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**GEOCHEMICAL AND GROUNDWATER FLOW
MODELING
OF MULTI-PORT-INSTRUMENTED COREHOLES
(GW-131 THROUGH GW-135)**

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GEOCHEMICAL AND GROUNDWATER FLOW MODELING OF MULTIPOINT-INSTRUMENTED
COREHOLES (GW131 THROUGH GW135)

By L.E. Toran and J.A. Saunders

ABSTRACT

Evolution of groundwater from Ca-HCO₃-type in recharge areas to Na-HCO₃-type further along flow paths is typically attributed to exchange of Na for Ca on exchange sites of clays. Geochemical modeling indicates that Na-HCO₃ waters can also be produced by aluminosilicate alteration and precipitation of secondary minerals. To test the feasibility of Na-HCO₃ production by silicate alteration on the Oak Ridge Reservation, groundwater samples from multipoint samplers at depths of 200 to 1000 ft were modeled with a reaction path geochemical model. Observed groundwater compositions were reproduced by the model without invoking cation exchange. Secondary minerals precipitated in the model are similar to those present along fractures in the shale host rocks. Residence times of the Na-HCO₃ zone calculated from a particle tracking groundwater flow model indicated this zone is stable after flushing thousands of pore volumes. This flow modeling provides further evidence that the proposed aluminosilicate alteration process is at least in part responsible for the observed groundwater geochemistry because if Na-HCO₃ groundwater was produced by cation exchange, then it should be flushed out by the Ca-Mg-HCO₃ recharge water when exchange sites are filled. Thus, the lower boundary of the Ca-Mg-HCO₃ groundwater may be an indicator of active circulation and important in



determining depth of monitoring for contaminants.

Evolution of Ca-Mg-SO₄-type water has been influenced by dedolomitization driven by gypsum dissolution. Secondary barite dissolution may also occur. Deeper Na-Ca-Cl-SO₄ type water may be the result of advective mixing, matrix diffusion, or upward diffusion, or some combination of these in a transition between fresh waters and brine.

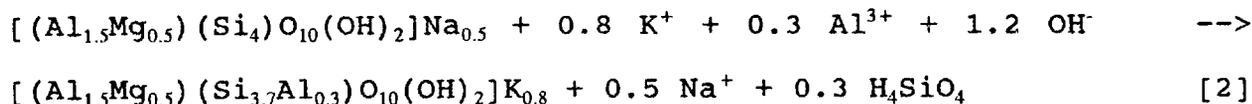
INTRODUCTION

Alkaline Na-HCO₃ groundwaters are hosted by formations of diverse lithologic composition including siliciclastic Cretaceous and younger aquifers of the Atlantic and Gulf Coastal Plain (Foster, 1950; Back, 1966; Lee, 1985; Lee and Strickland, 1988, and Sprinkle, 1989) and High Plains (Thorstenson et al., 1979), Miocene and younger basalts (Deutsch et al., 1982; Hearn et al., 1985; and Gislason and Eugster, 1987), Tertiary ash flow tuffs in the Great Basin (Benson and McKinley, 1985), Pennsylvanian siliciclastics of the Appalachian Plateau (Powell and Larson, 1985), Cambrian shales of the Valley and Ridge Province near Oak Ridge, Tennessee (Bailey and Lee, 1990; Early et al. 1991; and Dreier et al. 1991), and other shales of varying ages (Von Damm, 1987). The generally invoked mechanism to explain the origin of these waters includes dissolution of aluminosilicates and calcite to release Na⁺, Ca²⁺, and HCO₃⁻, and cation exchange reactions with phyllosilicates:



This mechanism is used to explain Ca depletion, which leads to further calcite dissolution and increases in alkalinity and pH. Cation exchange reactions are important in controlling the composition of natural waters over short-term time intervals, such as in soil-water reactions, but cannot represent a net sink or source for cations over longer time spans where steady-state conditions occur (e.g., Drever, 1988; Kenoyer and Bowser, 1992). Where natural conditions are modified, as in the case of acid deposition (Drever, 1988), or subsurface water injection (Richards et al., 1992), cation exchange becomes an important composition-controlling process.

Alternately, Hanor (1980) and Hanor and McManus (1988) argue against this process for an explanation of Na-HCO₃ waters in Coastal Plain formations, and suggest that aluminosilicate dissolution coupled with precipitation of secondary minerals (smectite and calcite) without cation exchange can lead to the evolution of Na-HCO₃ groundwaters. Deutch et al. (1982) and Hearn et al. (1985) reached a similar conclusion to explain secondary mineral formation and the evolution of Na-HCO₃ waters in Columbia River basalts. For example, the commonly observed conversion of smectite to illite in sedimentary basins (at about 70°C), which can be expressed for a Na-smectite as (e.g., Yariv and Cross, 1979):



This reaction could reverse during shale weathering, resulting in a more stable aluminosilicate phase. The reversal of this reaction is essentially a hydrolysis reaction, which causes an increase in solution pH, release of potassium, and the formation of a clay, which may have a higher cation exchange capacity.

In this study, we examine the chemical evolution of Na-HCO₃ water from shallower Ca-Mg-HCO₃ groundwater in a package of interbedded Cambrian clastic and carbonate rocks in Bear Creek Valley, near Oak Ridge, Tennessee in the vicinity of the U.S. Department of Energy's Y-12 Plant (Figure 1), and evaluate the hydrologic significance of the chemical zones formed. We present 2-dimensional flow and particle tracking models, which are used to evaluate the order of encounter of the different formations and to provide information on groundwater residence times. These data in turn provide constraints on the processes that produced significant changes in groundwater chemistry along discrete flow paths. This study benefitted from vertically-distributed data not usually available for hydrochemical studies, which aided in constraining geochemical processes operating on this relatively small scale. The data included: 1) diamond drill core from 5 relatively deep wells (200-450 m) for stratigraphic and mineralogic information; and 2) water analyses, hydraulic conductivity measurements, and hydraulic head values at numerous depth intervals, obtained from multi-port monitoring devices installed in the core holes. Details of the multi-port monitoring system, including sampling techniques and the relationship of contaminant hydrogeology to fluid flow and

ground-water chemistry in the study area, are presented in Dreier et al. (1991). The present study combines chemical, hydrologic, and mineralogic data to construct a general model of groundwater chemical evolution in the study area, excluding the processes in contaminated zones.

We show that the chemical evolution of groundwater is controlled primarily by water-rock reactions along relatively short (<1 km) flow paths. Even at this scale, it appears that groundwater approaches chemical equilibrium with the host rocks, primarily as a consequence of the long residence times. Most studies of the chemical evolution of groundwater are regional in nature (e.g., Thorstenson et al., 1979; Lee, 1985; Edmunds et al., 1987; Sprinkle, 1989; and Weaver and Bahr, 1991a,b; Gerla, 1992), involving flow systems ranging from 50 to several hundred kilometers in length. Results have implications for monitoring well network design because the depth of active circulation is often used as a control on monitoring well depths. We will show the importance of using both geochemical and hydrologic information to look for the zone of active circulation.

HYDROGEOLOGIC SETTING

The Oak Ridge area lies in the Valley and Ridge province of east Tennessee, which is underlain by folded and thrust-faulted Paleozoic rocks. Differential erosion produced the characteristic linear and parallel ridges and valleys that strike approximately N55°E in the vicinity of Oak Ridge (McMaster, 1963). Groundwater

in the Valley and Ridge province generally flows across strike from ridge to valley, where it either discharges to streams or is deflected along strike by more permeable zones (Seaber et al., 1988). The Paleozoic rocks typically have very low primary permeabilities resulting in fracture-controlled groundwater flow, although significant secondary permeability develops locally where fractures are enlarged due to dissolution in carbonate units (Seaber et al., 1988; Solomon et al., 1992). In the Oak Ridge area, groundwater flow primarily occurs in 3 poorly connected, mutually perpendicular fracture sets within the abundant shales and thinly-bedded carbonates in the valleys (Dreier et al., 1987; Dreier et al., 1991; and Solomon et al., 1992). Significant flow also occurs through solution pathways in massively bedded carbonate units commonly underlying ridges. In general, both the fracture density and dissolution features decrease with depth, and as a result, the active groundwater flow system is generally confined to relatively shallow depths (<100 m).

Along Pine Ridge, the outcrop of the Rome Formation receives recharge and groundwater flows down dip, and subsequently into the Conasauga group where it either discharges at the surface or flows parallel to strike. Along this general flow path, groundwater changes from a Ca-Mg-HCO₃ type in the shallow portions of the Rome Formation (Bailey and Lee, 1991) into the high pH, Na-HCO₃ water down dip in the Rome and in the Conasauga Group. A similar pattern is observed on Chestnut Ridge, except that the chemical evolution of water is affected by the shorter pathway from the recharge to

the discharge area and by differences in mineralogy encountered in the Knox.

STRATIGRAPHY AND MINERALOGY

The bedrock can be subdivided into 3 principal lithostratigraphic intervals that dip at about 45° to the southeast (Figure 2). These include the Cambrian Rome Formation, which crops out along Pine Ridge, the Cambrian Conasauga Group underlying the valley floor, and the Cambrian-Ordovician Knox Group underlying Chestnut Ridge (Figure 2). In the study area the Rome Formation consists of calcareous and locally dolomitic red and green shale, mudstone, and fine- to medium-grained sandstone. A sandstone interval at the top of the Rome Formation intersected by core hole GW132 (Figure 2) produced significant amounts of water under artesian pressure, which flowed to the surface. Subsequent hydraulic testing in the zone (Golder Associates, 1987) indicated significant, apparently primary, permeability ($K=10^4$ cm/s).

The Conasauga Group lies on top of the Rome Formation and consists of approximately 500 m of alternating shale, siltstone, and thin bedded limestone, with massive limestone at the top. The Conasauga Group is subdivided in east Tennessee into the basal Pumpkin Valley Shale, Rutledge Limestone, Rogersville Shale, Marysville Limestone, Nolichucky Shale, and Maynardville Limestone based mainly on the relative proportions of clastic and calcareous components (Hasson and Haase, 1988). The formations below the Maynardville Limestone have very low primary and secondary

permeability. At shallow depths, the massively bedded Maynardville Limestone has developed significant secondary permeability due to dissolution along fractures.

The mineralogy of the Conasauga Group shales is typical of most Paleozoic shales (e.g., Weaver and Beck, 1971), where illite and chlorite are the primary phyllosilicates. Detailed mineralogic studies have been conducted on the Pumpkin Valley and Nolichucky Shales (Haase, 1983, Baxter, 1989; and Lee et al., 1988a), and in addition to chlorite and illite, they contain abundant oligoclase (Na-plagioclase), calcite, quartz, and minor amounts of potassium feldspar, glauconite, pyrite, barite, and organic matter. In addition, the interbedded limestones typically contain low Mg-calcite, dolomite, and ferroan dolomite (Foreman, 1991). Conasauga shales commonly contain numerous veinlets up to 1 cm wide containing white calcite that apparently precipitated from hot (>100°C) brines during the Paleozoic (Foreman, 1991).

The Maynardville Limestone, regionally and in the study area, is predominantly dolostone at the top grading into a dolomitic limestone at the base. In addition, reddish anhydrite (CaSO_4) nodules up to 15 cm in diameter, authigenic barite (BaSO_4), and celestite (SrSO_4) are present at 1200 feet in drill core from the Maynardville in wells GW131 and GW135. In places, cavities of a size and shape similar to the evaporite nodules are lined with colorless euhedral calcite crystals, suggesting that locally anhydrite was dissolved and calcite precipitated in the resulting void. In addition, authigenic barite (BaSO_4) and celestite (SrSO_4)

occur along a fracture near the base of the Maynardville in GW135. Both minerals occurs as translucent, colorless to light blue, platy euhedral crystals up to a few mm in length..

Dolostone of the Copper Ridge Formation of the Knox Group overlies the Maynardville Limestone in the study area. At depths <100 m beneath the surface, the Copper Ridge Formation exhibits extensive dissolution features, consistent with its generally high hydraulic conductivity (Golder Associates, 1987). Gypsum nodules and veinlets locally are present within the Copper Ridge Formation. The shape and size of the gypsum nodules is similar to those containing anhydrite at greater depths within the Maynardville Formation, suggesting that anhydrite may have inverted to gypsum. Gypsum (?) dissolution cavities containing calcite are also present within the Copper Ridge Formation.

