PROJECT COMPLETION REPORT

Nature and Rates of Bacterial Metabolism in the Aquifers of Southeastern Louisiana

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Problem and Research Objectives:

This study addresses three problems relevant to the southeast Louisiana aquifers. The first is concerned with the rates and spatial distribution of excess CO_2 production. The second concerns whether CO_2 is derived from bacterially-oxidized organic matter. The final is to understand the origin and evolution of the groundwater major element chemistry and its high $Na\text{-}HCO_3$ levels. The specific objectives were:

1. To determine the in situ rate of CO_2 production.

2. To establish the effect of viable bacterial activity on groundwater chemistry, and to test the hypothesis that high bicarbonate levels are the result of deep seated bacterial metabolism.

3. To ascertain the distribution of bacteria in the subsurface, and to improve understanding of processes which lead to mineralization or corrosive development of secondary porosity in clastic sediment aquifers.

4. To distinguish between aerobic, sulfate-reducing, and methanogenic microbial metabolism.

5. To evaluate the relative roles of calcite dissolution, silicate dissolution, and ion exchange in modifying groundwater chemistry.

Methodology:

Carbon Sources in Groundwaters:

Stable carbon isotopes, ^{13}C and ^{12}C, occur in natural carbon compounds at about 1 and 99% abundance, respectively. Isotope ratios of $^{13}C/^{12}C$ in natural carbon-bearing compounds vary considerably with the source of the carbon and the pathway of carbon fixation during metabolic processes. Hence it is possible to use carbon isotope ratios to study both the source of the carbon and the biota affecting it.

During rainfall in recharge areas, CO_2-charged precipitation introduces carbon dioxide with atmospheric values of -6 to -7^{o}/oo into the aquifer system. As the waters percolate through the unsaturated zone, CO_2 derived from aerobic bacterial oxidation of organic material in the soil zone is added. The isotopic composition of the resultant CO_2 is substantially more depleted in ^{13}C relative to the atmospheric value because organic matter and its oxidation products preferentially sequester the ^{12}C isotope. An increase in CO_2 resulting from bacterial respiration in the soil or aquifer leads to the dissolution of carbonate and silicate minerals, thus adding excess bicarbonate to the groundwater. In the case of carbonate dissolution, the $\delta^{13}C$ composition of DIC is expected to yield intermediate values between those of CO_2 released from bacterial respiration, and those of the dissolved carbonate with typical values of 2 to -5^{o}/oo. In the case of silicate dissolution, DIC $\delta^{13}C$ is expected to remain unchanged, as no new carbon is added to the system.

Mass balance calculations using measured values of $\delta^{13}C$, DIC, alkalinity, sodium, and H_4SiO_4 can be used to evaluate chemical changes occurring between points along a groundwater flow path. The isotope composition of the added CO_2 can be calculated in order to determine its source using the mass balance equation below:

$$\delta^{13}C_f = (\delta^{13}C_i)(m_i) + (\delta^{13}C_a)(m_a) + (\delta^{13}C_c)(m_c)/m_i+m_a+m_c$$

$\delta^{13}C_f$ is the measured (final) isotope composition of the sample, $\delta^{13}C_i$ is the isotope composition of the original DIC, m_i is the number of moles of original DIC, $\delta^{13}C_a$ is the isotopic composition of the added CO_2, m_a is the number of moles of added CO_2, $\delta^{13}C_c$ is the isotopic composition of the dissolved carbonate mineral, and m_c is the number of moles of carbonate mineral dissolved.

Rates of excess CO_2 production along groundwater flow paths can be estimated by applying another mass balance equation:

$$CO_2\ (PR) = (R)(m_a)/L$$

where CO_2 (PR) is the production rate of CO_2 averaged over a flow path segment, m_a is the moles of CO_2 added, L is the length of the flow path, and R is the rate of groundwater flow.

Alkalinity and Total Dissolved Inorganic Carbon (DIC):

An important concept in the study of waters is *alkalinity*, defined as the hypothetical amount of strong base that must be neutralized in order to reach a pH corresponding to a solution of pure CO_2 and water. In a simple system, consisting of only NaOH and CO_2, alkalinity is given by:

$$A = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

In dilute natural waters, total alkalinity is generally taken to be equal to carbonate alkalinity. Between a pH of 5 and 9, bicarbonate is the dominant carbon-bearing species, and the bicarbonate concentration is essentially equal to the alkalinity.

Total dissolved inorganic carbon (DIC) is the amount of carbon in both charged and uncharged species in solution, and is represented by a mass balance on carbon:

$$DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

An important property of alkalinity is that it does not change when CO_2 is added to or withdrawn from the solution. Altering the amount of CO_2 in solution does change the total dissolved inorganic carbon (DIC). Adding or removing bicarbonate (HCO_3^-) changes both DIC and alkalinity in a one-to-one ratio, while adding or removing CO_3^{2-} changes alkalinity by two units and DIC by one unit.

A graphic technique developed by Deffeyes using alkalinity as the ordinate and DIC as the abscissa has a number of useful characteristics. Changes in solution chemistry move the point representing the solution on the diagram in definite directions depending on the reaction stoichiometry. Since reactions such as calcite dissolution and CO_2 addition alter the solution according to definite stoichiometries, the change in solution chemistry can be split into component vectors representing a calcite component and a CO_2 component. In this way, contributions to the carbon budget by various processes can be assessed and distinguished.

Principal Findings and Significance:

The primary goal of this study was to evaluate the contribution of bacterial metabolism to the development of high Na-HCO_3 waters in the Baton Rouge aquifer system. In so doing, the nature and rates of bacterial activity were explored, and the relative roles of ion exchange, silicate dissolution, calcite dissolution, and bacterial oxidation of organic material were elucidated.

The impact of silicate reactions on groundwater chemistry was found to be negligible, while the impacts of bacterial production of CO_2, calcite dissolution, and ion exchange on major element and isotope chemistry were found to be profound. Sodium, derived by a two-for-one ion exchange with calcium, was found to be a good predictor of the amount of calcite dissolved.

The contribution to the carbon dioxide budget by bacteria oxidizing organic matter deep in the aquifers was substantial (3.15 mmol/L), and coequal to the contribution by calcite dissolution (3.05 mmol/L). These contributions can be differentiated by plotting DIC versus alkalinity on a Deffeyes diagram, and by dividing them into their component vectors.

There is no evidence for methanogenic microbial activity on the basis of carbon isotope values. There is also little or no evidence for sulfate reducing bacteria, which can be distinguished from aerobic bacteria on the basis of their byproducts and on the sodium content of the waters. Aerobic bacteria produce CO_2, which causes calcite dissolution and ion exchange with sodium, while sulfate-reducers produce HCO_3^- and no subsequent calcite dissolution and sodium release. Sulfate-reduction can be detected by a sodium deficiency compared with HCO_3^- (alkalinity). In this aquifer system, sulfate-reduction occurs only in the deepest part of the 2800 foot aquifer, and its contribution to the total bacterial carbon budget is insignificant.

Bacterial activity is concentrated at particular zones in the deeper aquifers, and is minimal in the rest of the system. In those areas of high productivity ($6.4\text{x}10^{-2}$ versus an average productivity of $5.4\text{x}10^{-3}$), it is expected that porosity has been corrosively enhanced. The hydraulic conductivities of the 2000 and 2800 foot aquifers, are, in fact, higher than those of the shallower aquifers. Due to calcium uptake on clays, all the waters are undersaturated with respect to calcite, although saturation is approached in the deeper sand units. Local microenvironments may develop in which saturation or oversaturation is achieved, and in which calcite may precipitate. However, calcite cementation should be minimal overall.

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ABSTRACT

High Na-HCO_3 water in the stacked sand and clay aquifer system of Southeastern Louisiana was found to be caused by a combination of bacterial oxidation of organic matter, ion exchange, and calcite dissolution. Dissolution of feldspar had little impact on water chemistry. Na and alkalinity are highly correlated as a result of calcite dissolution and subsequent exchnage by clays of 2 Na ions for each Ca ion. Na content is a good indicator of the amount of calcite dissolved.

The contribution to the carbon budget by bacterially-mediated organic degradation is substantial and coequal to the contribution by calcite dissolution. Microbial activity is dominated by aerobic bacteria, and there is little or no contribution by either sulfate-reducers or methanogens.

Bacterial activity is concentrated within the deeper aquifers, and is much less important in the shallow and intermediate sands. The average rate of CO_2 production is estimated to be $5.4x10^{-3}$ $mmolL^{-1}yr^{-1}$, while in high CO_2 productivity areas, rates are more than ten times greater ($6.4x10^{-2}$ $mmolL^{-1}yr^{-1}$).

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1.0 DEFINITION OF THE PROBLEM

Oxidation of soil organic matter to CO_2 by shallow-seated bacteria is a well-known phenomenon, and, accompanied by dissolution of calcite, constitutes a dominant control over carbonate chemistry of groundwaters (Freeze and Cherry, 1979). In a number of aquifer systems consisting of stacked and stratified sands and clays, however, there is excess bicarbonate which cannot be attributed to soil gas and calcite dissolution. It was suggested, therefore, that deep-seated degradation of organic matter within the confined aquifers was responsible for the excess bicarbonate (Foster, 1950).

Until recently, there was no proof that viable bacterial populations existed deep within aquifers. However, a number of studies have now documented the presence of bacteria in deep, confined, clastic and carbonate aquifers from a variety of geographic locations (Dockins et al., 1980; Olson et al., 1981; Chapelle et al., 1987; Chapelle et al., 1988; Grossman et al., 1989; Fliermans, 1989). The proposed relationship between excess bicarbonate and bacterial degradation of organic matter (Foster, 1950) can be tested using carbon isotopes to trace the source of carbon (e.g. Pearson and Friedman, 1970; Rightmire and Hanshaw, 1973; Winograd and Farlekas, 1974; Chapelle et al., 1989; Grossman et al., 1989).

The freshwaters of the Southern Hills Regional Aquifer System of Louisiana have high sodium and high bicarbonate levels. Morgan and Winner (1962) and Khan et al. (1972) cited bacterial processes and ion exchange as the most likely controls over the water chemistry. This was challenged by Hanor (1980) on the basis of thermodynamic considerations; he suggested that feldspar dissolution and clay formation could explain the observed major element chemistry.

This study addresses three problems relevant to the southeastern Louisiana aquifers. The first is concerned with the rates and spatial distribution of excess CO_2 production. The second concerns whether CO_2 is derived from bacterially-oxidized organic material. The final is to understand the origin and evolution of the groundwater major element chemistry and its high Na-HCO_3 levels. The specific objectives were:

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2.0 BACKGROUND INFORMATION

2.1 The Aquifer System

The Southern Hills Regional Aquifer System (named by Buono, 1983) of southeastern Louisiana and southwestern Mississippi consists of a series of gulfward dipping, east-west trending, alternating sand aquifers and clay aquitards of Miocene to Pleistocene age (Figure 1). These are overlain by shallow Pleistocene upland deposits and Mississippi River alluvial deposits. The system is bounded hydraulically to the west by the Mississippi River, to the north by the outcrop limit, to the south by the Baton Rouge Fault Zone, and to the east by the Amite River, a groundwater divide (Figure 2). Discharge occurs in the southern-most part of the system, while recharge by rain and leakage from overlying aquifers occurs in the northern four-fifths of the region (Figure 2). The study area includes Amite County (Mississippi), East Feliciana Parish (Louisiana), and East Baton Rouge Parish (Louisiana) (Figure 3).

Tertiary and Lower Pleistocene sand and clay sediments were deposited during repeated transgressions and regressions of the Gulf of Mexico (Sellards et al., 1932; Dixon, 1963). Flood plain, deltaic, and fluvial sediments were deposited during the dominant regressive intervals, with thin interfingering marine clays and marls deposited during transgressions. As a result, beds are discontinuous over the area and many of the sand units are hydraulically connected (Morgan, 1963; Khan et al., 1972; Buono, 1983). In the study area, the sands are informally named according to their depth of occurrence at the Baton Rouge Fault Zone, a leaky hydrologic barrier (Figure 1) (Buono, 1983). Groundwater is salty on the downthrown (south) side of the fault.

