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TOPICAL REPORT

HYDROCHEMICAL STUDY OF THE UPPER  
CRETACEOUS AND LOWER TERTIARY  
FORMATIONS IN THE UINTA, PICEANCE  
AND GREEN RIVER BASINS:  
IMPLICATIONS FOR OIL- AND GAS-  
RELATED PROBLEMS

Project BE1

By

Michal Szpakiewicz and A. Gene Collins

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Fred W. Burtch, Technical Project Officer  
Bartlesville Project Office  
U.S. Department of Energy  
P.O. Box 1398  
Bartlesville, Oklahoma 74005

Prepared for U.S. Department of Energy  
Assistant Secretary for Fossil Energy



National Institute for Petroleum and Energy Research  
IIT Research Institute • P.O. Box 2128  
Bartlesville, Oklahoma 74005 • (918) 336 - 2400

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## ABSTRACT

Oilfield Water Analyses File (BRIN) from the Petroleum Data System (PDS), was used for this hydrogeochemical study of the oil and gas associated formation waters in the Upper Cretaceous and Lower Tertiary geologic sections of the Uinta, Piceance and Green River intermontane basins (Rocky Mountain region).

Most of the commercial oil and gas reservoirs of the Upper Cretaceous and the Lower Tertiary age in the Uinta, Piceance, and Green River Basins are located within the thick sequence of organic-rich, non-marine rocks of lacustrine, paludal and alluvial origin. Some productive or prospective reservoirs were also found in the marine, lower most Upper Cretaceous, mostly clayey parts of the basins.

Hydrochemical mapping used in this study permits a better recognition of the favorable or unfavorable environmental conditions that generate hydrocarbons, and the prediction of the most prospective zones that permit their survival and collection in traps. Postulates concerning the origin of the formation waters, their chemical characteristics, and causes of the associated crude oil alteration were formulated.

Chemical features of oil-and-gas associated formation waters reveal their mixed origin and stratification (zonality), depending on the proportions of participating fluids (meteoric, ancient marine and diagenetic), and alteration processes characteristic for changing environmental conditions down the geologic profile. The alteration of petroleum composition, within the basins is partially caused and reflected by the surrounding waters, and depends on the exposure of the hydrocarbons to the environmental conditions. Water mobility is an important factor, particularly within the uppermost and transitional zones where influxing meteoric water introduces oxygen, and aerobic bacteria, causing water washing and petroleum degradation.

Biochemical degradation related to anaerobic bacteria (particularly methanogenesis) is evident in the lower transitional zone, where significant amounts of carbon dioxide and biogenic methane can be produced. These zones are highly enriched in bicarbonates. Their origin is supposed to be different in hydrochemically identifiable individual sections.

The isolated, biologically inactive low-temperature zone, is favorable for oil survival in a relatively unaltered form which can be traced on the basis of associated water chemical characteristics. In the deep-seated, stagnant zone, where the formation temperature exceeds 176-212° F (80-100° C), petroleum is exposed to the low-grade thermal metamorphism. Formation waters might be diluted and enriched in bicarbonates by the thermal decarboxylation of organic acids and/or thermometamorphism of carbonates. Supporting chemical, isotopic and hydrodynamic research is needed to validate and possibly improve the proposed conceptual hydrochemical model of water-rock-organics interaction, within the geological zones considered in this study. The results obtained in this study can be tested in areas of current hydrocarbon exploitation, and therefore the concept can be extrapolated to comparable geologic areas.

## INTRODUCTION

This paper describes the chemical characteristics of oil and gas associated formation waters within the Upper Cretaceous and Lower Tertiary formations in the Uinta, Piceance and Green River Basins (Rocky Mountains region). Hydrogeochemical interpretations were determined to a depth of 12,000-14,000 feet (3660-4300m), where reliable water data are available.

Formation waters constitute an integral part of oil and gas reservoirs, and, when subjected to the interaction with surrounding rocks and organics, develop characteristic chemical features, which can be regionally traced and mapped. Circulating or stagnant waters of different origin can strongly affect both hydrocarbons and reservoir rocks. The degree of interaction is dependent upon chemical composition and mobility of the waters.

Formation water is also considered as a carrier and a perfect habitat for aerobic and anaerobic microorganisms, which, at favorable environmental conditions, can readily metabolize organic matter significantly affecting formation water chemistry. (Bailey et.al., 1973; Marquis, 1982; Douglas and Maxwell, 1980; and Bockmeulen et.al., 1983). Thus, as proven by many authors, the brackish, saline waters or brines, coexisting underground with hydrocarbons for a geologic period of time, can protect, significantly alter, or even destroy a hydrocarbon accumulation. This justifies studying and mapping environmental conditions of reservoirs reflected by the water chemistry, because water is more abundant than hydrocarbons in most reservoirs.

Also the current progress in applying the secondary or tertiary oil-gas recovery methods, within exploited or abandoned reservoirs, require a detailed recognition of local geochemistry, including formation water chemistry. Results obtained in this study suggest the usefulness of the incorporation of hydrochemistry in standard oil and gas related research programs. Formation water data were collected, by personnel of the Bartlesville Energy Technology Center. Later it was evaluated and computerized into the Petroleum Data System BRIN file, where it is available for use in hydrochemical studies for characterization of petroleum reservoirs. Data from the BRIN file were used in this study for mapping spatial distributions of water chemical types, their stratification, salinity (TDS) distributions and to attempt to develop a conceptual model of water-rock-organics interaction within the oil and gas

bearing Upper Cretaceous and Lower Tertiary formations of the Uinta, Piceance and Green River basins. Several thousand formation water chemical analyses are available in the BRIN file for these areas, but approximately 400 carefully selected analyses were chosen as the most representative and used in this study. The location of the study area is shown in Figure 1.

## METHODS USED

Formation water analyses chosen for consideration from the BRIN data file contain information on total dissolved solids (TDS), pH; and the following least 8 major ions properly balanced in reactive values as:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ , (expressed in mg/l or ppm). One group of them also contains water resistivity data and data on concentration of the minor components:  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{B}^-$ ,  $\text{NH}_4^+$ , organic acids like acetic acid,  $\text{Li}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Fe}$  (total),  $\text{Ba}^{2+}$  and  $\text{H}_2\text{S}$ . Very few of the analyses contained trace element data, or bottom hole temperature and pressure.

The raw chemical analyses data were converted into reacting values, and percents of milliequivalents. Then, the formation water chemical type was defined, according to the international standards recommended by the International Association of Hydrogeologists (IAH), on the basis of the amount of major ions in excess of 10 and 20 milliequivalent (meq) percent. (Anions as well as cations were counted as 100 meq. %). For example the symbol  $\text{Cl-HCO}_3\text{-Na}$  means that formation water contains at least 20 meq. % of  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{Na}^+$ , while  $\text{Cl}^-$  prevails over  $\text{HCO}_3^-$ . In a case where the percentage of  $\text{HCO}_3^-$  meq. % prevails over  $\text{Cl}^-$ , the formula  $\text{HCO}_3\text{-Cl-Na}$  was used. The ions present in amounts above 10 meq. %, but less than 20 meq. %, were also included in the chemical formula (in parentheses), for example  $\text{Cl-(HCO}_3\text{)-(SO}_4\text{)-Na}$ .

Four hydrochemical maps to the scale of 1:127,000 were drawn for the Uinta, North Piceance and two areas of the Green River Basins, showing isosalinity contours (TDS in g/L), and Stiff (1951) diagrams for the more characteristic water types plus spatial distribution of 6 major water chemical types for depths and formations related to pertinent documentary points. Superposition of 2 or 3 water types are shown on the maps in the areas where sufficient data were available. Hydrochemical cross-sections, based on published geological interpretations, help visualize the vertical distribution

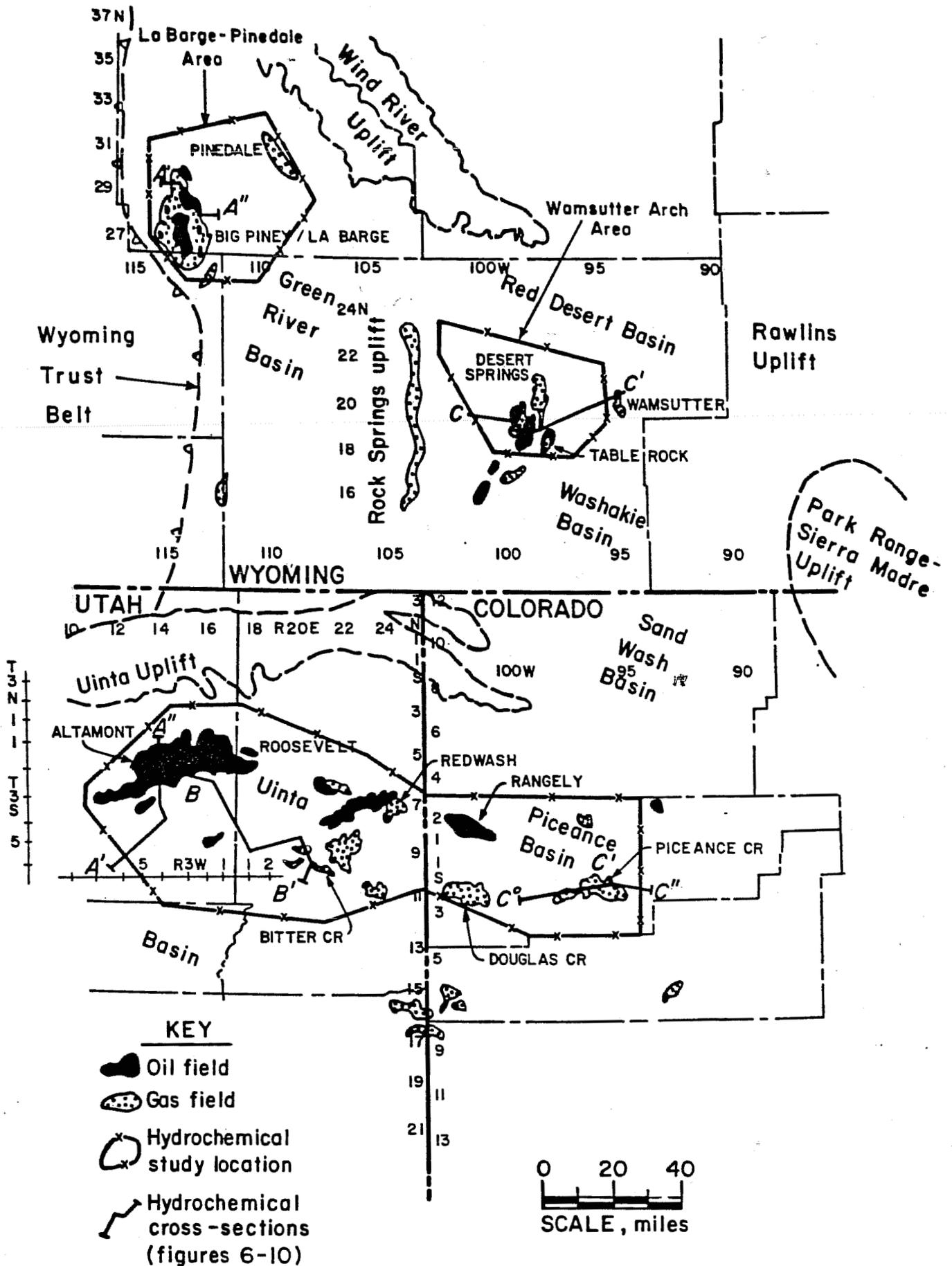


FIGURE 1. - The location of hydrochemical study area and the major oil and gas fields of the area (after Petroleum Information 1974).

of different formation waters. The isotherms of 167° F (75° C); 212° F (100° C) and 302° F (150° C), based on the Geothermal Gradient Map of North America (AAPG and USGS, 1976), also are shown on some of the cross-sections.

The hydrochemical data were computed according to the program developed by M. Ray at the BETC and with his assistance. The Sulin (1947) type and class of waters were determined, the Schoeller (1955) indices of the ion base exchange (IBE) were calculated, and Stiff (1951) diagrams, for the most typical waters from different formations, were drafted.

The "metamorphism indices" ( $r\text{Na}^+/r\text{Cl}^-$ ), the "reductivity indices" ( $r\text{SO}_4^{2-} \times 10^3 / r\text{Cl}^-$ ) and genetic indices ( $\text{Cl}^-/\text{Br}^-$ ) also were calculated. The genetic indices were calculated for 36 waters, where bromide analyses were available.

Several plots of major ion relations, showing their distributions with depth, were mapped to illustrate genetic variations, within the basins. The mapped data include: TDS,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  versus depth;  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  versus TDS;  $\log \text{Na}^+$  vs.  $\log \text{Cl}^-$ ;  $\log \text{HCO}_3^-$  vs.  $\log \text{Cl}^-$ ;  $\log \text{Cl}^-$  vs  $\log \text{Br}^-$ ;  $\text{HCO}_3^-$  vs  $\text{SO}_4^{2-}$ ;  $\text{SO}_4^{2-}$  vs  $\text{Ca}^{2+}$  and TDS vs resistivity\*.

The high enrichment of bicarbonates in these formation waters, as well as their unusual pattern of distribution with depth, obliged us to seek to determine their geological sources. All of the known chemical reactions, leading to significant  $\text{CO}_2$  generation, including biodegradation of organics, were examined and relevant findings were calculated and plotted on hydrochemical maps. On this basis a conceptual model of formation water-rock-organics interaction was developed and applied to the local environment of the sedimentary basins investigated in this study.

The conceptual model developed indicates the formations and depths particularly favorable for both immature and mature methane generation, and/or for crude oil survival in relatively unaltered form. This information also is shown on the hydrochemical maps. Zones of intensive meteoric water infiltration, definitely unfavorable for survival or accumulation of hydrocarbons also are shown. These maps are compared with published maps of

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\* Lack of data for constituents such as  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{NH}_4^+$  and organic acids, as well as lack of stable isotope determinations of  $^{18}\text{O}/^{16}\text{O}$ ,  $\text{D}/\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{34}\text{S}/^{32}\text{S}$ , and dissolved organic compounds and gases, significantly limited the final conclusions.

oil and gas accumulation and production in this region, to prove their validity, and applicability to less recognized, but geologically comparable areas. Hydrodynamic conditions were not considered quantitatively in this study, because of scarcity of data related to hydrostatic water levels and bottom hole pressures.

## GEOLOGIC SETTING

The regional geology of the Uinta, Piceance and Green River intermontane basins have been described by several authors, (Fouch, 1975; Ryder et.al., 1976; Johnson, 1979; Fouch, 1981; Law, 1981; Johnson and Keighin, 1981; Pitman et.al., 1982; and Spencer, 1983). The Upper Cretaceous and Lower Tertiary sedimentary zones represent mostly non-marine sequences of locally folded, discontinuous, lenticular, interbedded (rarely blanket-like) rocks, consisting of sandstones, siltstones, shales, mudstones, carbonaceous shales and some coal. However, considerable amount of marine and marginal marine deposits is represented in eastern part of mapped areas. The tertiary section was deposited entirely within non-marine-lacustrine, paludial and alluvial environments.

Sediments deposited in litoral or open marine environments are primarily restricted to the lower section of the Upper Cretaceous rocks (Frontier formation, Mancos or Baxter shale, part of the Mesaverde Group and Lewis shale). The total thickness of the Upper Cretaceous and Lower Tertiary sediments may be more than 20,000 feet (6000 m) in the deepest part of the Green River Basin (Law et.al., 1980) even though 3,500 feet (1070 m) of overburden has been eroded (Law et.al. 1982).

In the Uinta Basin, during the Lower Tertiary period, about 20,000 feet (6000 m) of sediments were deposited in lacustrine or alluvial environments (Tissot et.al, 1978). The Upper Cretaceous and Lower Tertiary sequences within the Piceance Basin may reach 18,000-20,000 feet (5500-6000 m) (Johnson and Keighin, 1981; Johnson, 1979).

The saline facies of substantial importance to local or regional hydrochemistry, contribute rather little to the total bulk of the investigated rock sequences. They are concentrated exclusively within the uppermost parts of the Tertiary Green River Formation, above the Mahogany Oil Shale in the Uinta Basin (Ryder et.al. 1976), and in the very central part of the Piceance

Basin, where saline minerals such as nahcolite, dawsonite and halite, associated with the oil shales, may reach a maximum thickness of 1100 ft. (350 m) within the Parachute Creek Member of the Green River Formation (Johnson and Keighin, 1981).

In both cases these saline facies are situated, as shown later in this study, within the uppermost, highly dynamic or upper transitional zone which is open for meteoric water invasion and very unfavorable for hydrocarbon survival or accumulation. The unconformity between the Cretaceous and Tertiary sections reported by several authors who investigated these basins. For example, Johnson and Keighin (1981) stated, that 2,000 to 4,600 ft (600-1400 m) of the Upper Cretaceous Mesaverde sediments have been eroded in the Piceance Basin, and that the section beneath the unconformity is highly weathered. This paleohydrologic criteria is of great importance to the hydrochemical history of these formation waters because descending meteoric waters probably penetrated Upper Cretaceous formations and mixed with waters of marine origin for long periods of time.

A thick load of rapidly deposited Tertiary age continental sediments increased the hydrostatic or petrostatic pressure. Most of the water in these sediments, presumedly fresh waters, probably was continental and meteoric. However also, squeezed upward, from deep-seated formations were saline waters with typical marine characteristics.

The intermontane sedimentary basins in the study area are surrounded by tectonized, precambrian, crystalline rock uplifts raised 6,500-7,000 ft. (2000-2130 m) above the basins floor. The regional tectonics is poorly recognized, although a major deep Wind River Thrust zone is shown along the northeastern margin of the Green River Basin and western edge is bordered by the Wyoming Thrust Belt (Law et.al, 1980). A similar thrust zone is known along the northern margin of the Uinta Basin (Fouch 1982; Ritzma 1969).

Local tectonic faults are depicted on geological maps, mostly within those sections of the basins where commercial oil and gas pools were discovered in the last half century. Somewhat controversial is to what extent these fault zones can act as conduits for vertical fluid migration. Some light on the problem was recently introduced by Pitman et.al. (1982). They classified the Pariette Bench oil and gas bearing Douglas Creek Member of the Tertiary Green River Formation in the Uinta Basin at depths up to 6,000 ft. as

a low permeability but fractured reservoir. Further they found stable isotope evidence that indicates that meteoric waters were important in the formation of authigenic carbonate cement; however, fluids and ions from other sources probably also circulated through the sandstones through vertical open fractures. This opinion is in agreement with the overall hydrochemical model presented in this study.

Rock porosity and permeability of these basins has been studied in some reservoirs by several oil companies, but good general quantitative values are not publicly available. Usually they are reported as "low or very low". A detailed study was recently initiated at the USGS in Denver, in cooperation with DOE BETC, on the properties of the Rocky Mountain "tight gas reservoirs". Spencer et.al (1977) stated that these tight gas sands occur at depths of less than 2,000 ft. (600 m) to greater than 19,000 ft. (5,800 m). Within the Green River Basin, however, all gradations exist, from good permeable reservoirs to tight sands. The last statement presumably is valid for all of the basins in this study.

The primary and secondary porosity and permeability of tight gas reservoirs were summarized by Spencer (1983). According to him the overall porosity for conventional and tight gas reservoirs is estimated as 14-25<sup>+</sup> and 3-12<sup>+</sup> percent respectively, but permeability to gas is highly differentiated and varies between 1.0-500 md and below 0.1 md respectively. The very low permeabilities undoubtedly restrict formation water mobility, but do not eliminate it where geologic time and high pressures are involved. The geothermal gradients for this part of the United States varies between 1.2 and 2.0° F/100 ft. (AAPG - USGS, 1976)

#### COMPREHENSIVE FORMATION WATER CHEMICAL CHARACTERISTIC

Formation waters within the oil and gas bearing zones of the Upper Cretaceous and Lower Tertiary formations of the three studied intermontane basins; represent the varied proportions of major components (chemical water types), and wide range of total dissolved solids. Total salinity ranges from very low (1-2 g/l) to much over 100 g/l (max. TDS reported 243 g/l), although, most values fall within the range of 50-70 g/l. Lower values were reported from Big Piney-La Barge oil and gas fields of the Green River Basin and the Piceance Creek Basin. In these fields the maximum TDS did not exceed 30 and

40 g/l respectively in water samples taken from wells 5,000-7,000 ft (1500-2100m) deep.

TDS distributions with depth, as shown in Figures 2 through 5, reveal irregular, but generally increasing water mineralization with depth, down to 5,000-7,000 ft., while a significant decrease, to 15 g/l or less, may be observed at depths below 7,000 ft. Within the Uinta Basin, however, the higher TDS values (up to 50-55 g/l) appear locally again at a depth of 11,000-12,000 ft. (3350-3650 m), and seem to decrease at depths greater than 12,000 ft. Besides this general tendency, in terms of highest TDS values distribution, both very low and very high formation water mineralizations may be also observed at any depth. This fact is reflected by highly differentiated vertical hydrochemical conditions within particular sections of the basins. Total water salinity is related, however, to different water chemical types and follows a commonly known rule that the higher the TDS the more dominant the chloride anion becomes.

Six principal water chemical types were distinguished within the studied areas - namely: Cl-Na; Cl-Na-Ca; Cl-SO<sub>4</sub>-Na; Cl-HCO<sub>3</sub>-Na; HCO<sub>3</sub>-Cl-Na and SO<sub>4</sub>-Cl-Na. Proportions of major ions differ significantly, and six additional chemical water formulas may be described. Chloride concentration usually exceeds 20 meq.%, while potassium or magnesium rarely exceed 10 meq.%.

Within the Piceance and Green River Basins the Cl-HCO<sub>3</sub>-Na, Cl-(HCO<sub>3</sub>)-Na and Cl-Na types of water predominate while within the Uinta basin the Cl-SO<sub>4</sub>-Na and Cl-(SO<sub>4</sub>)-Na types also frequently occur at different depths, but usually the TDS are less than 65 g/l. Calcium rich Cl-Na-Ca or Cl-Ca-Na waters are considered as characteristic of an isolated (stagnant) environment, at least for a significant period of geologic time, are less abundant, and were found locally within the Uinta, Piceance and Green River basins with TDS values, as low as 10 g/l. An unusual hydrochemical phenomena was observed, namely gaining of calcium often accompanied by low water mineralization. This suggests that water stagnation was followed by dilution with a fresher water, but not necessarily a recent meteoric water. B. Law, et al., 1983 suggest that water derived from dewatering of stratigraphically variable coal-bearing sequences in the Green River Basin is fresh relative to most formation fluids and may affect significantly local salinity of pore fluids, as well as cause some diagenetic alterations in the adjacent rocks.

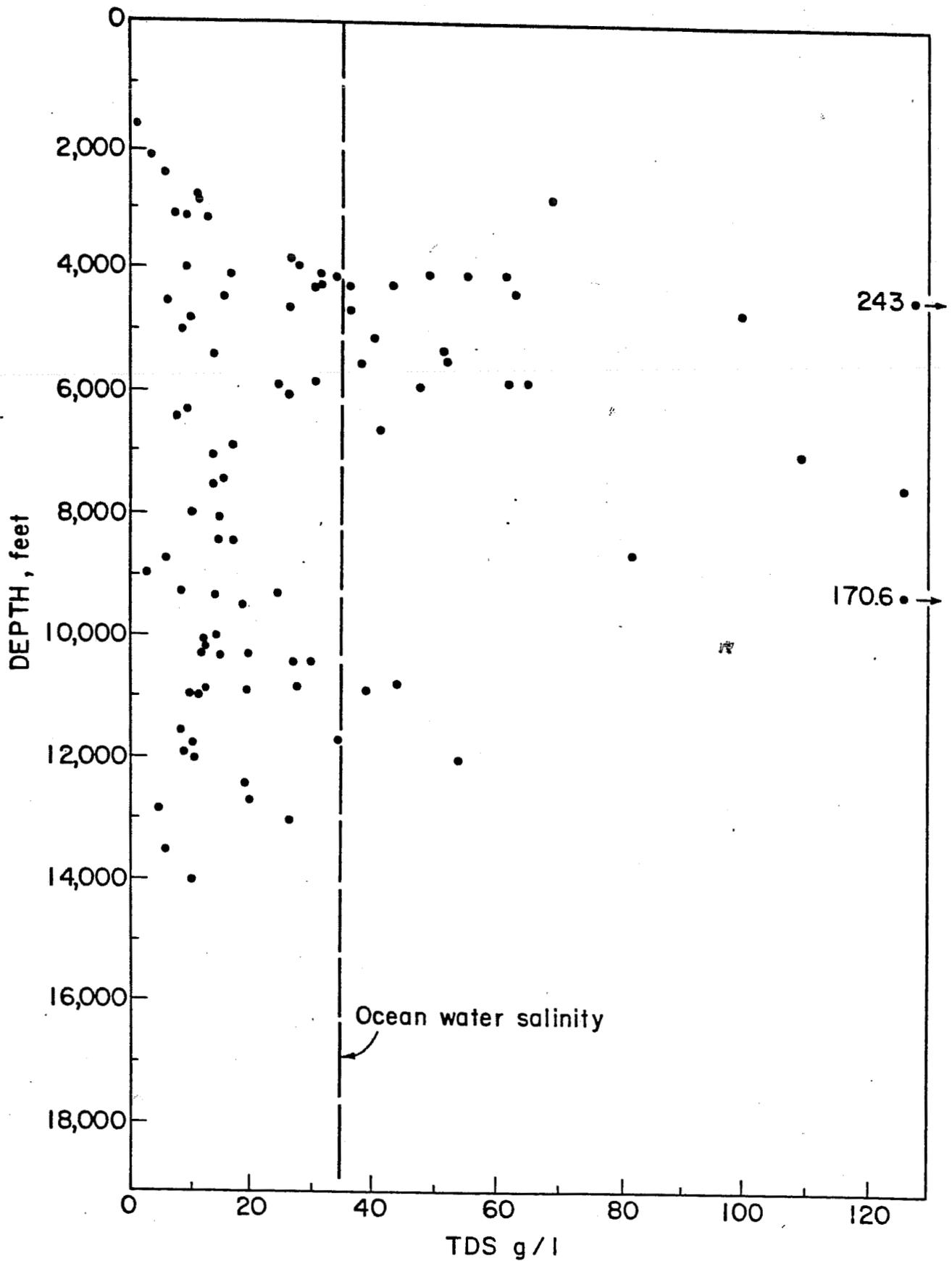


FIGURE 2. - Relationship between total salinity and depth in the Uinta Basin.