GROUNDWATER CHEMISTRY

A large data base of groundwater chemical analyses from literally hundreds of monitoring wells exists for the Oak Ridge Reservation and many technical reports have been written dealing with sub sets of the data, which document the general chemical characteristics of groundwater in the area (e.g., Haase and King, 1988; Geraghty and Miller, Inc., 1990, Dreier et al., 1991, Solomon et al., 1992). For this study, the new chemical data from the deep core holes (Figure 2), augmented by available data from existing wells, were used to study possible geochemical processes along discrete flow paths identified from the flow model.

Four chemically distinct groundwater types occur in the study area, and their characteristics are well illustrated by a trilinear diagram (Figure 3), and their general distribution is shown in Figure 2. Representative chemical analyses of each type are presented in Table 1, and include: Ca-Mg-HCO₃, Na-HCO₃, Ca-Mg-SO₄, and Na-Ca-Cl waters. Haase (1991) recognized the first 2 water types in a similar geologic setting within Bear Creek Valley 3 km to the southwest of the study area, as well as additional waters having higher levels of sulfate and chloride that may be transitional to the latter 2 water types recognized in the present study area.

In the study area, Ca-Mg-HCO₃ water occurs at shallow depths throughout the valley and to deeper levels under Pine and Chestnut Ridges (Figure 2). This water type typically has a total dissolved solids (TDS) content less than 300 mg/l, pH in the range of 7.5-8.5, and molar Ca/Mg ratios close to 1. The latter suggests that these waters have equilibrated with dolomite, which is present in most of the formations in the study area. Chemical speciation modeling using the computer program SOLMINEQ.88 (Kharaka et al., 1988), modified by incorporating the equilibrium solubility product for dolomite of Nordstrom et al. (1990), indicates that these waters are supersaturated with respect to both calcite and dolomite (e.g., saturation indices >0.5, analysis GW135-34, Table 1).

Na-HCO₃ groundwater occurs beneath the Ca-Mg-HCO₃ waters in the Rome Formation and Conasauga Group (Figure 2) and typically has a TDS >400 mg/l, pH >9, very low Ca and Mg contents, and typically

has higher silica than the shallower Ca-Mg-HCO₃ water (e.g., analysis GW132-5, Table 1). Even with the low Ca and Mg content, the Na-HCO₃ groundwaters are saturated with respect to calcite, and slightly undersaturated to saturated with respect to dolomite. The relatively high pH of the Na-HCO₃ waters throughout the Oak Ridge Reservation has been considered previously to be the result of grout contamination related to well construction. Many of these waters have pH in the 10-12 range and no doubt have been contaminated. However, because groundwater analyzed in this study comes from the multi-port monitoring systems installed without grout, the high pH must be a product of water-rock reactions.

Ca-Mg-SO₄ groundwater is present in the Maynardville and Copper Ridge Formation, where abundant gypsum occurs. These waters typically have TDS contents exceeding 2000 mg/l, pH <8, and are supersaturated with respect to calcite and dolomite, and locally are close to saturation with respect to gypsum (e.g., analysis 135-23, Table 1).

The remaining groundwater type is a Na-Ca-Cl(>SO₄) type (mixed ion on the Piper diagram) that has been encountered only at the bottom of the deep wells GW135 and GW134 (Figure 2) in the study area. These waters have TDS contents ranging from 3000-27,000 mg/l, pH <8, and are saturated with respect to calcite and dolomite, and undersaturated with respect to gypsum (e.g., analysis GW135-6, Table 1). Saline Na-Ca-Cl brines (TDS >150,000 mg/l, e.g., analysis 4SE400RC, Table 1) have been encountered within the Conasauga Group at depths >300 m in Melton Valley, approximately 15

km southwest of the study area. The deep saline waters may represent a zone of dilution at the top of a similar brine.

GEOCHEMICAL MODELING

NA-HCO₃ EVOLUTION

Chemical evolution of groundwater flowing from the recharge zone along Pine Ridge toward the center of Bear Creek Valley can be conveniently illustrated by a plot of molar Ca+Mg/Na ratios versus pH for some representative groundwaters along this flow path (Figure 4). Dilute groundwater from a shallow monitoring well is used to simulate recharge on Figure 4. Equilibration with dolomite and calcite leads to an increase in the Ca+Mg/Na ratio and pH. This process was modeled by using SOLMINEQ.88 assuming closed system conditions with respect to CO₂ and a relatively high initial P_{CO₂} of 10^{-1.5} b. The resulting model value is also shown Figure 4. Alternatively, similar results can be obtained by assuming open system conditions and lower but constant values for P_{CO₂}. Calculated P_{CO₂} values for Ca-Mg-HCO₃ waters in the Rome Formation are approximately 10⁻² b, a value that is significantly greater than atmospheric conditions of 10^{-3.5} b. This suggests that additional sources of CO₂ are required to account for the observed water chemistry, which probably comes from a combination of oxidation of organic matter in soil and in the rocks themselves (e.g., Drever, 1988).

Preliminary geochemical modeling by Haase (1991) using the computer program EQ3/6 (Wolery, 1979) indicates that chemical

differences between the Ca-Mg-HCO₃ and Na-HCO₃ waters in Bear Creek Valley are related to the increased ground-water residence time with depth. In the present study, we test this hypothesis within the framework of the overall flow regime and the order of encounter of host rocks.

The evolution of groundwater to the high pH, Na-HCO₃ water along the Pine Ridge flow path appears to be related to residence time (Haase, 1991) and water-mineral reactions involving aluminosilicates in the shales, which are indicated by higher silica contents in the Na-HCO₃ waters than in the Ca-Mg-HCO₃ waters. Laboratory experiments by Von Damm and Johnson (1987) provide some support for the shale alteration process proposed in this study. Von Damm and Johnson (1987) ground a sample of Pumpkin Valley Shale and leached it with distilled water at 20°C for 43 days at a water/rock ratio of 4. They then analyzed the leachate and the reacted shale. The leachate composition plots close to the chemical evolution trend proposed for the Pine Ridge flow path (Figure 4). More significantly, the reacted shale contained subequal amounts of smectite and illite, whereas the unreacted shale contained no smectite (Von Damm and Johnson, 1987). This experiment was not specifically designed to reproduce the natural water-rock reactions in the Pumpkin Valley Shale, and it is likely that mineral abrasion during grinding probably had an effect on the results. However, the results can be taken as at least qualitative support to the concept that the shales in the study area have undergone water-rock reactions in response to the present meteoric

water system.

To test the hypothesis that shale-water reactions are capable of producing the high pH, Na-HCO₃ groundwater, the computer program CHILLER (Reed, 1982; Spycher and Reed, 1989) was employed. CHILLER is a chemical equilibrium reaction path model applicable to heterogeneous systems (e.g., containing solid and aqueous phases). The program solves a series of mass balance and mass action equations by a Newton-Raphson numerical solution to the algebraic form of the governing equations. CHILLER computes the heterogeneous equilibrium conditions as a reaction progress variable (e.g., composition, temperature, or pressure) is changed incrementally. For this study, a Ca-Mg-HCO₃ groundwater similar in composition to GW135-34 (Table 1) was incrementally titrated at 14°C with increasing amounts of Pumpkin Valley Shale. For the model, the shale contained the following minerals, in decreasing abundance: illite, quartz, chlorite, albite, dolomite, anorthite, and pyrite.

Results of the model can be illustrated by tracking the composition of the aqueous solution (Figure 5a) and the secondary minerals precipitated (Figure 5b) as a function of the amount of shale reacted with 1 kilogram of initial solution. The dissolution of primary albite and dolomite, coupled with precipitation of secondary muscovite, clinocllore (Mg-chlorite), kaolinite, and calcite cause the water to rapidly become enriched in sodium and bicarbonate, and the pH steadily increases to 9.05 at the end of the model run. The final composition of the water from the model

is also shown on Figure 4, where it plots close to the natural Na-HCO₃ waters. Therefore, it appears that the evolution from a Ca-Mg-HCO₃ to a high pH, Na-HCO₃ water can be accomplished solely by mineral dissolution and precipitation. Ion exchange can not be ruled out as possible parallel process, but ion exchange alone would not explain increases in TDS, pH, and silica contents.

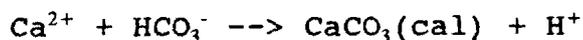
A number of limitations are inherent to this and all quantitative geochemical modeling attempts. For this study, it is difficult to quantify a reasonable water:rock ratio due to the complexity of fracture flow coupled with matrix diffusion (e.g., Toran et al., 1991). However, the chemical trends established in the model hold over a large span of water:rock ratios (varying amounts of shale titrated) and so the implications from the model do not appear to be affected greatly by this parameter. Other considerations are probably more important, such as the quality and quantity of thermodynamic data for minerals and aqueous species, the quality of the aqueous chemistry data, and the role of kinetics in the water-rock reactions. Kinetics are required to address such issues as whether ground-water residence times are sufficient to approach chemical equilibrium with the aluminosilicates, and whether the secondary mineral phases produced in the model are realistic. For example, muscovite is the most thermodynamically stable potassium aluminosilicate under the model conditions, but a kinetically favored phase (e.g., illite or possibly smectite), probably forms at this temperature (e.g., Reed 1991). Even with these uncertainties, the results of the model agree favorably with

textural and mineralogic studies of the Pumpkin Valley Shale. For example, SEM studies by Baxter (1989) documented extensive dissolution of primary feldspars and the presence of nearby well-crystallized, apparent authigenic kaolinite. In addition, Lee et al. (1988) recognized authigenic chlorite, quartz, illite, pyrite, and calcite in micropores and fractures. It is not possible to conclusively relate the timing of the formation of some or all of these authigenic phases to the present fresh groundwater system. However, at the very least, their presence and textural morphology indicate that the current groundwater is probably in chemical equilibrium with them.

Gypsum dissolution and evolution of Cl-type water

Recharge along Chestnut Ridge flows primarily through relatively shallow (<50 m) solution cavities and fractures in the Copper Ridge Formation and into the underlying Maynardville Limestone, and then ultimately discharges at the surface in springs near Bear Creek as Ca-Mg-HCO₃ water (Figure 2). Somewhat deeper flow paths encounter gypsum in the Copper Ridge and Maynardville Formations (Figure 6), and groundwater evolves to high sulfate water by gypsum dissolution. Geochemical modeling indicates that gypsum dissolution should cause a decrease in pH in a solution initially in equilibrium with calcite and dolomite. The pH decreases primarily due to ionic strength effects and to the removal of un-associated bicarbonate and carbonate to form the CaHCO₃⁺ and CaCO₃⁰ aqueous complexes, respectively. This results in

a re-establishment of the carbonate-species equilibria by dissociation of carbonic acid, resulting in a lower pH. Even with decreasing pH, dissolution of gypsum causes supersaturation with respect to calcite, and to a lesser extent dolomite, due to the common ion effect of adding Ca^{2+} to solution. Additionally, if calcite then precipitates by the following reaction:



pH will decrease further, Ca^{2+} will be removed from solution, and the result may be subsaturation of dolomite and its dissolution. This is the "dedolomitization" process described in detail by Back et al. (1983). The dedolomitization process can be modeled for the Chestnut Ridge flow path using analysis GW135-34 (Table 1) as a starting solution composition and CHILLER to titrate increasing increments of gypsum into the solution. Results of the numerical model (Figure 7) indicate that the solution precipitates initially dolomite and calcite, then only calcite, resulting in an increase in Ca, Mg, and SO_4 and a decrease in HCO_3^- and pH in the solution.

Three lines of evidence provide support for the occurrence of dedolomitization along the deeper Chestnut Ridge flow paths. The presence of euhedral calcite crystals lining cavities that were apparently once filled with gypsum (Figure 8) is consistent with dedolomitization. In addition, a plot of SO_4 versus pH for analyses from the Copper Ridge and Maynardville Formations indicate that pH decreases with increasing SO_4 content (Figure 9). Back et al.