Sand units south of the Baton Rouge fault are saturated with brackish connate waters; on the north side of the fault, the sands have been flushed with freshwater (Rollo, 1969; Whiteman, 1979). As a result of incomplete flushing, the deepest "2800 foot sand" (Whiteman, 1979) unit contains remnant connate water for several miles north of the fault (Whiteman, 1979). Saltwater encroachment through the barrier has also occurred to a limited extent in the upper sand units (Rollo, 1969; Whiteman, 1979).

Aquifer sands are dominated by quartz with subordinate amounts of feldspar some of which has been altered to clay (Meyer and Turcan, 1955; Hanor, 1980). Calcium carbonate is locally abundant. Aquitard sediments consist of a mixture of sand, silt, and clay minerals; the fine-grained layered silicates are in exchange equilibrium with the nearby aquifer waters. Organic carbon in the aquicludes comprises between 0.1 and 3 wt% of the bulk sediment (Hanor, 1980).

Recharge rates, established from tritium isotope profiles (Aharon, unpubl. data), vary from 0.3 to 0.6 meters per year. Groundwater generally flows southerly in response to topographic gradients from north to south, with an estimated horizontal flow velocity of 78m/yr and 200 m/yr in the shallow (400-600 foot sands) and deeper (2000 foot sands) aquifers, respectively (Buono, 1983). Upward flow and discharge from the system occur at lower elevations near the Baton Rouge fault zone. Accelerated withdrawal rates, however, have resulted in a cone of depression centered at the Baton Rouge industrial complex. This cone of depression has disrupted natural flow patterns. The age of the oldest fresh water in the system was calculated from Darcy's law to lie between 4000 and 8000 years, indicating that most of the groundwater postdates both glacial precipitation and glacial melt (Gonthier, 1989).

Bicarbonate content was computed on the basis of mass and charge balance by Khan et al. (1972), and was used to divide the freshwater into three zones: (1) shallow, unconfined aquifers containing approximately 2 mmol/L of bicarbonate; (2) transition zone between zones 1 and 3 in the "400", "600", and "800 foot sands;" and (3) "1000" to "2800 foot sands" with increasing Na and HCO_3 contents with depth.

2.2 Previous Work

The groundwater hydrology of Southeast Louisiana has been comprehensively studied over the previous fifty years (e.g. Cushing and Jones, 1945; Meyer and Turcan, 1955; Morgan, 1961, 1963; Morgan and Winner, 1962; Smith, 1969; Kazmann, 1970; Rollo, 1969; Khan et al., 1972; Nyman and Fayard, 1978; Martin and Whiteman, 1989). Geochemistry of the waters has been studied by Meyer and Turcan (1955), Morgan (1961), Morgan and Winner (1962), Khan et al. (1972), Hanor (1980), and Gonthier (1989).

Several different hypotheses have been developed to explain the origin of elevated Na-HCO_3 contents in the Southern Hills Regional Aquifer complex. The classic work was by Foster (1950), whose experiments showed that waters in contact with lignite, calcite, and ion exchange material became similar in composition to the natural waters occurring in coastal plains aquifers. Foster hypothesized that oxidation of organic material was the source of excess CO_2 in the system, and that subsequent dissolution of calcium carbonate was accompanied by base exchange of sodium for calcium on clays.

Hanor (1980) rejected the role of ion exchange in forming $Na-HCO_3$ rich waters, and instead invoked silicate breakdown reactions with subsequent incorporation of Ca and Mg on newly formed clay lattice sites. Excess Na was produced by the breakdown of Na-bearing smectite and feldspar. He suggested that in situ bacterial alteration of organic matter during earliest clay diagenesis produced bicarbonate that migrated outward into the sands. Ion exchange was rejected on the basis that connate waters were riverine and were therefore already in exchange equilibrium with the sediments.

Isotopic studies of the total dissolved carbon phase in groundwaters from other aquifer systems tend to support Foster's model (Pearson and Friedman, 1970; Winograd and Farlekas, 1974; Rightmire and Hanshaw, 1973). The $\delta^{13}C$ composition of the excess dissolved carbon phases generally indicates an organic source. Thus far, little work has been done to delineate the relative roles of ion exchange, carbonate dissolution, and silicate dissolution, and few attempts have been made to distinguish between possible bacterial pathways (e.g., aerobic oxidation and sulfate reduction).

Although Foster (1950) speculated that bacterial oxidation of organic material occurs deep within aquifers, until recently, most evidence of bacterial activity was indirect. Several studies have now documented the presence of bacteria in shallow and deep groundwaters by enumeration and incubation. Aerobic, sulfate-reducing, methanogenic, and facultatively anaerobic bacteria have each been identified from different sites and depths (Olson et al., 1981, Chapelle et al., 1987, Chapelle et al., 1988, Grossman et al., 1989, Fliermans, 1989). The occurrence of viable bacterial assemblages as deep as 1800 meters (Olson et al., 1981) supports the feasibility of Foster's model.

3.0 METHODS

Groundwater samples from fifty-four (54) active freshwater wells in East Baton Rouge Parish, East Feliciana Parish, and Amite County (Figure 3) were collected at the well heads between January and June of 1990. Collection sites were selected to achieve reasonable coverage of each of the major sands from the recharge area to the discharge area. Active wells were sparse in the area between the recharge zone (towns of Norwood, Clinton, Wilson, Jackson, Centerville), and the discharge zone (Zachary, Baker, Baton Rouge).

Temperature (+/- 0.5°C) and pH (+/- 0.01 standard pH unit) were measured on-site, and tightly sealed 100 mL bottles were removed to the laboratory. A few grains of mercuric chloride were added to each bottle before sealing in order to prevent subsequent bacterial activity. In most cases, alkalinity titrations were performed within twenty-four hours. Dilute hydrochloric acid (0.01N) was used to titrate 5 to 10 mls of water in a covered, stirred beaker using an Orion pH meter and combination pH electrode. The equivalence point was determined using Gran calculations (Gran, 1952). The reproducibility of the alkalinity measurements was +/-0.1 meq/L.

Total dissolved inorganic carbon (DIC) and $\delta^{13}C$ were determined within a week of collection using the technique described in Graber and Aharon (in prep; Appendix 2). In this method, 2 ml samples are injected into a temperature-controlled, evacuated reaction vessel containing phosphoric acid. The evolved CO_2 is removed from the solution by stirring and dynamic cold pumping using a series of dry ice/alcohol and liquid nitrogen-cooled traps. The amount of CO_2 is measured with the mass spectrometer and the gas is analyzed for its isotopic composition. Accuracy and precision for DIC measurements were both within 0.1 mmol/L, and for $\delta^{13}C$, were within 0.1°/oo. Results are reported in the delta notation ($\delta^{13}C = ({}^{13}C/{}^{12}C_{(sample)} - {}^{13}C/{}^{12}C_{(standard)})/\ {}^{13}C/{}^{12}C_{(standard)}) \times 1000$ in parts per thousand (°/oo) with respect to the Peedee Belemnite Standard (PDB). Mass spectrometer corrections as reported by Craig (1954) were followed.

$\delta^{18}O$, Na content, and Cl content were analyzed by Gonthier (1989) from water samples collected from these same wells in 1987. $\delta^{18}O$ was determined using the Epstein and Mayeda (1953) equilibration method with a reproducibility of 0.1°/oo. Chloride was determined by the Mohr titration method with a reproducibility of +/- 1ppm. Ca, Mg, Na, and H_4SiO_4 contents of the 1990 samples were determined by inductively coupled plasma (ICP) analysis (std. dev.: H_4SiO_4 = +/- 2%, Na = +/- 2%, Ca = +/- 2%, Mg = +/- 2%).

Calcite and dolomite saturation states (defined as the free energy of dissolution) were computed using the collected data and temperature dependent equilibrium constants reported by Butler (1982). For saturation calculations, sulfate (not measured) concentrations were taken to be 8 mg/L, the average value reported by Khan et al. (1972) for Baton Rouge waters. The calculations were also performed using values ranging between 2 and 14 ppm (2 standard deviations). The difference in computed saturations was less than 2 percentage points.

The data generated for this report is tabulated in Appendix 1. Data from Gonthier's (1989) study is also presented in Appendix 1.

4.0 THEORY AND METHODOLOGY

4.1 Carbon Sources in Groundwaters

Stable carbon isotopes, ^{13}C and ^{12}C, occur in natural carbon compounds at about 1 and 99% abundance, respectively. Isotope ratios of $^{13}C/^{12}C$ in natural carbon-bearing compounds vary considerably with the source of the carbon and the pathway of carbon fixation during metabolic processes. Hence it is possible to use carbon isotope ratios to study both the source of the carbon and the biota affecting it. Carbon sources in groundwater, bacterially-mediated chemical reactions, and the effects of bacterial activity on $\delta^{13}C$, carbonate alkalinity, and DIC, are summarized in Table 1.

During rainfall in recharge areas, CO_2-charged precipitation introduces carbon dioxide with atmospheric values of -6 to -7°/oo into the aquifer system (Keeling et al., 1979). As the waters percolate through the unsaturated zone, CO_2 derived from aerobic bacterial oxidation of organic material in the soil zone is added. The isotopic composition of the resultant CO_2 is substantially more depleted in ^{13}C relative to the atmospheric value because organic matter and its oxidation products preferentially sequester the ^{12}C isotope (Deines, 1980). An increase in CO_2 resulting from bacterial respiration in the soil or aquifer leads to the dissolution of carbonate and silicate minerals, thus adding excess bicarbonate to the groundwater. In the case of carbonate dissolution, the $\delta^{13}C$ composition of DIC is expected to yield intermediate values between those of CO_2 released from bacterial respiration, and those of the dissolved carbonate with typical values of 2 to -5°/oo (Milliman, 1974). In the case of silicate dissolution, $\delta^{13}C_{DIC}$ is expected to remain unchanged, as no new carbon is added to the system.

Mass balance calculations using measured values of $\delta^{13}C$, DIC, alkalinity, sodium, and H_4SiO_4 can be used to evaluate chemical changes occurring between points along a groundwater flow path. The isotope composition of the added CO_2 can be calculated in order to determine its source using the mass balance equation below (Chapelle et al., 1987):

$$\delta^{13}C_f = (\delta^{13}C_i)(m_i) + (\delta^{13}C_a)(m_a) + (\delta^{13}C_c)(m_c)/m_i+m_a+m_c \quad (1)$$

$\delta^{13}C_f$ is the measured (final) isotope composition of the sample, $\delta^{13}C_i$ is the isotope composition of the original DIC, m_i is the number of moles of original DIC, $\delta^{13}C_a$ is the isotopic composition of the added CO_2, m_a is the number of moles of added CO_2, $\delta^{13}C_c$ is the isotopic composition of the dissolved carbonate mineral, and m_c is the number of moles of carbonate mineral dissolved.

Rates of excess CO_2 production along groundwater flow paths can be estimated by applying another mass balance equation (Chapelle et al., 1987):

$$CO_2\ (PR) = (R)(m_a)/L \quad (2)$$

where CO_2 (PR) is the production rate of CO_2 averaged over a flow path segment, m_a is the moles of CO_2 added, L is the length of the flow path, and R is the rate of groundwater flow.

4.2 Alkalinity and Total Dissolved Inorganic Carbon (DIC)

An important concept in the study of waters is *alkalinity*, defined as the hypothetical amount of strong base that must be neutralized in order to reach a pH corresponding to a solution of pure CO_2 and water (Butler, 1982). In a simple system, consisting of only NaOH and dissolved carbon species, alkalinity is given by:

$$\bar{A} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (3)$$

The operational definition (titrate the sample with standard HCl to the methyl orange endpoint) applied to a natural water may also include other weak acids and bases such as borate, ammonia, hydrolized ferric ion, or organic acid anions, and is called total alkalinity. In dilute natural waters, total alkalinity is generally taken to be equal to carbonate alkalinity (Butler, 1982). Between a pH of 5 and 9, bicarbonate is the dominant carbon-bearing species, and the bicarbonate concentration is essentially equal to the alkalinity.

Total dissolved inorganic carbon (DIC) is the inventory of carbon in both charged and uncharged species in solution, and is represented by a mass balance of carbon:

$$DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \quad (4)$$

An important property of alkalinity is that it does not change when CO_2 is added to or withdrawn from solution, because the combination of charged concentrations given by Eq. (3) are unaffected. Altering the amount of CO_2 in solution does change tha total dissolved inorganic carbon (DIC). Adding or removing bicarbonate (HCO_3^-) changes both DIC and alkalinity in a one-to-one ratio, while adding or removing CO_3^{2-} changes alkalinity by two units and DIC by one unit.

