DH42A-d	DHP401-u	GSEEP-d	L1X00-d	NG252-d
anhydrite	-0.043s	-0.093s	0.122s	0.086s	0.082s	-0.086s
barite[b]	0.727ss	0.275s	0.934ss	0.350s	0.486ss	0.421ss
bassanite	-0.742us	-0.792us	-0.590us	-0.615us	-0.624us	-0.788us
celestite[b]	-0.866us	-0.956us	0.048s	-0.283s	-0.547us	-0.639us
dolomite	2.072ss	-0.691us	-1.821us	-1.602us	-1.150us	-0.885us
fluorite[b]	1.214ss	1.255ss	1.357ss	1.003ss	1.314ss	1.247ss
glauberite	-0.071s	-0.133s	-0.008s	0.425ss	0.082s	-0.114s
gypsum	-0.168s	-0.218s	-0.055s	-0.043s	-0.070s	-0.219s
halite	-0.027s	-0.033s	-0.022s	-0.001s	-0.002s	-0.011s
magnesite	0.959ss	-0.392us	-0.667us	-0.813us	-0.513us	-0.436us
polyhalite	-0.795us	-0.876us	0.330s	-0.140s	0.135s	-0.808us
sylvite	-0.672us	-0.667us	-0.595us	-0.757us	-0.507us	-0.676us
syngenite	-0.701us	-0.742us	-0.521us	-0.432us	-0.283s	-0.790us
thenardite	-0.886us	-0.897us	-0.987us	-0.518us	-0.857us	-0.884us

[a]SI=[log(ion-activity product/solubility product)]
[b]Mineral SI obtained with the Pitzer ion-interaction parameters

TABLE VI.   SATURATION INDICES (SI)[a] BASED ON EQ3NR MODELING RESULTS
FOR BRINES IN TABLE III

Letters following SI number indicate undersaturation (us), saturation (s)
or supersaturation (ss). Only minerals with SI > -1 are listed.

	A1X02-u	BX01-d	DH36-d	DH38-d	DH42A-d	GSEEP-d	NG252-d
anhydrite	-0.159s	-0.294s	-0.210s	-0.267s	-0.252s	-0.085s	-0.275s
bassanite	-0.859us	-0.989us	-0.906us	-0.960us	-0.947us	-0.780us	-0.969us
celestite[b]	-0.064s	-0.553us	-0.786us	-1.014us	-1.034us	-0.353s	-0.750us
fluorite[b]	0.948ss	1.173ss	0.952ss	0.862ss	0.932ss	0.784ss	0.995ss
glauberite	-0.305s	-0.417us	-0.302s	-0.357s	-0.356s	0.228s	-0.411us
gypsum	-0.288s	-0.402us	-0.319s	-0.366us	-0.359s	-0.193s	-0.377us
halite	-0.094s	-0.116s	-0.097s	-0.130s	-0.101s	-0.076s	-0.132s
magnesite	-1.090us	-0.860us	-0.899us	-0.883us	-0.826us	-1.027us	-0.789us
polyhalite	-0.760us	-1.326us	-1.148us	-1.316us	-1.266us	-0.547us	-1.339us
sylvite	-0.710us	-0.735us	-0.682us	-0.705us	-0.664us	-0.783us	-0.729us
syngenite	-0.880us	-0.989us	-0.805us	-0.836us	-0.815us	-0.520us	-0.935us
thenardite	-1.003us	-0.980us	-0.948us	-0.947us	-0.961us	-0.544us	-0.992us