(1983) demonstrated that this pH-SO₄ relationship is characteristic of dedolomitization attending gypsum dissolution. Also shown in Figure 9 is the modeled result of pH versus molar SO₄ content (which equals moles of gypsum dissolved) from Figure 7. The model results closely approximate the observed trend of pH decrease with increased SO₄ content for the modeled interval. The third indication is the increase in magnesium content of these groundwaters with increasing sulfate, as a result of magnesium dissolved from dolomite.

Gypsum dissolution also appears to have an effect on the barium content of groundwaters in the Chestnut Ridge area. Many groundwaters on the Oak Ridge Reservation are approximately saturated with respect to barite (Haase, 1991), and the identification of barite within the Pumpkin Valley Shale (Baxter, 1989) suggests that the mineral may control barium levels in the study area. Gypsum dissolution would lead to barite supersaturation and precipitation (Figure 7) as a result of adding SO₄ to solution. Figure 10 is a plot of Ba²⁺ versus SO₄ content for groundwaters beneath Chestnut Ridge, which shows that some of the low-sulfate waters, and all of the high-sulfate waters are close to saturation with respect to barite, or are supersaturated, and that barite could be precipitating along the Chestnut Ridge flow path. However, the coarse barite observed in a veinlet near the bottom of GW135 (Figure 11) may only be indirectly related to gypsum dissolution. The association of barite with the more soluble celestite in this setting suggests that the deeper low sulfate

brines, containing up to 2000 mg/l strontium and 770 mg/l barium (Switek et al., 1987), mixed with the sulfate-rich shallow groundwaters to cause precipitation of barite and celestite. Celestite is a relatively rare mineral, in part due to the ease of substitution of Sr^{2+} for Ca^{2+} in calcium-bearing minerals. However, Saunders et al. (1988) have documented the occurrence of massive amounts of celestite in a salt dome caprock, and it appears to have formed by a process similar to the mixing process proposed here. Sr-isotope and mass balance calculations indicate that celestite in Tatum salt dome, Mississippi, precipitated in response to the mixing of Sr-rich Na-Ca-Cl brines with sulfate-rich waters in the caprock, the latter of which originated by anhydrite dissolution (Saunders et al., 1988).

Further support for mixing of the shallow groundwater with brines at depth comes from analyses of the deep chloride-rich waters encountered at the bottom of GW134 and GW135, which contain elevated amounts of Sr (up to 22 mg/l) and appear to be diluted equivalents of brines present at depth in nearby Melton Valley (compare analysis 135-6 with 4SE400RC, Table 1). However, given the probable sluggish nature of groundwater flow at this depth, the role of diffusion must also be considered. Hendry and Schwartz (1988 and 1990) have interpreted increases in salinity along a flow path in the Milk River aquifer (Canada) to be the result of diffusion of Na and Cl out of the shale confining layer in response to a concentration gradient. From the studies of Hendry and Schwartz, it appears that other solutes such as Ca did not diffuse

in the process. The higher charge and ionic radius of Ca^{2+} compared to Na^+ apparently make it less mobile than sodium and chloride during diffusion (White, 1965). Therefore, if diffusion is the main process by which the saline waters form in the study area, the process should enrich them in Na and Cl relative to Ca, Ba, Sr, etc.

In addition to upward diffusion of solutes from brines thought to be present at depth, it is also possible that matrix diffusion could play a role in the chemical evolution of the groundwater in the transition zone between fresh water and brines. It is likely that the brines occupied a structurally higher position in the past, and are continuously being "flushed-out" by the fresh groundwater system. Therefore, it is possible in these low permeability units that diffusion of solutes out of the matrix could continue for quite some time after the brine had been removed from the intervening fractures. However, there is no way from the present data to determine whether advective mixing, matrix diffusion, or upward diffusion, or some combination of these, has the predominant influence on groundwater chemistry in the transition between fresh waters and brine.

Figure 12 illustrates some of the important chemical evolution trends observed in the Copper Ridge flow path. Open system dissolution of dolomite and calcite appears to account for the Ca-Mg- HCO_3 water at shallow depths. Dissolution of gypsum would cause an increase in the molar Ca+Mg/Na ratio and that process has been modeled and the resulting water composition is shown on Figure 12.

Two water samples (GW135-23 and GW135-6) that are close to or at saturation with respect to gypsum, have similar TDS values as the model water, but much lower molar Ca+Mg/Na ratios due to higher sodium contents. The additional sodium is somewhat problematic because the Maynardville limestone lacks such sodium sources as albite and clays capable of cation exchange. We have conducted leaching experiments where gypsum and anhydrite from the Copper Ridge and Maynardville Formations, respectively, were dissolved in triple distilled water, and sodium was released in the same approximate molar Ca/Na ratios present in the high-sulfate groundwater samples. Upward diffusion of Na is another possible source.

The remainder of the groundwater analyses from the Chestnut Ridge area do not plot on the carbonate-gypsum dissolution trend, nor do they plot on a trend defined by an advective mix with brines (Figure 12). These compositions appear to represent waters that are in equilibrium with dolomite and calcite and have dissolved variable amounts of gypsum, but are enriched in sodium relative to the advective mix trend on the plot of $\log m(\text{Ca}+\text{Mg}/\text{Na})$ versus \log (TDS in mg/l). These waters appear to have been affected by matrix or upward diffusion of Na and Cl. Additional data will be required to better understand the chemical evolution of the deeper groundwaters in the study area.

FLOW MODELING AND REACTION RATES

A two-dimensional groundwater flow model was constructed to

confirm that the geochemical patterns observed are hydrologically reasonable, and in turn, to use the geochemical data to help calibrate a non-unique set of data that could be used to better understand the intermediate scale flow system between Pine Ridge and Chestnut Ridge. This model was not constructed to understand the shallow flow system that is the location of several waste disposal areas, nor the NO₃ contamination that has penetrated to the base of GW134, apparently via density-driven flow. For this corehole, pressure observations must be corrected for density to calculate flow potentials and specialized models used to predict flow. As such, only GW132, -133, and -135 are used for calibration. Nonetheless, an understanding of the flow system between the ridges contributes to our understanding of the relationship between contaminated and uncontaminated zones and the stability of these zones. Furthermore, rates and directions of movement in the deep flow systems are important for contaminants that sink due to density.

The USGS code MODFLOW (McDonald and Harbaugh, 1988) was used in a 2D (one layer) cross-section. The steady state, heterogeneous, anisotropic groundwater flow equation was solved. The grid was oriented with the bedding (45° to land surface) to allow for anisotropy perpendicular to bedding, and the grid size was 47 by 47 with 70 sq ft blocks.

The boundary conditions consisted of no flow at the base in a low permeability zone at a depth of 1200 ft. At the top, a specified head boundary was used based on potentiometric surface

maps of the shallow zone (Geraghty and Miller, Inc., 1989). Beneath the ridges, a no flow boundary condition was used, assuming the ridges are groundwater divides. However, the low heads at the base of GW135 were lower than most of the rest of the model region, suggesting the divide may not fully penetrate the model depth, and underflow occurs. A specified head boundary condition was used to create underflow flux for the bottom 400 ft of the Chestnut Ridge boundary.

Two different hydraulic conductivity (K) zonations were tested in modeling. The first model incorporated variable K with stratigraphy (heterogeneous model) as well as variation in K with depth. The second model used only vertical variation in K but incorporated bedding-oriented anisotropy (anisotropic model). While both models could be calibrated to observed data, the results indicated anisotropy was an important factor in determining the K values of the heterogeneous model.

The conceptual model of the K pattern decreasing with depth and specific estimations of shallow and deep K's were based on observations elsewhere on the Oak Ridge Reservation (Solomon et al., 1992). The decrease is attributed to a reduction in number of open fractures at depth. The depth of these K zones varies and is based on somewhat limited K and geochemical data; in the model area, the Ca-Mg-HCO₃ zone was selected as the base of the shallow zone, and the first appearance of Cl-type water was the top of the lowest permeability zone (Table 2). There is limited evidence for variation in K with stratigraphy, but the model was set up with

slanted zones to allow for stratigraphically-controlled K. Initial values for these zones were based on geometric means in each formation from packer tests (Golder Associates, 1987) in the GW wells (Table 2). The K's varied from 1.4×10^{-6} to 3.6×10^{-9} ft/s. Because these packer tests were conducted in intervals selected as fracture zones, trends in K with depth were not observed.

The K's in the formations that produced a reasonable fit for the heterogeneous model to observed heads were nearly the same as the geometric means calculated from packer tests. Two formations differed from initial guess: in the Pumpkin Valley a K one order of magnitude lower was used to reproduce the steep head gradient observed between elevation 600 to 300 ft in GW132. A higher K was used in the Rogersville/Rutledge formations where the gradients were not as steep. The lower K in the Pumpkin Valley may be justified on several grounds. First, only 2 measurements were available in this formation, and the intervals for measurement were selected to try to intersect fractured intervals which should have a higher K than the surrounding matrix or an average of fractures and matrix. Second, flow through the Pumpkin Valley, assuming the regional flow model from ridges to valley is correct, would be nearly perpendicular to bedding. This is likely to be a low permeability direction and thus require a low K in the model. The contrast could be greater for the Pumpkin Valley than for other formations. Thus, it may be simpler to consider the heterogeneous K's as also encompassing anisotropy, as appears to be the case in the Pumpkin Valley.

Most of the model assumptions concerning boundary conditions, the governing equation, and K patterns have been described above. It is worth re-iterating that the cross-sectional model assumes 2D flow, although a 3D component may occur in the valley. Since the valley well (GW134) is contaminated and the heads may be affected by transient, density-driven flow, neither the heads nor the geochemistry were used in this calibration. The 3 wells used for calibration are located in areas of 2D flow. Another model assumption was that the fractured sedimentary rocks could be represented as an equivalent porous media. On the scale of the cross-section, and for the regional geochemical processes considered (describing flow not transport), this is likely to be an adequate representation.

The flow paths, as expected from the selected boundary conditions, are from the ridges to the valley. The modeled heads match observed trends reasonably well in GW132, -133, and -135 (Figure 13) for both models. There appears to be no advantage to use heterogeneous K's with stratigraphy, and thus anisotropy is considered the more important factor in model calibration. A bedding plane anisotropy of 1:10 produced the best fit. The model was not very sensitive to the K values selected in the shallow and deep zone, since there is little head data there to calibrate to. Some details are not fitted and no attempt to do so was made for the purposes of this study (to represent the overall flow system). Discrepancies are likely due to fracture effects or other local variations in permeability. As noted earlier, to reproduce the low

heads observed in the lower 600 ft of GW135, outflow beneath Chestnut Ridge was required. When a fully penetrating no flow boundary is used, the modeled heads were 60 ft higher than observed. An outflow rate of ~ 1 in/yr was used in the model, which is similar to the recharge rate and seems to confirm a regional underflow could exist here.

The modeled recharge to the water table is quite low, 1 in/yr or less, and occurs only over the ridges but not in the valley. This rate is similar to other model results by the USGS on the Reservation (Tucci, 1992; Bailey and Lee, 1990) and estimates from well hydrographs (Solomon et al., 1992). If the shallow flow system was included in the model in more detail, recharge would likely be distributed over the valley as well. Bear Creek has reaches that lose water and represent recharge to the valley not just discharge. Approximately 94% of the flow occurs in the upper high K zone of the model (150 ft zone), which again is similar to previous model results, and agrees with the low recharge estimates representing recharge only to the deep system (since the upper boundary in the shallow zone has a fixed head).

Velocities and flow paths were calculated using a particle tracking code (Pollock, 1989) implemented with MODFLOW input (Figure 14), using the anisotropic model (results of the same order of magnitude were obtained with the heterogeneous model), and assuming a uniform porosity of 1% (discussed below). Model velocities were up to 50 ft/y or 40 years from Pine Ridge to the valley. In the shallow Ca-Mg-HCO₃ zone, some local system discharge

to the Maryville Formation occurs from the Ca-Mg-HCO₃ zone in 3 to 40 years. On Chestnut Ridge, recharge may exit to the valley with flow rates of around 3 ft/y and travel times ranging between a few years and 100 years. Alternately, recharge may enter the deeper system and discharge as underflow in 30 to 40 years at velocities of around 10 ft/y. In the deep zone, where a Na-Cl zone may develop, model flow rates were less than 0.03 ft/y with travel times of 100,000 years or more from Pine Ridge to beneath Chestnut Ridge. This long travel time implies some connate groundwater could be mixed in with portions of the deep system. However, a porosity lower than 1% might be more realistic for this zone, which would decrease the travel times proportionally.