A graphic technique developed by Deffeyes (1965) using alkalinity as the ordinate and DIC as the abscissa has a number of useful characteristics. Changes in solution chemistry move the point representing the solution on the diagram in definite directions depending on the reaction stoichiometry. For example, in Figure 4a, adding CO_2 changes only the concentration of DIC, and thus the initial solution moves from point 1 to point 2. Addition of OH- increases only alkalinity, and moves the solution from point 2 to point 3. As depicted in Figure 4b, the dissolution of calcite contributes 2 units to alkalinity for each additional unit of DIC. Since reactions such as calcite dissolution and CO_2 addition alter the solution according to definite stoichiometries, the change in solution chemistry can be split into component vectors representing a calcite component and a CO_2 component. In this way, contributions to the carbon budget by various processes can be assessed and distinguished.

5.0 RESULTS

A number of the measured chemical parameters display a general increase with depth. Water temperature measured at the well head increases from approximately 20°C in the shallow recharge zone to 35°C in the discharge zone (Figure 5). This represents a minimum geothermal gradient of 15°C/km. Other parameters which generally increase with depth include pH (5 to 9 standard pH units) (Figure 6), DIC (0.7 to 7.5 mmol/L) (Figure 7), alkalinity (0.1 to 6.5 meq/L) (Figure 8), $\delta^{13}C$ (-22 to -13°/oo) (Figure 9), Na (5 to 150 mg/L) (Figure 10), and calcite saturation (0% to 97%) (Figure 11). All the waters were found to be completely undersaturated with repect to dolomite (Appendix 1).

Calcium and magnesium are highly positively correlated (Figure 12), and display substantial, though non-linear, decreases with depth (Figures 13 and 14). Chloride is invariant and low, except for four shallow (400-600 foot aquifer) wells with elevated contents (Figure 15). Although the 400-600 foot aquifers suffer from saltwater intrusion (Whiteman, 1979), the absence of corresponding elevated Na contents suggests an anthropogenic source for the chloride (Gonthier and Aharon, 1990). Except for low values in the shallowest recharge wells, silica content of the waters seems to decrease with depth, albeit with large scatter, from a maximum of 30 ppm to a minimum of 10 ppm (Figure 16).

Although DIC, alkalinity, and sodium generally increase with depth, their behavior within each sand unit is complex and non-linear (Figures 17, 18, and 19). In each case, the recharge zone is impoverished and the 2800 foot aquifer is enriched. All the intervening sands (400, 600, 1000, 1200, 1500, 1700, 2000, and 2400 foot) have intermediate and variable compositions unrelated to absolute depth. This zonation varies markedly from that reported by Khan et al. (1972) (Section 2.1). The discrepancy is probably due to the fact that Khan et al. did not measure alkalinity, but computed it from a charge balance. Their empirical method of alkalinity estimate is deficient because values incorporate the measurement errors of all the parameters.

Sodium and alkalinity display a marked linear covariance with depth (Figure 20). This correlation can also be seen within each sand unit by comparing trends along lithologic layers (Figures 18 and 19). Importantly, although DIC and alkalinity are also highly correlated ($r^2=0.93$) (Figure 21), Na tracks DIC much less well than it tracks alkalinity (compare Figures 17 and 19 with Figures 18 and 19).

$\delta^{13}C$ is quite variable at all depths, and can be relatively high even in the recharge zone (Figure 22). This is because at low DIC levels, $\delta^{13}C$ is very sensitive to additions of carbon which can make up a large percentage of the total. Overall, there is a ^{13}C enrichment with increasing depth from approximately -22°/oo to -13°/oo.

Chemical patterns are contoured on projections (Figure 1) along a north-south cross-section line (Figure 23a-f). Several trends common to the measured parameters are noted. First, chemical gradients are gentle over most of the cross sectional area, both along recharge flow paths from the north to the south, and along discharge flow paths from deep to shallow aquifers. Second, there are steep chemical gradients at intermediate depths in the 1700, 2000, 2400, and 2800 foot aquifers. Third, steep gradients in the 2400 and 2800 foot aquifer occur in the deepest portion of the sands and are nearly horizontal. Because the wells are projected into a single plane, steep contoured gradients do not necessarily represent changes parallel to flow.

The patterns for DIC, alkalinity, Na, and calcite saturation are very similar (Figure 23a-d). In the discharge area, the gradients are small until the 2400 and 2800 foot sands are reached. Further north, there are steep chemical gradients in the 1700, 2000, 2400, and 2800 foot sands. In the discharge area and deep aquifers, $\delta^{13}C$ (Figure 23e) contours are similar to DIC, alkalinity, Na, and % calcite saturation. In the recharge area and shallow aquifers, however, the pattern of ^{13}C-enrichment differs because $\delta^{13}C$ is more sensitive to small changes in DIC and alkalinity when the initial DIC content is low. The chemical contours of H_4SiO_4 (Figure 23f) are quite different from the others in two ways: (i) where all the other parameters increase, H_4SiO_4 decreases; and (ii) H_4SiO_4 content is variable in the shallow aquifers throughout the whole area. This suggests that local mineralogy may more impact on H_4SiO_4 concentrations than does overall, downflow, chemical change.

6.0 DISCUSSION

6.1 The Rejected Model - Sodium-rich Silicate Dissolution

There are a number of lines of evidence suggesting that feldspar dissolution is not responsible for downflow increases in sodium as suggested by Hanor (1980). First, incongruent dissolution reactions involving a sodium-rich silicate such as albite and a clay such as kaolinite, would release approximately twice as much silicic acid to solution as Na:

$$NaAlSi_3O_8\ (ab) + H_2CO_3^* + 9/2H_2O\ -\ Na^+ + HCO_3^- + 2H_4SiO_4 + 1/2Al_2Si_2O_5(OH)_4\ (kaol) \quad (5)$$

However, Na content of the waters varies from 0.5 to 7 mmol/L while H_4SiO_4 content varies only 0.1 to 0.35 mmol/L, a twentyfold increase of Na over H_4SiO_4.

Second, feldspar dissolution does not contribute new carbon atoms to the DIC system, and $\delta^{13}C_{DIC}$ should remain unchanged. In fact, though, $\delta^{13}C_{DIC}$ increases from $-22^{o}/_{oo}$ to $-13^{o}/_{oo}$ from the recharge area to the deepest part of the aquifer complex.

Third, during the breakdown of feldspar to clay, dissolved CO_2 is converted to HCO_3^-, thus the overall amount of DIC remains fixed while alkalinity increases. On a Deffeyes plot of DIC versus alkalinity (Figure 4), the point representing the solution will move up parallel to the alkalinity axis during feldspar dissolution. In an actual groundwater system, where CO_2 is also being added, the samples will plot in the field above the bicarbonate line marked in Figure 21. In this study, the samples plot well below the bicarbonate line.

Fourth, if feldspar dissolution is the source of sodium, the observed increase in sodium with depth should be accompanied by an increase in silicic acid. However, silicic acid concentrations in the groundwaters generally decrease in concentration with depth in the intermediate and deep aquifers (Figure 16).

Based on the evidence above, feldspar dissolution cannot account for the chemical changes observed in these waters. The hypothesis suggested by Hanor (1980) is insupportable and is thus rejected.

6.2 The Accepted Model - Calcite Dissolution, Ion Exchange, and Bacterial CO_2 Production

All the evidence suggests that the processes of calcite dissolution, ion exchange, and bacterial CO_2 production combine to result in the observed water chemistry.

6.2.1 Calcite Dissolution

One way to explain the increase of $\delta^{13}C_{DIC}$ with depth (Figure 22) is by dissolution of calcite with an average carbon isotope composition of 0°/oo. The increase in bicarbonate concentration downflow can also be attributed to calcite dissolution, a process which increases DIC by one unit and alkalinity by two on a Deffeyes diagram. Groundwater samples should and do plot in the field below the bicarbonate line marked in Figure 21 when the combined processes of calcite dissolution and CO_2 addition occur. The amount of CO_2 added versus the amount of calcite dissolved can be resolved by plotting the solution compositions on a Deffeyes diagram and by dividing the components into their respective vectors (Figure 4b). This has been discussed Section 4.2.

There is an increase in calcite saturation with depth, from 0% saturated to nearly 100% saturated (Figure 11). The increase corresponds to that of alkalinity through the section (Figure 23b and d), suggesting a relationship between the two.

One parameter which should increase as calcite is dissolved is calcium. However, calcium decreases downflow (Figure 13). This can be explained by calcium uptake on clays with the concommitant release of ions such as sodium. If ion exchange is occuring, sodium would increase downflow, as is observed in Figures 10 and 23c.

6.2.2 Ion Exchange

In rejecting ion exchange of Ca for Na on clays in the aquifers and aquitards, Hanor (1980) assumed that the initial connate waters were riverine and are still extant in the aquifer system. This means that the water and sediments would have been in exchange equilibrium at the time of deposition, and that there would have been no thermodynamic drive for ion exchange. However, initial connate waters were brackish (Rollo, 1969; Whiteman, 1979), and have been subsequently flushed by fresh water recharge (Morgan, 1961; Buono, 1983; Gonthier, 1989). Using Darcy's law, Gonthier (1989) calculated the age of the oldest fresh water in the system to be only 8000 years.

The cation exchange capacity (CEC) of the bulk clay, a mixture of kaolinite, illite, and montmorillonite (Hanor, 1980), ranges from 36 to 76 meq/100 grams, and for bulk sediment, from 13 to 53 meq/100 grams (Hanor, 1980). These sodium-saturated clays (originally in equilibrium with brackish connate waters) were thus the most probable source of Na for exchange with Ca brought into the system by recharge waters and by calcite dissolution.

In addition to providing a source of Na and a sink for Ca, ion exchange drives calcite dissolution forward beyond its natural equilibrium and causes undersaturated conditions to linger. The amount of calcite dissolved can be determined by the stoichiometry of calcite dissolution, which requires that moles of calcite dissolved are equal to the moles of calcium and half the moles of HCO_3^- in solution.

$$CaCO_3 + H_2CO_3^* - Ca^+ + 2HCO_3^- \qquad (6)$$

If ion exchange results in a 2:1 substitution of Na for Ca (Stumm and Morgan, 1981, p. 643), then moles of calcite dissolved should also equal half the moles of Na in solution. The good correlation observed between Na and alkalinity (Figure 20) supports this relationship.

Mass balances computed using both Na and alkalinity can provide a test of the importance of ion exchange in controlling groundwater chemistry. Na can also be used to evaluate minor contributions by feldspar dissolution. For example, excess Na over alkalinity may be ascribed to feldspar contributions. Similarly, excess alkalinity over Na can be used to differentiate between bicarbonate derived from calcite dissolution and bicarbonate derived via sulfate reduction. This will be discussed in a later section.

6.2.3 Sources and Rates of CO_2 Production Across the Aquifer System

A single mass balance calculation based on initial and final water compositions can serve to preface the following discussion of sources and rates of CO_2 generation in the subsurface. Equation (1), presented earlier and reproduced below, will be used. This equation has terms for the initial DIC, an addition of CO_2, and an addition of dissolved calcite. Using this equation, the isotopic composition of the added CO_2 will be computed.

Recharge waters are best represented by an initial DIC content of 1.2 mmol/L and HCO_3^- of 0.2 mmol/L; the oldest (deepest) water contains 7.4 mmol/L DIC and 6.3 mmol/L HCO_3^-. Na content of the recharge waters is approximately 0.4 mmol/L; Na content of the deepest water is 6.5 mmol/L. $\delta^{13}C_i$ (initial) is $-22^o/oo$; $\delta^{13}C_f$ (final) is $-13^o/oo$. H_4SiO_4 remains nearly unchanged at approximately 0.1 mmol/L. The dissolved calcite (moles of dissolved calcite = m_c) is assumed to have a $\delta^{13}C$ ($\delta^{13}C_c$) value of $0^o/_{oo}$ (marine carbonate generally varies between -5 to $+2^o/oo$, with $0^o/oo$ being a reasonable average value).