[a]SI=[log(ion-activity product/solubility product)]
[b]Mineral SI obtained with the Pitzer ion-interaction parameters
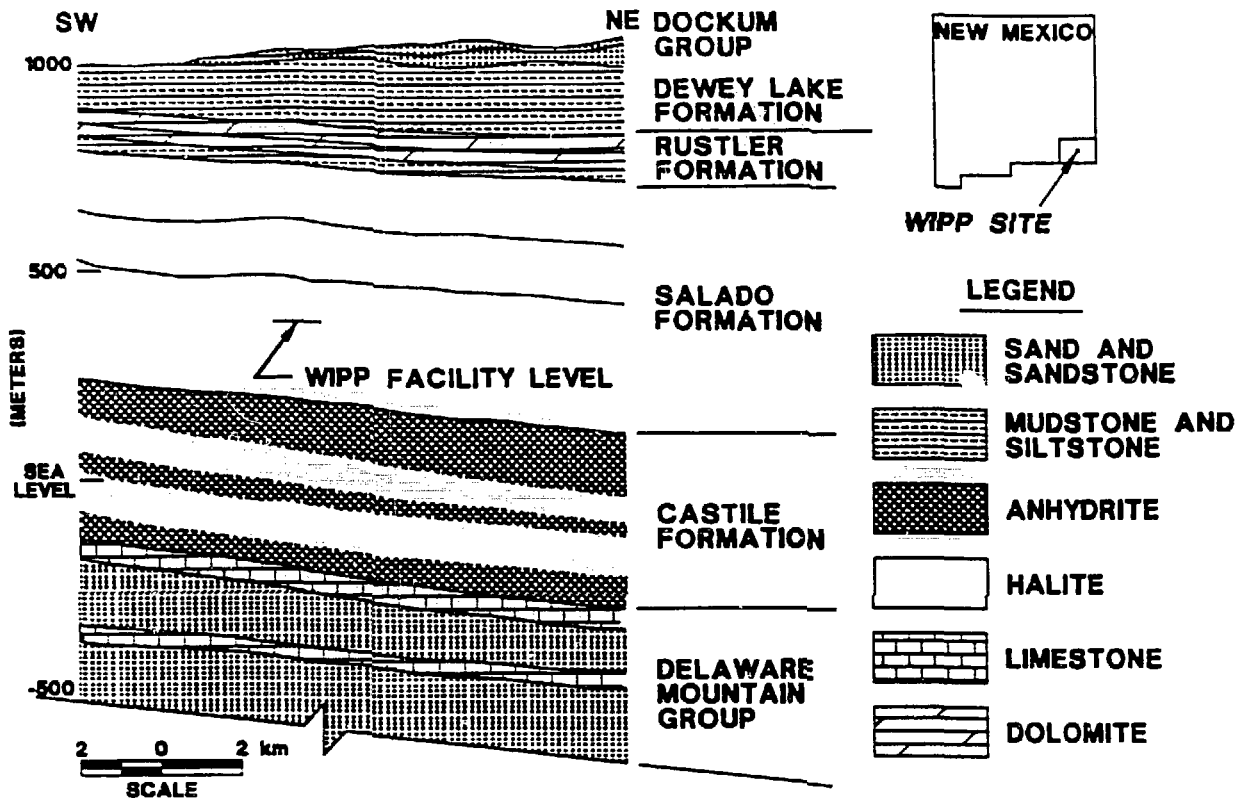
Fig. 1. Location map of the WIPP site and stratigraphic cross section through the site. Repository horizon lies within the Permian Salado Formation.
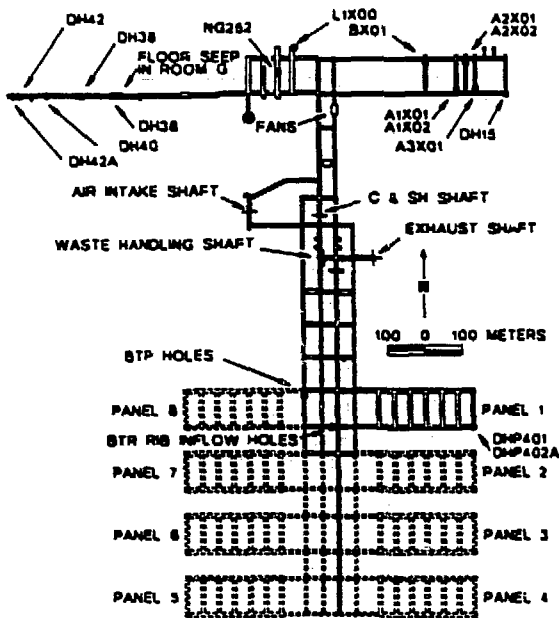
Fig. 2. Schematic plan of the WIPP repository horizon showing drill hole locations where brine has been recovered. Dashed lines indicate future excavations.
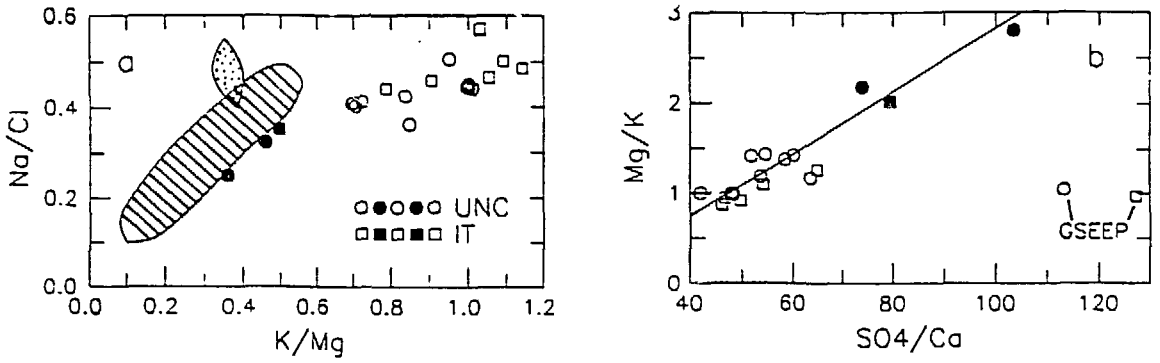