In the Na-HCO₃ zone, velocities were on the order of 10 ft/yr. The high K layer from 0 to 150 ft creates convergent discharge from the Na-HCO₃ zone to the center of the valley, and is consistent with the observed Ca-HCO₃ geochemistry at shallow depths in the rest of the valley. Without this layer, discharge would be spread throughout the valley. Further evidence of a convergent rather than divergent discharge area comes from geochemical data in shallow wells. We plotted data from Bailey and Lee (1990) by formation and found only the Nolichucky had any shallow water trending toward Na-HCO₃-type. Mineralogy rather than flow rates likely plays the major roll in the deeper penetration of Ca-HCO₃ waters in GW135 beneath Chestnut Ridge. The Knox and Maynardville formations lack silicate minerals or exchange sites apparently required for the production of Na-HCO₃-type water.

Given modeled travel times from Pine Ridge to the valley, the Na-HCO₃ zone would be flushed every 100 to 500 years over most of the zone, and thousands of years would be required near the contact with the Na-Cl zone. This flow rate would result in flushing 1000's of pore volumes given that the regional structural regime developed in the Paleozoic. These flushing rates depend on the model-calibrated K and i, which seem to be reasonable, and on the uniform porosity selected. An effective porosity of 1% was used in these calculations. This value is believed to be a reasonable estimation of equivalent porous media porosity, primarily reflecting porosity of the matrix. Estimates have been obtained by 10 laboratory measurements on coreholes (reported in Solomon et al., 1992). The porosity could vary, but is likely to be within an order of magnitude. Thus, the flow rates are thought to represent order of magnitude estimates. Despite this repeated flushing, the Na-HCO₃-type water has persisted as a geochemical zone.

DISCUSSION

The rapid rate of flushing implied by the flow modeling suggests that the Na-HCO₃ zone is stable through time, which in turn suggests that continuous silicate alteration is at least in part responsible for the observed water chemistry. If cation exchange alone were the geochemical process, the exchange sites should fill up eventually. The units are believed to have low exchange capacity based on limited measurements (Lee et al., 1988b). After the exchange sites fill up, fresh Ca-HCO₃ water would flush the

system. In contrast, silicate hydrolysis can occur rapidly (e.g., Stauffer and Witchen, 1991; Kenoyer and Bowser, 1992; and Richards et al., 1992) and silicate minerals are abundant in the Pine Ridge portion of the model. However, some combination of cation exchange and silicate hydrolysis may be important. For example, production of secondary clays along fractures could create new exchange sites over time.

Groundwater geochemistry is often used as an indicator of evolution of flow paths, and thus suggests how dissolved contaminants may travel. The most important places to monitor groundwater are likely to be shallow, active systems (where contaminants are placed), but these cannot always be easily distinguished. For example, Na-HCO₃-type groundwater is typically assumed to be "evolved". However, depending on the geochemical reactions and groundwater flow paths, this zone could be either a stable or unstable boundary. In the case of cation exchange, three stages occur: first, Ca-HCO₃ water is present; second, sufficient exchange occurs that Na becomes the dominant cation; and third, exchange sites fill up so that Ca-type water will flush out Na-type water. Thus, the Na-HCO₃ boundary eventually gets pushed down and out (e.g., Poth, 1973). Groundwater compositions alone cannot indicate which state is operating, so the presence of Na-HCO₃-type water is only an ambiguous indicator of "evolved" water. In the case of feldspar dissolution/clay alteration, the presence of Na-HCO₃ type waters indicates water in its final equilibrium stage, and thus, marks a stable circulation zone. The rate at which the

system reaches chemical equilibrium and the quantity of metastable clays are the factors that determine the rate of evolution of Na-HCO₃ waters by this mechanism.

CONCLUSIONS

The 4 chemically distinct ground-water types, present at depths less than 400 m in the study area, result from 2 principal processes: 1) the partial flushing of Na-Ca-Cl brines with TDS contents >150,000 mg/l from the deeper portions of the host formations; and 2) water-rock reactions. As a result of brine flushing, substantial solute concentration gradients exist between the shallow fresh-water flow system and the deeper brines, as well as between the rock matrix and the fresh water in the transition zone. Diffusion of Na and Cl up from the brines and out of the matrix apparently produced the Na-Ca-Cl groundwaters in the study area. However, the presence of authigenic celestite suggests that advective mixing also occurred to some extent. The remaining ground-water types are a consequence of calcite and dolomite dissolution at shallow depths that produces the Ca-Mg-HCO₃ waters, which in turn are then modified by additional water-rock reactions depending on their flow paths. Reactions with aluminosilicates and dolomite in shales produces high pH, Na-HCO₃ waters that exist beneath the Ca-Mg-HCO₃ waters throughout most of the study area. Under Chestnut Ridge, dissolution of gypsum in the massive limestones results in calcite and barite precipitation, dolomite dissolution, and a Ca-Mg-SO₄ groundwater results.

This hydrogeochemical study provides two insights into geochemical evolution of Na-HCO₃-type waters. First, the geochemical processes (dissolution of plagioclase and dolomite, and precipitation of muscovite, clinocllore, kaolinite, and calcite) could reach chemical equilibrium even at the scale of this model (approximately one km as opposed to hundreds of kilometers). Second, silicate hydrolysis may be more important than previously believed, and future studies should examine this mechanism as an alternative to cation exchange for producing Na-HCO₃ waters in geologically "old" formations. The persistence of this zone over hundreds of flushing cycles (as evidenced by groundwater flow modeling) suggests an ongoing process produced the Na-HCO₃ water. If cation exchange is the dominant process, cation exchange sites would eventually fill and fresh Ca-HCO₃ water would push the Na-HCO₃ water out. Some combination of cation exchange and silicate hydrolysis may be important. The relative importance of these processes needs to be studied through additional mineralogic and geochemical analysis.

This study of the Oak Ridge Reservation differs from previous studies in the scale of modeling, both in the detail of vertical data and the smaller horizontal scale. We also benefited from the use of both geochemical models and flow models to interpret the data. The geochemical data helped suggest zonation for K in the flow model and the flow model indicated reaction times and flushing rates were more rapid than previously expected for these Na-HCO₃ waters. Although we still don't know the mechanism for production

of mixed cation-Cl-type water at depth in GW135, the data suggest the presence of Na-Cl-type water somewhat below the current depth of monitoring.

The study of stability of groundwater geochemical zones can be an aid in designing monitoring plans for groundwater contamination which require monitoring of active circulation zones. However, geochemistry can only be used if the processes producing the observed water type are understood, and if complementary flow modeling is conducted to estimate residence times and understand these processes.

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TABLE 1
 REPRESENTATIVE GROUNDWATER CHEMICAL ANALYSES

Well	GW135-34	GW132-5	GW135-23	GW135-6	4SE400RC ¹
Formation	CR	RM	CR	MN	PV
Temp. (°C)	19.7	24.0	18.9	20.6	20.4
pH (SU)	8.3	9.4	7.9	7.5	7.5
Sp. C. (umhos/cm)	295	500	2,150	3,225	189,000
log P _{CO2} (bars)	-3.08	-4.16	-2.87	-2.31	-
Ca	32	0.82	540	340	20,000
Mg	20	0.11	130	100	3,400
Na	0.56	120	20	510	48,000
K	0.10	0.96	26	7.1	ND
Fe (tot)	0.013	0.099	0.21	ND	130
Mn	0.005	0.008	0.41	ND	31
Sr	0.016	0.024	4.7	2.4	2,000
Ba	0.58	0.041	0.02	0.037	650
SiO ₂	6.4	15.2	6.8	7.2	<100
HCO ₃	183	300	144	195	<2
Cl	1	1	3	580	120,000
SO ₄	2	11	1,820	1,620	<50
TDS (calculated)	245	450	2,690	3,360	192,000
SI _{cal}	0.55	0.03	0.83	0.40	-
SI _{dol}	1.19	-0.50	1.15	0.52	-
SI _{gyp}	-3.53	-4.51	-0.04	-0.29	-
SI _{bar}	-0.36	-0.86	0.44	0.63	-

Note: Units for all dissolved constituents are in mg/l

Abbreviations: Formations- CR= Copper Ridge; RM= Rome; PV= Pumpkin Valley; MN= Maynardville. Minerals- cal= calcite; dol= dolomite; gyp= gypsum; bar= barite. Other- Sp. C.= specific conductance; TDS= total dissolved solids; ND= not determined; SI= saturation index (log (IAP/Kt)).

¹Data from Switek et al., (1987).

Table 2: Hydraulic conductivities

Isotropic model

Unit	Geom Mean Measured, ft/s	Modeled ft/s
Rome	3.66e-7	3.66e-7
PV	1.50e-7	1.00e-8
Rt/Rg	3.58e-9	1.00e-7
Mary	1.16e-8	1.16e-8
Nol	1.54e-8	1.54e-8
Mayn	2.45e-7	2.45e-7
Knox	1.36e-6	1.36e-6
Base (below 1000 ft)		1.00e-9

Anisotropic model, bedding plane direction

Depth, feet	K, ft/s
0-150	1.5e-6
150-1000	1e-7
1000-1200	1e-9

FIGURE CAPTIONS

Figure 1. Map showing the location of the study area and coreholes. Contours are land elevation in feet above mean sea level. Adapted from Dreier et al., 1991.

Figure 2. Geologic cross-section A-A' showing the location of the deep core holes and sampling intervals and distribution of principal water types in the study area. Adapted from Dreier et al., 1991. Location of the cross section is shown on Figure 1.

Figure 3. Trilinear diagram for water analyses from the study area.

Figure 4. Plot of $\log m(\text{Ca}+\text{Mg}/\text{Na})$ versus pH for water analyses along the Pine Ridge flow path, illustrating interpreted chemical evolution processes.

Figure 5. Results of the CHILLER reaction path model for shale-water reactions. A. aqueous species as a function of the amount of shale reacted. B. secondary minerals precipitated as a function of the amount of shale reacted.

Figure 6. Photo of gypsum nodules in GW135 at 610 ft.

Figure 7. Results of CHILLER reaction path model for gypsum dissolution. Aqueous species are shown with dashed lines and minerals precipitated shown in solid lines.

Figure 8. Photo of cavities lined with calcite in GW135 at 465 ft.

Figure 9. Plot of SO_4 versus pH for groundwaters in the Copper Ridge and Maynardville Limestone.

Figure 10. Plot of SO_4 versus Ba content for groundwaters in the Copper Ridge Dolomite and Maynardville Limestone.

Figure 11. Photo of barite at 1226 ft in GW135.

Figure 12. Plot of $\log m(\text{Ca}+\text{Mg}/\text{Na})$ versus $\log (\text{TDS in mg/l})$ for groundwaters in the Copper Ridge Dolomite and Maynardville Limestone, illustrating interpreted chemical evolution processes.

Figure 13. Results of the 2-dimensional flow models (A. heterogeneous model, B. anisotropic model) and (C.) comparison of modeled and observed heads in GW wells. Location corresponds to the that of the geologic cross section (Figure 2).

Figure 14. Flow paths and travel times calculated from particle tracking model of the anisotropic case.