In order to determine the molar contributions of calcite and CO_2, the initial and ending DIC and alkalinity contents are plotted on a Deffeyes diagram (Figure 24). The calcite and CO_2 are broken into component vectors and their respective contributions are read from the plot. In this case, 3.15 mmol/L of CO_2 are added, and 3.05 mmol/L of calcite are dissolved.

We wish to solve for $\delta^{13}C_a$, the carbon isotope composition of the added CO_2:

$$\delta^{13}C_f = (\delta^{13}C_i)(m_i) + (\delta^{13}C_a)(m_a) + (\delta^{13}C_c)(m_c)/(m_i+m_a+m_c)$$

$$-13 = (-22)(1.2) + (\delta^{13}C_a)(3.15) + (0)(3.05)/1.2 + 3.15 + 3.05$$

hence: $\delta^{13}C_a = -22.16$

Using a calcite of $\delta^{13}C$ equal to -5°/oo instead of 0°/oo yields -17.3°/oo for the incoming CO_2.

Sediment samples were unavailable for this study, and thus neither organic matter nor carbonate were measured directly for $\delta^{13}C$. It is assumed that the organic material of the aquifers and aquitards consists of a mixture of C3 and C4 terrestrial plants, marine plankton, and marine plants. The more labile organic components of these are enriched in ^{13}C (Deines, 1981; Degens, 1969), but bacteria selectively use ^{12}C-enriched functional groups (Rosenfield and Silverman, 1959; Kaplan and Rittenberg, 1964). Based on probable sources, organic matter may vary in composition between -15 to -30°/oo. The average $\delta^{13}C$ of organic matter among all marine sediments is -23°/oo (Anderson and Arthur, 1982). This value is certainly in good agreement with the $\delta^{13}C$ values of -22.2 and -17.3 calculated above for the incoming CO_2.

In this instance, the change in sodium content is exactly equal to the change in alkalinity. Thus sodium content could also be used to indicate how much calcite was dissolved. This demonstrates the importance of ion exchange in controlling groundwater chemistry.

A similar general calculation can be made to ascertain the average rate of CO_2 production from the surface to the deepest point in the aquifer using equation (2). The total distance between these two points is approximately 41 miles. An average horizontal flow velocity is taken to be 0.07miles/yr, which is an average of the velocities in the 2400 and 2800 foot sands (Buono, 1983). Simply regarded, the CO_2 production rate can be calculated as the flow rate multiplied by the amount of CO_2 added, all divided by the length of the flow path:

CO_2 (PR) = Rm_a/L

CO_2 (PR) = (0.07) x (3.15)/41

CO_2 (PR) = 5.4×10^{-3} $mmolL^{-1}yr^{-1}$

The calculated average production rate (using 3.15 mmol/L of added CO_2 as determined from the Deffeyes diagram in Figure 24) is 5.4×10^{-3} $mmolL^{-1}yr^{-1}$.

6.2.4 Sources and Rates of CO_2 Production in High Productivity Zones

The rate of CO_2 production is not uniform across the aquifer system, but is concentrated in particular zones: at intermediate depths in the 1700, 2000, 2400, and 2800 foot aquifers, and at the deepest reaches of the 2400 and 2800 foot aquifers (Figure 23). Two additional mass balance calculations in high productivity areas are shown in Figure 25. In the first area, labeled 2-2′ on Figure 23a, the carbon isotope composition of the incoming CO_2 is calculated to be -21.7°/oo, and in the second, labeled 3-3′, -18.1°/oo. Again, these values indicate an organic source of carbon. The rates of CO_2 production were calculated to be 4.9×10^{-2} and 6.4×10^{-2} $mmolL^{-1}yr^{-1}$, respectively. This is more than a tenfold increase over the average production rate.

The results of all these calculations indicate that the source of additional CO_2 is in situ bacterial alteration of organic matter. The rates of CO_2 production vary throughout the system, and production is concentrated in the lower sand units. The amount of bacterially-generated CO_2 is substantial, and is overall slightly higher than the amount of bicarbonate contributed to the system by calcite dissolution.

6.3 Nature of Bacterial Activity

The computed carbon isotope values for incoming CO_2 of -17 to -22°/oo preclude contributions from methane oxidation or methanogenesis. This is because methanogenesis causes intense fractionation of carbon isotopes between the two products, CO_2 and methane (CH_4). CO_2 produced during methanogenesis will be very enriched in ^{13}C, and will have a carbon isotope composition of +10 to +30°/oo. The mass balances above, however, indicate that the composition of the incoming CO_2 was only -22 to -17°/oo. $\delta^{13}C_{DIC}$ from other aquifers in which methanogenesis occurs is as heavy as 0°/oo, and mass balances clearly identify the heavy CO_2 source (Grossman et al., 1989).

There is also little or no evidence for substantial contributions by sulfate-reducing bacteria. In all but 5 wells from the deepest portion of the 2800 foot aquifer, no H_2S was detected by smell, indicating less than 25 ppb H_2S (Standard Methods, 1985). Second, the SO_4^{--} content is essentially invariant throughout the section (Khan et al. 1972). If sulfate-reducing bacteria were active, H_2S would be more prevalent, and sulfate levels would decrease downflow (Foster, 1950).

In the deepest wells, a faint H_2S odor indicated that sulfate reduction was occurring. Significant contributions by sulfate-reducers can, in this system, be determined on the basis of HCO_3^- and Na contents. The reduction of sulfate to sulfide and the oxidation of organic matter liberates HCO_3^-, not CO_2. If sulfate-reduction is considerable, some of the excess alkalinity will be derived from sulfate reduction, and only some from calcite dissolution. The change in Na, as the calcite dissolution index, would be less than the change in alkalinity, and the difference between Na and alkalinity would be a measure of the amount of sulfate reduction. In the 2800 foot sand, sodium is essentially equal to the alkalinity (Appendix 2), indicating that no significant contribution to the carbon budget was made by sulfate-reducers.

Thus we conclude that the vast majority of the bacterial activity in this aquifer is aerobic in origin.

7.0 CONCLUSIONS

The primary goal of this study was to evaluate the contribution of bacterial metabolism to the development of high Na-HCO_3 waters in the Baton Rouge aquifer system. In so doing, the nature and rates of bacterial activity were explored, and the relative roles of ion exchange, silicate dissolution, calcite dissolution, and bacterial oxidation of organic material were elucidated.

The impact of silicate reactions on groundwater chemistry was found to be negligible, while the impacts of bacterial oxidation of organic matter, calcite dissolution, and ion exchange on major element and isotope chemistry were found to be profound. Sodium, derived by a two-for-one ion exchange with calcium, was found to be a good predictor of the amount of calcite dissolved.

The contribution to the carbon dioxide budget by bacteria oxidizing organic matter deep in the aquifers was substantial (3.15 mmol/L), and coequal to the contribution by calcite dissolution (3.05 mmol/L). These contributions can be differentiated by plotting DIC versus alkalinity on a Deffeyes diagram, and by breaking them into their component vectors.

There is no evidence for methanogenic microbial activity on the basis of carbon isotope values. There is also little or no evidence for sulfate reducing bacteria, which can be distinguished from aerobic bacteria on the basis of their byproducts and on the sodium content of the waters. Aerobic bacteria produce CO_2, which causes calcite dissolution and ion exchange with sodium, while sulfate-reducers produce HCO_3^- and no subsequent calcite dissolution and sodium release. Sulfate-reduction can be detected by a sodium deficiency compared with HCO_3^- (alkalinity). In this aquifer system, sulfate-reduction probably occurs only in the deepest part of the 2800 foot aquifer, and its contribution to the total bacterial carbon budget is insignificant.

Bacterial activity is concentrated at particular zones in the deeper aquifers, and is minimal in the rest of the system. In those areas of high productivity ($6.4x10^{-2}$ versus an average productivity of $5.4x10^{-3}$), it is expected that porosity has been corrosively enhanced. The hydraulic conductivities of the 2000 and 2800 foot aquifers, are, in fact, higher than those of the shallower aquifers (Buono, 1983). Due to calcium uptake on clays, all the waters are undersaturated with respect to calcite, although saturation is approached in the deeper sand units. Local microenvironments may develop in which saturation or oversaturation is achieved, and in which calcite may precipitate. However, calcite cementation should be minimal overall.

8.0 REFERENCES

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9.0 FIGURE CAPTIONS

Figure 1. Hydrogeologic section showing the freshwater bearing units in East Feliciana and East Baton Rouge Parishes (from Morgan, 1963). The numbers represent the locations of the wells sampled in this study projected into the field of view.

Figure 2. Map view of study area (hatched) and the regional groundwater system.

Figure 3. Map showing sample locations and cross section line of Figure 1.

Figure 4. DIC plotted versus alkalinity in Deffeyes (1965) diagrams. (A) Reactions cause solutions to change according to a definite stoichiometry. In this case, the addition of CO_2 causes DIC to increase and alkalinity to remain the same. Similarly, addition of a strong base will increase the alkalinity without changing DIC. (B) Calcite dissolution causes alkalinity to increase by two units and DIC to increase by one unit. Since the total change in DIC can be split into component vectors representing a calcite dissolution component and a CO_2 addition component, the amount that each has contributed to the carbon budget can be read from the plot.

Figure 5. Water temperature versus depth of well. Temperature increases with depth from approximately 20°C in the shallow recharge zone to 35°C in the discharge zone.

Figure 6. Hydrogen ion concentration in pH units versus depth of well. Note that pH increases with depth from 5.2 to 8.9 pH units.

Figure 7. Total dissolved inorganic carbon (DIC) versus depth of well. DIC increases with depth from 0.7 mmol/L to 7.5 mmol/L.

Figure 8. Alkalinity versus depth of well. Alkalinity increases with depth from 0.2 meq/L to 6.5 meq/L.

Figure 9. $\delta^{13}C_{DIC}$ versus depth of well. $\delta^{13}C$ is variable, but becomes more enriched with increasing depth. At low DIC concentrations, $\delta^{13}C$ is sensitive to additions to the carbon budget and is therefore more variable at shallow depths where DIC is low overall, than at deeper depths where DIC is considerably higher.

Figure 10. Sodium ion concentration versus depth of well (some data is from Gonthier, 1989). Note that Na increases overall from 5 mg/L to 150 mg/L with increasing depth.

Figure 11. Percent calcite saturation versus depth of well. There is a general increase in calcite saturation with increasing depth.

Figure 12. Crossplot depicting the linear correlation ($r^2 = 0.93$) between calcium and magnesium in mg/L.

Figure 13. Calcium ion concentration versus depth of well. Calcium concentrations are highest in the shallow aquifers, and decrease non-linearly to nearly constant and low values in the deeper aquifers. Recharge waters are also low in calcium.

Figure 14. Magnesium ion concentration versus depth of well. Magnesium concentrations are highest in the shallow aquifers, and decrease non-linearly to essentially zero in the deeper aquifers. Recharge waters are also low in magnesium.

Figure 15. Chloride ion concentration versus depth of well (data from Gonthier, 1989). Chloride is invariant and low, except for four shallow (400-600 foot aquifer) wells with elevated contents . Although the 400-600 foot aquifers suffer from saltwater intrusion (Whiteman, 1979), the absence of corresponding elevated Na contents suggests an anthropogenic source (Gonthier and Aharon, 1990).

Figure 16. Silicic acid content versus depth of well. Silicic acid content of the waters appears to decrease (albeit with considerable scatter) with depth in the deeper aquifers, and is variable in the recharge and shallow aquifer zones.

Figure 17. Changes in DIC content of the waters within each aquifer sand unit. Water from the recharge zone has a low DIC content while the deepest "2800-foot" sand has the highest overall DIC content. All of the intermediate aquifers have intermediate values. The variability within each sand unit reflects their heterogeneity and also indicates that the sampled wells are not always aligned along flow paths.

Figure 18. Changes in the alkalinity content of the waters within each aquifer sand unit. Water from the recharge zone has a low alkalinity content while the deepest "2800-foot" sand has the highest overall alkalinity content. All of the intermediate aquifers have intermediate values. The variability within each sand unit reflects their heterogeneity and also indicates that the sampled wells are not always aligned along flow paths.

Figure 19. Changes in Na content of the waters within each aquifer sand unit. Water from the recharge zone has a low Na content while the deepest "2800-foot" sand has the highest overall Na content. All of the intermediate aquifers have intermediate values. The variability within each sand unit reflects their heterogeneity and also indicates that the sampled wells are not aligned along flow paths. The patterns for Na match those for alkalinity very well; the match between Na and DIC is less good.