Fig. 3.   Major—element mass ratios for WIPP brines. (a) Na/Cl versus
K/Mg.   Stippled field bounds analyses obtained on seawater in equilibrium
with modern evaporites in Peru (7) and hatched field encloses analyses
obtained on fluid inclusions in WIPP halite (1).   (b) Mg/K versus SO4/Ca.
Linear trend defined by up—hole samples results from evaporation.   GSEEP
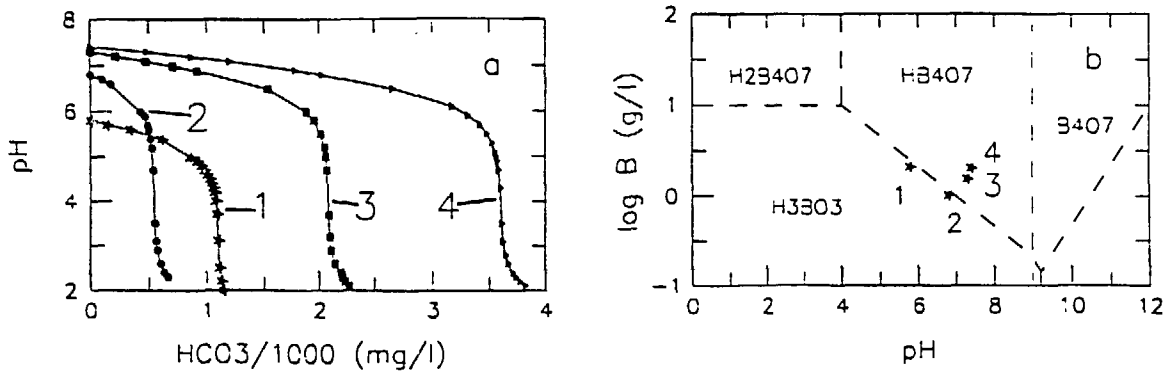chemistry may reflect fluid equilibrated within anhydrite marker bed 139.
Symbols: up holes filled; down holes open.