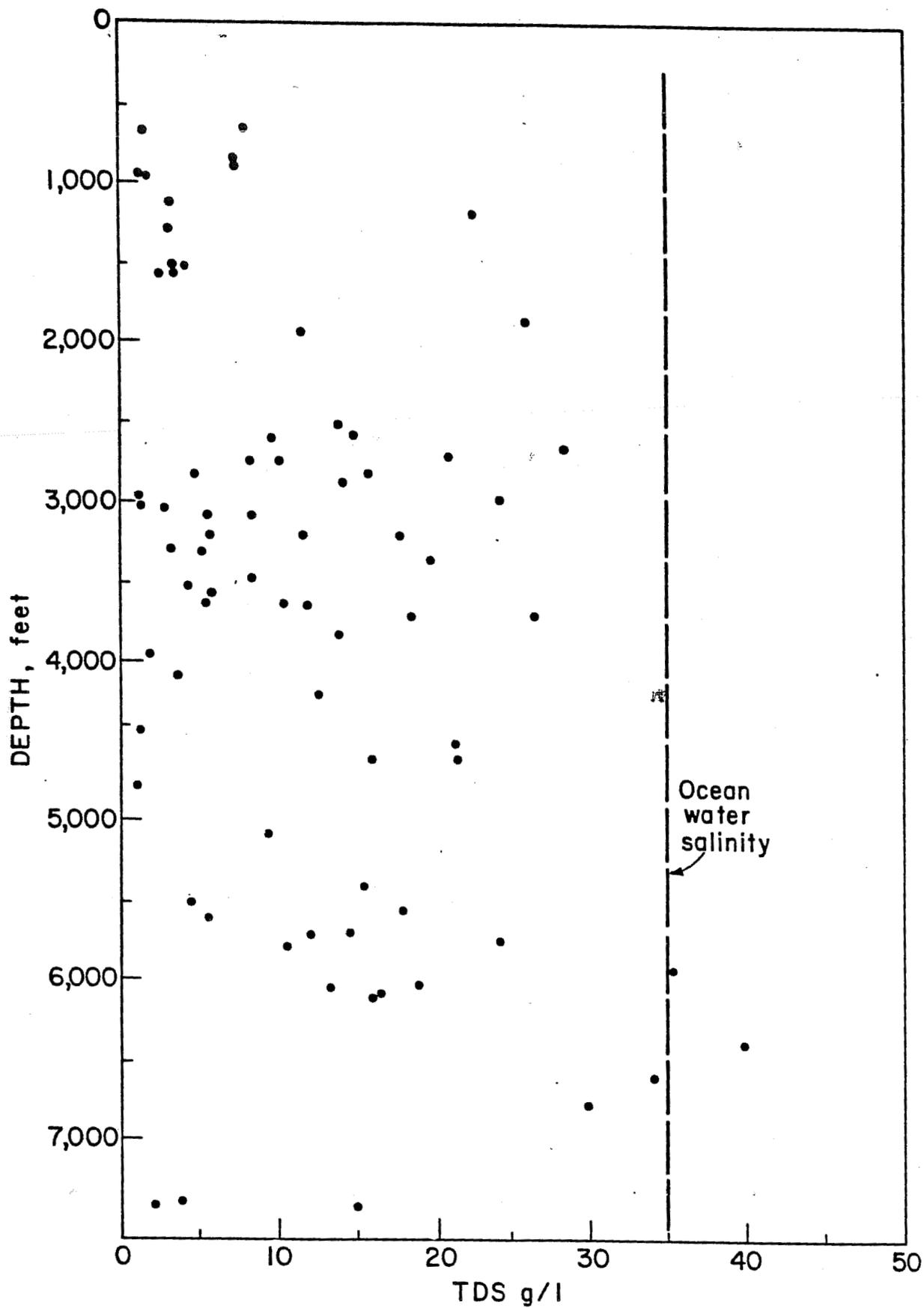


FIGURE 3. - Relationship between total salinity and depth in the North Piceance Basin.

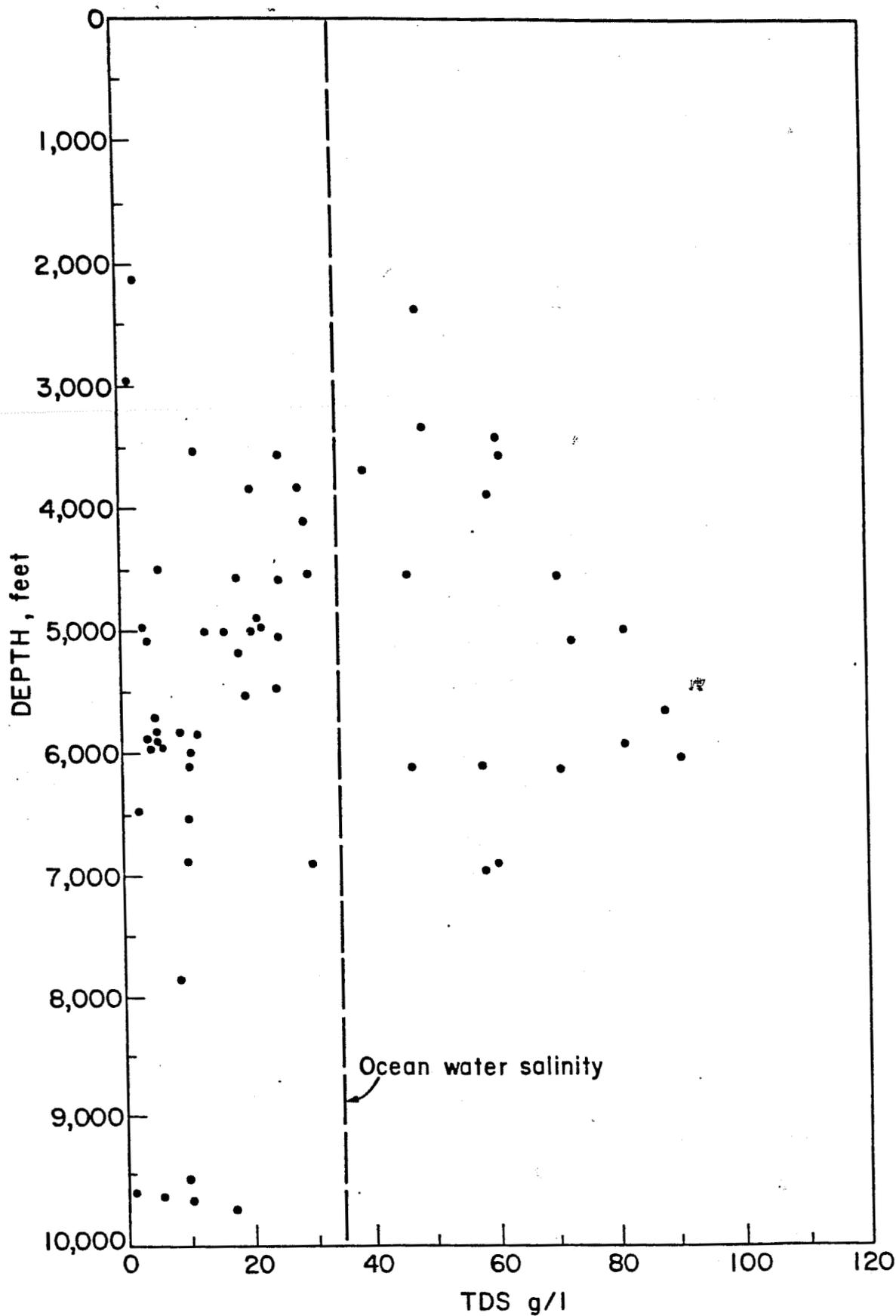


FIGURE 4. - Relationship between total salinity and depth in the Greater Green River Basin, east of the Rock Springs uplift.

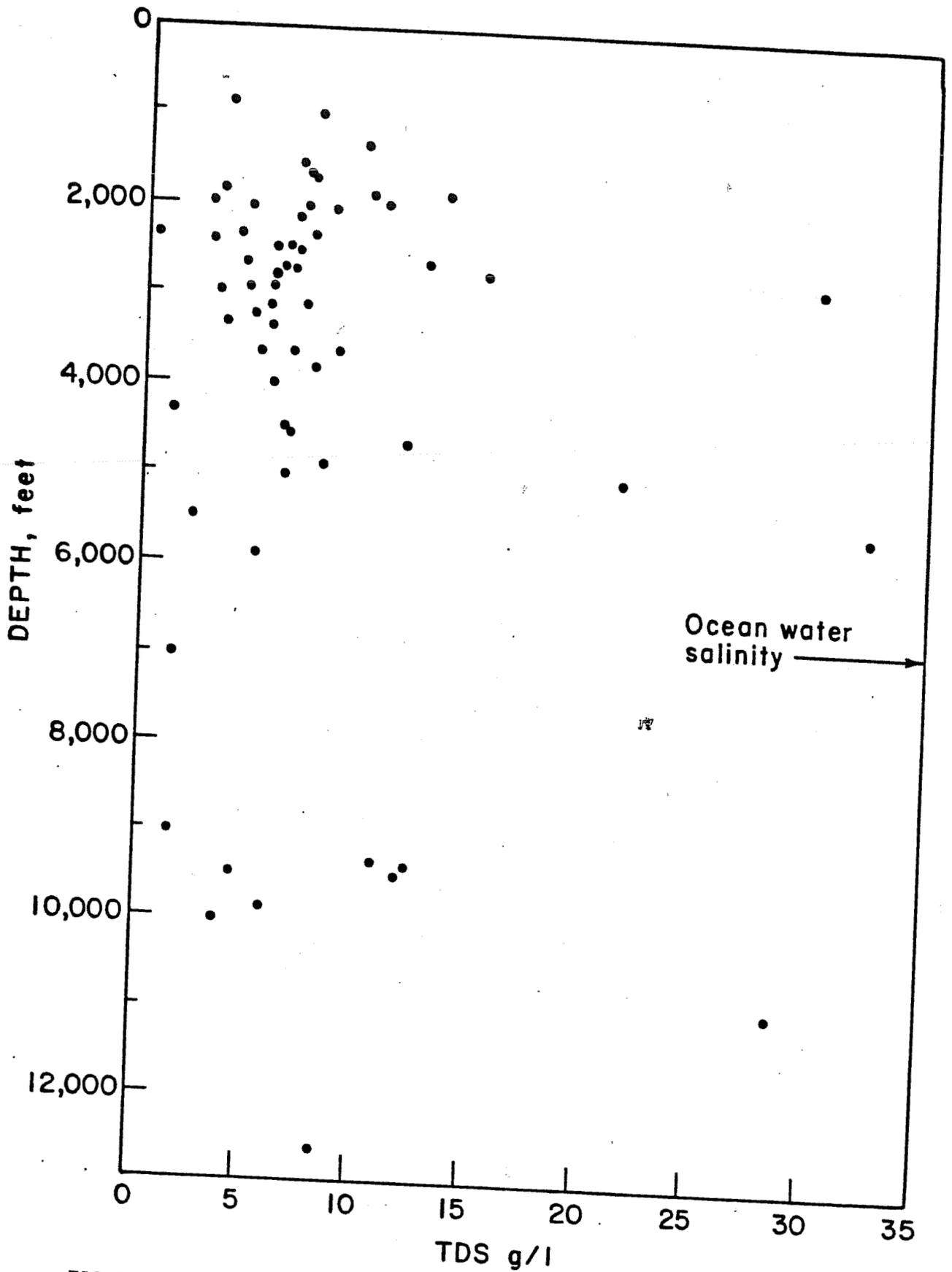


FIGURE 5. - Relationship between total salinity and depth in the Greater Green River Basin - Big Piney - La Barge area.

The pH of most of the formation waters studied fall within a range of 6.5-8.9, although, slightly alkaline or alkaline waters of pH, 7.2-8.5 significantly, prevail. The spatial distribution of the dominant water types was depicted on 4 hydrochemical maps drafted to the scale of 1:127,000 which are not presented here. However, the general image and distribution can be seen on the cross-sections (Figs. 6-10).

The hydrochemical sequences found with increasing depth are  $\text{HCO}_3\text{-Cl-Na}$ ,  $\text{Cl-HCO}_3\text{-Na}$ ,  $\text{Cl-Na}$  with some stratification of the  $\text{Cl-SO}_4\text{-Na}$  and  $\text{Cl-Na-Ca}$  types of water. There is a general trend, however, local chemical inversions also may occur. The occurrence of  $\text{HCO}_3\text{-Cl-Na}$  and  $\text{Cl-HCO}_3\text{-Na}$  water types down to 7,000 ft (2130 m) is characteristic at the edges of the basins as shown in Figure 6, 7 and 9, where the meteoric waters descension through outcropping zones is particularly intensive. In the central deeper parts of the basins the amount of original formation water affected by infiltrating waters is dependent upon the local rock permeabilities and also upon any local tectonic events.

The deep encroachment of meteoric waters (recent or paleoinfiltrated) was locally confirmed by the isotopic composition of the carbonate cements in the Parriette Bench field (Green River Formation of the Uinta Basin) down to about 6,000 ft., where "the authigenic carbonate was formed at low temperatures in the presence of meteoric waters by a process of solution-precipitation" (Pitman, et.al, 1982).

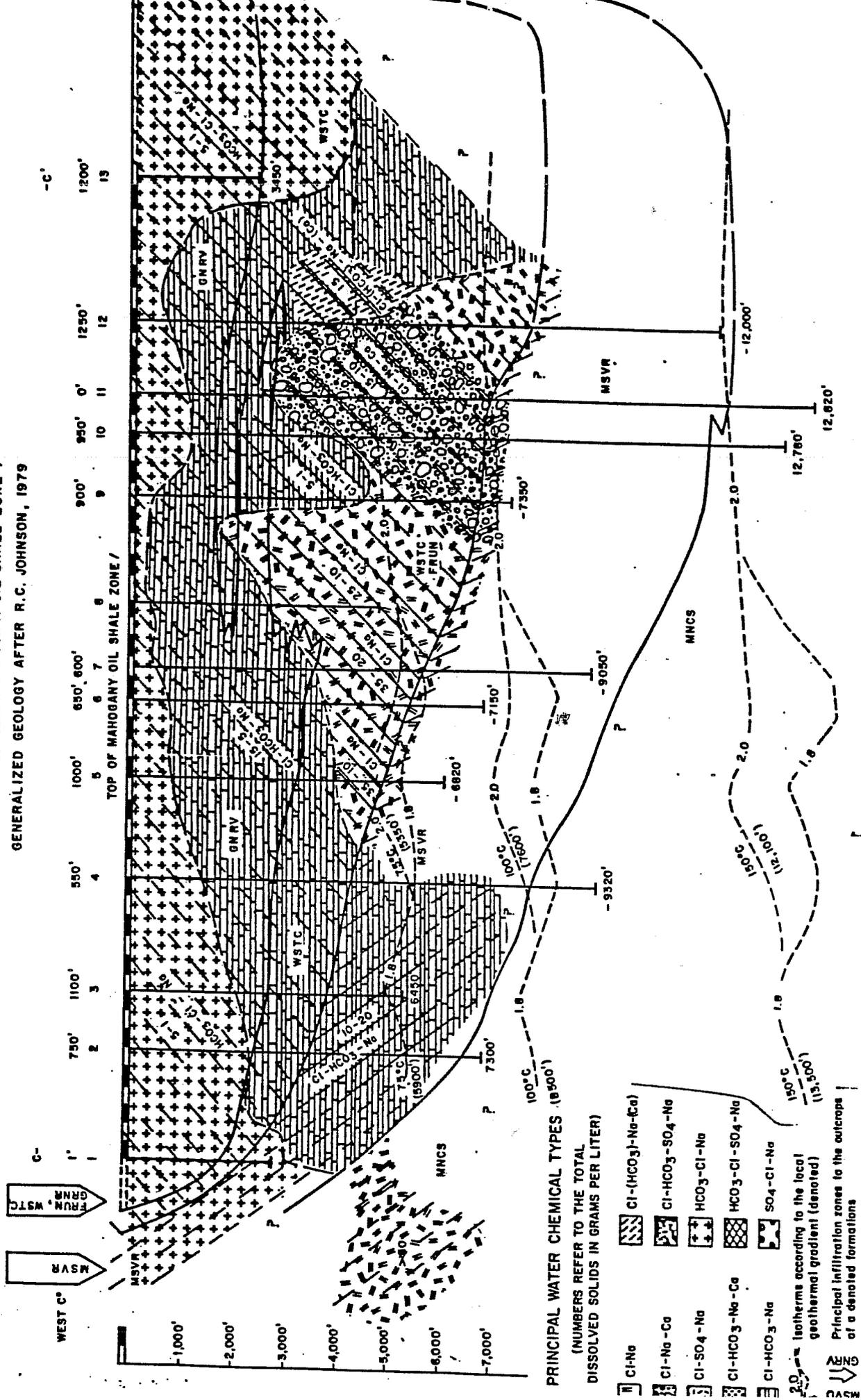
Significant data were obtained by carbon-14 dating of the fresh waters in the Lower Tertiary Wasatch Formation of Pinedale Unit, Green River Basin, where the age of water at a depth of 2,300 ft (700 m) was determined as only 20,800 years. However, at a depth of about 5,000 ft (1500 m) a water sample, with a TDS of 21 g/l and  $\text{Cl-Ca-Na}$  chemical type, was carbon -14 dated dead; and found to be older than 30,000 years (Dinwiddie, 1973).

Water chemical data reported in this study from the Fort Union Formation taken at the Pinedale Unit from a depth of 9,000-10,000 ft. (3000 m) contained about 1.6-10.0 g/l of TDS and the chemical types were  $\text{Cl-(HCO}_3\text{)-Na}$  or  $\text{Cl-Na}$ . A similar situation was observed for samples from the Wamsutter

FIGURE 6.

PICEANCE CREEK BASIN

APPROXIMATE HYDROCHEMICAL CHART C'-C'  
/ INTERPRETED BELOW MAHOGBANY OIL-SHALE ZONE /  
GENERALIZED GEOLOGY AFTER R.C. JOHNSON, 1979



PRINCIPAL WATER CHEMICAL TYPES (NUMBERS REFER TO THE TOTAL DISSOLVED SOLIDS IN GRAMS PER LITER)

- CI-Na
- CI-(HCO<sub>3</sub>)-Na-Ca
- CI-Na-Ca
- CI-HCO<sub>3</sub>-SO<sub>4</sub>-Na
- CI-SO<sub>4</sub>-Na
- HCO<sub>3</sub>-Cl-Na
- CI-HCO<sub>3</sub>-Na-Ca
- HCO<sub>3</sub>-Cl-SO<sub>4</sub>-Na
- CI-HCO<sub>3</sub>-Na
- SO<sub>4</sub>-Cl-Na

150°C  
(13,500')  
100°C  
(8500')

Principal infiltration zones to the outcrops of a denoted formations

FIGURE 7.

UINTA BASIN  
 APPROXIMATE HYDROCHEMICAL CHART A-A'  
 GENERALIZED GEOLOGY AFTER T.D. FOUCH, 1981

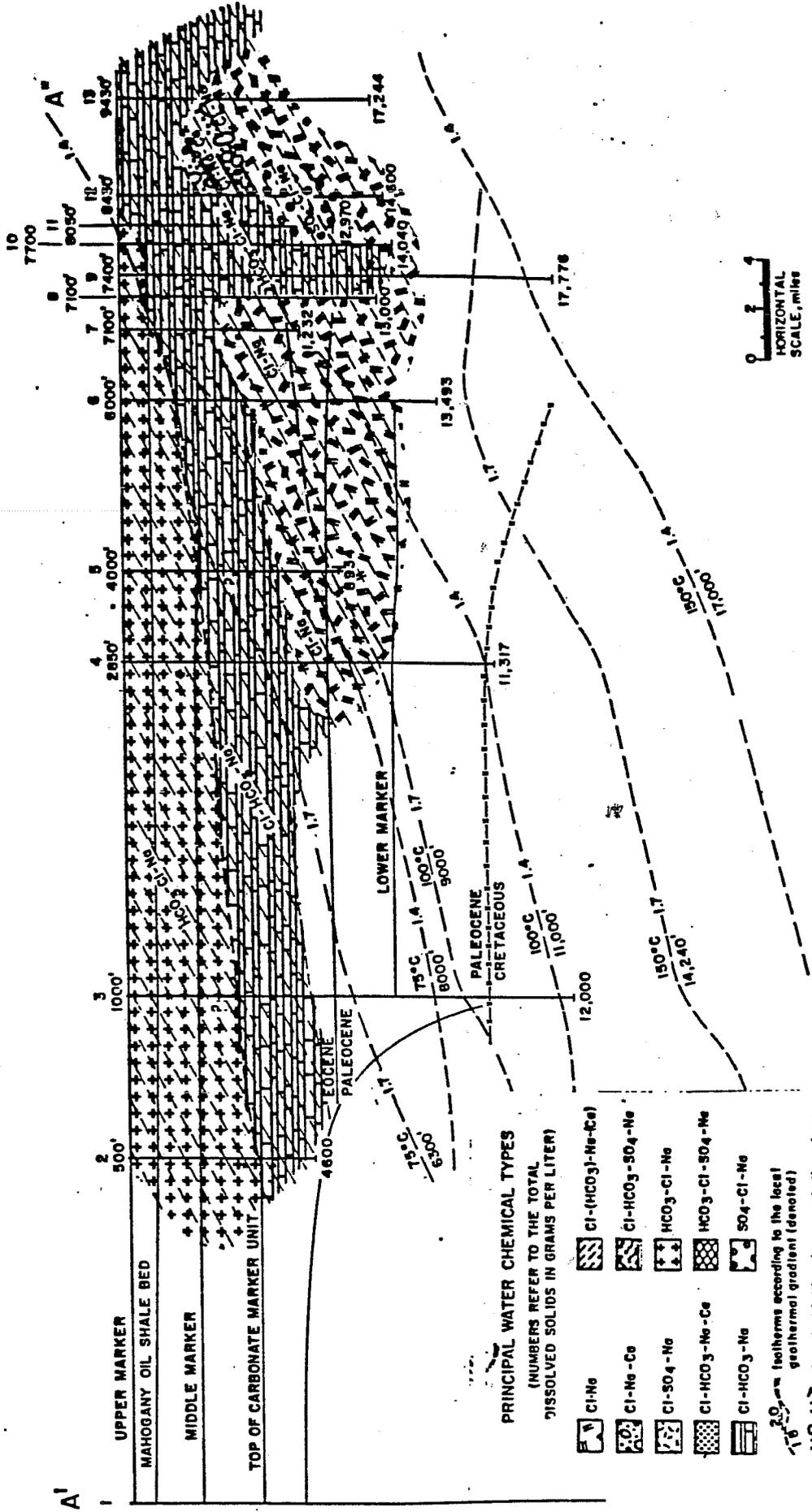
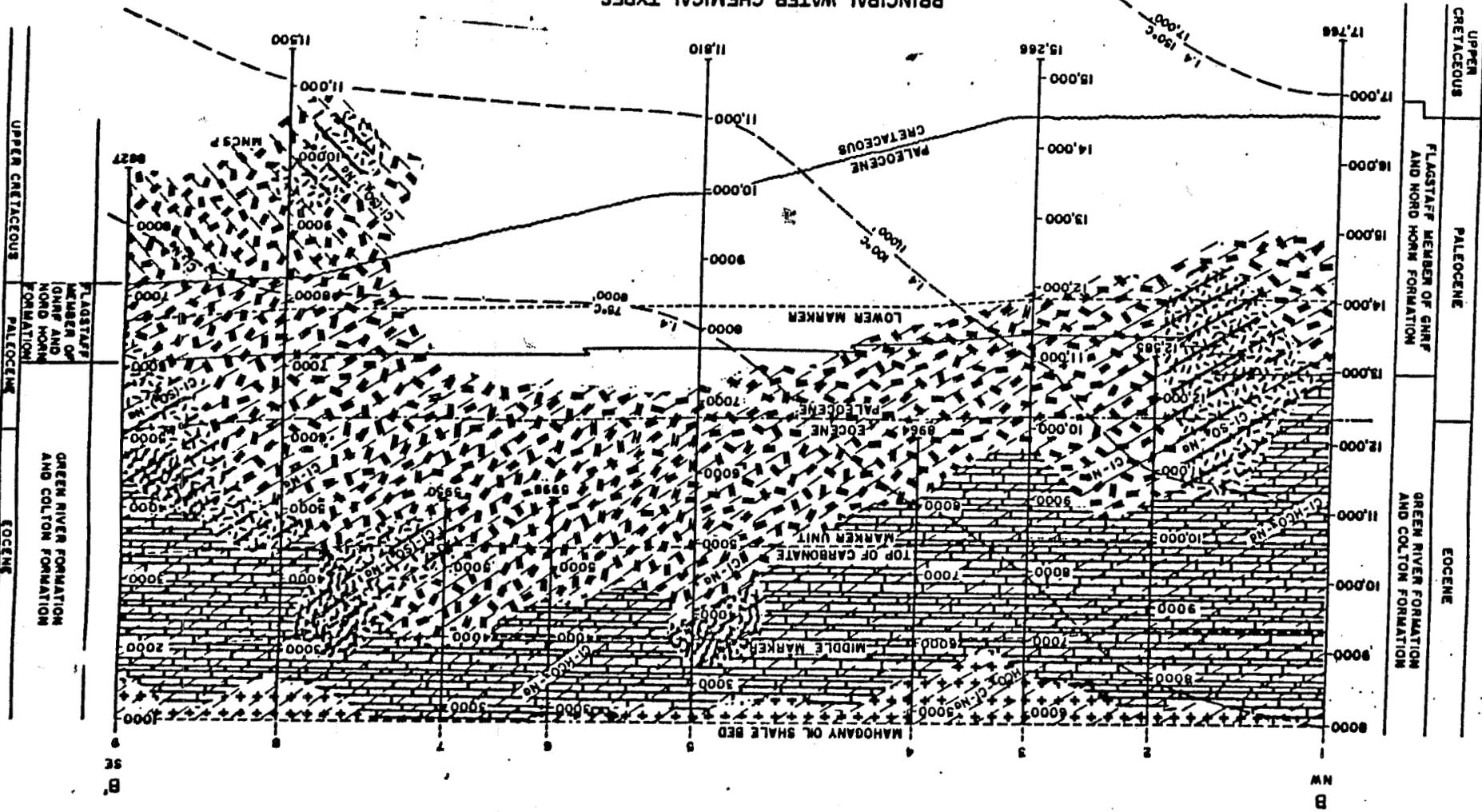


FIGURE 8.