Figure 20. Linear correlation between Na and alkalinity. There is nearly a 1:1 relationship between these two parameters.

Figure 21. DIC versus alkalinity for the water samples. Note that DIC and alkalinity are linearly correlated. The departure of the points from the "bicarbonate" line suggests the presence of excess CO_2 (see text).

Figure 22. Changes in $\delta^{13}C$ composition of DIC within each aquifer sand unit. $\delta^{13}C$ is quite variable at all depths, and can be relatively heavy even in the recharge zone. Overall, there is a ^{13}C enrichment with increasing depth from approximately -22°/oo to -13°/oo. $\delta^{13}C$ is very sensitive to small changes in DIC or alkalinity at low concentrations overall, and thus shows irregular responses down flow.

Figure 23. Contours of chemical parameters across a north-south section of the Southeast Louisiana aquifer system. Well locations were projected onto a general cross section line running from Amite County, Mississippi to East Baton Rouge Parish, Louisiana (Figures 1 and 3). Concentrations of various parameters have been plotted and contoured on the general cross section. The patterns for each parameter are similar, but vary in distinctive ways. (a) DIC (mmol/L), (b) alkalinity (meq/L), (c) Na (mg/L), (d) % calcite saturation, (e) $\delta^{13}C$ (°/ooPDB), (f) H_4SiO_4 (mg/L). Generally, in the discharge area, the gradients are low until the 2400 and 2800 foot sands are reached. Further north, however, there

are steep chemical gradients in the 1700, 2000, 2400, and 2800 foot sands. In the discharge area and deep aquifers, $\delta^{13}C$ (e) contours are similar to DIC, alkalinity, NA, and % saturation (a-d). In the recharge area and shallow aquifers, the pattern of $\delta^{13}C$ enrichment is different, because $\delta^{13}C$ is more sensitive to small changes in DIC and alkalinity when the initial DIC content is low overall. The chemical contours of H_4SiO_4 (f) differ from the others in two significant ways: (1) where (a) through (e) increase, (f) decreases; and (2) H_4SiO_4 content is very variable in the shallow aquifers throughout the whole area. This suggests that local mineralogy and other conditions have more impact on H_4SiO_4 concentrations than does overall, downflow, chemical change. All the waters plot in the kaolinite stability field.

Figure 24. Deffeyes plot of DIC versus alkalinity used to determine the relative proportions of CO_2 added by organic degradation versus bicarbonate added via calcite dissolution. In this example, the amount of additional CO_2 brought into the system is 3.15 mmol/L and the amount of HCO_3^- derived from calcite dissolution is 3.05 mmol/L. The $\delta^{13}C$ value of the incoming CO_2 is calculated to be -22.2.

Figure 25. Deffeyes plot of DIC versus alkalinity used to determine the relative proportions of organically-derived CO_2 versus HCO_3^- from calcite dissolution in two high productivity areas marked on Figure 23a as 2-2′ and 3-3′.

Table 1: Bacterially-mediated processes and resultant carbon isotope ($\delta^{13}C$), total dissolved inorganic carbon (DIC), and alkalinity (Alk.) changes.

CO_2 Source	Reaction Type	$\delta^{13}C$ (°/oo PDB)	DIC	Alk.
Rainwater infiltration	$CO_2+H_2O \longrightarrow H_2CO_3{*}$	-6:-7	inc.	dec.
Bacterial oxidation	$CH_2O+O_2 \longrightarrow CO_2+H_2O$	-12:-26	inc.	dec.
Carbonate dissolution	$CaCO_3+H_2CO_3{*} \longrightarrow 2HCO_3{}^-+Ca^{++}$	2:-5	inc.	inc.
Sulfate reduction	$2CH_2O+SO_4{}^{--} \longrightarrow H_2S+2HCO_3{}^-$	-12:-26	inc.	inc.
Anaerobic fermentation	$CH_3COOH \longrightarrow CH_4+CO_2$	10:30	inc.	dec.
Aerobic methane oxidation	$CH_4+2O_2 \longrightarrow CO_2+2H_2O$	-30:-60	inc.	dec.

FIGURE 1

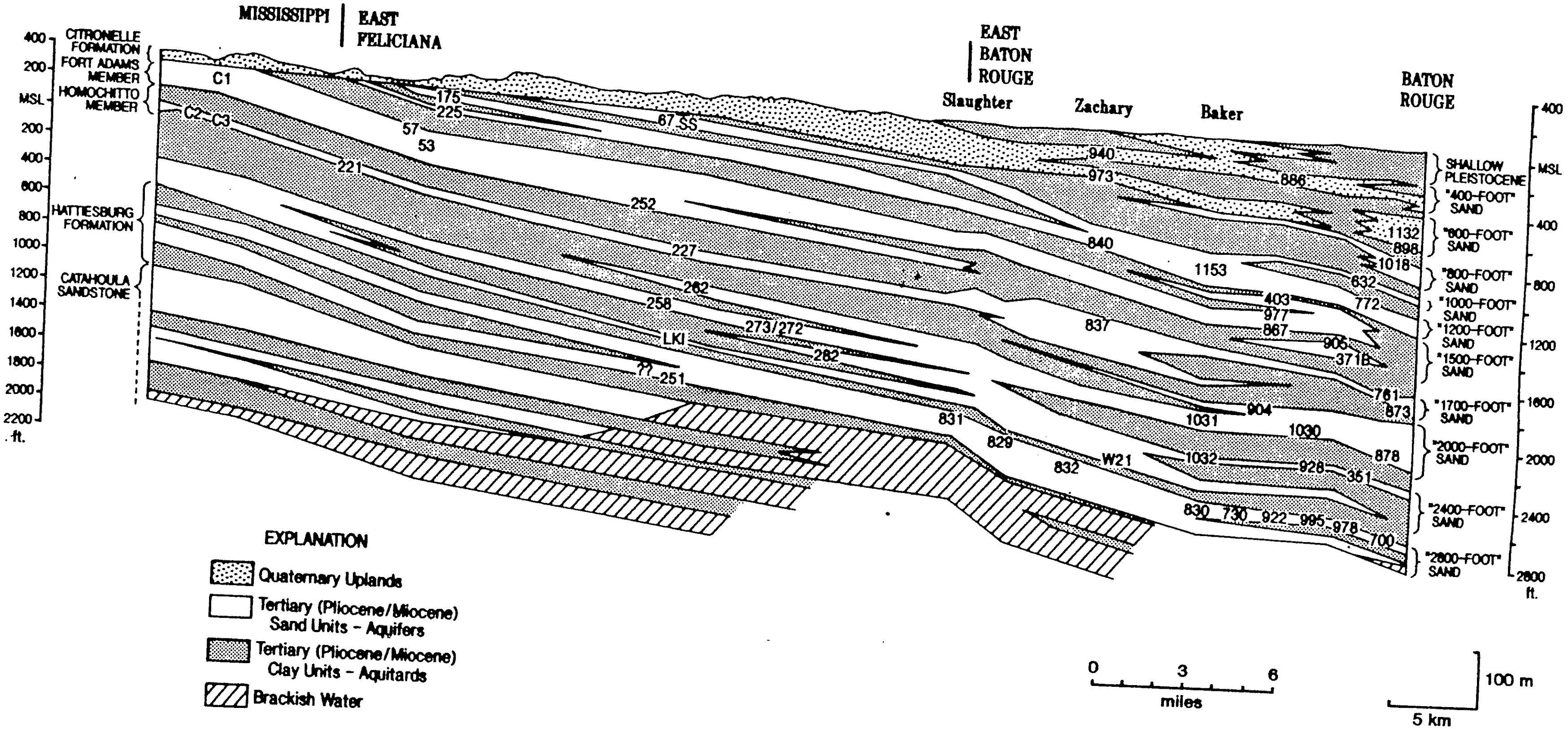

MISSISSIPPI
EAST FELICIANA
EAST BATON ROUGE
Slaughter
Zachary
Baker
BATON ROUGE
400
200
MSL
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
ft.
CITRONELLE FORMATION
FORT ADAMS MEMBER
HOMOCHITTO MEMBER
HATTIESBURG FORMATION
CATAHOULA SANDSTONE
C1
C2
C3
175
225
57
53
67
SS
221
252
227
262
258
LKI
273/272
282
??
251
940
973
886
840
1132
898
1018
1153
632
403
772
977
867
837
905
371B
761
873
904
1031
1030
831
829
832
W21
1032
928
351
878
830
730
922
995
978
700
SHALLOW PLEISTOCENE
"400-FOOT" SAND
"600-FOOT" SAND
"800-FOOT" SAND
"1000-FOOT" SAND
"1200-FOOT" SAND
"1500-FOOT" SAND
"1700-FOOT" SAND
"2000-FOOT" SAND
"2400-FOOT" SAND
"2800-FOOT" SAND
400
MSL
400
800
1200
1600
2000
2400
2800
ft.
EXPLANATION
Quaternary Uplands
Tertiary (Pliocene/Miocene) Sand Units - Aquifers
Tertiary (Pliocene/Miocene) Clay Units - Aquitards
Brackish Water
0
3
6
miles
100 m
5 km

FIGURE 2

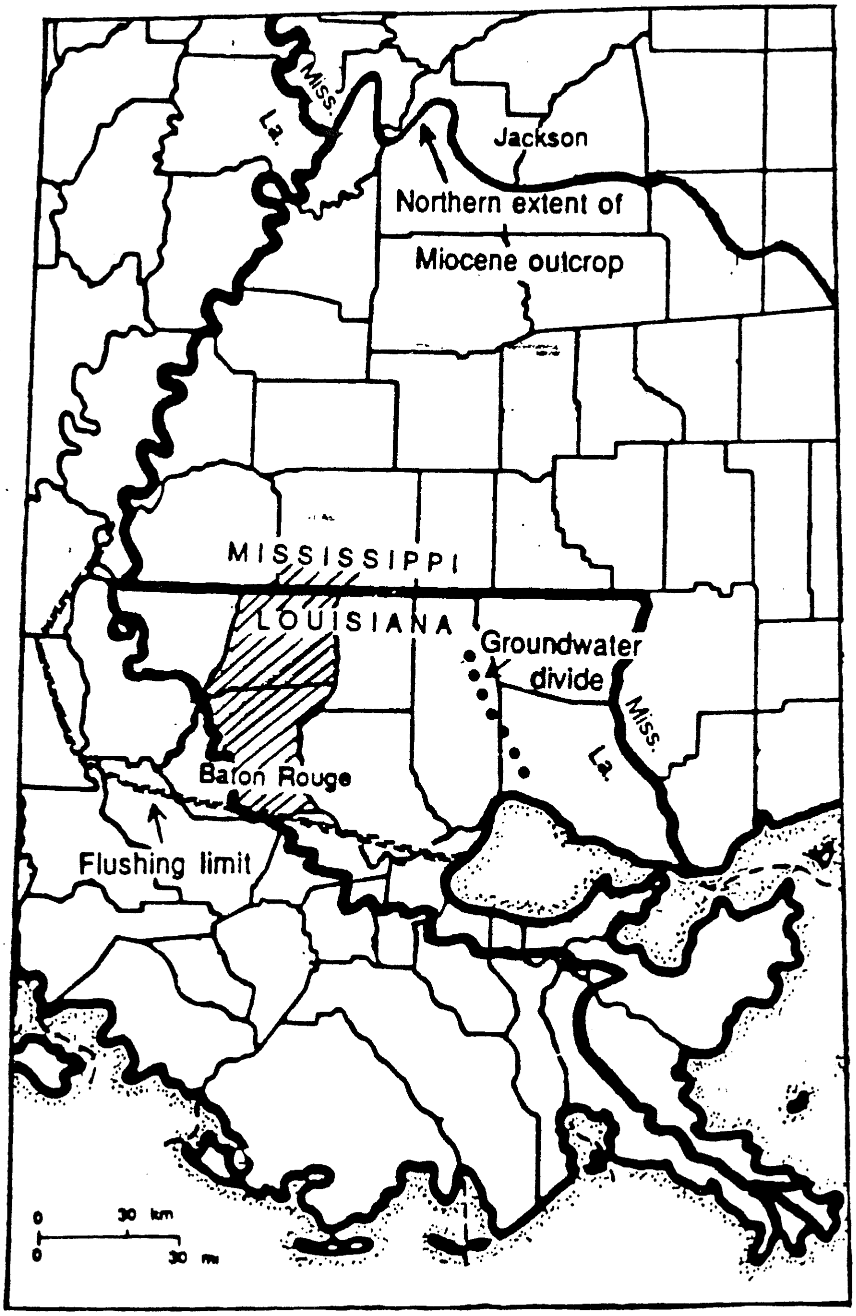

Miss.
La.
Jackson
Northern extent of
Miocene outcrop
MISSISSIPPI
LOUISIANA
Groundwater
divide
Miss.
La.
Baton Rouge
Flushing limit
0
30 km
0
30 mi