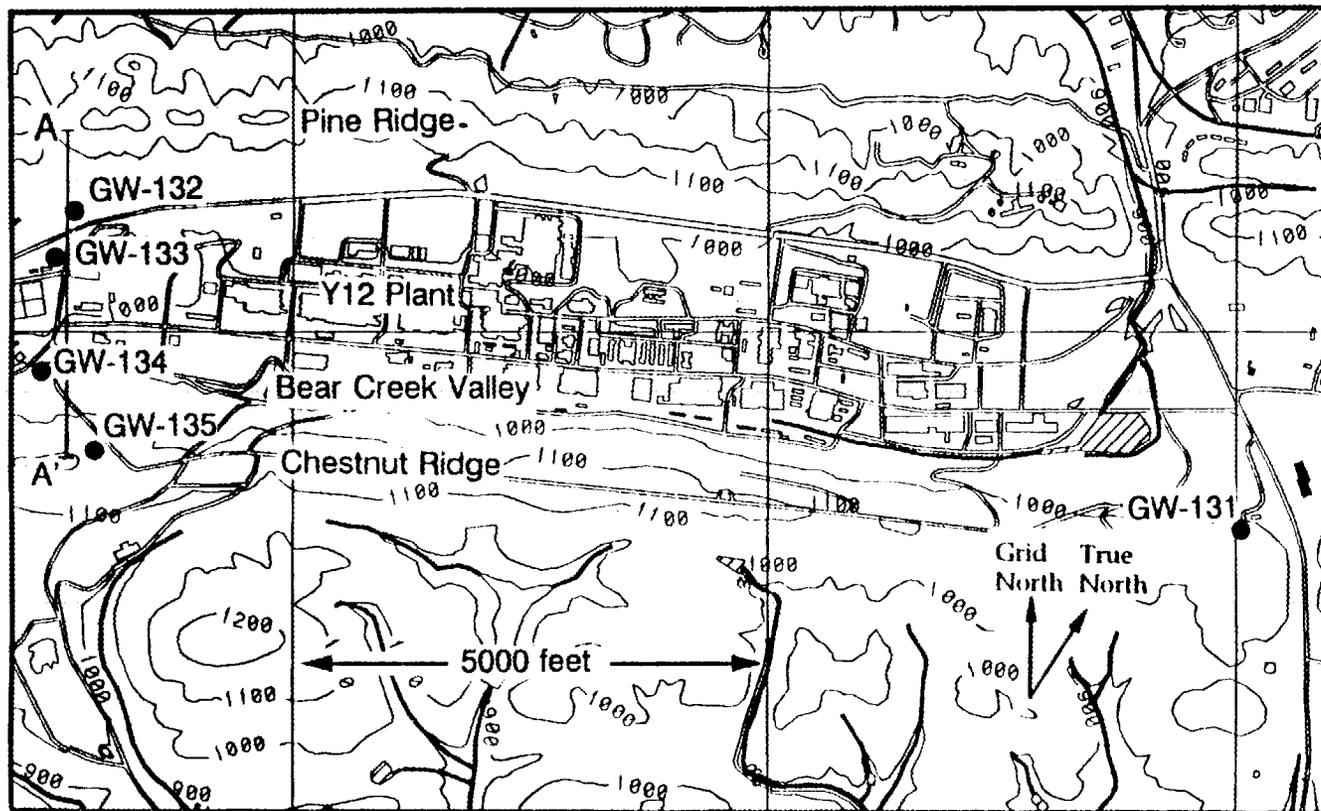


FIG. 1

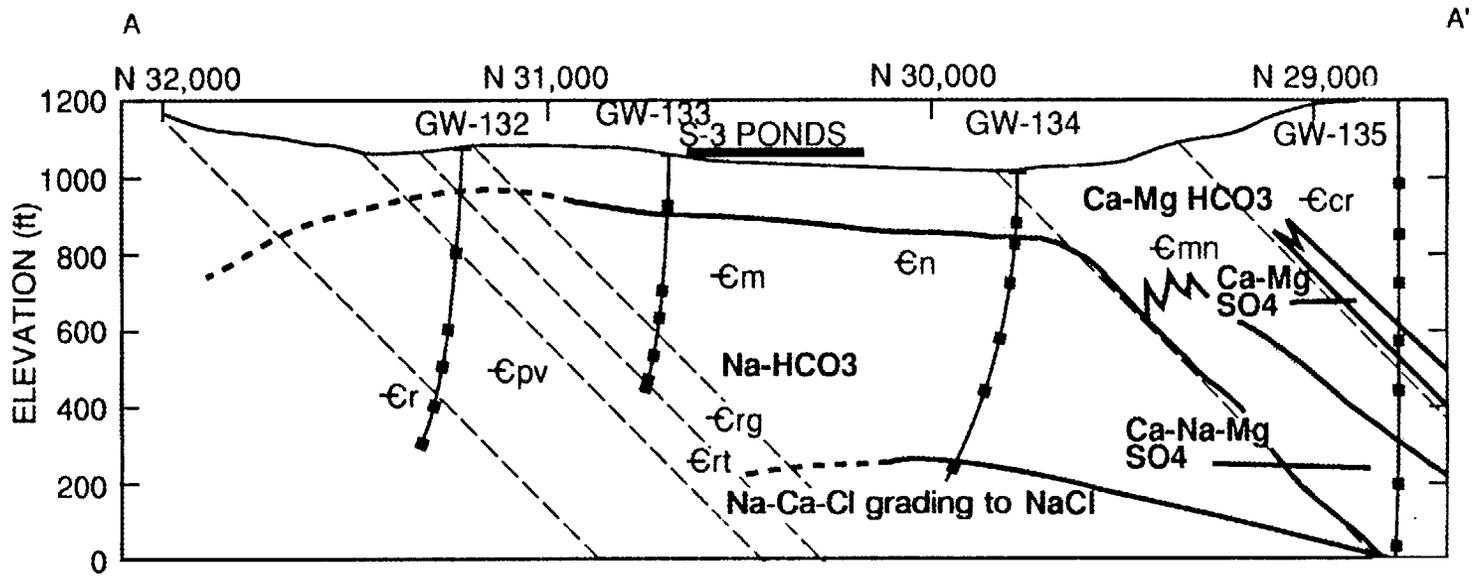


FIG. 2

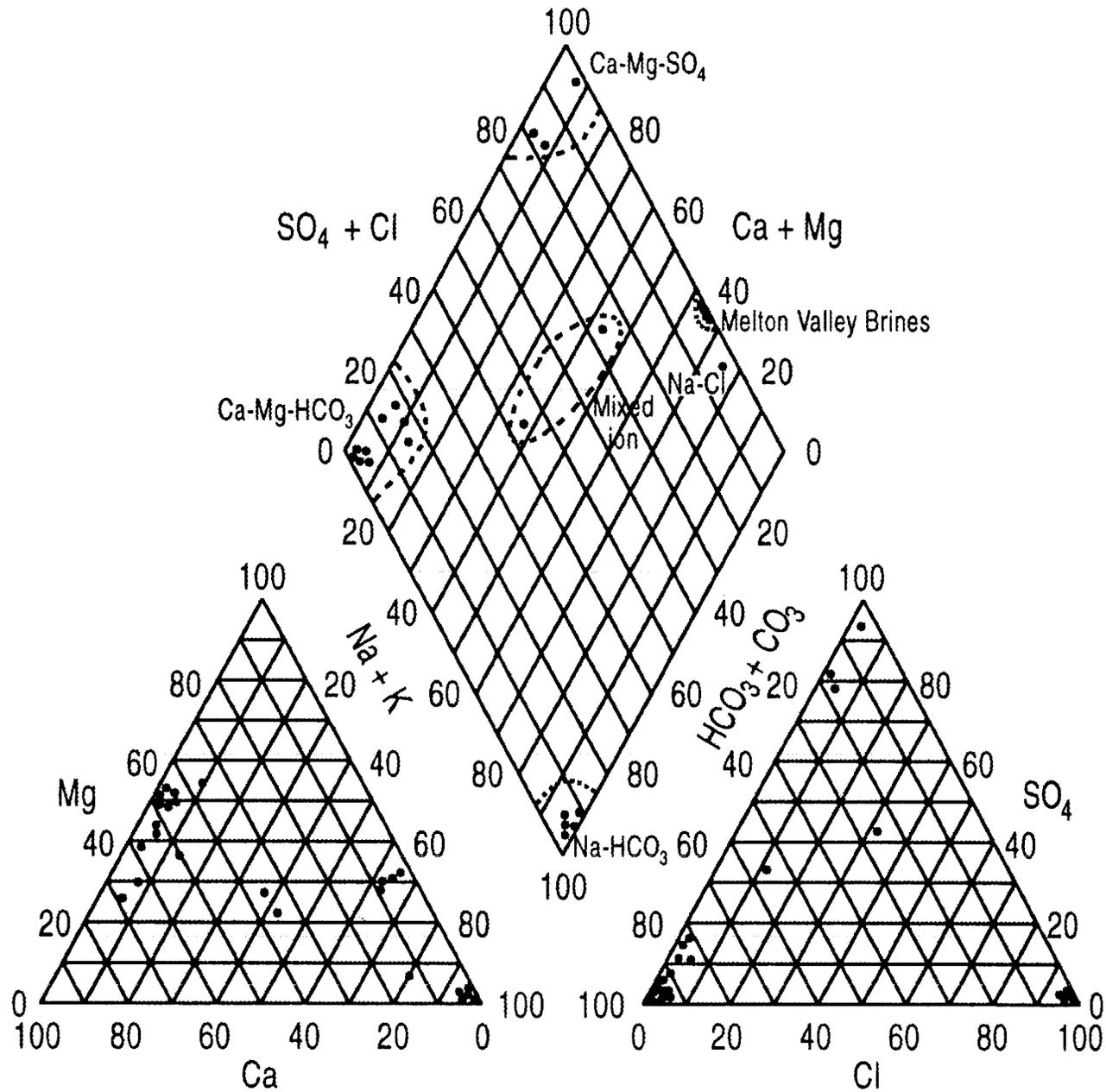


FIG. 3

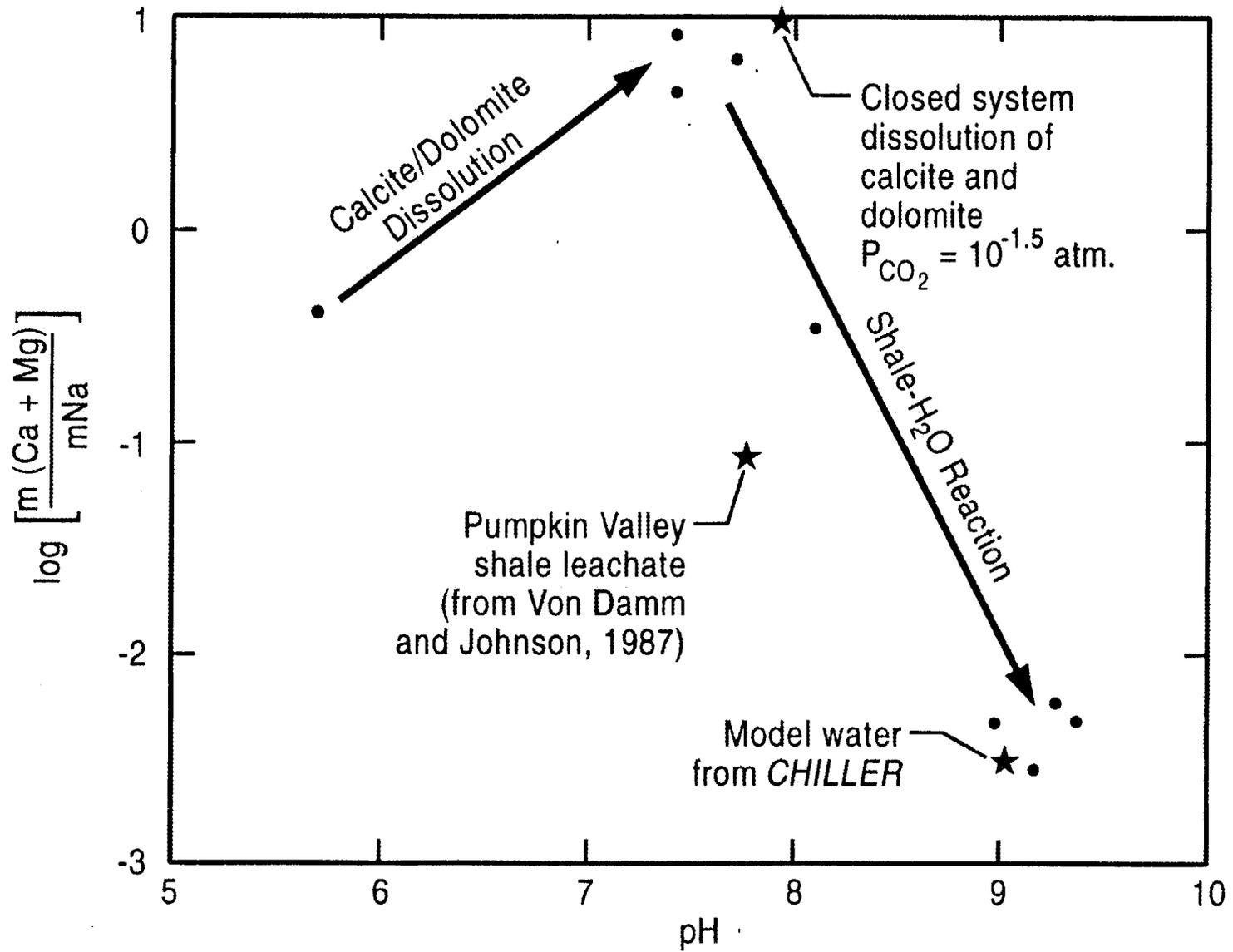
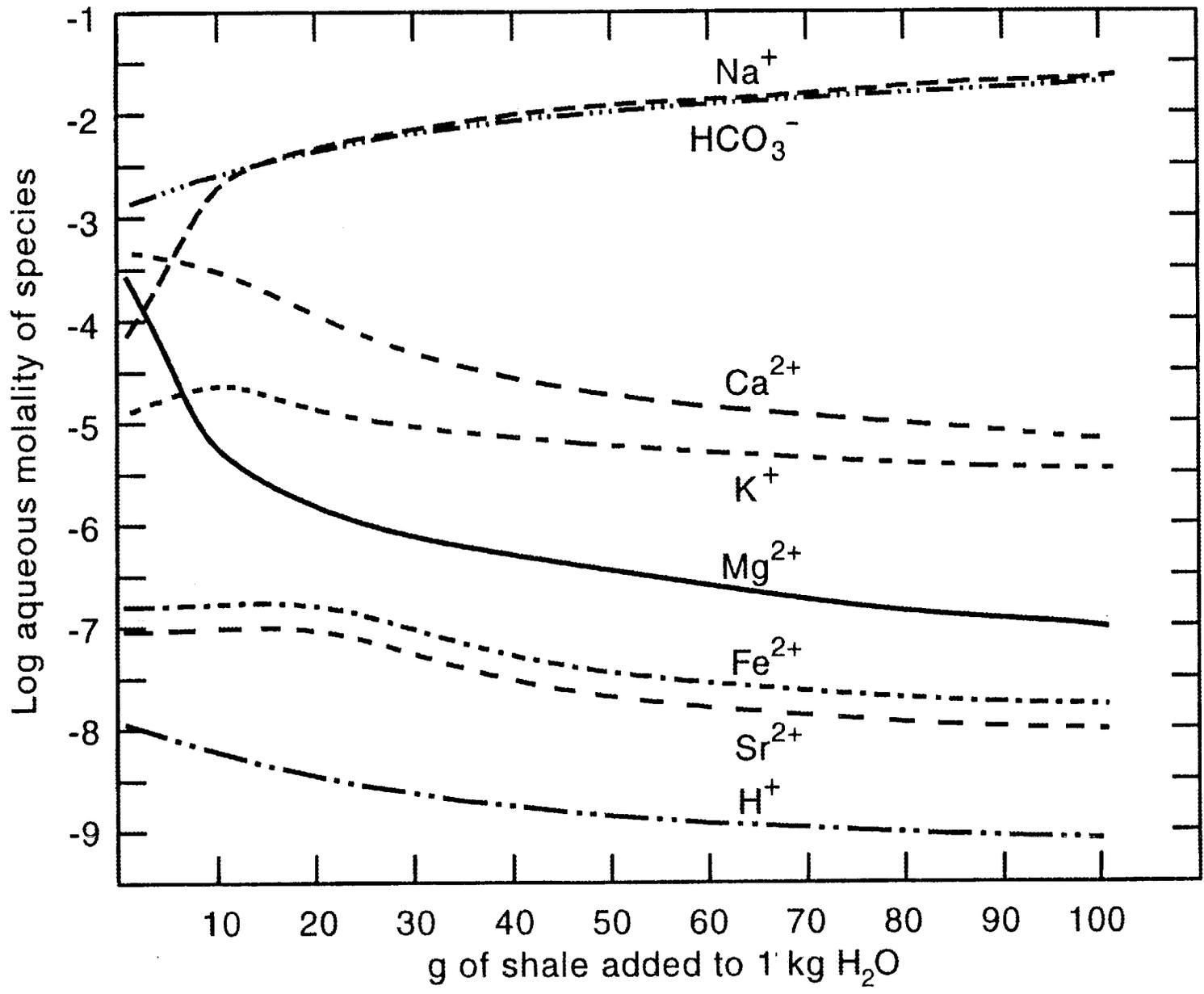