UNITA BASIN

APPROXIMATE HYDROCHEMICAL CHART B-B'  
 /INTERPRETED BELOW MAHOAGANY OIL-SHALE ZONE/  
 GENERALIZED GEOLOGY AFTER T.D. FOUCH AND W.B. CASHION, 1978



HORIZONTAL SCALE, miles  
 0 1 2

FIGURE 9.

HYDROCHEMICAL CROSS-SECTION EAST OF ROCK SPRINGS UPLIFT  
 - GREATER GREEN RIVER BASIN  
 ALMOND FORMATION INTERPRETED

GEOLOGY BASED ON THE LOG CORRELATION BY TYLER T.F. 1979 (CROSS-SECTION C-C')

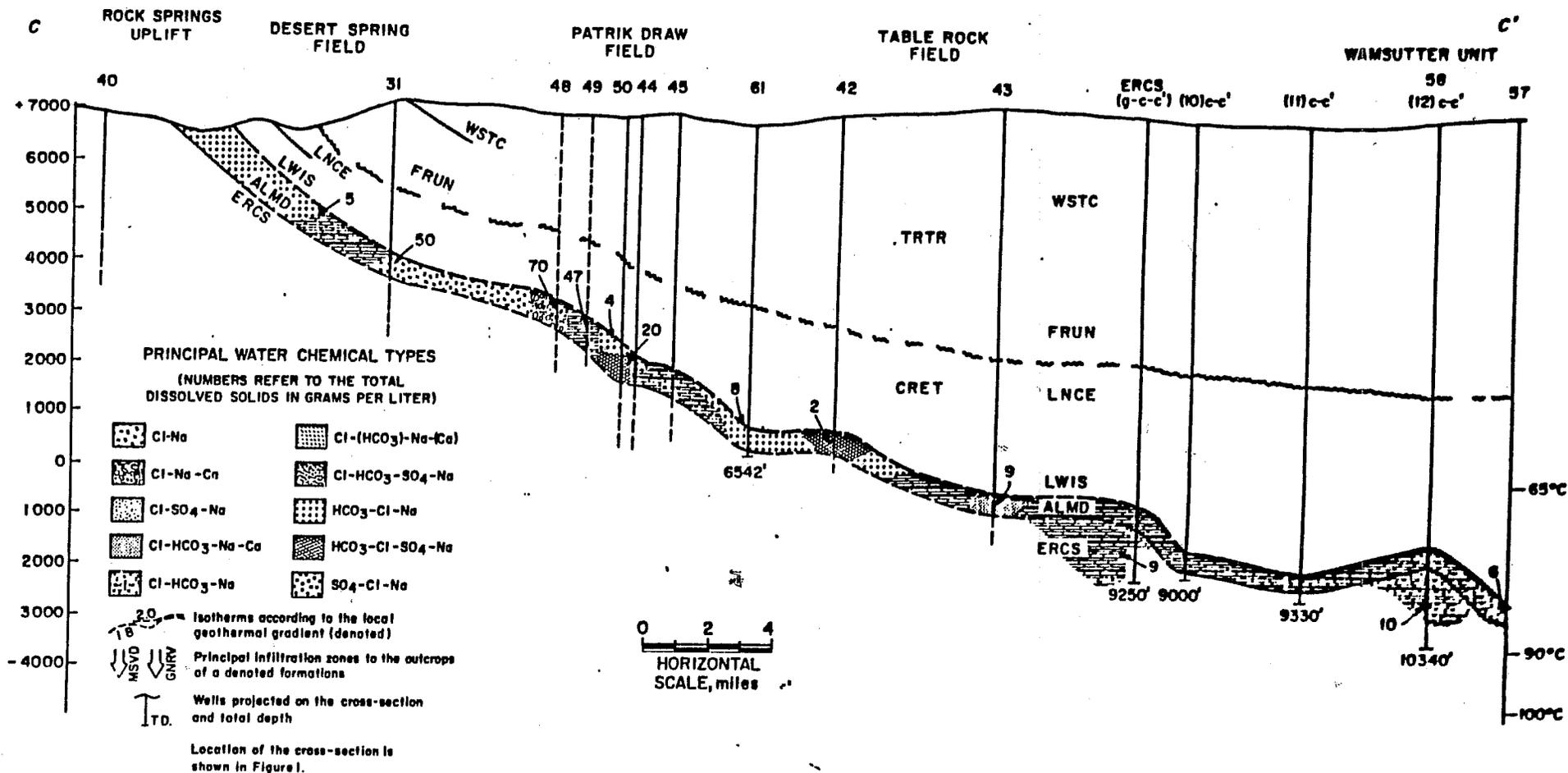
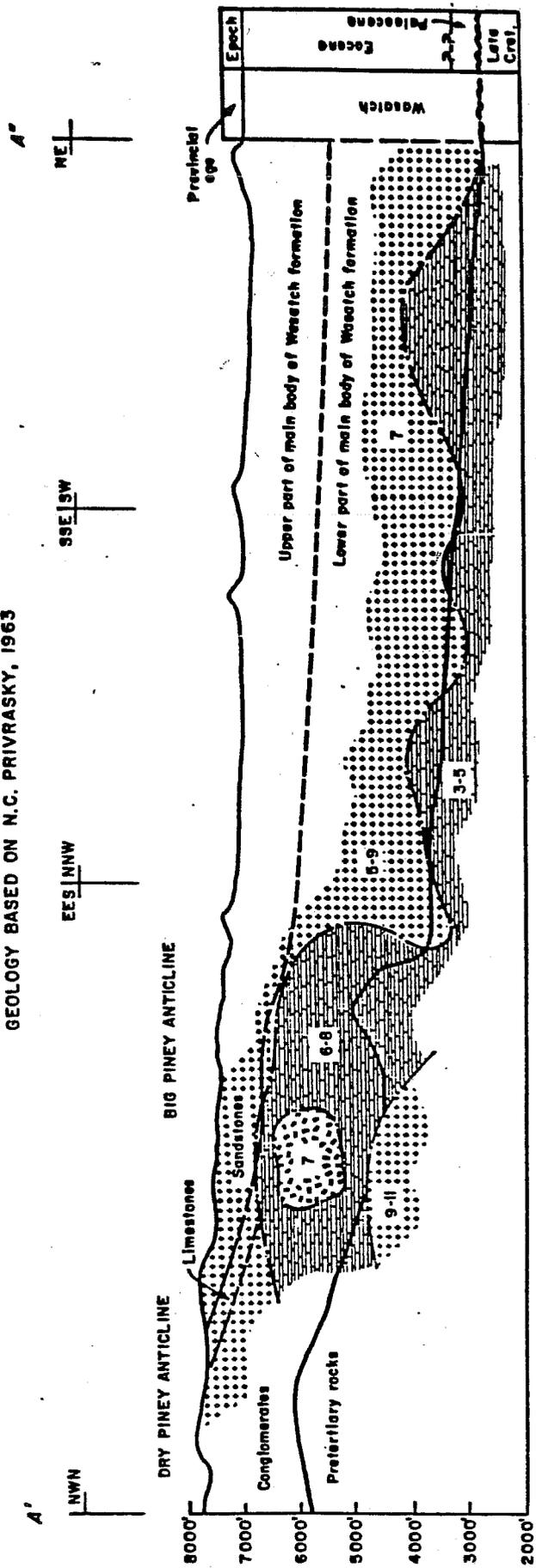


FIGURE 10.

APPROXIMATE HYDROCHEMICAL CROSS-SECTION THROUGH THE BIG PINEY LA BARGE  
OIL-GAS FIELD SUBLETTE COUNTY, WYOMING

GEOLOGY BASED ON N.C. PRIVRASKY, 1963



PRINCIPAL WATER CHEMICAL TYPES  
(NUMBERS REFER TO THE TOTAL  
DISSOLVED SOLIDS IN GRAMS PER LITER)

- |  |                            |  |  |
|--|----------------------------|--|--|
|  | Cl-Na                      |  | Cl-(HCO <sub>3</sub> )-Na-Ca             |
|  | Cl-Na-Ca                   |  | Cl-HCO <sub>3</sub> -SO <sub>4</sub> -Na |
|  | Cl-SO <sub>4</sub> -Na     |  | HCO <sub>3</sub> -Cl-Na                  |
|  | Cl-HCO <sub>3</sub> -Na-Ca |  | HCO <sub>3</sub> -Cl-SO <sub>4</sub> -Na |
|  | Cl-HCO <sub>3</sub> -Na    |  | SO <sub>4</sub> -Cl-Na                   |

- Isotherms according to the local geothermal gradient (denoted)
- Principal infiltration zones to the outcrops of a denoted formations
- Wells projected on the cross-section and total depth
- I.T.D.
- Location of the cross-section is shown in Figure 1.

Unit, east of Rock Springs Uplift, Washakie or Greater Green River Basin where formation waters from the Upper Cretaceous Almond Formation at 9,500-10,000 ft (3000 m), have mineralizations of 1.5-11.0 g/l TDS and a Cl-HCO<sub>3</sub>-Na chemical type.

Another situation was observed in a through-like structure shown on Figure 7 near the Altamont oil field in the Uinta Basin, where Cl-HCO<sub>3</sub>-Na type waters of 8-9 g/l TDS, overlap the Cl-Na; Cl-Na-Ca or Cl-Ca-Na type of waters, indicating that an isolated, stagnant zone, occurs at about 13,000 ft. (5150 m). It is unlikely that meteoric water encroachment down to those depths is possible. Another factor must have been involved to dilute the original fluids and to generate the bicarbonates. It is very difficult to solve this problem without stable isotope data, but an attempt is undertaken as described later to determine the different sources of bicarbonates and their relationship to the hydrocarbons.

On the basis of available chemical data one can trace and determine some aspects of the formation water origin and alteration, within this thick sequence of mostly non-marine rocks. As can be seen on Figures 11-14, the distribution of chloride concentrations versus total dissolved solids (TDS), of most of the formation waters from all of the basins considered closely follow the ocean water dilution-concentration line defined by the relation:  $TDS = 1.805 Cl$  (Horne, 1969). This suggests an ascension of relict, connate waters from deep-seated marine formations into the shallower non-marine sections of the basins, followed by dilution by mixing with fresh waters from other sources, and an alteration caused by interaction with the surrounding rocks and hydrocarbons. ✓

A slight parallel deviation from the sea water dilution line is caused by a gain of the anions HCO<sub>3</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup> shown by points below this line, or cations, mostly Ca<sup>2+</sup> shown by points above the line. Some points depart significantly from this line. There are waters located within the uppermost portions of the basins, of very low TDS (below 5 g/l). This and other features suggest their origin as undoubtedly meteoric. For example they are deficient in chloride, are of the HCO<sub>3</sub>-Cl-Na, HCO<sub>3</sub>-Na, SO<sub>4</sub>-Cl-Na chemical water types, their metamorphism index (rNa/rCl) usually is much higher than 1.6, and their reductivity index (rSO<sub>4</sub> x 10<sup>3</sup>/rCl) is much higher than 200, indicating oxidizing environmental conditions.

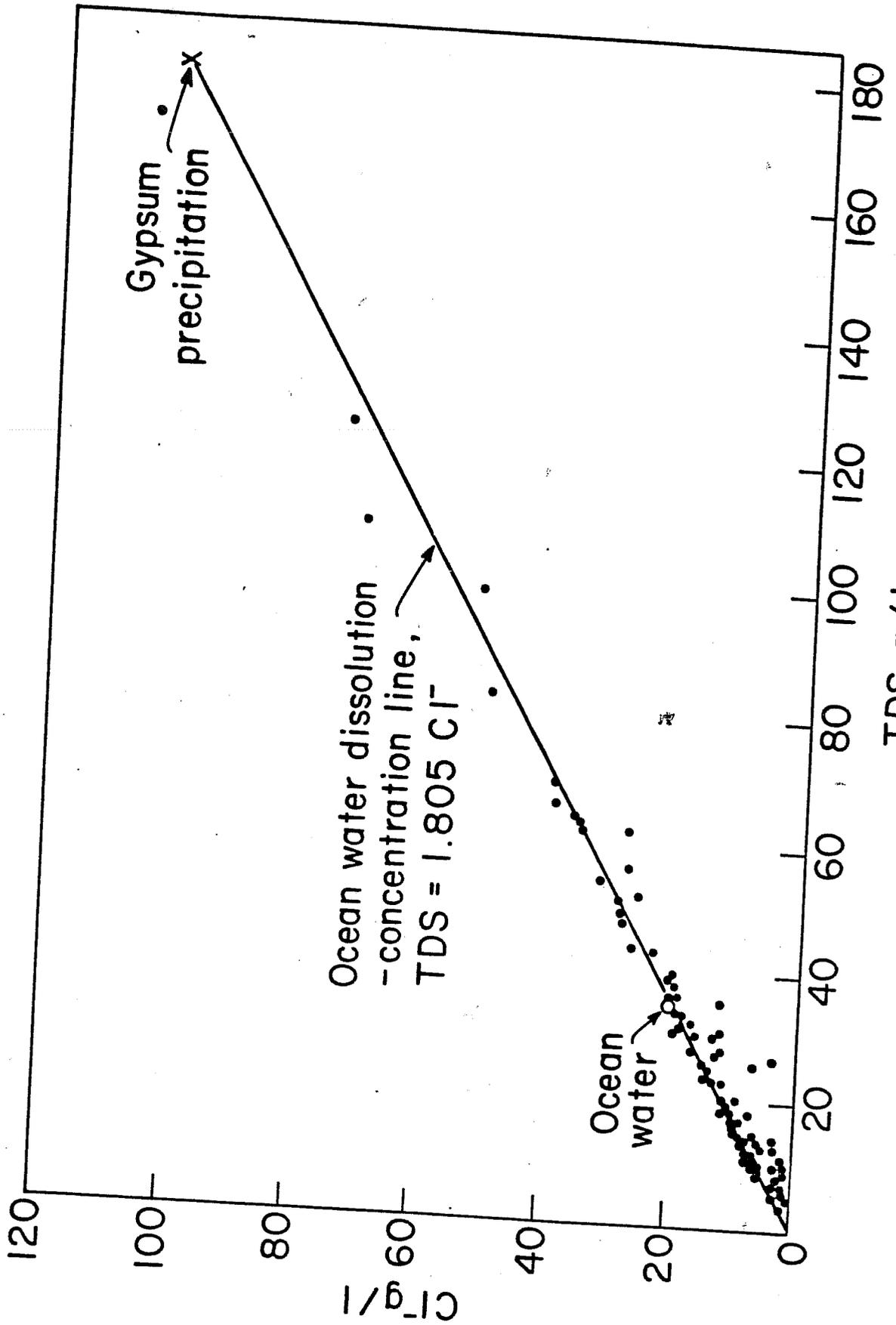


FIGURE 11. - Relation between dissolved solids and chloride concentration in the formation waters of the Upper Cretaceous and Lower Tertiary formations within the Illinois Basin.

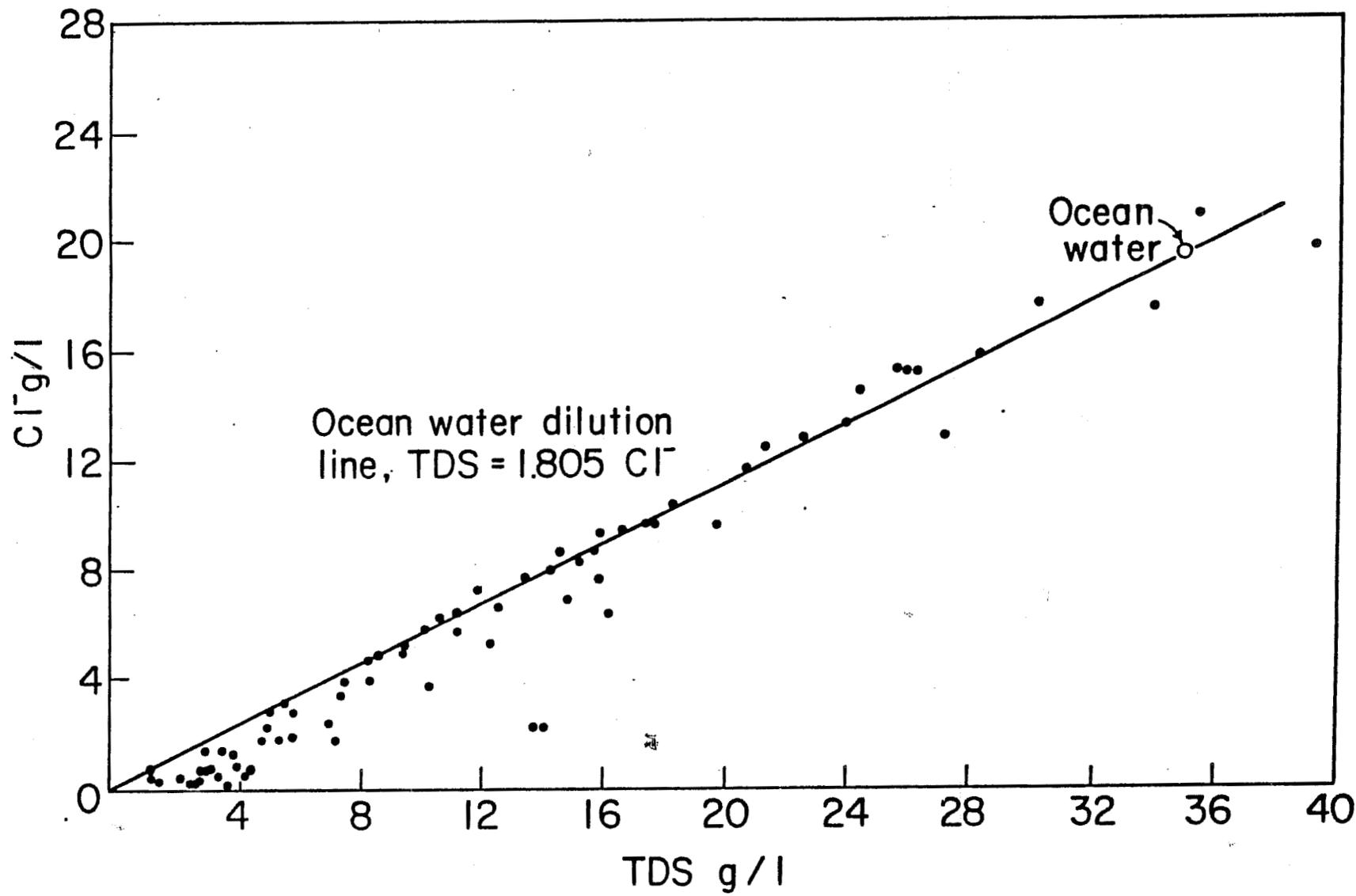


FIGURE 12. - Relation between dissolved solids and chloride concentration in the formation waters of the Upper Cretaceous and Lower Tertiary marine and continental deposits within the Northern Piceance Creek Basin, Colorado.

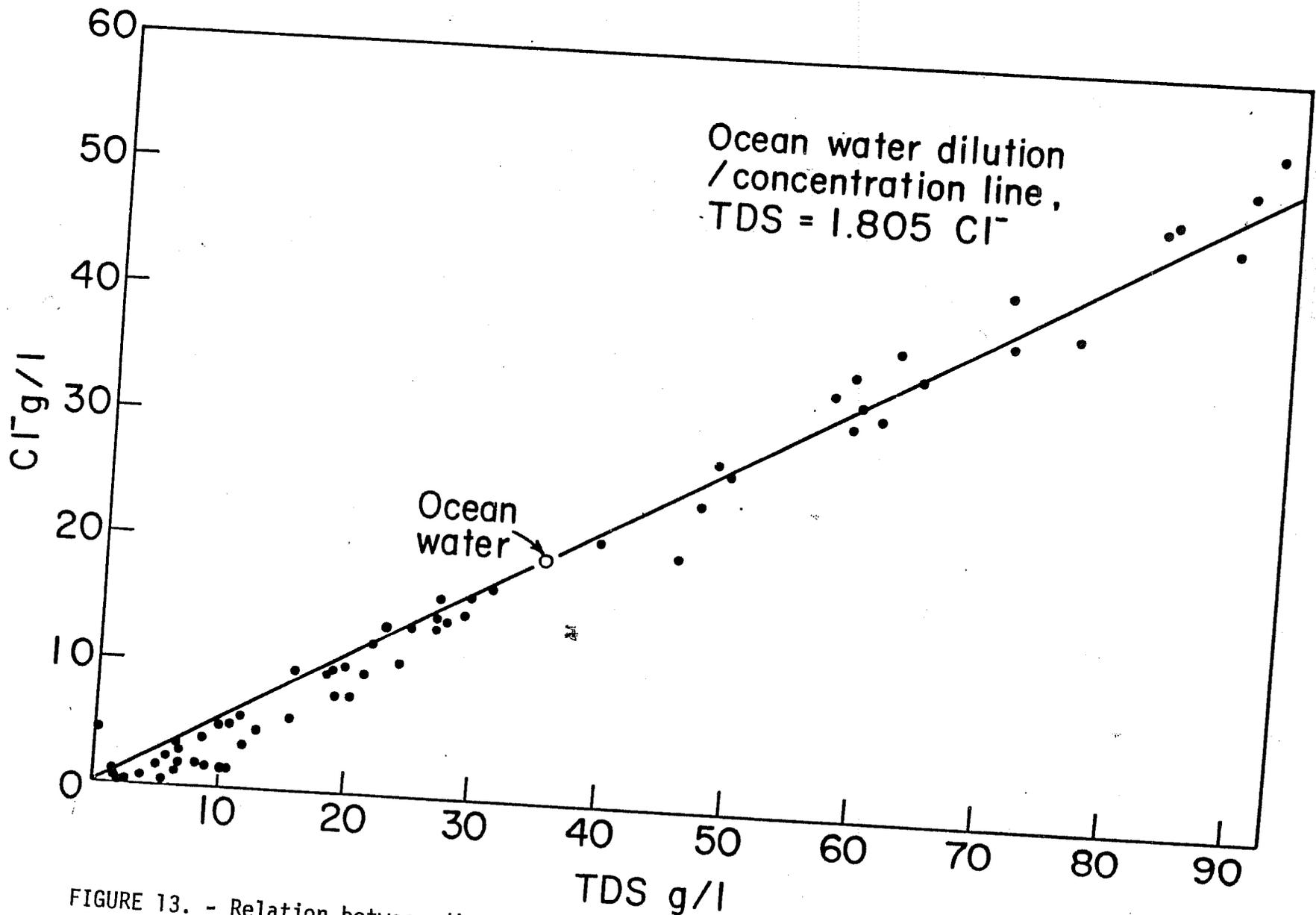


FIGURE 13. - Relation between dissolved solids and chloride concentration in the  
 of some Upper Cretaceous deposits in the  
 Springs

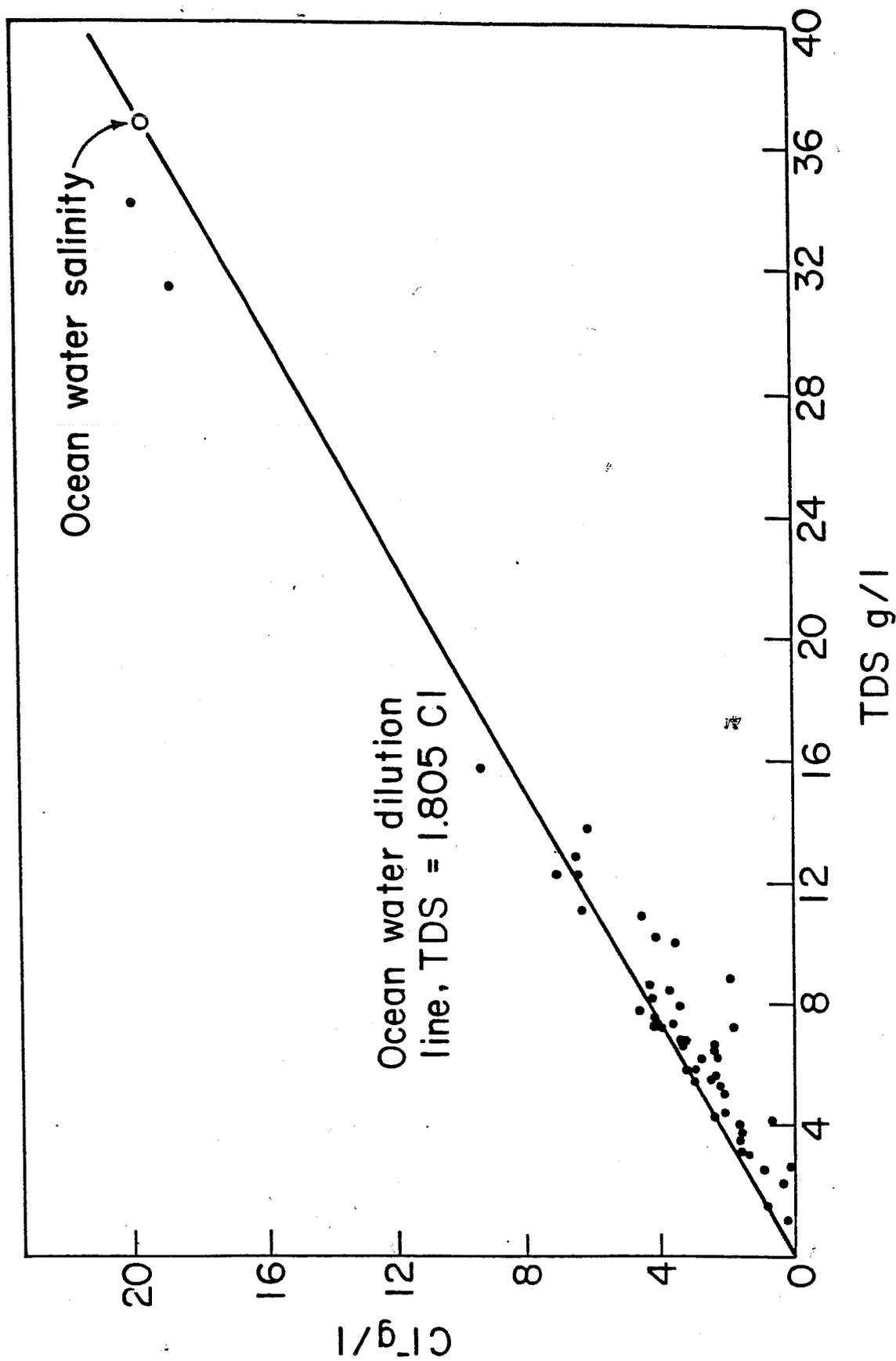


FIGURE 14. - Relation between dissolved solids and chloride concentration in the formation waters of the Upper Cretaceous and Lower Tertiary deposits within the Greater Green River Basin; Big Piney-La Barge area.