FIGURE 3

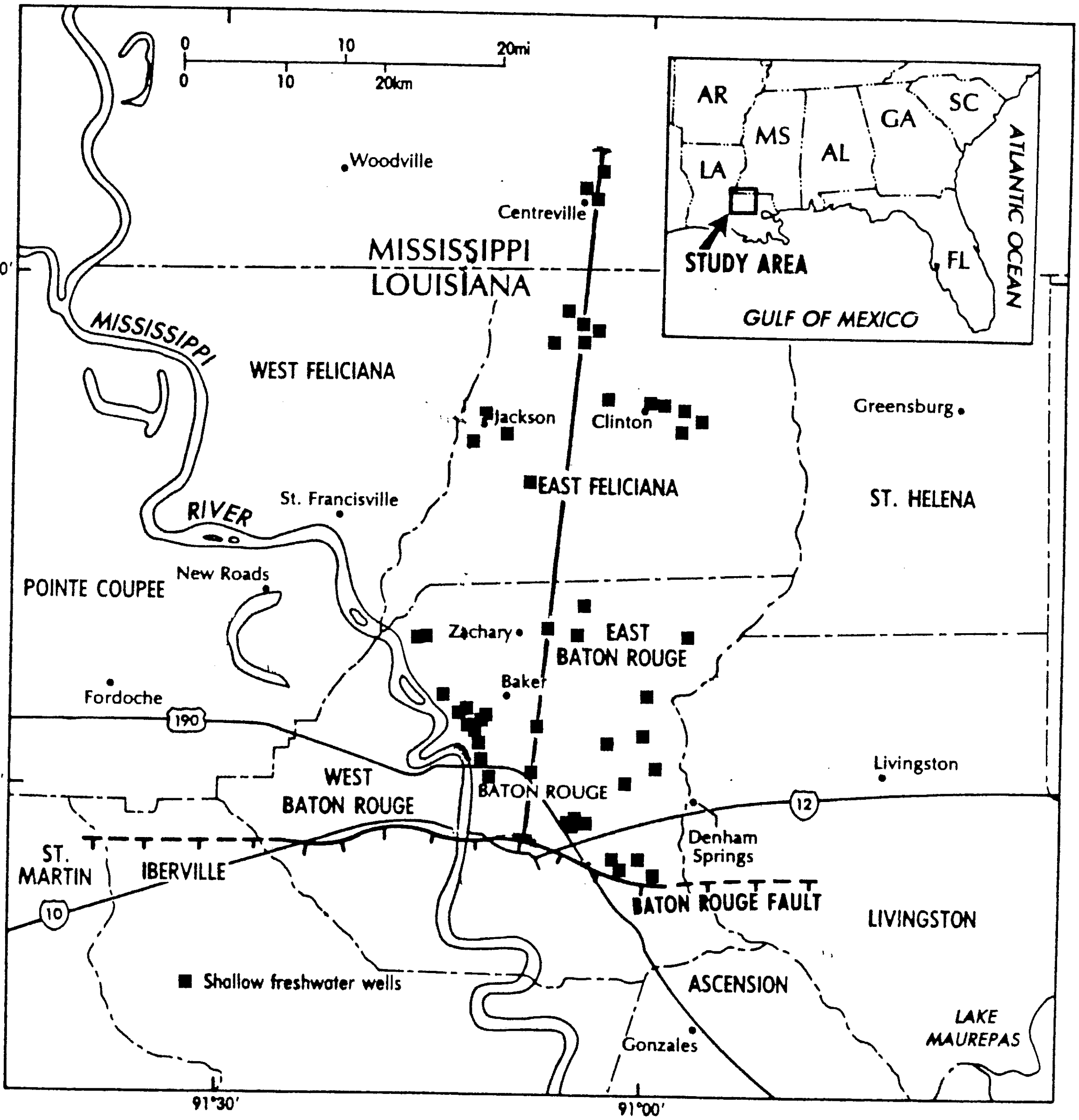
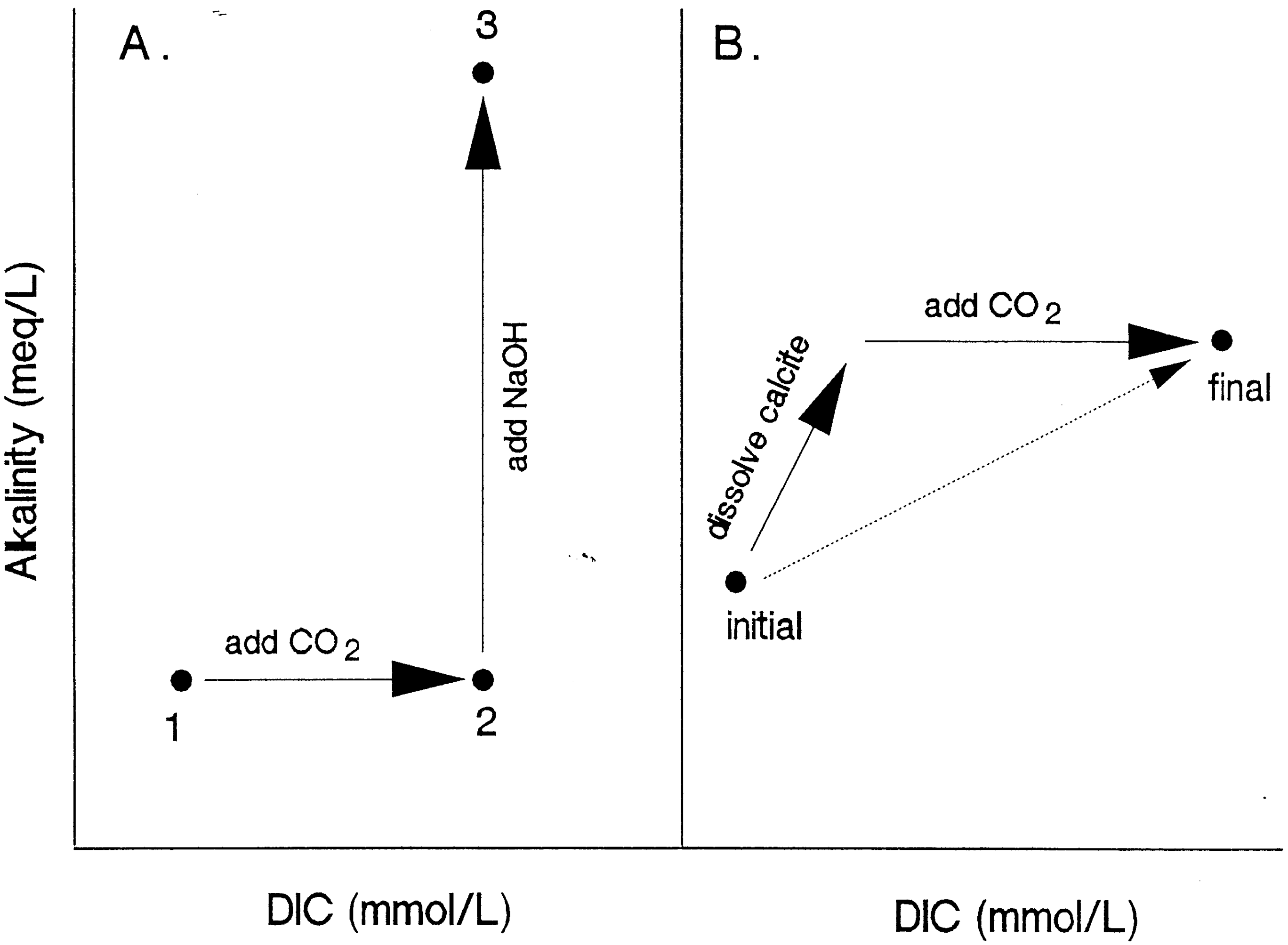

0
10
20mi
0
10
20km
Woodville
Centreville
MISSISSIPPI
LOUISIANA
31°00′
MISSISSIPPI
RIVER
WEST FELICIANA
Jackson
Clinton
Greensburg
EAST FELICIANA
St. Francisville
ST. HELENA
POINTE COUPEE
New Roads
Zachary
EAST
BATON ROUGE
Baker
Fordoche
190
30°30′
WEST
BATON ROUGE
BATON ROUGE
Livingston
12
Denham
Springs
ST.
MARTIN
IBERVILLE
10
BATON ROUGE FAULT
LIVINGSTON
Shallow freshwater wells
ASCENSION
LAKE
MAUREPAS
Gonzales
91°30′
91°00′
AR
MS
AL
GA
SC
LA
STUDY AREA
FL
ATLANTIC OCEAN
GULF OF MEXICO

FIGURE 4



A.
3
add NaOH
add CO_2
1
2
Alkalinity (meq/L)
DIC (mmol/L)
B.
add CO_2
final
dissolve calcite
initial
DIC (mmol/L)

FIGURE 5

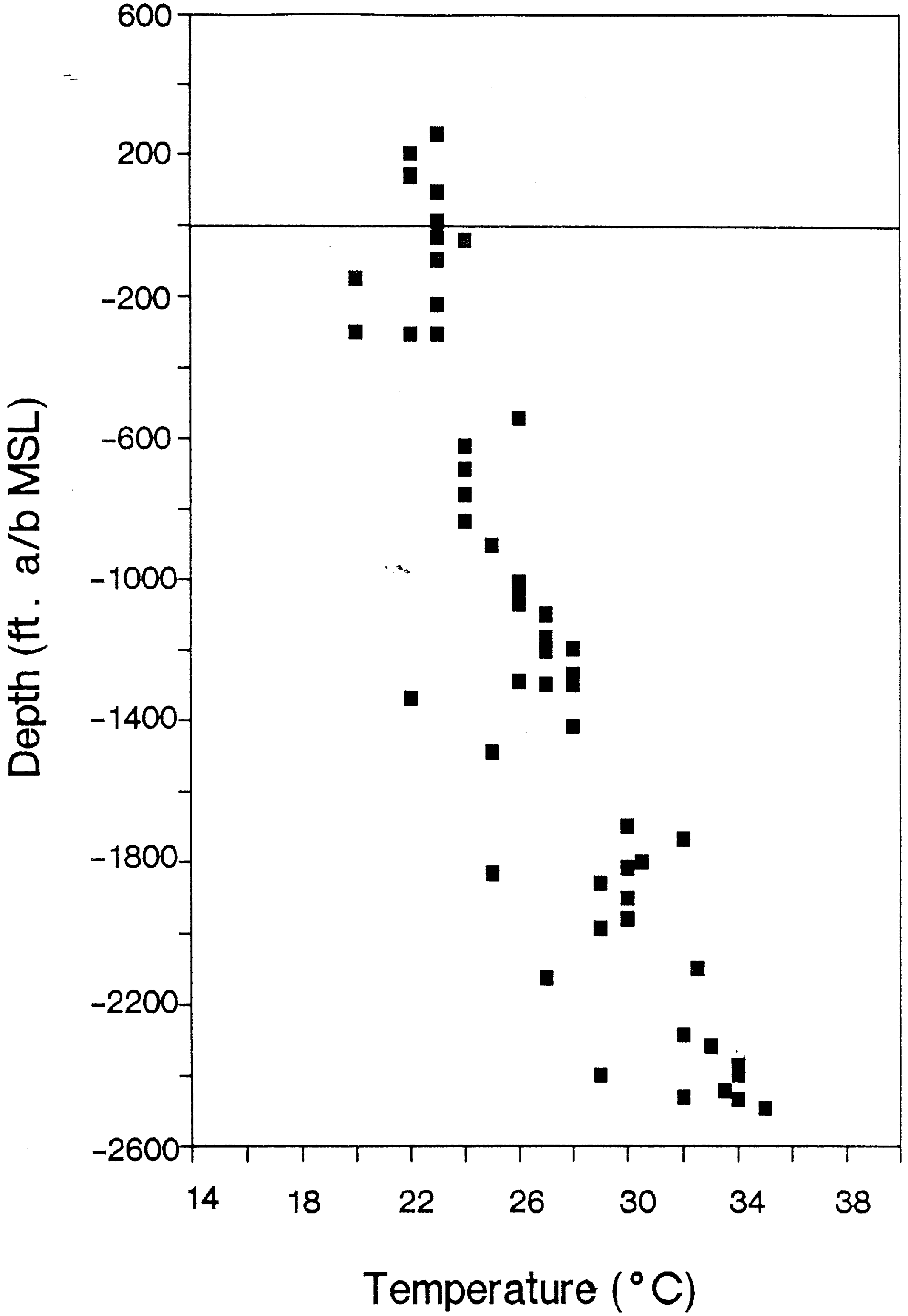

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft . a/b MSL)
14
18
22
26
30
34
38
Temperature (°C)