Fig. 4. Results of the titration–alkalinity test for brine spiked with sodium tetraborate. (a) Titration curves for: 1) undiluted brine, 2) diluted brine, 3) diluted brine + 500 mg B/l, and 4) diluted brine + 1000 mg B/l. (b) The system B–H2O at 25 degrees C (9), and test–sample points prior to titration. See text for discussion.
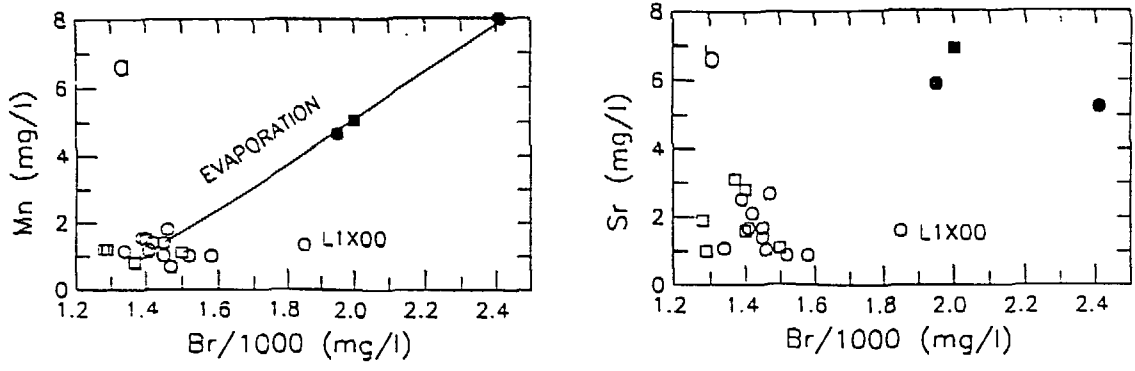
Fig. 5.　　　Selected trace elements versus Br for WIPP brines.
(a) Mn variation with Br is linear, because both elements exhibit
incompatible behavior during evaporation.　(b) Sr variation with Br
is not linear, because Sr is a compatible element when the solubility
product of celestite is exceeded.　Note anomalous Br concentration for
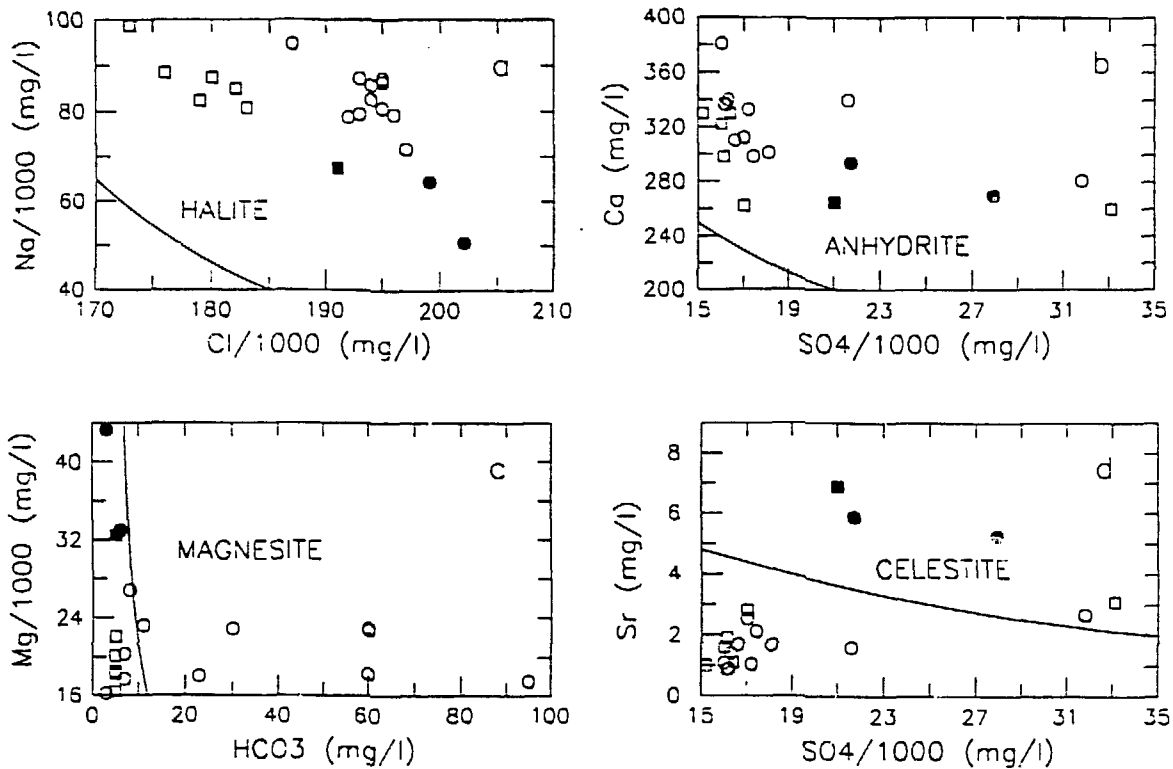L1X00, relative to other down holes.　Symbols as in Fig. 3.

Fig. 6. Saturation fields for (a) halite, (b) anhydrite, (c) magnesite and (d) celestite, based on solubility calculations with the EQ3NR code. Symbols as in Fig. 3.