Similar relationships were observed in Figures 15-18 where the log Na<sup>+</sup> concentration versus log Cl<sup>-</sup> concentration were plotted. The formation water data again closely follow the sea water dilution/concentration line, expressed by the relation:  $\log Cl = 1.06 \log Na$ . Points located far off this line on the right, represent marine waters from relatively isolated environments, where Na<sup>+</sup> from solution was exchanged with Ca<sup>2+</sup> in the surrounding clayey rocks - mostly shales, mudstones or carbonaceous sandstones.

Points located on the left side in these figures represent waters which gained mostly bicarbonates and sometimes sulfates (in the Uinta Basin) while chloride was depleted. This can be attributed to leaching processes and/or interaction with organic matter. This will be discussed in detail later. The lower concentrations of TDS, and the divergence from the ocean water line is interpreted as an increased contribution of meteoric waters to the formation fluids.

That a chemically altered, originally marine water component exists within an overwhelmingly continental rock is strongly confirmed by the presence of iodide and bromide in 36 water samples from the Uinta Basin. The reported iodide content in waters from the continental Wasatch and Green River formations ranges from trace concentrations to 32 mg/l., with most of the values between 5-22 mg/l (sea water contains 0.05 mg/l). Bromide content varies in these samples between 5 and 381 mg/l (seawater contains about 68 mg/l). Unfortunately, data concerning I<sup>-</sup> and Br<sup>-</sup> are very scarce from the other areas, however, bromide was found "in all of the Big Piney - La Barge oil-field waters" in the Green River Basin (Crawford 1964). J. Dyni, et. al. (1970) reported significant amount of bromide from bedded halite, nahcolite, and trona evaporative facies of lacustrine Green River formation in the Piceance Creek Basin and the Green River Basin, suggesting its origin from "contemporaneous volcanic sediments or gaseous emanations and older marine evaporites."

Bromide may originate directly from ancient sea water, or from dissolution of some non-marine evaporites containing bromide salts. The only known and significant source of high enrichment in iodide is bioconcentration in marine organisms, deposited later with marine sediments and eventually transformed to hydrocarbons. W. Carothers and Y. Kharaka (1978, p. 2452) observed that iodide concentrations increased with increasing concentration of

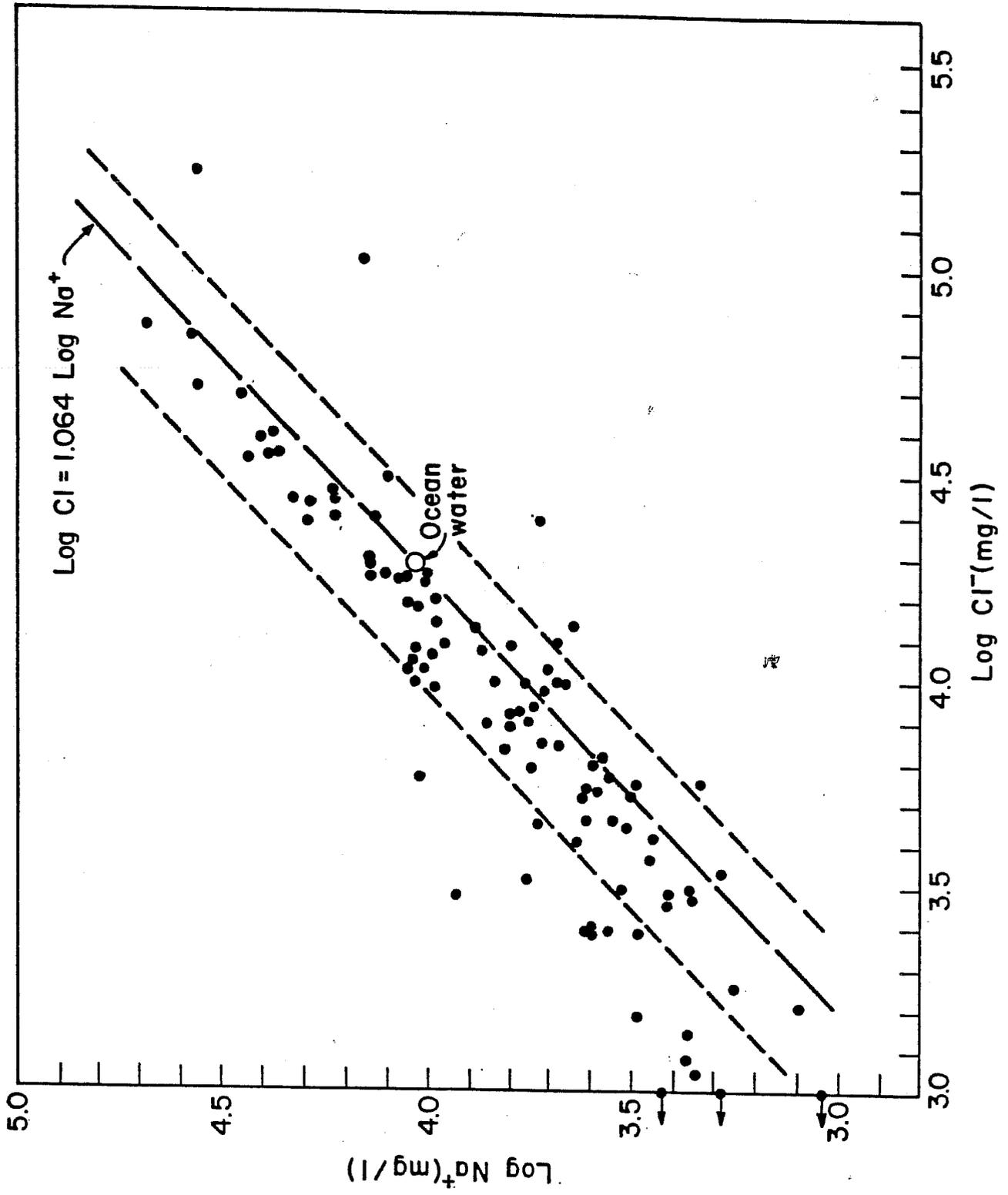
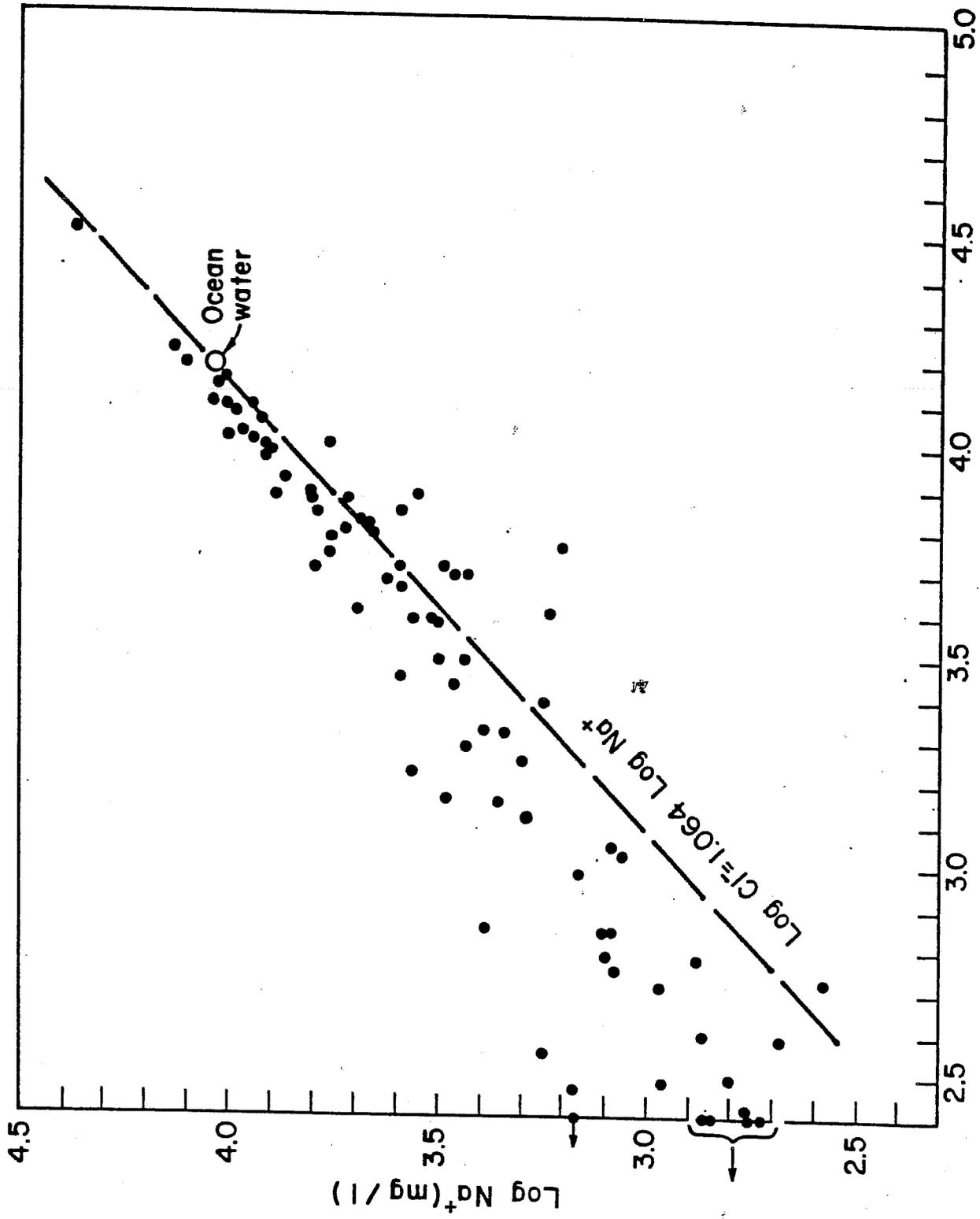


FIGURE 15. - Relationship between sodium and chloride concentration in the studied formation waters of the Uinta Basin. Middle line indicates the marine water dilution-concentration trend.



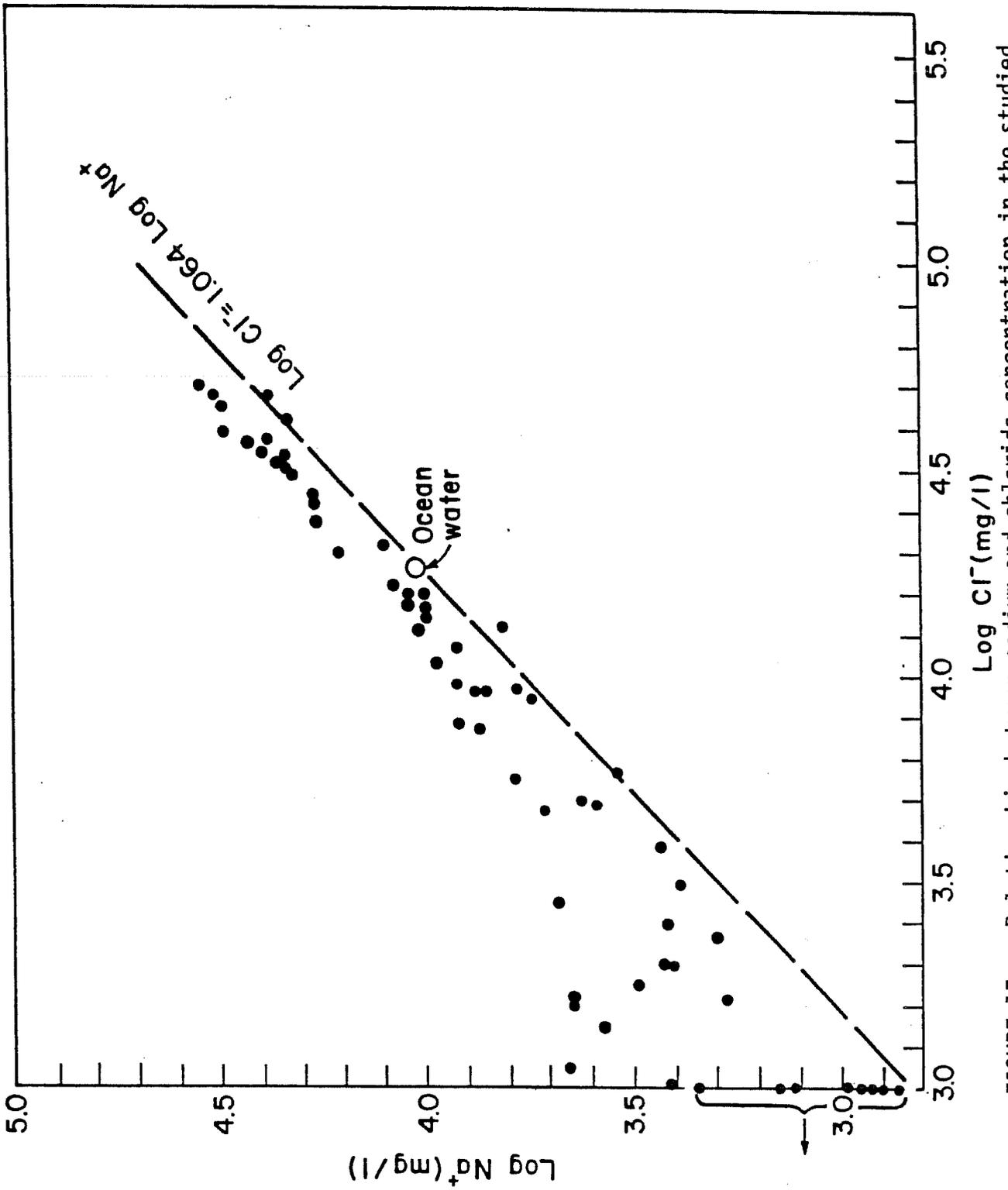
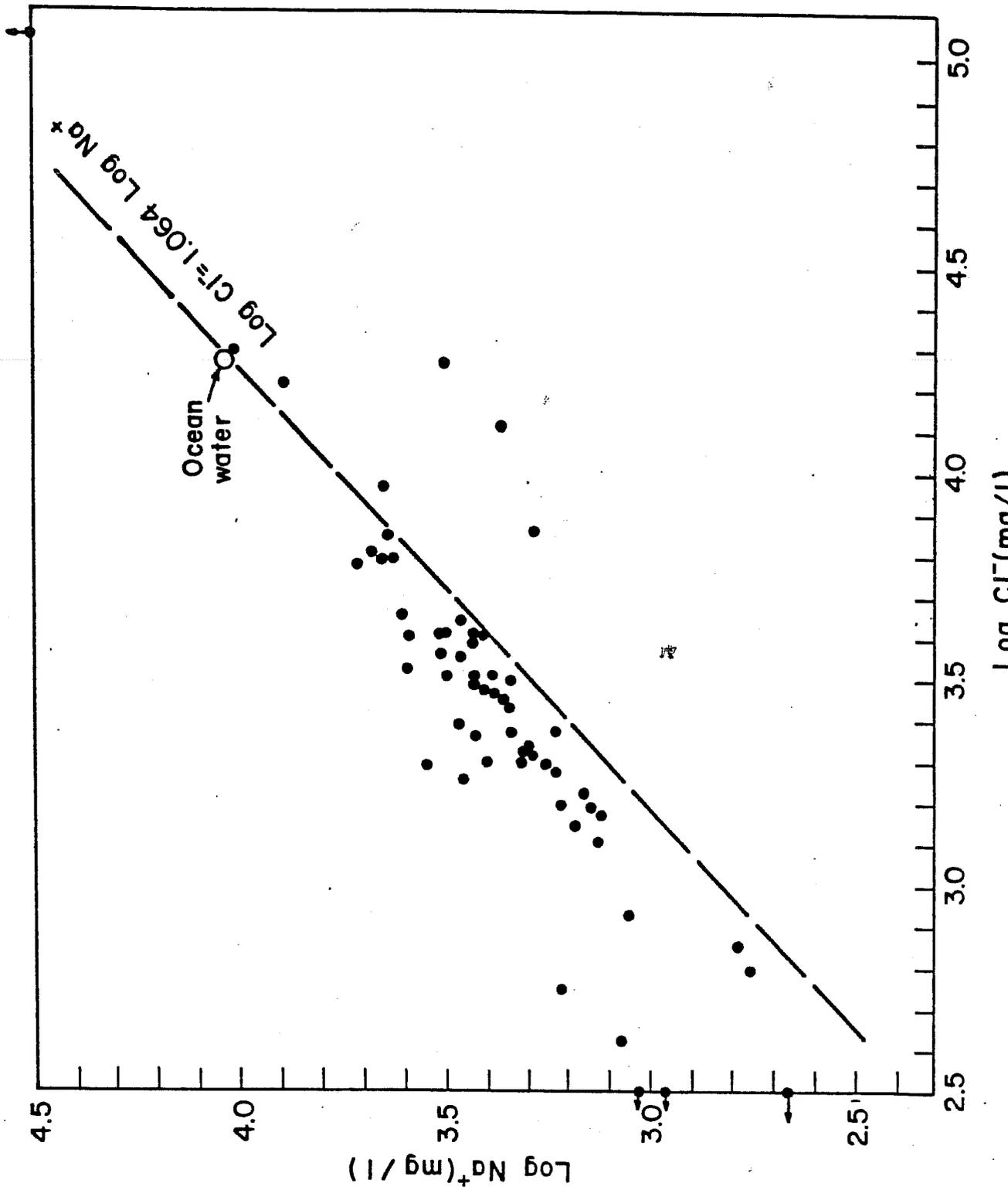


FIGURE 17. - Relationship between sodium and chloride concentration in the studied formation waters of the Greater Green River Basin - east of the Rock Spring Uplift.



aliphatic acid anions in oil-field waters in California and Texas. This fact supports the common belief that marine organisms are the source of iodide in oilfield waters. They also stated, that iodide concentrations are a good indicator of petroleum, even when aliphatic acid anions have been degraded biologically or thermally.

Bromide, because of its geochemical behavior, is also considered a useful indicator of water origin (Rittenhouse, 1967; Collins, 1975; Carpenter, 1978a, 1978b). Figure 19 depicts a relationship between log of Cl<sup>-</sup> concentration versus log of Br<sup>-</sup> concentration in some Uinta Basin waters. Plotted points scatter within different genetic fields (Carpenter, 1978a), but a group of them concentrates around the sea water dilution line. A few of the points may indicate halite dissolution (bromide depleted) and others indicate some admixture of bitterns or interaction with organic matter (bromide enriched). Only vague genetic conclusions can be drawn so far because of the scarce bromide and iodide data.

The origin of water mineralizations much higher than 35-40 g/l TDS is not clear and difficult to explain on the basis of existing hydrochemical data. These are usually the Cl-Na type, containing minor amounts of Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> ions. The dissolved solids in these correspond to the ocean water concentration line and most of them never reached the point of CaSO<sub>4</sub> precipitation stage as shown in Figures 11 and 13.

Most of the highly mineralized waters were found within sections of the Uinta Basin and Wamsutter arch area of the Green River Basin, both in the Upper Cretaceous and Lower Tertiary formations. A deflection from the ocean water concentration line was evident in a few waters from the Uinta Basin (Fig. 11). These waters probably contain dissolved halite as suggested by the plots shown on Figure 19, even though halite is not readily available within the deeper section of Wasatch and Green River formation, where these waters were located. There also is no clear evidence of a bitterns admixture because the Mg<sup>2+</sup>, Br<sup>-</sup> and B<sup>-</sup> concentrations are too low.

There are many indications of relict sea water and meteoric water mixing in the rocks down to about 7,000 ft (2100m). In spite of the present observed low porosity and very low rock permeability, fluids of different origin had to migrate upward and downward for distances of several thousands of feet, then mix and interact with surrounding rocks and hydrocarbons during geologic

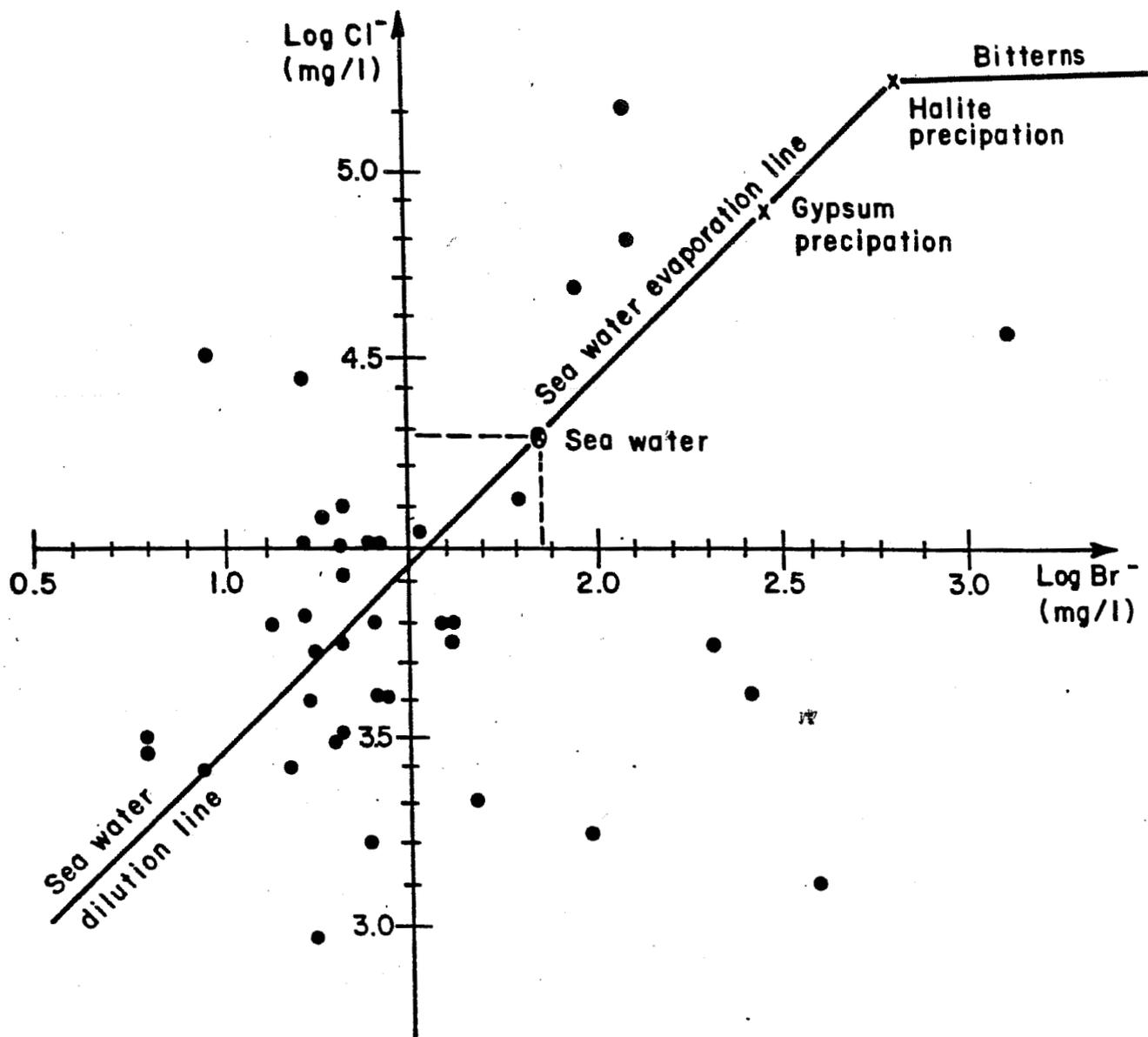


FIGURE 19. - Relationship between chloride and bromide in the studied formation waters of the Uinta Basin.

time. The time and mechanism of this circulation is not yet clear, but there is good reason to assume that rapid deposition of continental deposits since the latest Cretaceous period, uplifting of mountain ranges nearby, and folding or faulting of deposited sediments, provided the high pressures necessary to set in motion compaction processes and initiate primary migration of squeezed off pore fluids.