FIG. 4



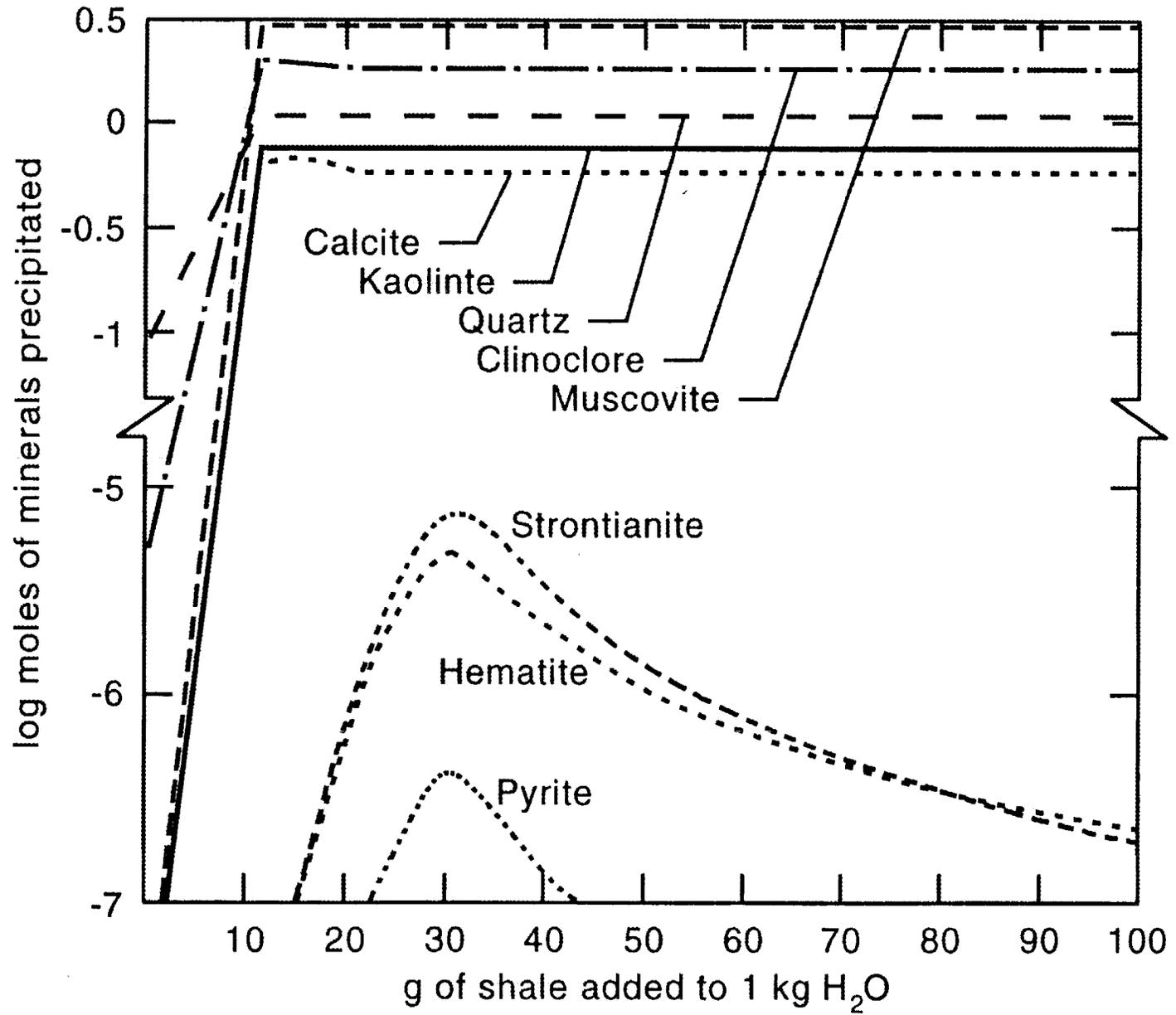


FIG. 5B

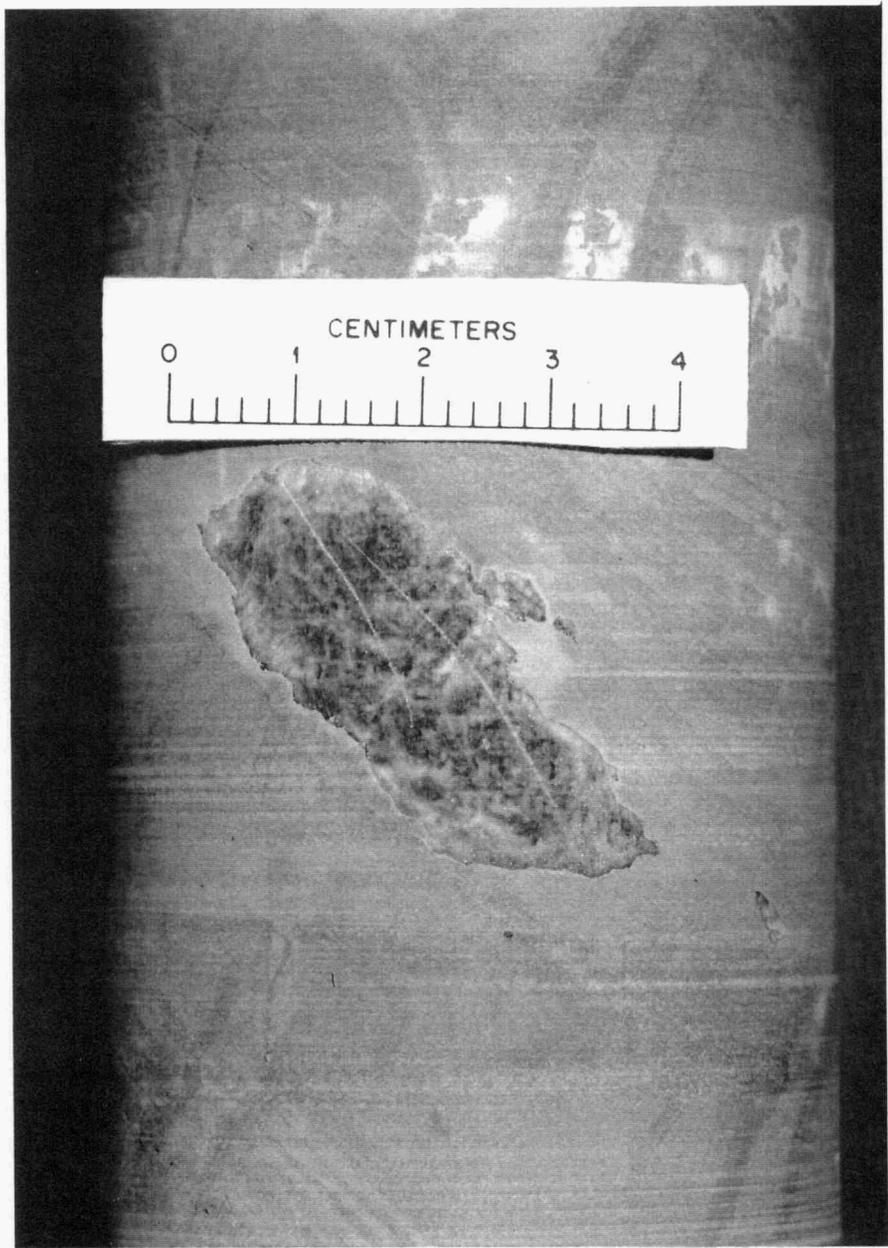


FIG. 6

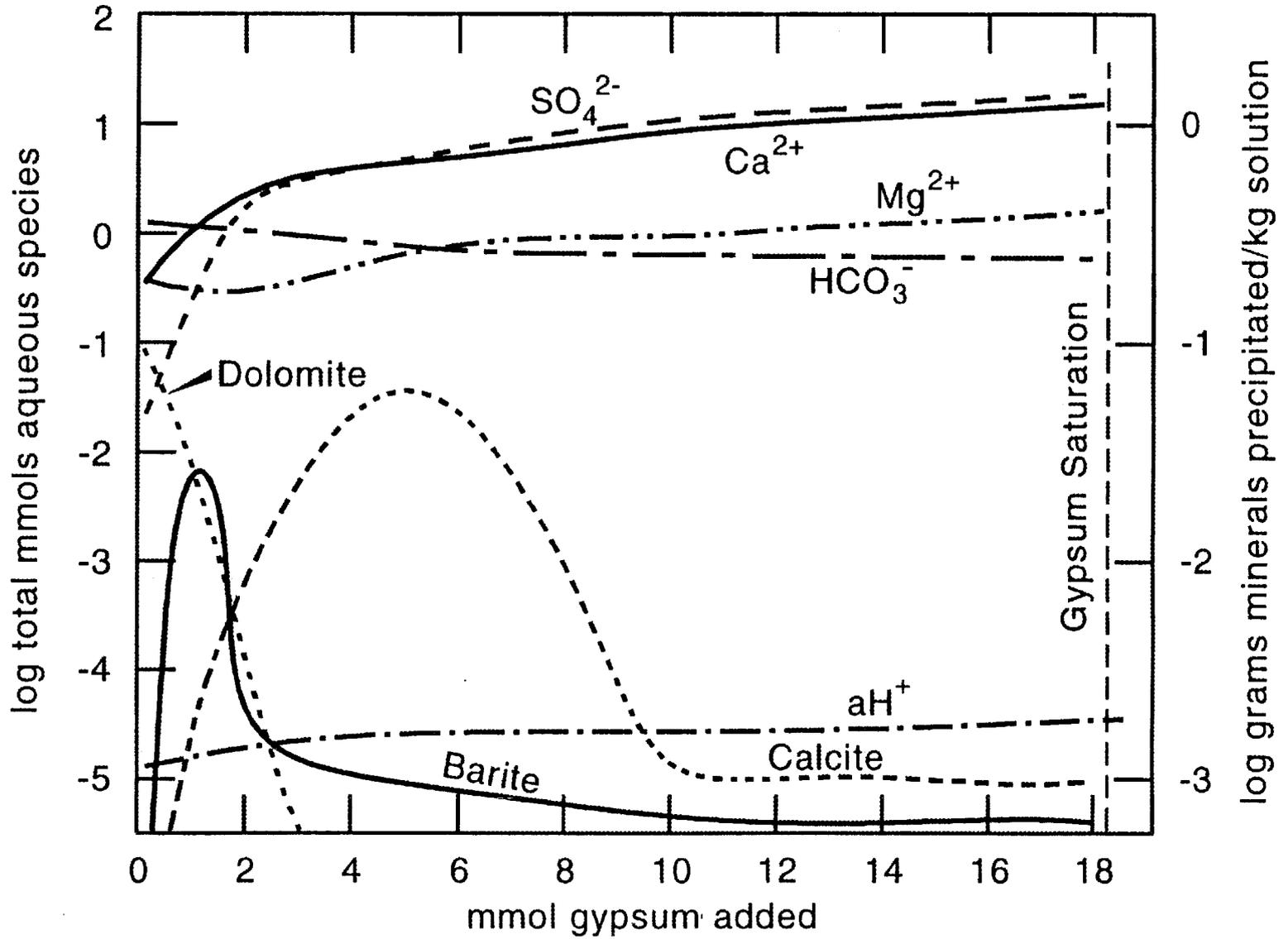


FIG. 7