FIGURE 6

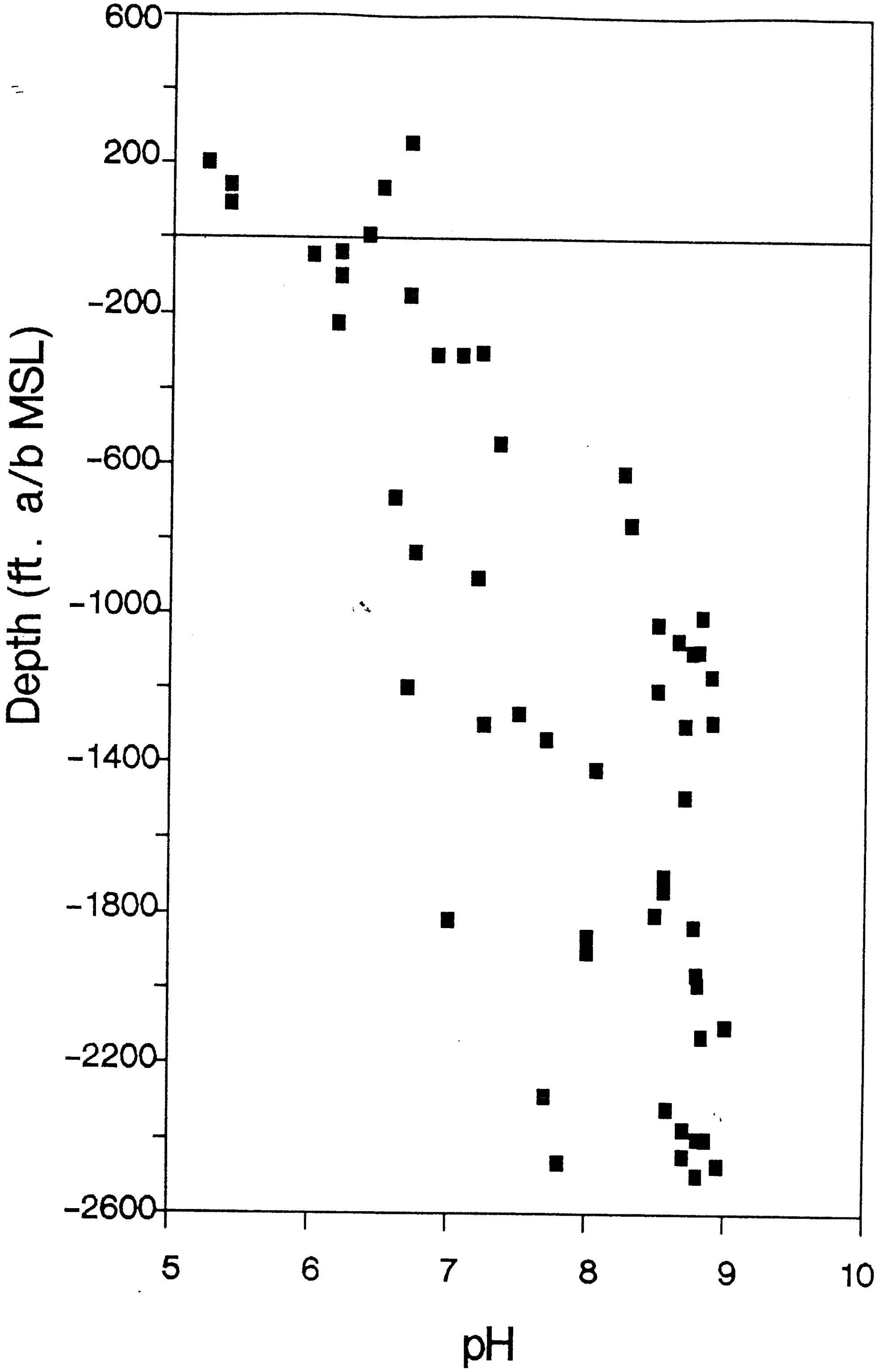
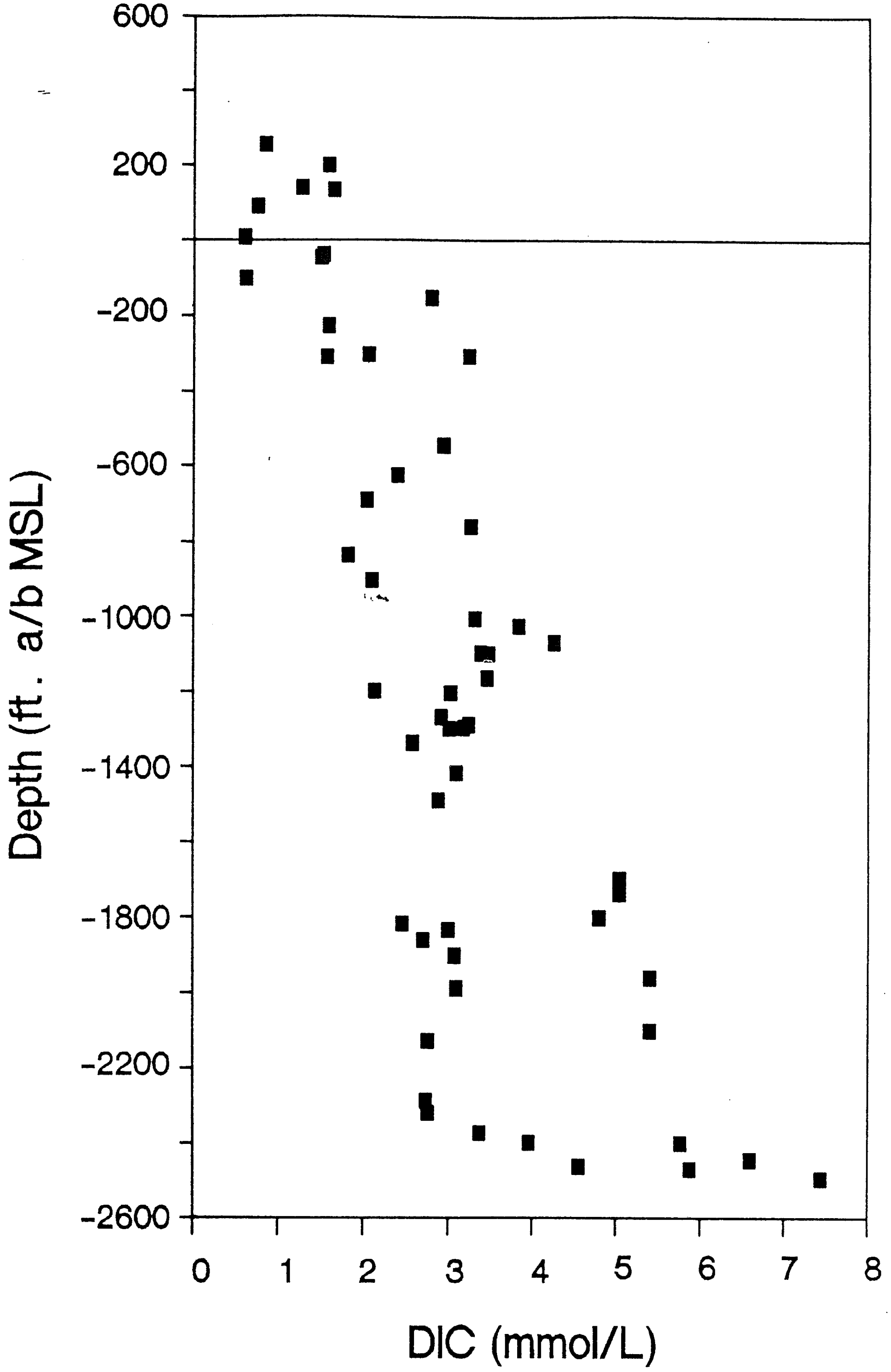

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
5
6
7
8
9
10
pH

FIGURE 7



600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
1
2
3
4
5
6
7
8
DIC (mmol/L)

FIGURE 8

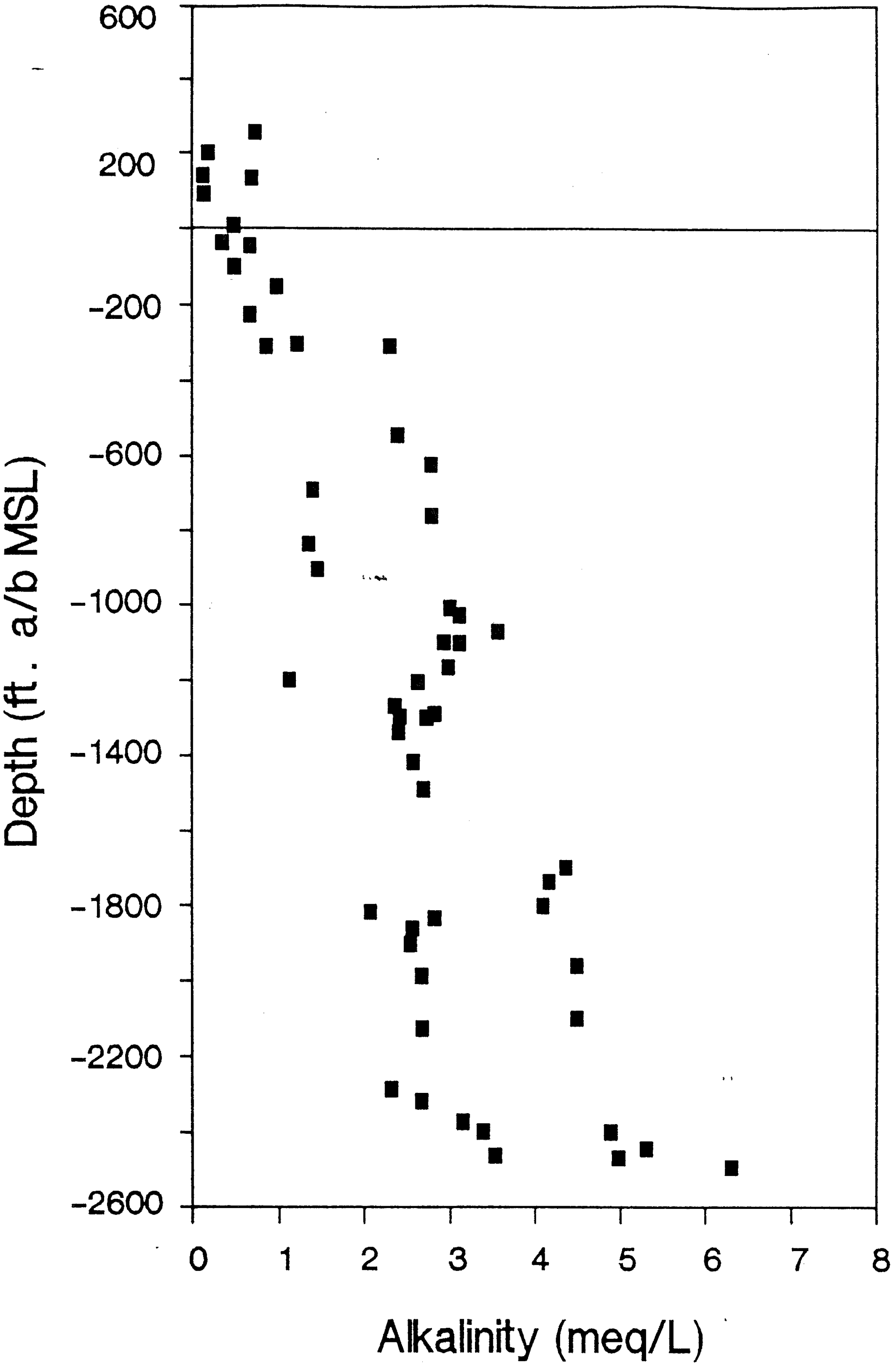

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
1
2
3
4
5
6
7
8
Alkalinity (meq/L)