The exposure of the Upper Cretaceous deposits (unconformity) to the atmosphere for a long period of time, enabled a meteoric water invasion and desalting of Cretaceous aquifers. During the Tertiary deposition, portions of deeply-seated marine fluids probably were introduced to Tertiary aquifers through open fractures along a major fault zone. Low rock porosity and permeability as well as discontinuous formations prevented complete local mixing.

Migration of crude oil, from deep-seated source rocks to the present collectors probably occurred in a similar manner. This is particularly true within these sections of the basins, where the geothermal gradient and formation temperatures are below "oil-window," which will not justify thermal maturation of organic matter from within the continental deposits. Examples are the Big Piney-La Barge, Table Rock, Patrick Draw oil fields, as well as oil fields in the Piceance Basin and eastern-central part of the Uinta Basin.

A better recognition of hydrodynamics could help solve many of the migration problems involved. On the basis of the few bottom hole pressure data available from the Piceance Basin, one can only assume that confined-artesian or subartesian conditions-occur down to at least 7500 feet (2300 m). Overpressured tight gas reservoirs have been identified within six Rocky Mountains basins (Spencer, 1983), including all of the three considered here. An abrupt increase in pressure gradient from 0.43 psi/ft - (9.7 kPa/m) to 0.84 psi/ft - (19.0 kPa/m), were identified by Law et.al. (1980) in the Pacific Creek area of the Green River Basin at a depth of about 11,600 ft (3500 m). This overpressuring was interpreted to be the result of active thermal generation of gas, associated with very low formation permeability and sealing the reservoir at the top. At similar depth ranges the formation water demineralization in the other areas was described earlier in this discussion.

The real piezometric surface gradient and the directions of the water flow, as well as water discharge areas for the basin's deep regional flow

network, are not yet determined. Water chemistry indicates, however, those sections of the basins where stagnant or semi-stagnant conditions prevail and the environment is isolated from outside influences. Also, local or intermediate hydraulic flow systems, where the aquifers are entirely or somewhat open to the meteoric water encroachment, are fairly well indicated by the hydrochemical data, and will be described later. However, there still are some genetic and hydrodynamic questions or uncertainties that remain unanswered.

### THE ORIGIN OF BICARBONATES ( $\text{HCO}_3^-$ ): IMPLICATION FOR OIL AND GAS RELATED PROBLEMS

Most of the formation water investigated in this study are chloride waters of mixed origin. Many of those within a lower range of mineralization, are highly enriched in bicarbonates, up to 9,000 mg/l or 90 meq.% of the total anions. These waters are represented primarily as Cl- $\text{HCO}_3$ -Na; Cl-( $\text{HCO}_3$ )-Na or  $\text{HCO}_3$ -Cl-Na chemical types. In an attempt to explain the origin of the bicarbonate type, its zonality, and to determine its relationship to hydrocarbons, the following principal natural processes, responsible for  $\text{CO}_2$  and/or  $\text{CH}_4$  generation, were considered:

- 1) inorganic and bacterial oxidation of oil
- 2) bacterial reduction of sulfates
- 3) bacterial reduction of organic acids
- 4) thermal decarboxylation of aliphatic acid anions
- 5) regional carbonate rock metamorphism
- 6) coalification

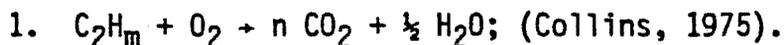
Chemical reactions related to these processes are listed in Table 1.

The inorganic oxidation of petroleum by fresh, meteoric waters carrying oxygen is rather restricted to near-surface reservoirs at depth not exceeding 3,000-3,500 ft (900-1060 m) (Bailey et al., 1973). Similar decomposition of oil, leading to the  $\text{CO}_2$  generation, may be caused by the encroachment in the reservoir of meteoric waters carrying aerobic bacteria, where free oxygen and organics are available, and the underground temperature does not exceed 200° F (90° C) (Collins, 1975).

→ TABLE 1. Principal chemical reactions leading to generation of CO<sub>2</sub> and/or CH<sub>4</sub> - their alleged zonality; water mobility and formation temperatures

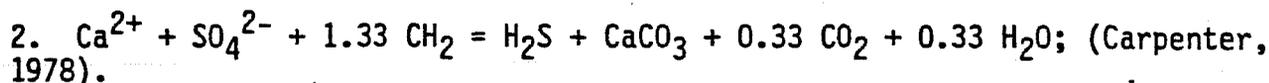
UPPERMOST ZONE - high water mobility - depth: to 700-2,000', locally deeper; temperature below 86° F (30° C).

Inorganic or bacterial oxidation of organic matter:



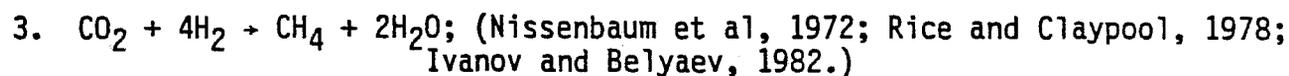
UPPER TRANSITIONAL ZONE - fair water mobility - temperature not crucial; depth: to several thousand feet.

Bacterial sulfate reduction:



LOWER TRANSITIONAL ZONE - poor water mobility (semi-stagnation) temp. 86-167° F (30-75° C) depth: 2,000-9,000 ft.

Reduction of CO<sub>2</sub> introduced from upper zones to the anoxic environment:

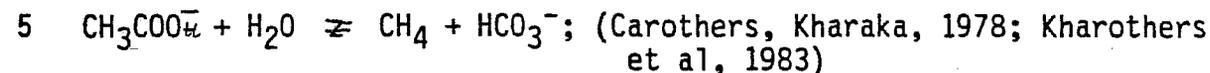


Bacterial reduction of organic acids: bacteria

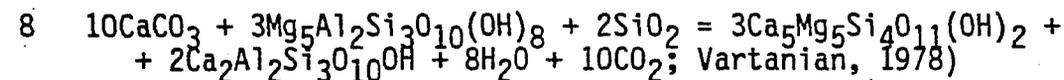
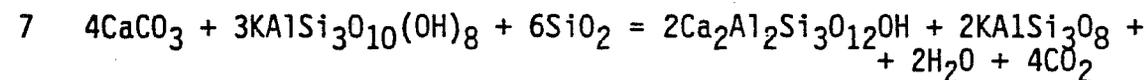
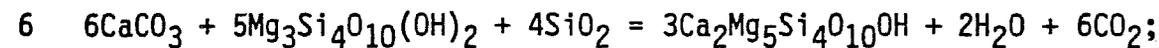


DEEP-SEATED ZONE - stagnation or ascension from depths. Temp. above 176° F (80° C); depth: below 9-10,000 feet.

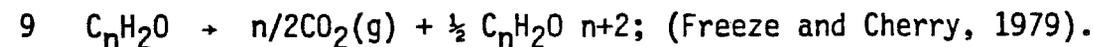
Thermal decarboxylation of aliphatic acid anions:



Thermometamorphism of carbonates:



Coalification of lignite:



This destruction of an oil accumulation results, as Ivanov and Belyaev (1982) stated, in an increase in concentration of soluble organic compounds and carbon dioxide in formation water, which after entering the anaerobic zone stimulate bacterial methanogenesis. When organic matter (crude oil) is abundant near the surface, the oxygen will be easily exhausted, and a reductive environment may occur at relatively shallow depths.

A zone of oxidation within the investigated intermontane basins is believed to be represented primarily by meteoric waters, low in total dissolved solids (TDS below 5-10 g/l) and  $\text{HCO}_3\text{-Na}$ ;  $\text{HCO}_3\text{-(Cl)-Na}$ ;  $\text{HCO}_3\text{-Cl-Na}$ ;  $\text{Cl-HCO}_3\text{-(SO}_4\text{)-Na}$  and  $\text{SO}_4\text{-Cl-(HCO}_3\text{)-Na}$  chemical water types. Their reductivity indices are very high ( $r\text{SO}_4 \times 10^3/r\text{Cl}$  usually much over 200), and these points fall farthest out of the sea water dilution line -  $\text{TDS} = 1.805 \text{ Cl}^-$ . The distribution of bicarbonates with depth ( $\text{HCO}_3^-$  vs depth) can be seen in figures 20-23.

The most characteristic and significant feature of bicarbonate vertical distribution is their rapid increase in the formation waters, below a depth of 1,000-3,000 ft. (300-900 m), reaching a maximum at about 3,000-6,000 ft. (900-1800 m), and then a significant decrease below 7,000 ft. (2100 m). Within the Uinta and Green River basins, the next slight increase, up to 2-3 g/l  $\text{HCO}_3^-$ , can be observed at depths of 9000-10,000 ft. (3000 m), with decreasing tendency in concentration at greater depths. It seems to suggest, that the most effective generation of bicarbonates ( $\text{CO}_2$ ) is related to a depth range of 2,000-7,000 ft. with the optimum range found at 3,000-6,000 ft. Then, an eventual second optimum source occurs at 9,000-12,000 ft.

Log  $\text{HCO}_3^-$  versus log  $\text{Cl}^-$  plots shown in Figures 24-27 reveal a scattered distribution of points with a noticeable tendency toward increasing bicarbonate concentration with decreasing chloride concentration. This tendency is more pronounced in the Uinta Basin than in the other areas studied. These facts strongly suggest that in contrast to chloride concentration the bicarbonates do not follow the dilution line, and that they are generated within the 2,000-7,000 ft zone rather than delivered from the deep-seated formation as the result of thermal decarboxylation of aliphatic acid anions or regional thermometamorphism of carbonates. It also is evident that in zones with small influx of meteoric water into the outcrop, the bicarbonate generation is reduced.

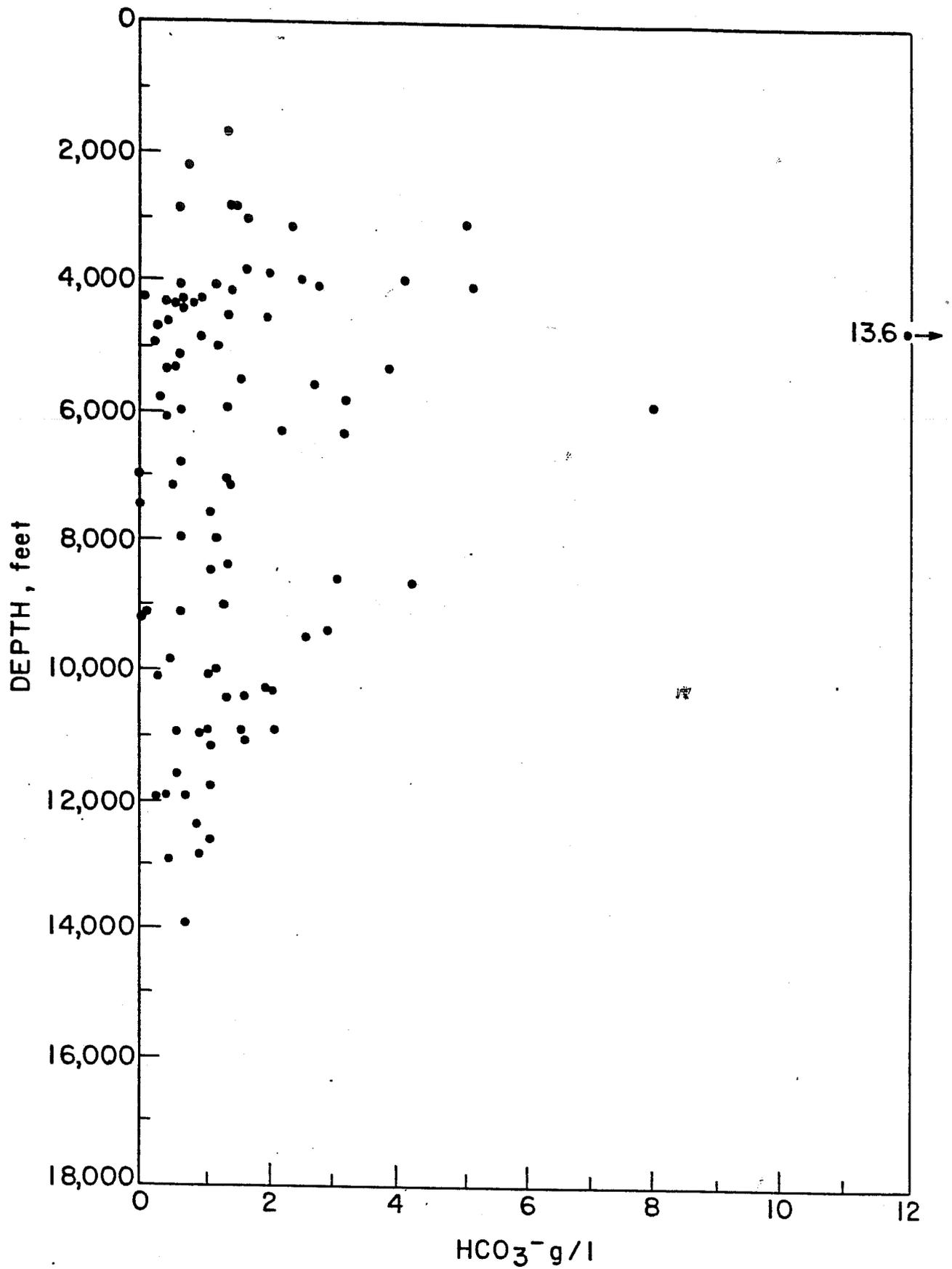


FIGURE 20. - Relationship between bicarbonates and depth in the Uinta Basin.

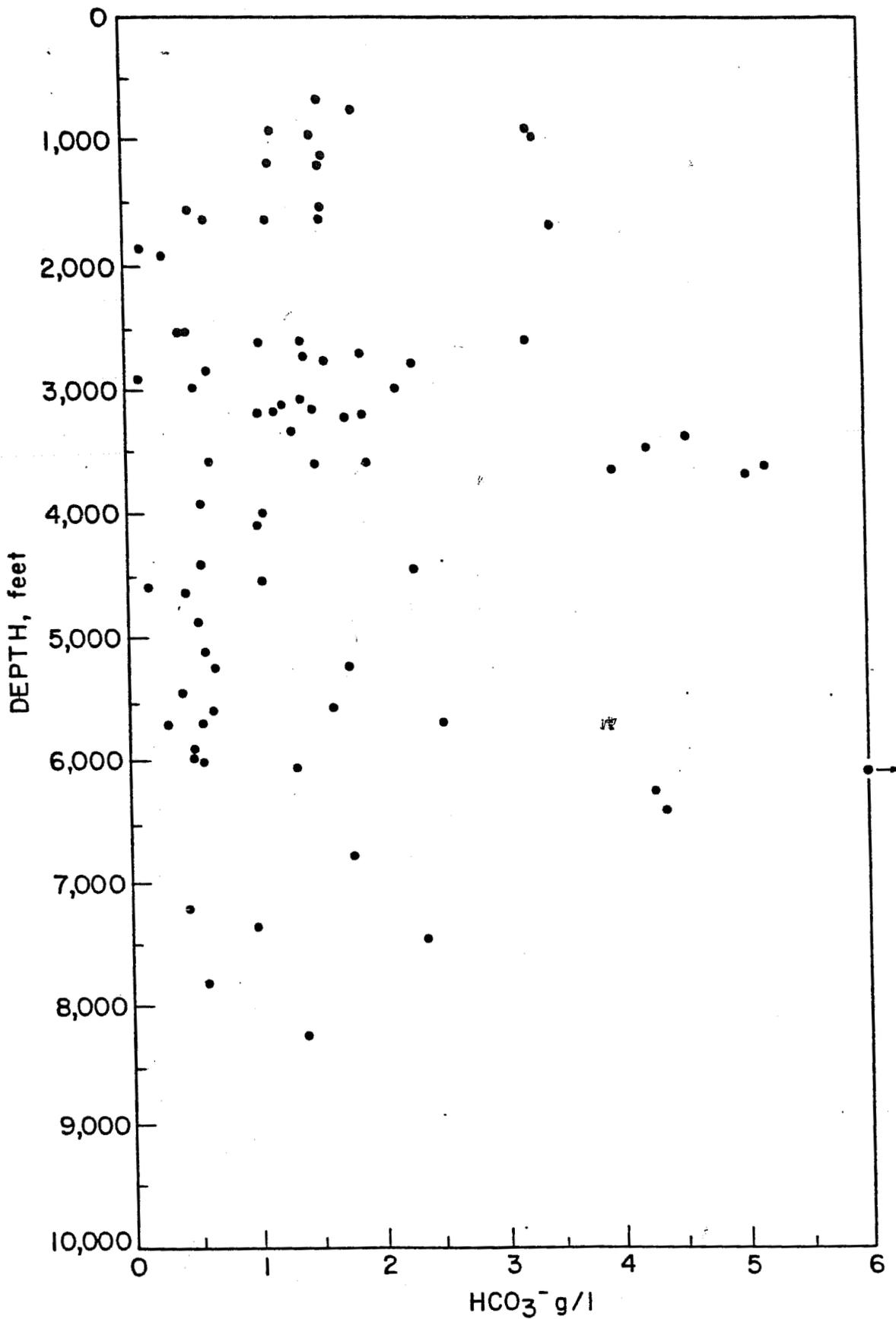


FIGURE 21. - Relationship between bicarbonates and depth in the Northern Piceance Basin.

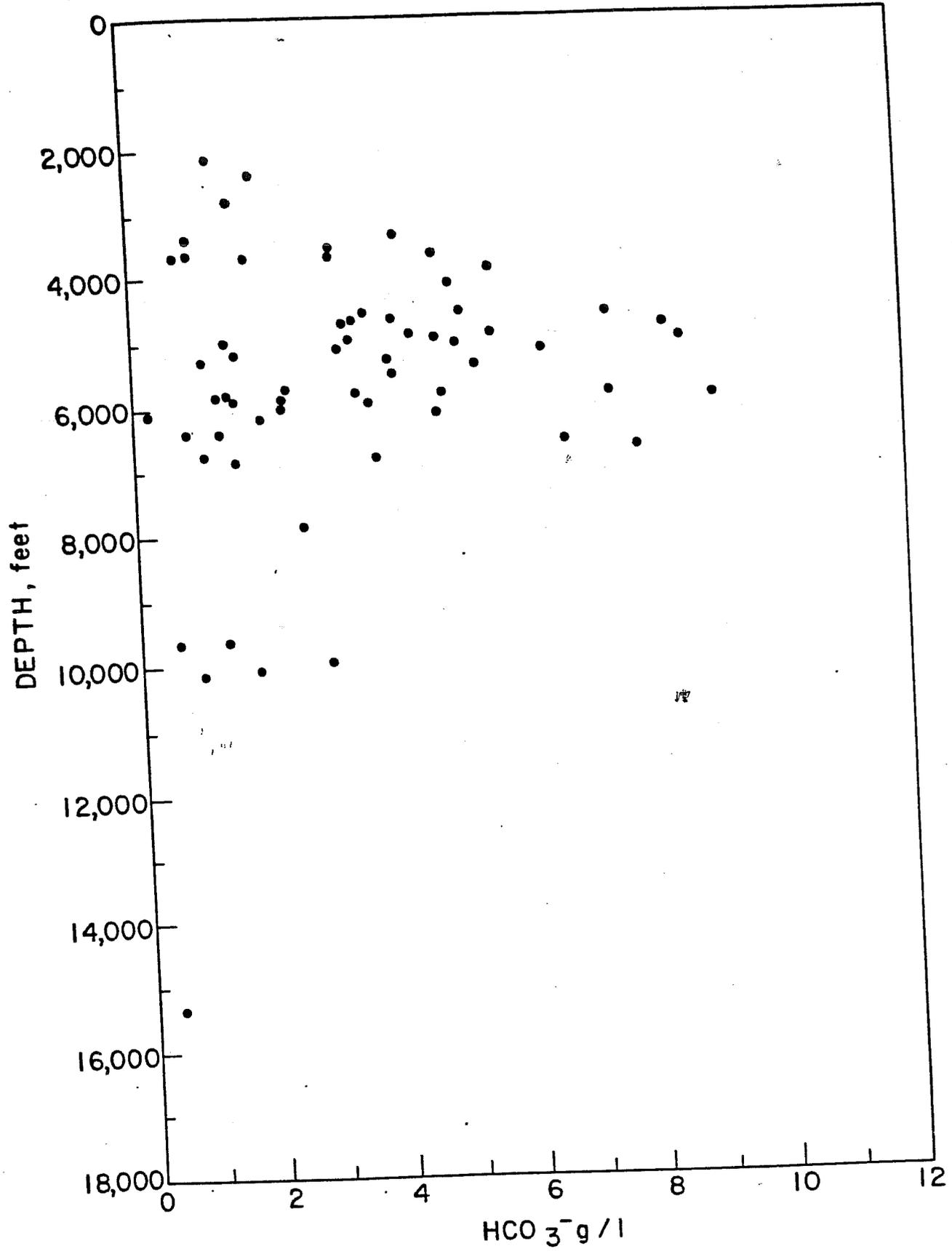


FIGURE 22. - Relationship between bicarbonates and depth in the Greater Green River Basin, east of the Rock Springs Uplift.

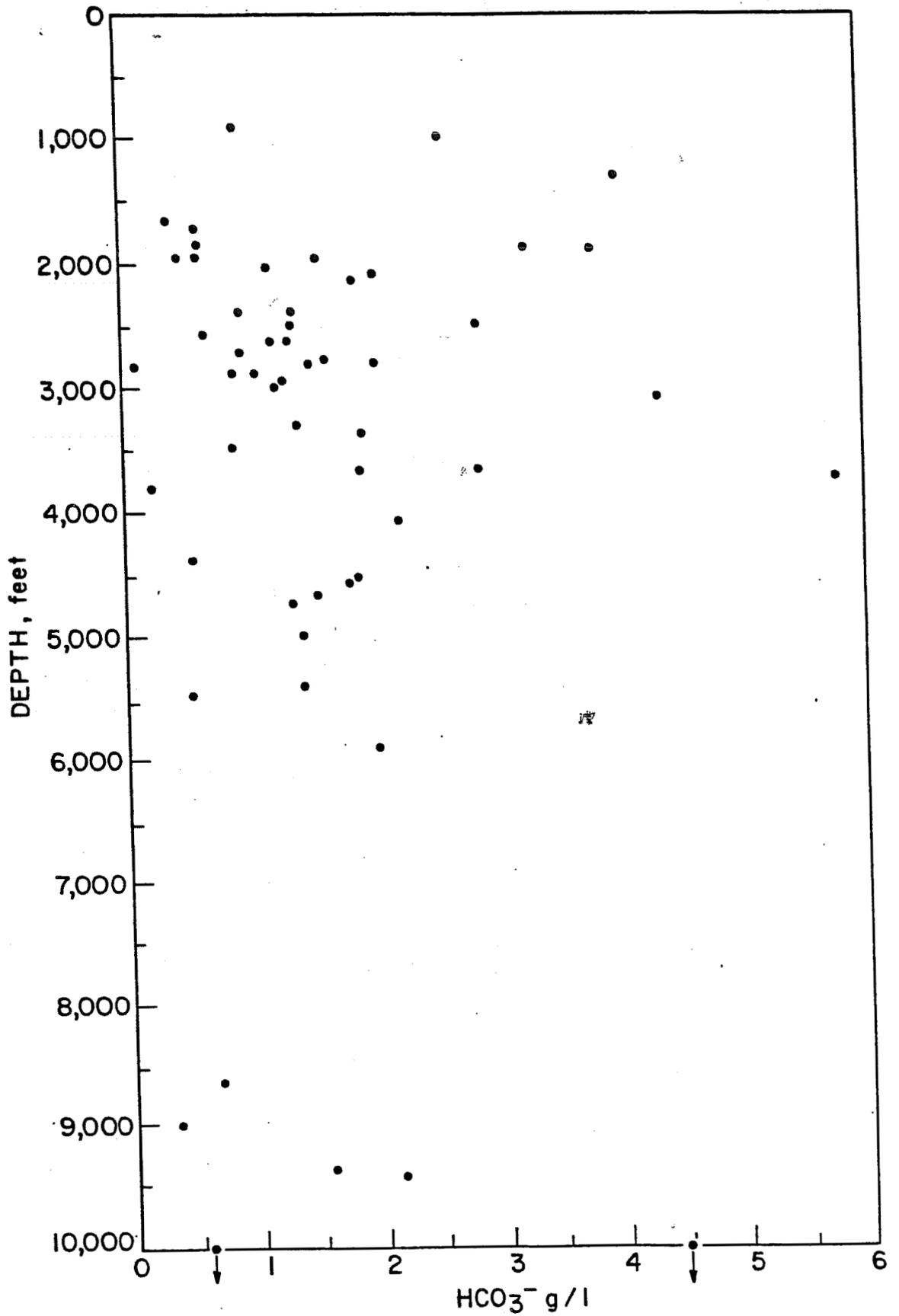


FIGURE 23. - Relationship between bicarbonates and depth in the Greater River Basin; Big Piney - La Barge area.