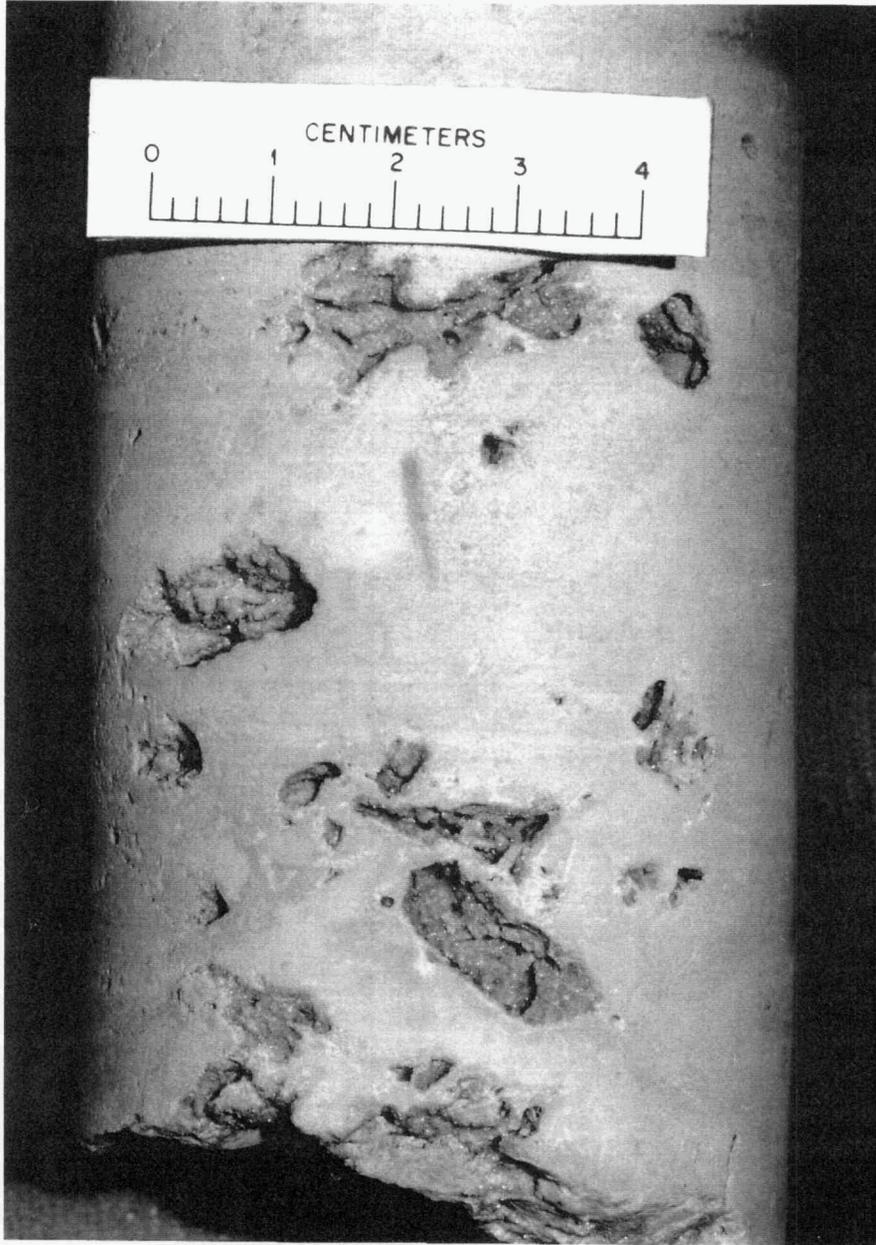


FIG. 8

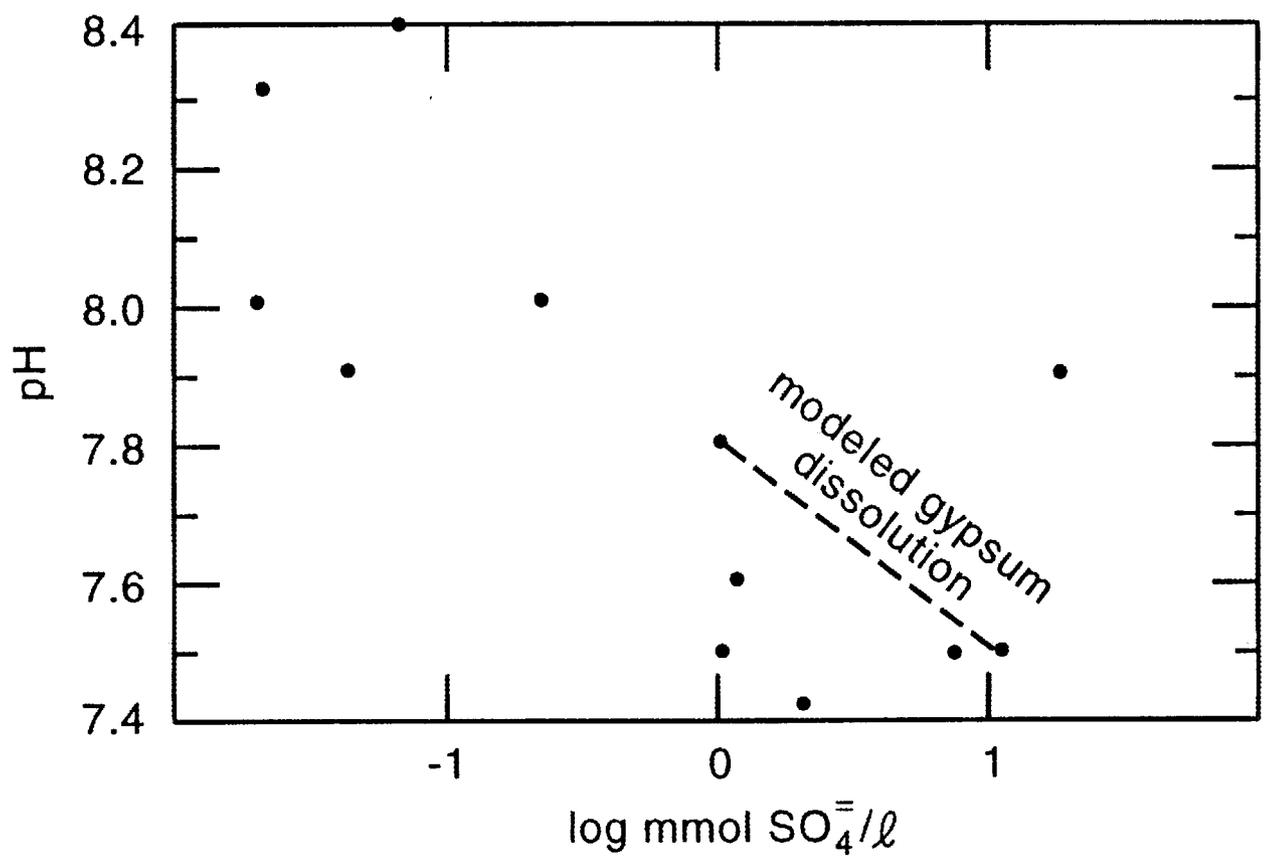


FIG. 9

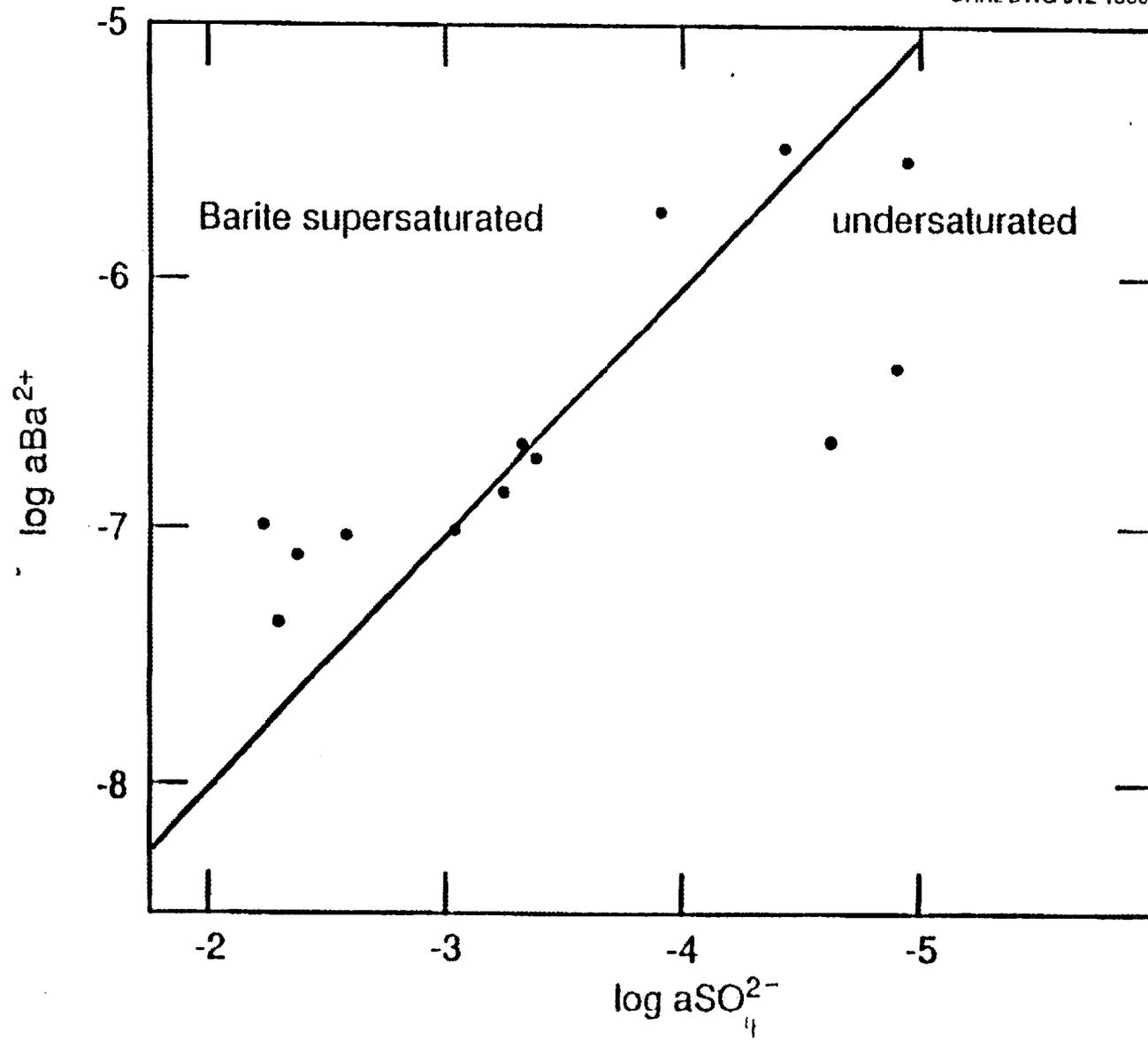
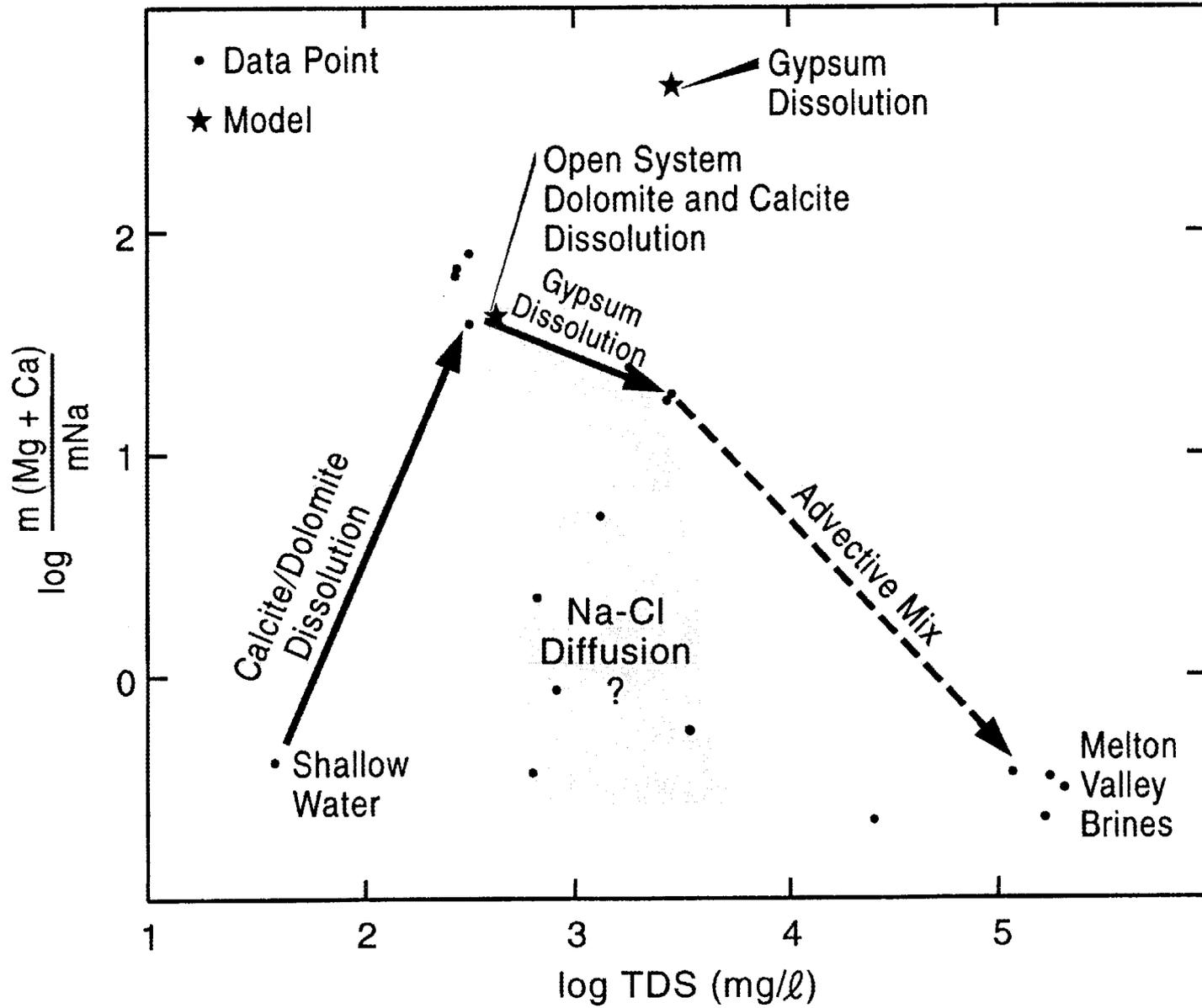