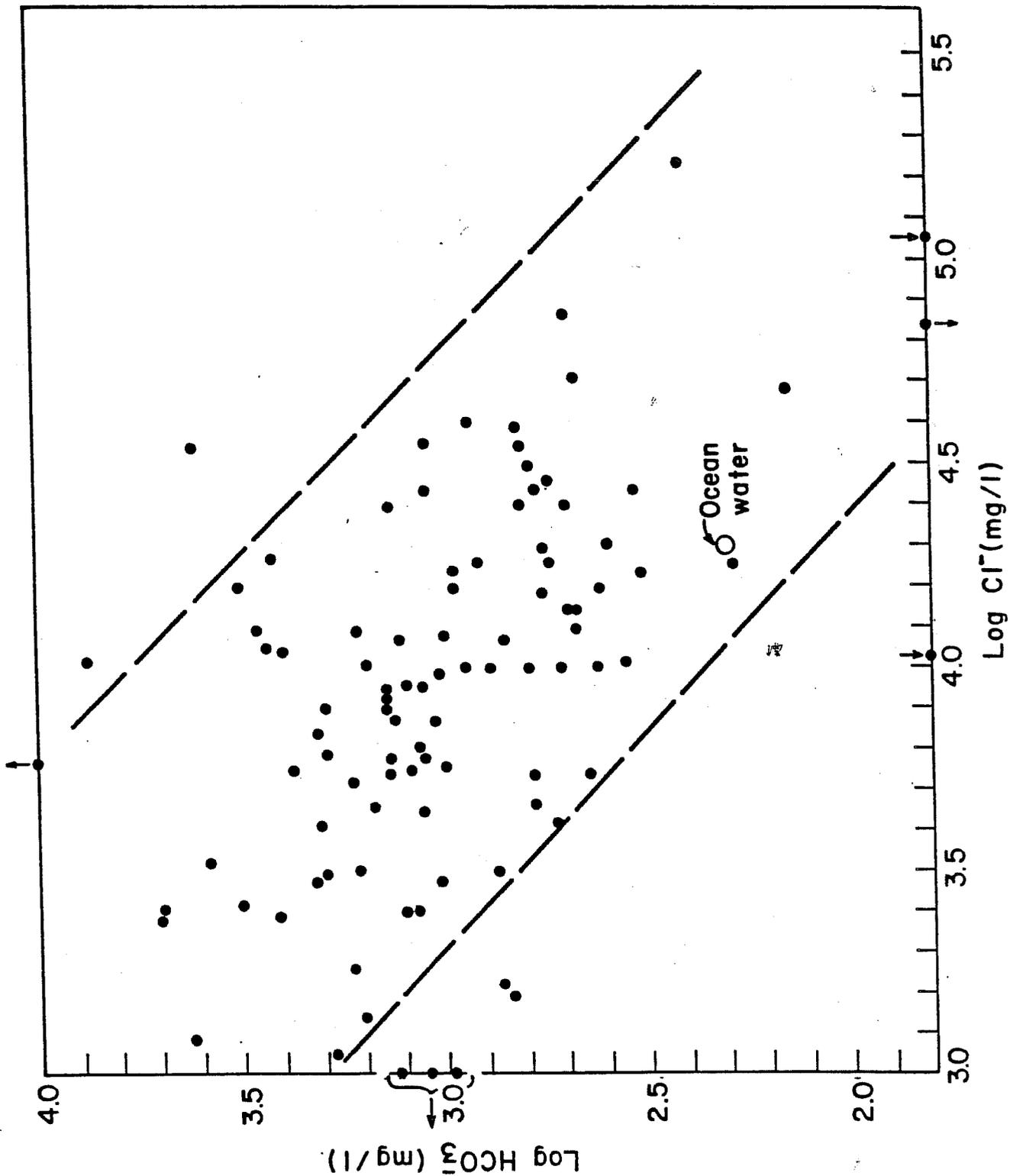


FIGURE 24. - Relationship between bicarbonates and chloride in the Uinta Basin.

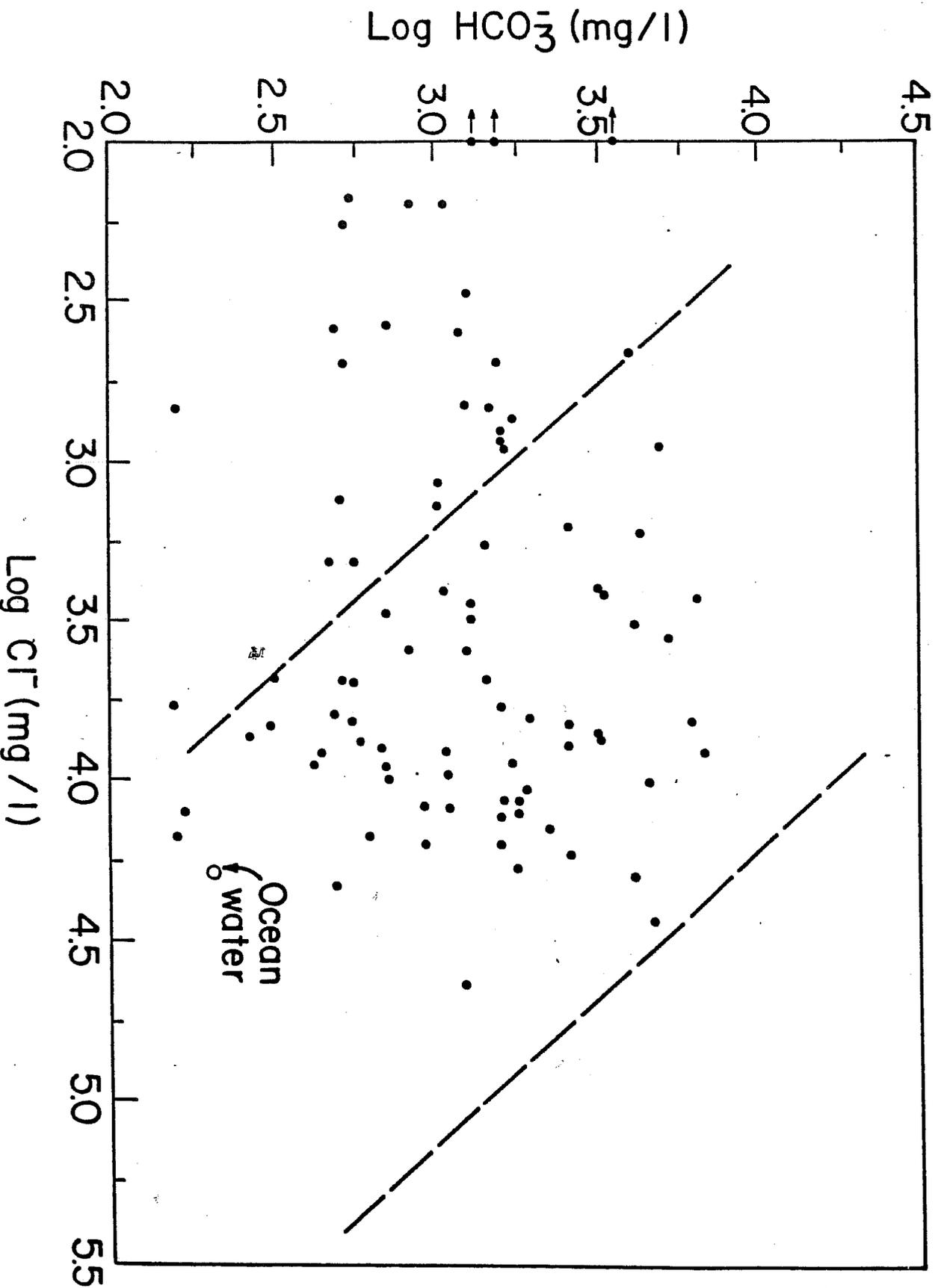


FIGURE 25. - Relationship between bicarbonates and chloride in the Northern Piccance Creek Basin.

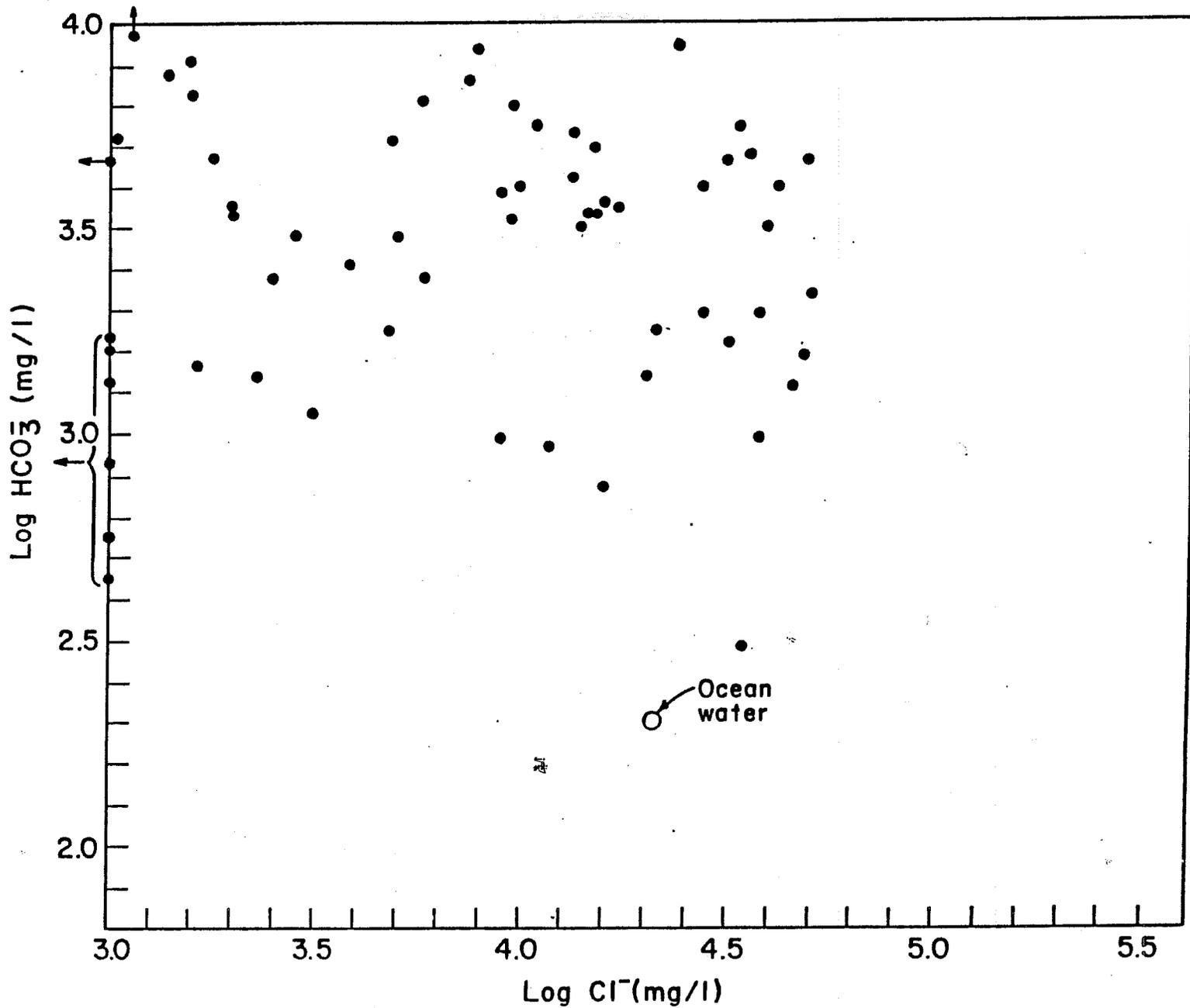


FIGURE 26. - Relationship between bicarbonates and chloride in the Greater Green River Basin, east of the Rock Springs Uplift.

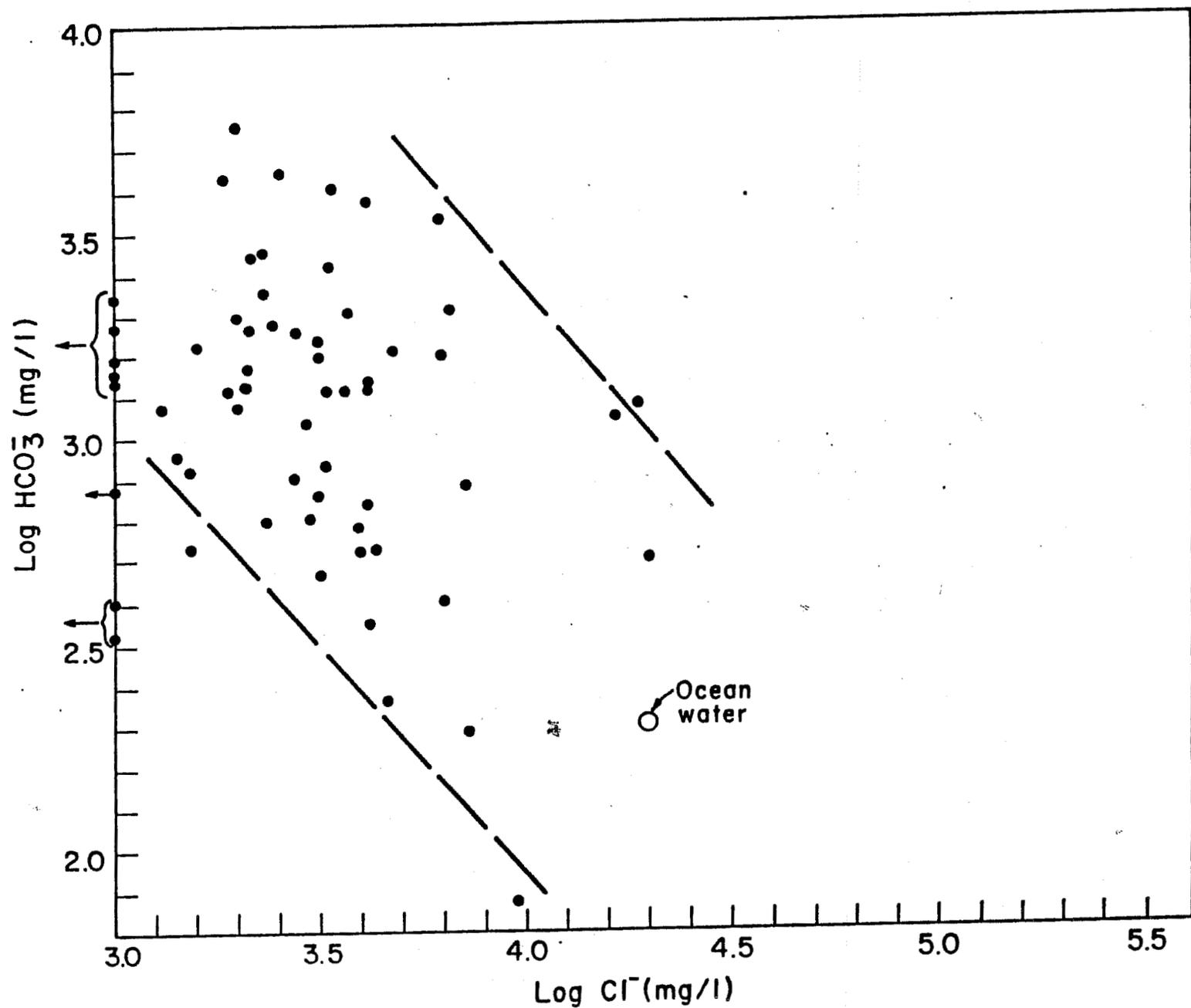


FIGURE 27. - Relationship between bicarbonates and chloride in the Greater Green River Basin: Big Pine - la Barge area.

The next important characteristic feature of bicarbonate-rich formation waters below the depth of 2,000-3,000 ft. is their low sulfate content, and their reductivity indices are usually much below 103, the value for sea water. In most cases  $rSO_4^{2-} \times 10_3 / rCl^-$  indices are lower than 30, and often near zero, which indicates a highly reductive environment. It is exemplified by a distribution of the  $rSO_4^{2-} \times 10_3 / rCl^-$  index with depth within the area east of the Rock Springs Uplift in the Green River Basin (Desert Springs, Table Rock, Patric Draw and Wamsutter oil and gas fields), where 70% of the formation waters at depths between 2,000-10,500 feet (600-3200 m) are characterized by very low reductivity indices (Fig. 28). Some waters may occur at similar depths with very high reductivity values 1000 or higher. Such waters reflect local differences in water mobility along geologic discontinuities. Similar patterns of distributions of reductivity indices have been recognized in other investigated areas.

However, the sulfate rich waters are more widespread in the Uinta Basin, than in the other basins studied. This is shown on Figures 7 and 8. Some waters appear to be oversaturated with respect to gypsum. Figure 29 depicts the sulfate content of the Uinta Basin water plotted versus calcium, with a line dividing the waters oversaturated (on the right) and undersaturated with respect to gypsum. Approximate saturation calculated on the basis of Schoeller's (1955) equation yields arbitrary limit of 70 for  $SO_4^{2-} \times Ca^{2+}$ . All waters rich in  $HCO_3^-$  are extremely sulfate-and-calcium-deficient and concentrate in the very corner of this plot.

Bacterial sulfate reduction, if performed here on the larger scale, should have produced precipitated calcite, released gaseous hydrogen sulfide, and carbon dioxide, according to reaction no. 2 in Table 1. However, 106 out of 108 water analyses from the Uinta, Piceance and Green River Basins, where  $H_2S$  was determined, revealed their absence. This fact contradicts bacterial reduction of sulfate as a major process responsible for the high enrichment of bicarbonates in these formation waters. A similar situation was reported by Szpakiewicz (1980) in the geologically comparable eastern part of Polish Carpathians. Also plots of  $HCO_3^-$  versus  $SO_4^{2-}$ , Figure 30-33 reveal poor relationships between these major anions and support the last suggestion. This process, however, seems to contribute to the enrichment in bicarbonates, particularly within the Uinta Basin (Fig. 30).

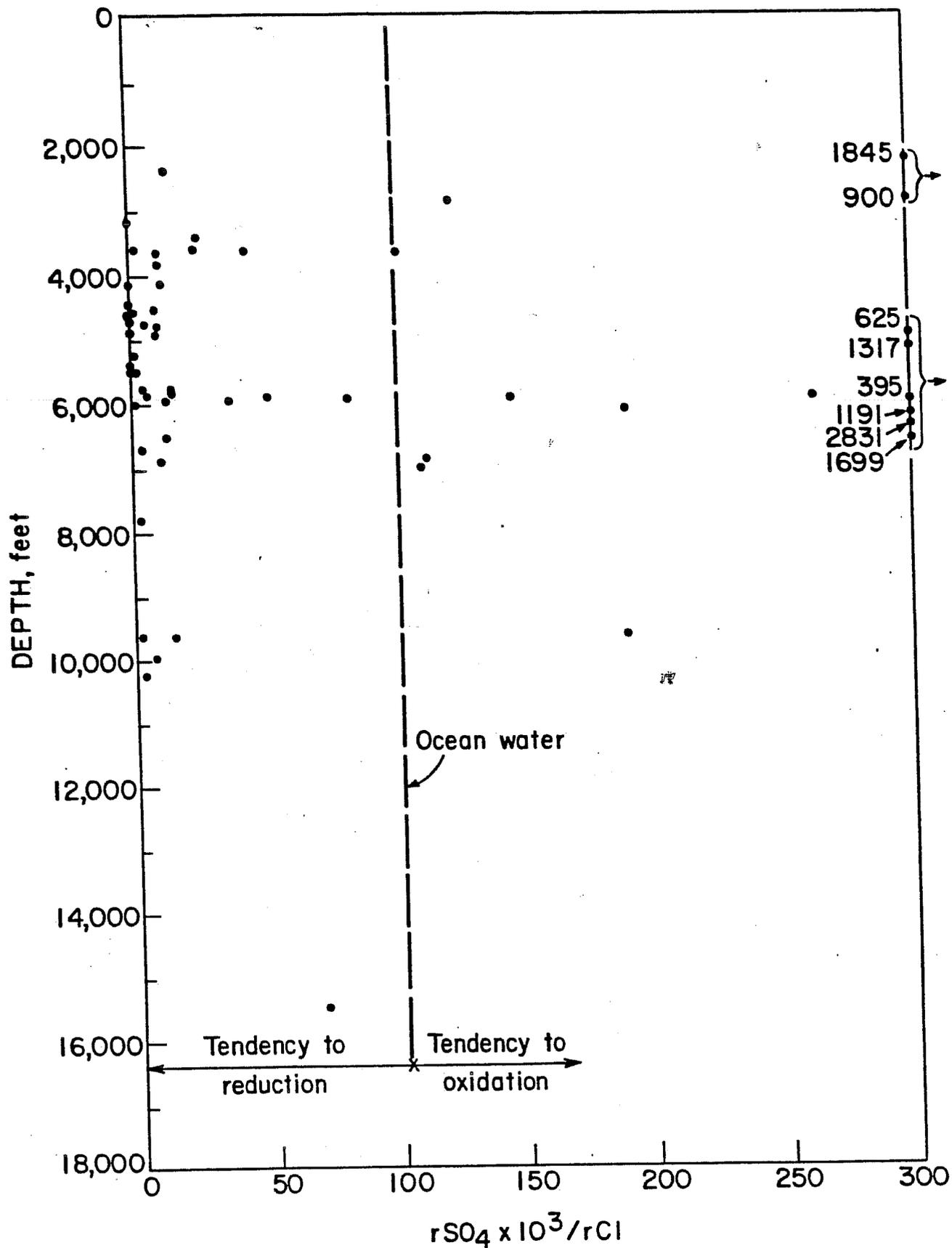


FIGURE 28. - Distribution of reductivity indices with depth in the Greater Green River Basin - east of the Rock Springs Uplift.

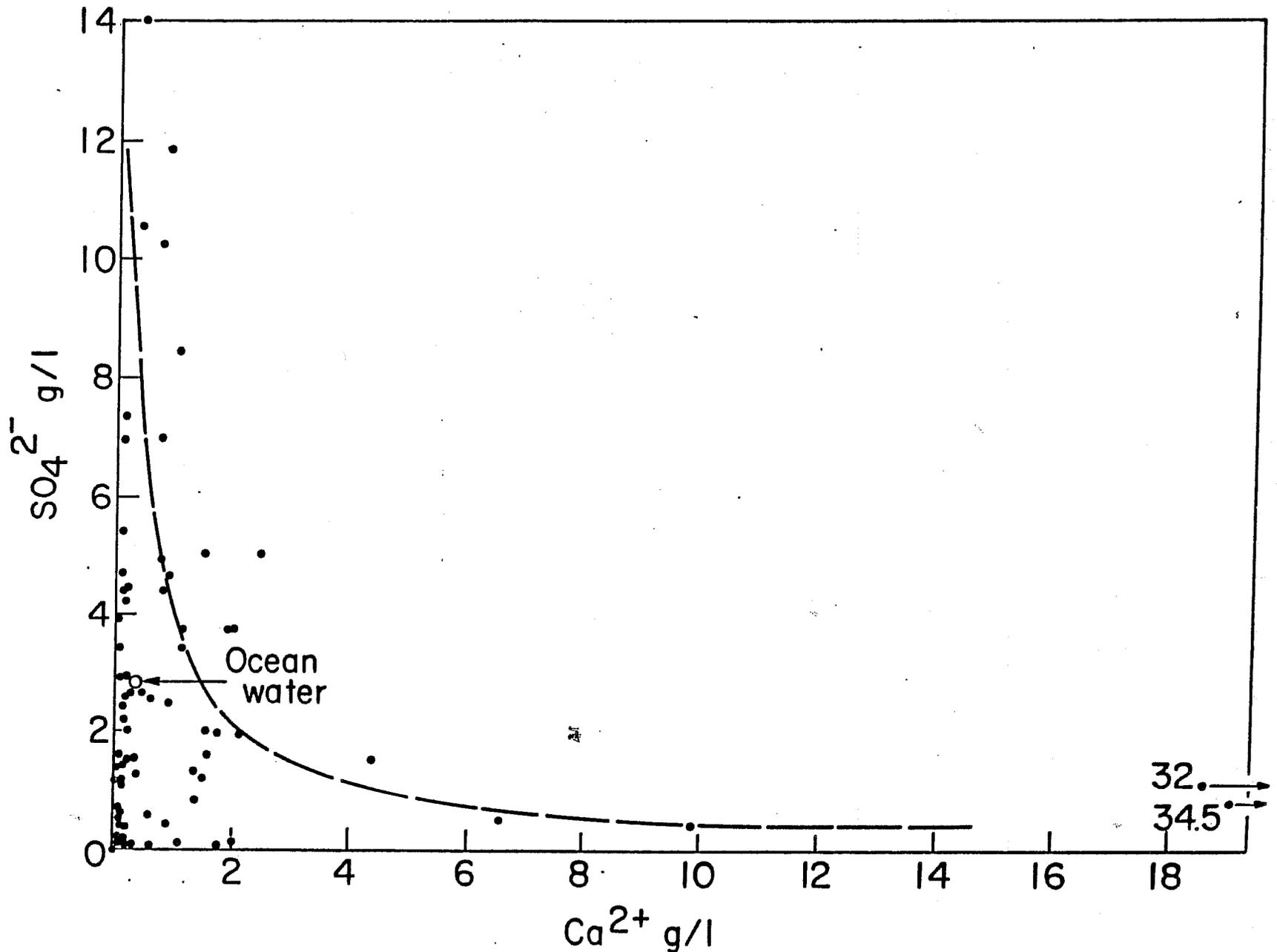


FIGURE 29. - Relationship between sulfate ion and calcium ion in the Uinta Basin. Dashed line indicates saturation of the formation waters with respect to  $\text{CaSO}_4$ . (Points situated on the left indicated undersaturation and on the right oversaturation with respect to gypsum.)

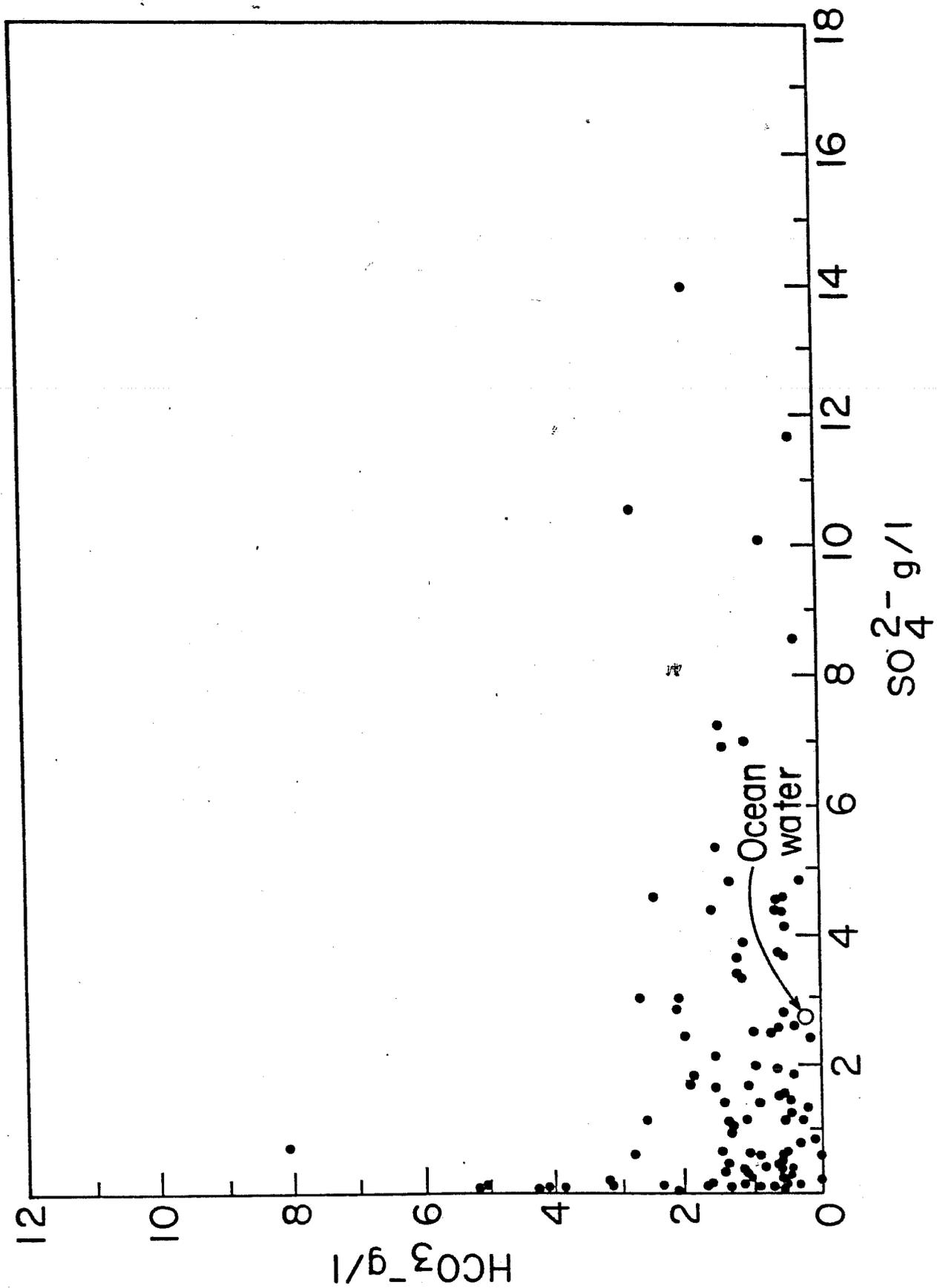


FIGURE 30. - Relationship between bicarbonates and sulfates in the Uinta Basin.

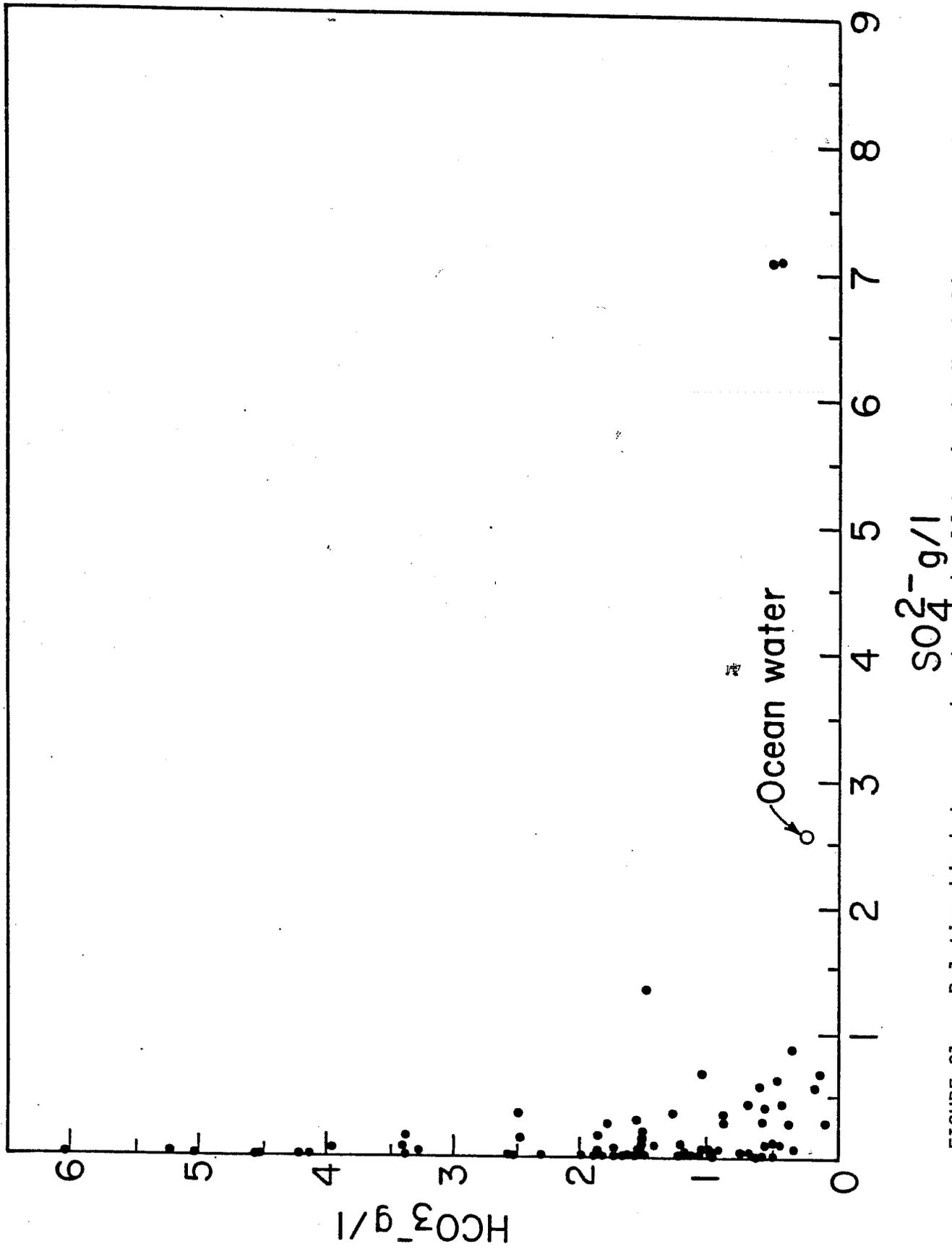
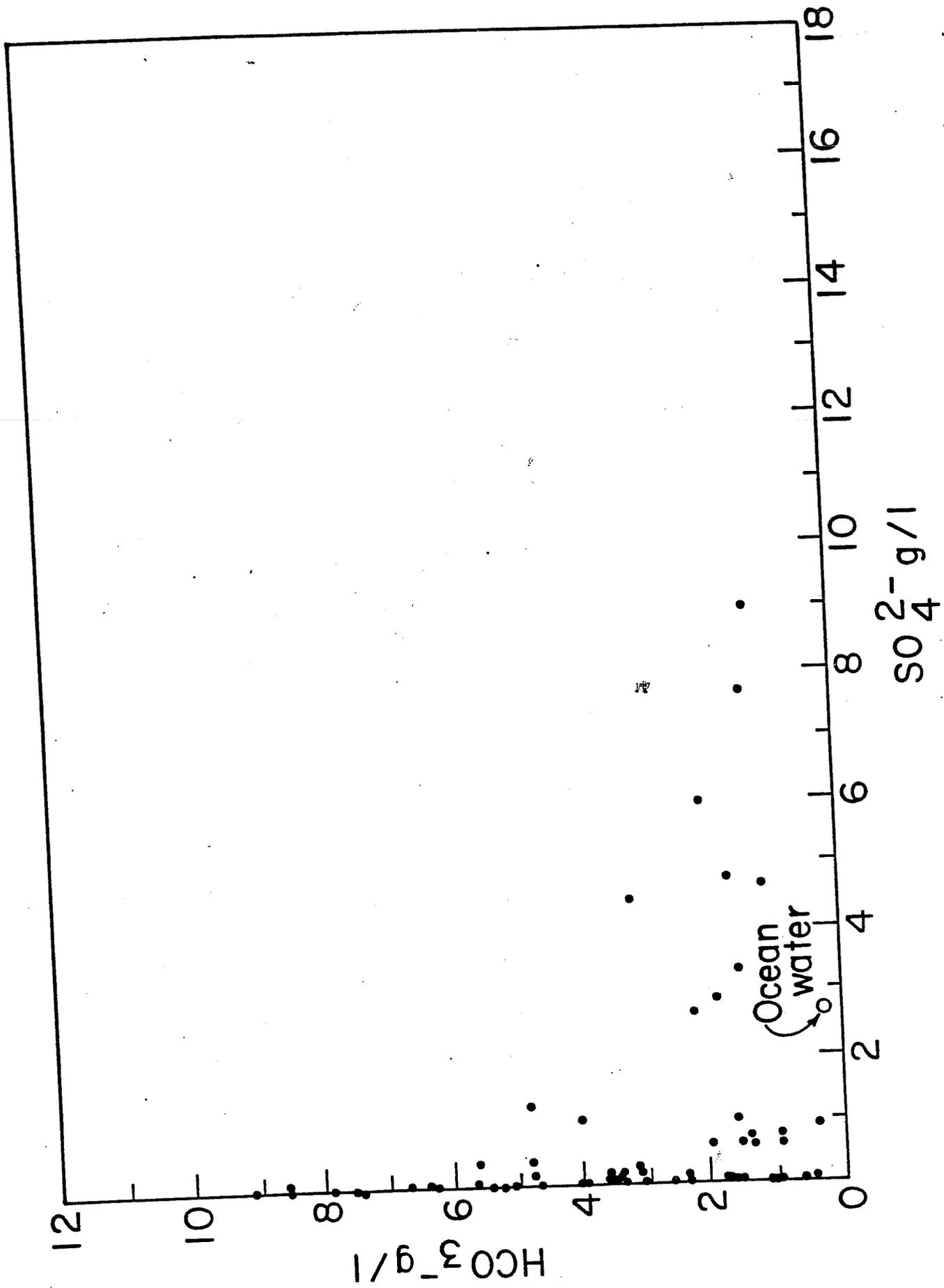


FIGURE 31. - Relationship between carbonates and sulfates in the North Piceance Creek Basin.



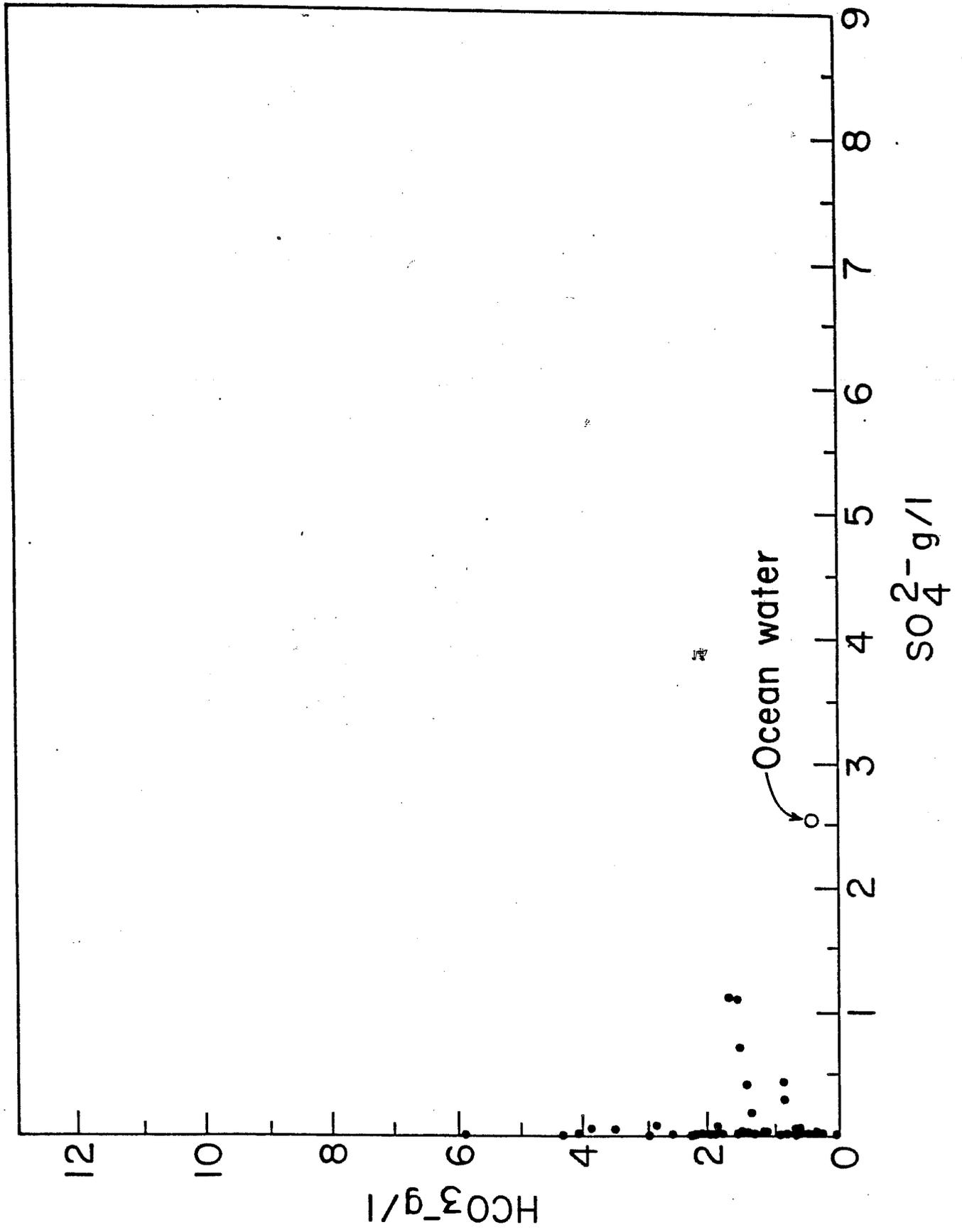


FIGURE 33. - Relationship between bicarbonates and sulfates in the Greater Green River Basin - Big Piney - La Barge area.

The highest enrichment in bicarbonates is observed: within a depth range of formation water temperatures between 86-167° F (30-75° C); where water mineralization does not exceed 90 g/l (usually 5-35 g/l); isolation is poor to fair and the IBE indices are negative, and the  $rNa/rCl$  is above 0.86; the environment is reductive ( $rSO_4 \times 10^3/rCl = 0$  to 30), and toxic  $H_2S$  is not reported present. These features are considered to be the perfect habitat for an anaerobic, methanogenic bacteria, provided that metabolizable organic matter also is available (Rice and Claypool, 1981). All of these conditions seem to be present within the investigated basins. Therefore, the most plausible and effective process responsible for bicarbonate generation within the described Rocky Mountains sedimentary basins down to about 8,000-9,000 ft (2400-2700 m), appears to be the bacterial reduction of organic acids see Table 1, reaction 4. Acetate degradation probably was particularly intensive near the formation water-crude oil contacts.

Part of the  $CO_2$  produced by degradation of organic matter was added to the anoxic environment. Inorganic or bacterial oxidation of organic matter in the uppermost zone, where invasion of meteoric waters is particularly intensive, Table 1, reaction 1, could have been reduced by reaction with molecular or organically available hydrogen yielding methane and water, (Table 1, reaction 3). There are only 13 determinations of organic acids as acetic acid available for the Uinta Basin formation waters. Concentrations as high as 200 mg/l as acetic acid are reported.

The final products of the methanogenic bacterial activity in the reductive zone within the organic rich sediments are biogenic methane, carbon dioxide, and bicarbonates. Thus, the carbonated or acidulous waters of mixed origin, and of  $Cl-HCO_3-Na$  and  $Cl-(HCO_3)-Na$  chemical type, may serve as a positive indicator of biogenic gas generation and crude oil accumulations, if the other favorable environmental requirements described above also are fulfilled. Contribution of bicarbonates, originated from bacterial reduction of sulphates, and/or bicarbonates with mature methane, generated during the thermal cracking of hydrocarbons at greater depths (Table 1, reactions 2 and 5 respectively) cannot be excluded, particularly in the Uinta Basin and southern

part of Green River Basin. Definite genetical recognition could be obtained by an appropriate investigation of  $^{13}\text{C}/^{12}\text{C}$  proportions in the  $\text{HCO}_3^-$ ,  $\text{CO}_2$  and  $\text{CH}_4$ . Within better isolated, stagnant zones, where formation waters are deficient in bicarbonates, a crude oil accumulation could survive in relatively unaltered form.

At depths below 9,000-10,000, feet diluted, bicarbonate-rich waters are reported again within the Uinta and Green River basins as shown in Figures 20 and 22. The bacterial activity should be restrained there by high formation temperatures, above  $212^\circ\text{F}$  ( $100^\circ\text{C}$ ). B. Law, 1984 reports results of  $\delta^{13}\text{C}$  analysis of methane from 10 samples obtained at depth range 9,000-13,500 feet in the Green River Basin.  $\delta^{13}\text{C}$  values range there from about -34 to -42‰, what indicates non-biogenic origin of methane (Table 2). Relatively low water mineralization observed locally at these depths, and a high water alkalinity (as reported by the  $\text{HCO}_3^-$  content) may be related to at least two major temperature dependent processes:

- 1) thermal decarboxylation of organic acids (Table 1, reaction 5).
- 2) low grade regional thermometamorphism of carbonate rocks (Table 1, reactions 6-8).

Carothers and Kharaka (1978) and Kharaka et.al. (1983) reported up to 4,900 mg/l of aliphatic acid anions, which contributed up to 90% of alkalinity in oil field waters from California and Texas in the temperature range of  $176-284^\circ\text{F}$  ( $80-140^\circ\text{C}$ ). Their content decrease significantly above  $140^\circ\text{C}$ , probably because of thermal cracking. These authors recommend titration of water samples to an inflection point of pH 3.5 rather than 4.5, to distinguish "bicarbonate" and "acetate" alkalinity.

The second potential temperature dependent source of demineralized, bicarbonate rich waters within deep-seated sections of sedimentary basins is regional thermometamorphism of carbonate rocks (Polanski and Smulikowski, 1969); (J. Barnes and O'Neil, 1976); (Vartanian, 1978), and (Dowgiallo, 1976). This process is believed to be restricted exclusively to young,

mountain-fold regions. Appropriate reactions are listed in Table 1, nos. 6-8. Lesniak (1980) estimated the approximate quantity of fluids produced by reaction 7 in Table 1. From a rock volume of  $1000 \text{ km}^3$ , 18 percent of  $\text{CO}_2 + \text{H}_2\text{O}$  will be released, which is equivalent to 165 and 15 cubic kilometers of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively.

This process could significantly contribute to dilution and alteration of deep-seated fluids in the Rocky Mountains area, but a source of carbonate rocks should be sought below the Upper Cretaceous formations. It would imply also the ascension of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  through the thick sequence of Mancos shales, which is more doubtful. Law et.al. (1983) relate the observed dilution of deep formation waters within the Upper Cretaceous and Lower Tertiary formations of the Green River Basin to the dewatering of coal-bearing rocks and other carbonaceous lithologies. The coalification process of lignite in an anaerobic environment leads to  $\text{CO}_2$  and  $\text{CH}_4$  generation according to reaction 9, Table 1.

Coal layers are relatively common within the non-marine formations of the Upper Cretaceous Mesaverde Group (mostly Rock Springs Formation) and the Lower Tertiary, Fort Union Formation of Green River Basin, as well as the Mesaverde Formation of Piceance and Uinta basins, (Law et.al., 1983; Fouch et.al., 1982). Their proportions, however, are very low in comparison with the bulk of the non-organic rocks, and it seems unlikely that they could strongly affect the structural units, as far as regional water dilution and natural gas generation is considered. Thus, the occurrence of highly diluted and bicarbonate enriched formation waters, at depth of 9,000-14,000 ft or more, might be related to at least three processes, two of which may also contribute to the generation of methane. Additional chemical and isotopic research would be necessary, however, to distinguish them and make quantitative estimates.

## PROPOSED APPLICATION OF HYDROGEOCHEMISTRY TO HYDROCARBON EXPLORATION AND DEVELOPMENT

The uppermost zones and the permeable rock outcropping sections of the basins down to at least 2,000 ft.+, where an intensive recent infiltration of meteoric waters accompanied by water flushing and oxidizing occur, seems to be very unfavorable for oil and gas survival. Ascending natural gas can escape to the atmosphere, unless there are appropriate traps. Any crude oil entering this shallow zone, would become highly degraded or destroyed.

Formation waters in this highly dynamic zone are very low in total dissolved solids and chloride (TDS usually below 10 g/l), but rich in bicarbonates and/or sulfates. Their metamorphism indices are high ( $rNa/rCl > 1.6$ ), and they are represented by the formation water formulas:  $HCO_3-Ca$ ;  $HCO_3-Na$ ;  $HCO_3-(Cl)-Na$ ;  $HCO_3-Cl-Na$ ;  $HCO_3-SO_4-Na$ ;  $HCO_3-Cl-SO_4-Na$ ;  $SO_4-HCO_3-(Cl)-Na$ ;  $SO_4-Cl-(HCO_3)-Na$ ;  $SO_4-HCO_3-Na$  and  $SO_4-Cl-Na$ .

The saline facies: gypsum, halite, nahcolite, trona, dawsonite, etc., leached by the infiltrating waters, can locally change the formation water chemical characteristic, but their oxidizing potential is still high and these waters would be poor in the biophile components or their products such as  $I^-$ ,  $Br^-$ ,  $NH_4^+$ , and organic acid salts. Saline facies occur within the Green River Formation in the Piceance basin (Johnson and Keighin, 1981), however, only within the uppermost part of the profile and of limited spatial extent. The eventual attempt at enhanced recovery of the heavier, mostly asphaltic crudes or oil shales from this zone does not appear feasible or profitable except perhaps by steam. Mining methods may be effective.

Within the deeper, upper transitional, still poorly isolated zone, represented by the  $HCO_3-Cl-Na$ ;  $HCO_3-Cl-(SO_4)-Na$ ;  $Cl-HCO_3-SO_4-Na$  and  $Cl-HCO_3-Na$  waters, where an atmospheric water component predominates, oxidizing and water flushing processes are still active, but their intensity decreases, as the oxygen gradually is exhausted and ground water mobility slowed down. The aerobic bacteria thrive at 140° F (60° C) and can survive at temperatures as high as 194°F (90°C) (Davis, 1967). Within the Rocky Mountain geothermal gradient ranges (AAPG-USGS Map, 1976) this process might have affected zones at depths of 4,000-5,700 ft (1200-1740 m) and 6,700-9,600 ft (2040-2920 m) respectively, if oxygen were available at these depths.\* This is probably a very rare case.

The oil alteration within the upper transitional zone should be high, and chances for biogenic gas generation are poor. This zone occurs within the basins under consideration at depth 1,000-5,000 ft (300-1500 m). The high bicarbonate concentration in formation waters within this zone may be a positive indicator of the presence of altered oil, because bicarbonate originates here primarily from bacterial or inorganic oxidation of organic matter. The non-organic related formation waters within this zone, should be sulfate rich, chloride-sodium type, if an endogenous CO<sub>2</sub> ascension is excluded.