FIG. 10



FIG 11



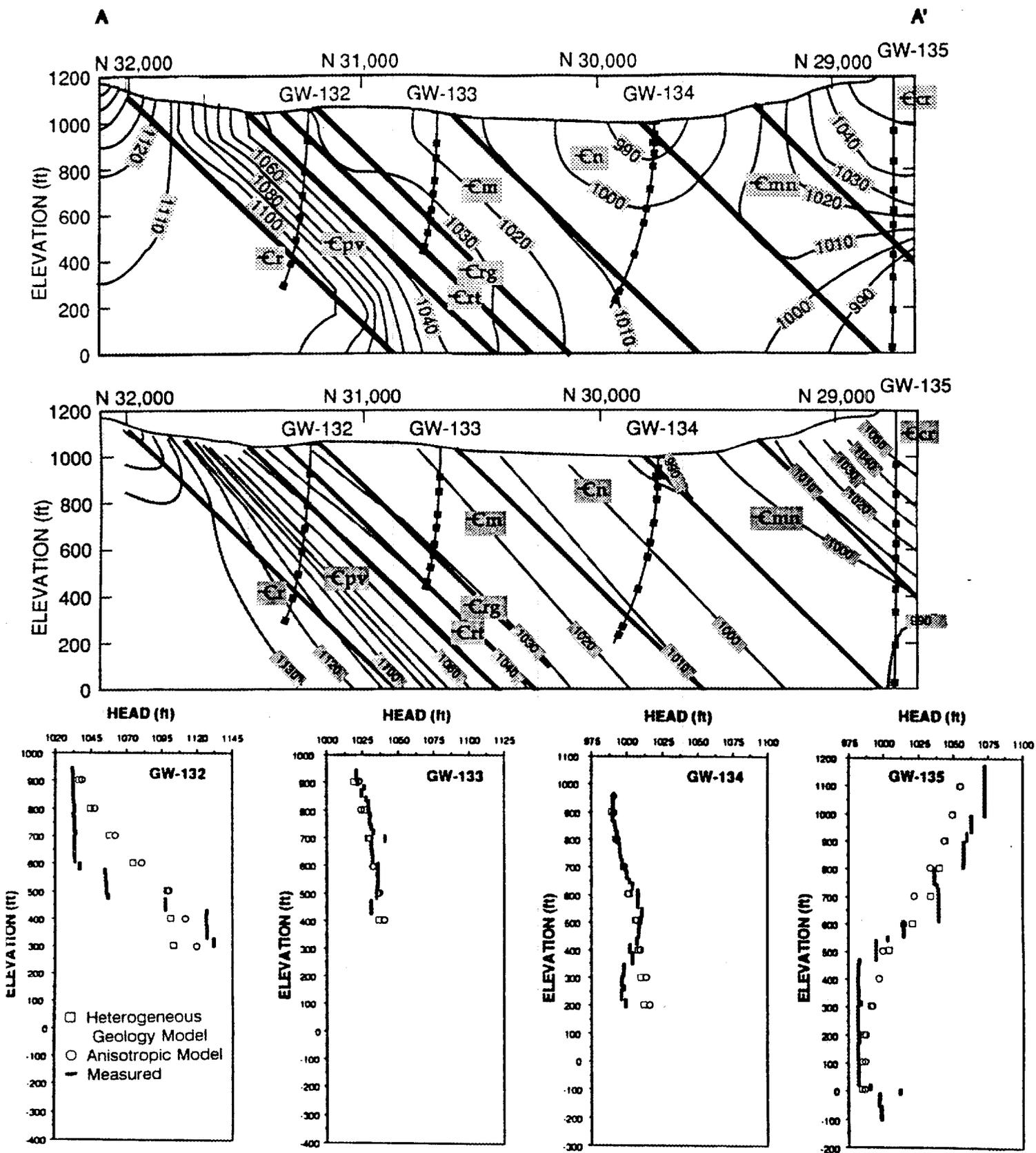


Fig 13

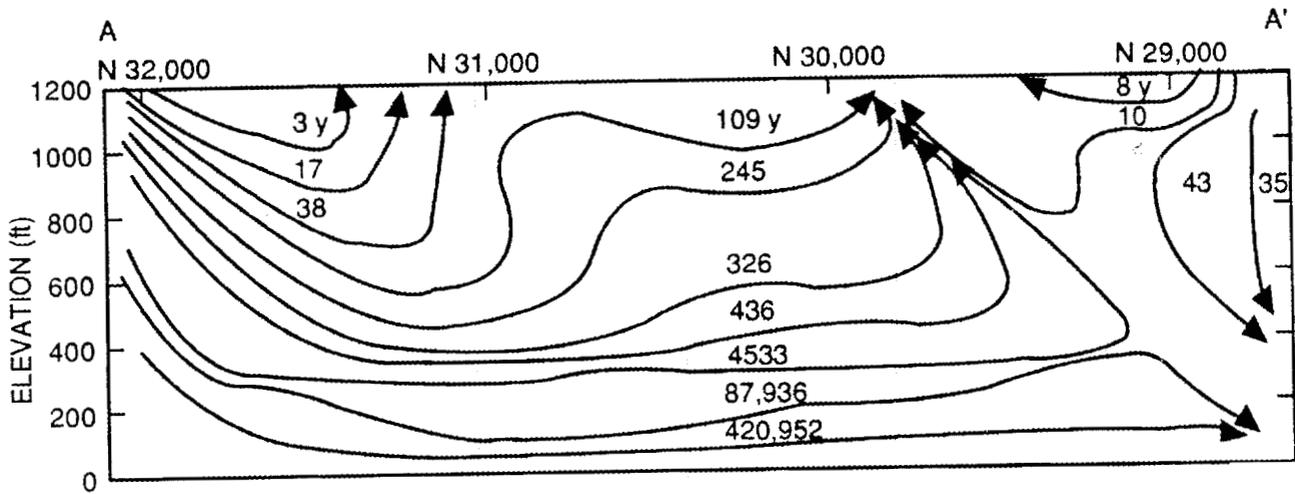


FIG. 14

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