The lower transitional, fairly isolated zone, at depths of about 2,000-7,000 ft (600-2100 m); is primarily represented by the HCO<sub>3</sub>-Cl-Na; Cl-HCO<sub>3</sub>-Na; Cl-(HCO<sub>3</sub>)-Na or Cl-(HCO<sub>3</sub>)-Na-(Ca) chemical types of formation waters. In most cases the TDS varies between 5-30 g/l, water metamorphism indices are high ( $rNa/rCl = 0.85$  to  $1.6$ ), IBE indices are negative and the environmental conditions are highly or extremely reductive ( $rSO_4 \times 10^3/rCl = 0$  to  $30$ ). Within this anoxic, low temperature zone, ideal for anaerobic bacterial activity, provided that organic material is abundant, very effective methanogenesis may occur, primarily at the edges of oil accumulations (bacterial corrosive effect), followed by bacterial oil degradation.

The presence of NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup> and CO<sub>2</sub>, the CO<sub>2</sub> primarily from oil oxidation within the upper zone, may highly promote methanogenesis (Ivanow and Belyaev, 1982). Methanogenic bacteria metabolize organics most effectively at temperatures of 104-150° F (40-65° C) (Games et.al. 1978). Vogel et.al. 1982 and other researchers concluded that biogenic methanogenesis usually is associated with temperatures below 176° F (80° C).

At the geothermal gradient of 1.4°F/100 ft to 2.0°F/100 ft (AAPG-USGS, 1976) bacterial methanogenesis might operate in the considered basins to a maximum depth of 5,500'-8,000' (1700-2400 m) respectively. Reduction of sulfates should be completed at an earlier stage of diagenesis, following with some pore plugging with CaCO<sub>3</sub> and H<sub>2</sub>S generation. Hydrogen sulfide, however, is considered to be highly toxic to methanogenic bacteria, and high accumulations would strongly inhibit methanogenesis. As previously stated most

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\* In the Greater Green River Basin, B. Law and C. Smith (1983) show temperature of 180° F (82° C) at depth range of 9,000-12,000 feet. (2740-3660 m).

of these investigated waters contained no  $H_2S$ . It is possible that hydrogen sulfide either escaped to the atmosphere, or was transformed into ferrous sulfide.

Tightly isolated, stagnant sections of the basins, located below the lower transitional zone, often interfingering or even overlapping, often are filled with highly mineralized formation waters of: Cl-Na; Cl-( $HCO_3$ )-Na; Cl-Na-(Ca); Cl-Na-Ca; Cl-Ca-(Mg)-Na or Cl- $SO_4$ -Na type. The latter type may originate from dissolution of dispersed gypsum, for example in the Uinta Basin. The isolation and sometimes high TDS and formation temperature or even lack of space (if highly compacted shales), prevent most bacterial activity. Formation waters within this zone are recognizable also by the metamorphism indices below 0.85 (often below 0.6), positive IBE indices, and reductivity indices usually below 100. Waters with such characteristics provide excellent protection for oil accumulations against water washing and bacterial degradations by aerobic or anaerobic bacteria. High iodide, bromide, ammonia and acetic acid concentrations are positive indicators of oil in the area, since these compounds are derived, from organic matter.

All of the described low temperature zones located above the "oil window" zone, may occur at different depths because of local hydrodynamics, tectonics and/or rock porosity/permeability changes. Chemistry of formation waters reflects the characteristic chemical and/or biological processes locally at work, and aids in finding hydrocarbon prospects in an area. Hydrochemical identification of these zones aids in predicting the degree and extent of oil alteration thus permitting a better choice of the most effective method of its extraction.

At depths below 8,000-10,000 ft (2400-3000 m), where present temperatures or paleotemperatures are or were higher than 194-212° F (80-100° C) bacterial activity should significantly decrease. However it should be noted that desulfobrio thermophilus bacteria were isolated from western Siberian oils by Rozanova and Nazina at depth of 10,170-10,820 ft (3100-3300 m) and at formation temperatures of 183° F (84° C) (R. Marquis, 1982, p. 4).

The high alkalinity of some diluted formation waters (reported as  $HCO_3^-$ ) from depths of 9,000-14,000 ft, within Pinedale, Pacific Creek and Wamsutter Units of the Green River Basin, could be partially related to the presence of aliphatic acid anions. Thermal decarboxylation of these acid anions by

increasing temperature could release bicarbonates and mature methane. ~~Garothers~~ Garothers and Kharaka (1980) stated that, at a temperature of 100° C half the concentration of acetic acid in a solution will be decarboxylated to CH<sub>4</sub> and CO<sub>2</sub> in only 13 years. Thus the concentration of acetic acid in a solution that originally contained 10,000 mg/l will be only 10 mg/l after about 130 years. If simultaneously the abnormal pressure gradients are recorded (Spencer, 1983), which are related in the Pacific Creek area (Law et.al. 1980), to the active thermal generation of gas associated with low permeability reservoirs, then low water salinity must not be correlated with descending meteoric waters, but rather with deep-seated processes releasing fresh water and gases, as described in a previous section.

Table 2 illustrates indicators associated with formation waters that are useful in distinguishing favorable environmental conditions for the origin, alteration, and survival of petroleum. A wide range of hydrochemical and geological data should be collected in any attempt to select a potential petroleum target and/or determine its probable degree of alteration. Parameters interpreted separately can yield inconclusive and confusing results. For example, correct interpretation of the source of HCO<sub>3</sub><sup>-3</sup> is necessary before one can say it is related to a diluted water component or mature methane.

The indicators in Table 2 must be carefully considered with respect to distribution and interrelationships among the major and minor ions in particular: TDS, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> versus depth; SO<sub>4</sub><sup>2-</sup> versus TDS and Ca<sup>2+</sup>; HCO<sub>3</sub><sup>-</sup> vs. SO<sub>4</sub><sup>2-</sup>; log HCO<sub>3</sub><sup>-</sup> vs log Cl<sup>-</sup>; log Na<sup>+</sup> vs log Cl<sub>-</sub>; Cl<sub>-</sub> vs TDS; log Cl<sub>-</sub> vs log Br<sup>-</sup> and log MCl<sub>2</sub>\* vs log Br<sup>-</sup>. All of these tabulated indicators and plots can be computed and synthesized to draw the final maps of potential prospects.

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\* Chlorides of divalent cations counted as: Ca+Mg+Sr-SO<sub>4</sub>-HCO<sub>3</sub> meq/l (Carpenter 1978).

TABLE 2. Favorable indicators in formation waters of biogenic gas generation and oil alteration (A): and preservation of oil in unaltered form (B) - down TO 10,000 feet

FACTOR	QUALITATIVE OR QUANTITATIVE INDICATOR	
	<u>Biogenic Gas Generation and Crude Oil Alteration (A)</u>	<u>Preservation or Crude Oil in Unaltered Form (B)</u>
Total Dissolved Solids (TDS in g/l)	3-90 preferably 5-30	10 + no upper limitation
Chemical water type	Cl-HCO <sub>3</sub> -Na; Cl-(HCO <sub>3</sub> )-Na; HCO <sub>3</sub> -Cl-Na; Cl-HCO <sub>3</sub> -Na-(Ca)	Cl-Na; Cl-(HCO <sub>3</sub> )-Na; Cl-Na-Ca; Cl-Ca-Na; Cl-(SO <sub>4</sub> )-Na
Depth	2,000-9,000' (600-2750 m) preferably 3,000-7,000' (900-2100 m)	3,000-10,000' (900-3000 m) preferably 6,000-10,000' (1800-3000 m)
Temperature	86-176° F (30-80° C) methanogens thriving at 150° F (65° C)	86-284° F (30-140° C)
Origin of water	mixed waters with significant contribution of meteoric component (recent or paleo-infiltrated)	altered marine or polygenetic waters
Age of water	exceptionally less than 30,000 years (tritium and radiocarbon dead)	ancient waters-millions years old. (4He method)

TABLE 2. Favorable indicators in formation waters of biogenic gas generation and oil alteration (A): and preservation of oil in unaltered form (B) - down TO 10,000 feet (cont'd)

FACTOR	QUALITATIVE OR QUANTITATIVE INDICATOR	
	<u>Biogenic Gas Generation and Crude Oil Alteration (A)</u>	<u>Preservation or Crude Oil in Unaltered Form (B)</u>
Hydrodynamics	transitional (fairly mobile) zone within intermediate flow system	isolated (stagnant) zone
Methanogenic bacteria	Abundant and vital	not numerous
Sulfate reducing bacteria	present	not numerous
Bicarbonates (in % meq)	over 10 preferably 20-50	below 10 preferably below 5
Sulfates (in % meq)	below 5 preferably absent	variable preferably low
Reductivity index ( $rSO_4 \times 10^3 / rCl$ )	0-10	below 100
Sulfides ( $H_2S + HS^-$ in mg/l)	very low preferably NIL or traces	low
Biophile elements ( $I^-$ , $Br^-$ in mg/l)	enriched relative to sea water	highly enriched relative to sea water (iodide more than 100 times)

TABLE 2. Favorable indicators in formation waters of biogenic gas generation and oil alteration (A): and preservation of oil in unaltered form (B) - down TO 10,000 feet (cont'd)

FACTOR	QUALITATIVE OR QUANTITATIVE INDICATOR	
	<u>Biogenic Gas Generation and Crude Oil Alteration (A)</u>	<u>Preservation or Crude Oil in Unaltered Form (B)</u>
Ammonium (NH <sub>4</sub> <sup>+</sup> in mg/l)	abundant	abundant
Organic acids (as acetic acid)	present (below 100 mg/l)	abundant increasing above 176° F (80° C)
Index of Base Exchange (IBE)	negative	positive (above 0.129).
Metamorphisation <sup>m</sup> (rNa/rCl)	0.85 - 2.0 preferable 1.1 - 1.6	below 0.85 preferably below 0.60
Cl <sup>-</sup> /Br <sup>-</sup> (in mg/l)	variable	below 300
Gaseous hydrocarbons ratio C <sub>1</sub> /C <sub>1</sub> -C <sub>5</sub>	>0.98	below 0.98
Stable isotopes:		
δ <sup>13</sup> C (CH <sub>4</sub> )	lighter than -55%	-35 to -55%
δ <sup>13</sup> C (HCO <sub>3</sub> <sup>-</sup> )	-20 to -28%	-
δD (CH <sub>4</sub> )	-180 to -280%	-

On the basis of all the hydrochemical and geological information available for this study, and a concept of water-rock-organics interaction, the most favorable zones for oil survival in relatively unaltered form and for the biogenic gas generation were drawn on the hydrochemical map of the Uinta, Piceance and Green River basins. A synthesized image, in the scale of 1:500,000, Figures 34-37, was compared with a published map of oil and gas fields in this region (Petroleum Information Co. 1974 figure 1). General compatibility of the presented prospective areas, on the basis of formation water chemistry with discovered, exploited, or abandoned oil and gas fields, is quite good. Some deviations in particular areas may be related primarily to the unequal distribution and quality of the water data.

It is also obvious, that actual gas reservoirs may consist only partially of biogenic gas. The proportions of biogenic and thermal gas can be calculated exclusively on the basis of stable isotope data.

The presented drafts indicate areas of local potential of biogenic methane generation and simultaneous oil alteration. The same is true for prospective survival zones of unaltered oil. A joint coincidence of geological and environmental factors is required for the creation and survival of a commercial oil and gas accumulation. The chemistry of formation waters, as an important environmental factor, deserves much more attention in prospecting for new petroleum resources as well as development and redevelopment of known ones.

## SUMMARY AND CONCLUSIONS

A hydrogeochemical study was conducted of the Upper Cretaceous and Lower Tertiary oil and gas bearing formations of the Uinta, Piceance and Green River intermontane basins, using formation water chemical analysis from the Petroleum Data System BRIN file (Oilfield Water Analyses). Hydrochemical maps depict spatial distribution of chemical water types, isosalinity contours, and sections of these basins where the environmental conditions appear particularly favorable for biogenic or thermal gas generation, or crude oil survival in relatively unaltered form.



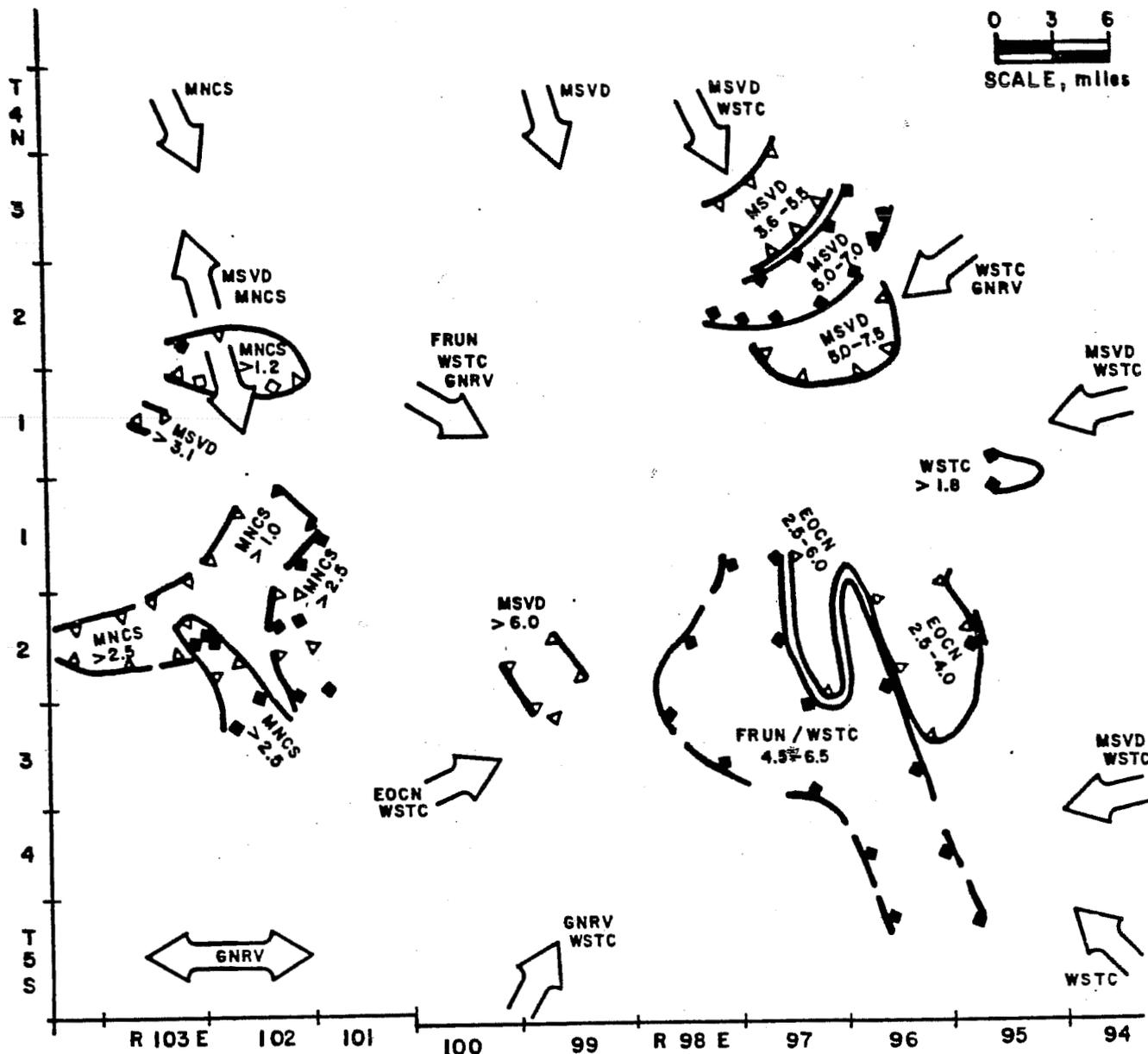


FIGURE 35. - Hydrochemical indications of oil and gas prospects in the Northern Piceance Creek Basin. Explanations are the same as given in Figure 34.

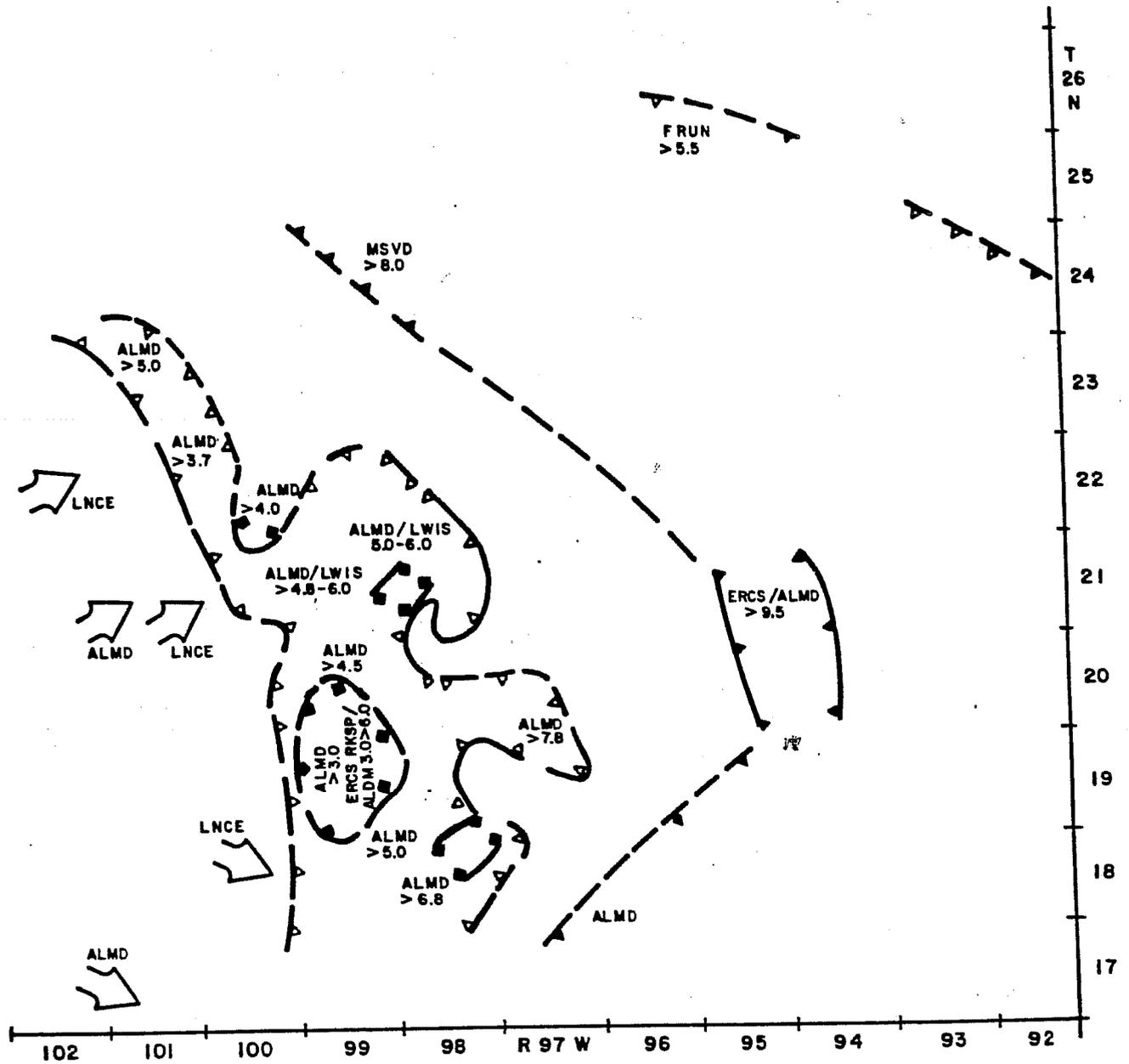


FIGURE 36. - Hydrochemical indications of oil and gas prospects in the Wamsutter arch area of the Greater Green River Basin . Explanations are the same as given in Figure 34.

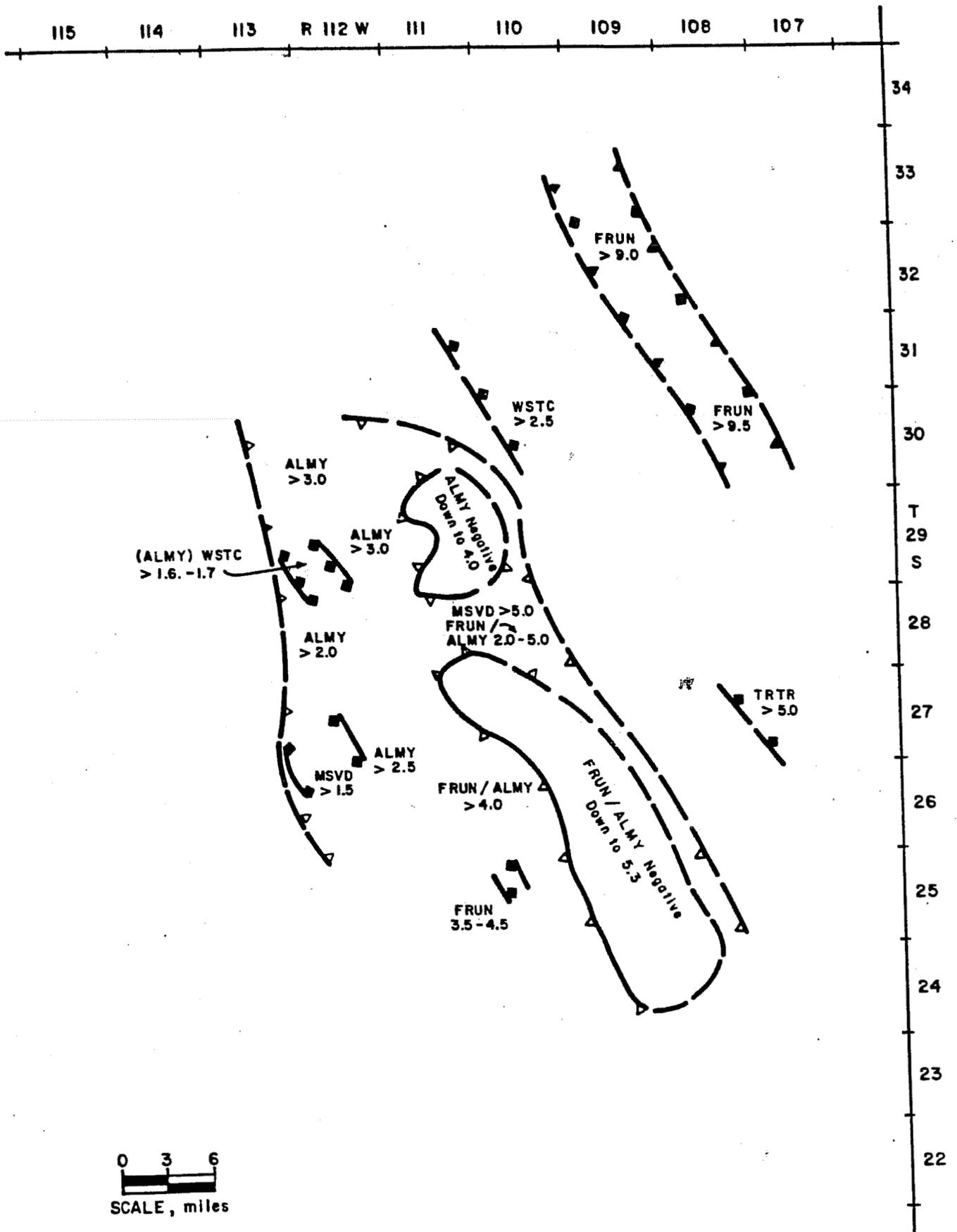


FIGURE 37. - Hydrochemical indications of oil and gas prospects in the Greater Green River Basin; Big Piney - La Barge area. Explanations are the same as given in Figure 34.

Five hydrochemical zones were distinguished, characterizing different formation water-rock-organics interaction processes. Their impact on the water chemistry and hydrocarbon alteration was theorized as:

1) An uppermost, highly mobile zone, where intensive meteoric water encroachment and oxidizing conditions prevail and where hydrocarbons are altered or destroyed.

2) An upper transitional zone - still poorly isolated from descending waters, where oxidation significantly decreases and formation water mobility is slowed down.

3) A lower transitional, fairly isolated or semi-stagnant, highly reductive zone, where waters from sources other than meteoric are the major component, and where effective bacterial action may occur.

4) An isolated, stagnant, low temperature zone, providing the best protection for hydrocarbon accumulation and protection from alteration processes.

5) A deep-seated, thermometamorphic zone, where thermal decarboxylation of organic acids and other temperature-dependent processes may affect the formation water chemistry.

The first four low temperature zones, are located above the main oil generation zones and they may occur at different depths - overlap or interfinger each other - because of recent and/or paleo- hydrodynamics, tectonics, rock porosity and permeability distribution and availability of organic matter. A mixed origin of the formation waters, consisting of recent or paleo-meteoric, relict-marine, plus diagenetic components, are characteristic features, within both non-marine and marine formations.

Most of the waters are also highly enriched in bicarbonates. Sources of  $\text{HCO}_3^-$  ion can be identified within individual zones on the basis of overall hydrochemical and geological interpretations, where the interpretations are linked to a theory of interaction between the formation water and the organics. The bicarbonate-rich waters are recognized as a positive indicator of hydrocarbon alteration and natural gas generation, provided that combined requirements listed in table 2 are fulfilled.

The validity of the proposed hydrochemical conceptual model as an indicator for oil and gas prospecting, depends on the availability of a wide range of geologic and hydrologic data. Consideration of individual parameters is less conclusive and can be confusing.

The reliability of this model can be proved in areas of current hydrocarbon exploitation in the Uinta, Piceance and Green River basins. It can be extrapolated to geologically comparable, but less explored areas. Supporting chemical, isotopic and hydrodynamic information would improve the understanding of on-going processes and their relation to the oil and gas reservoirs.

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