FIGURE 9

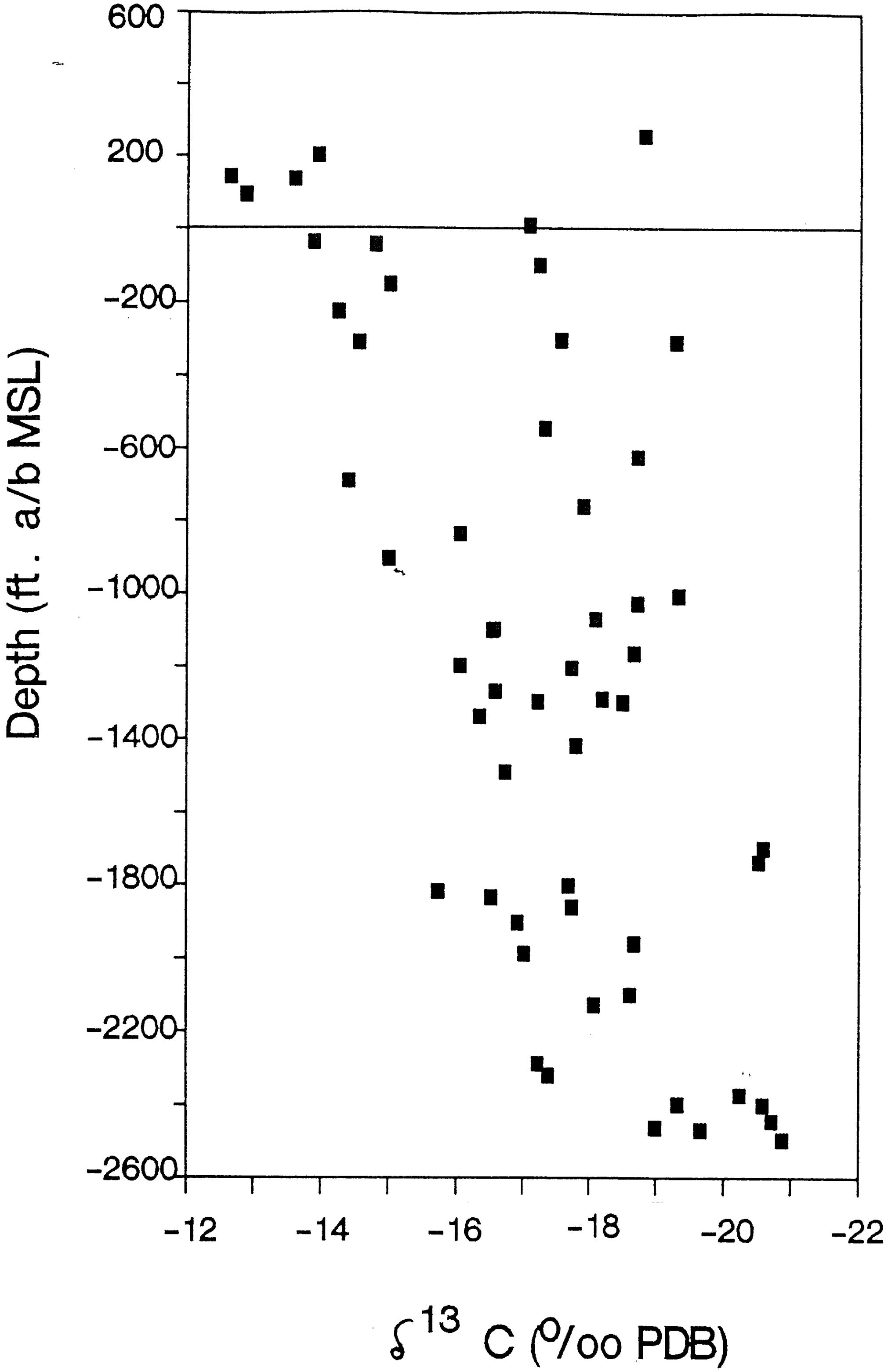

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
-12
-14
-16
-18
-20
-22
δ13 C (0/oo PDB)

FIGURE 10

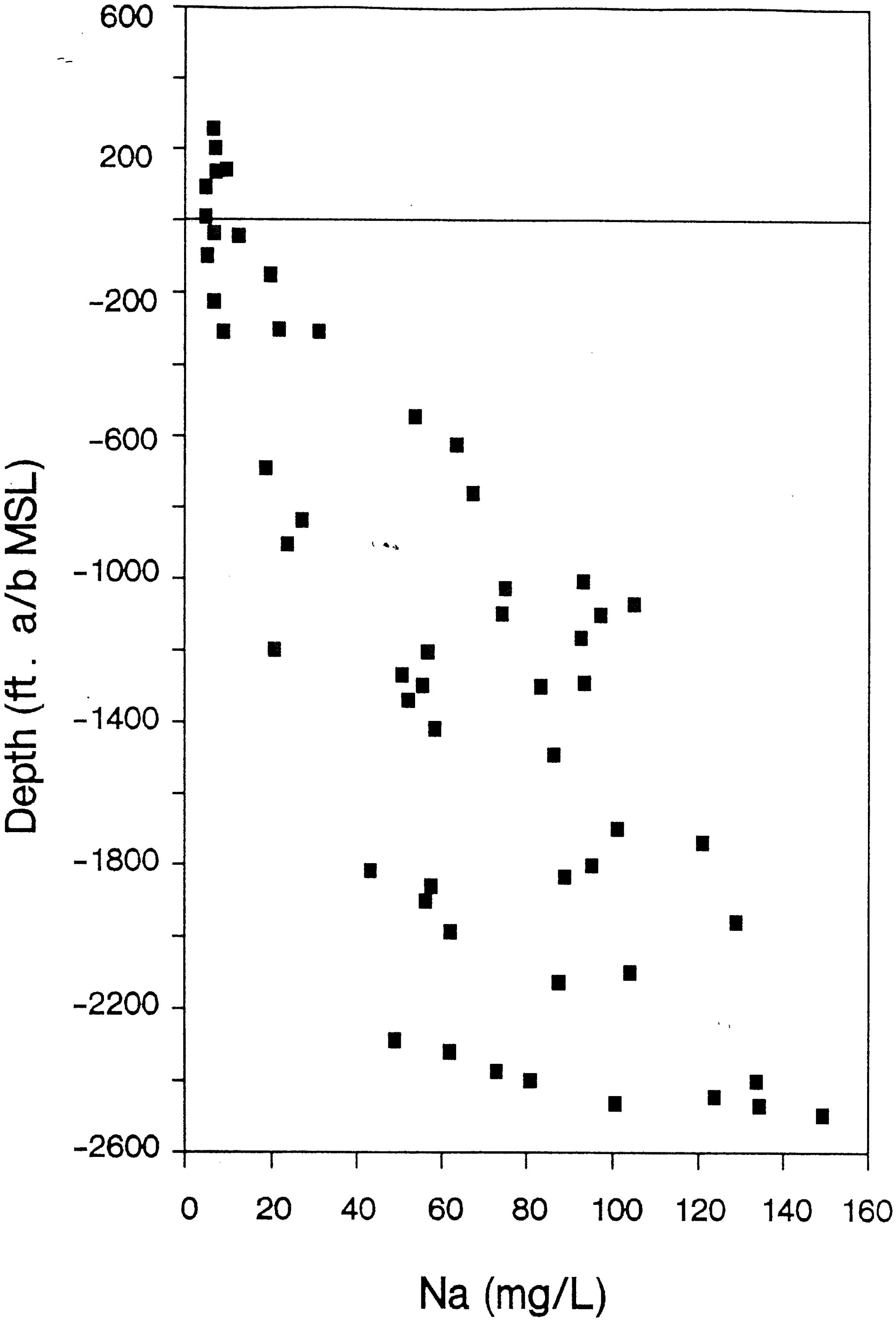

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
20
40
60
80
100
120
140
160
Na (mg/L)

FIGURE 11

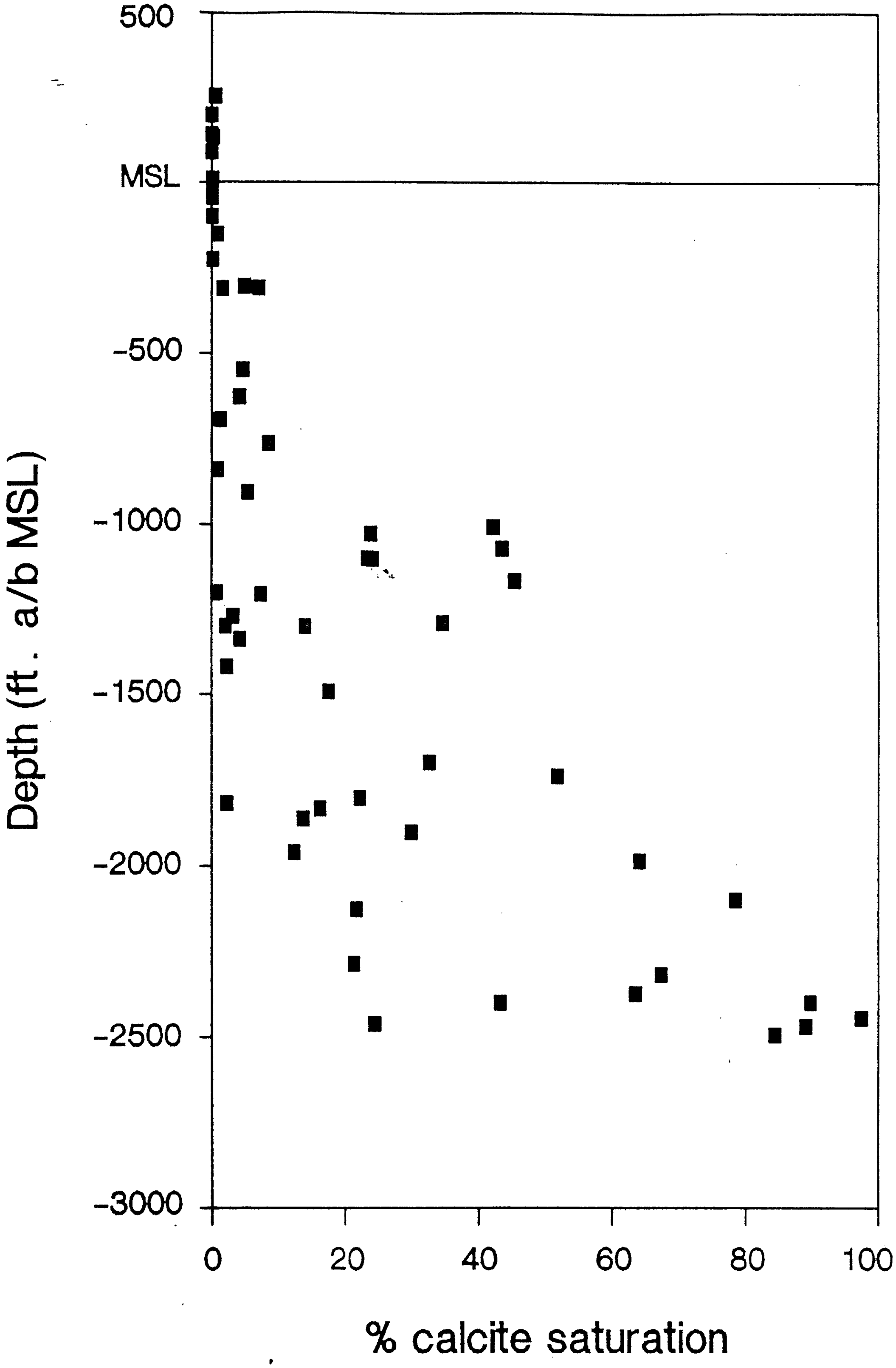
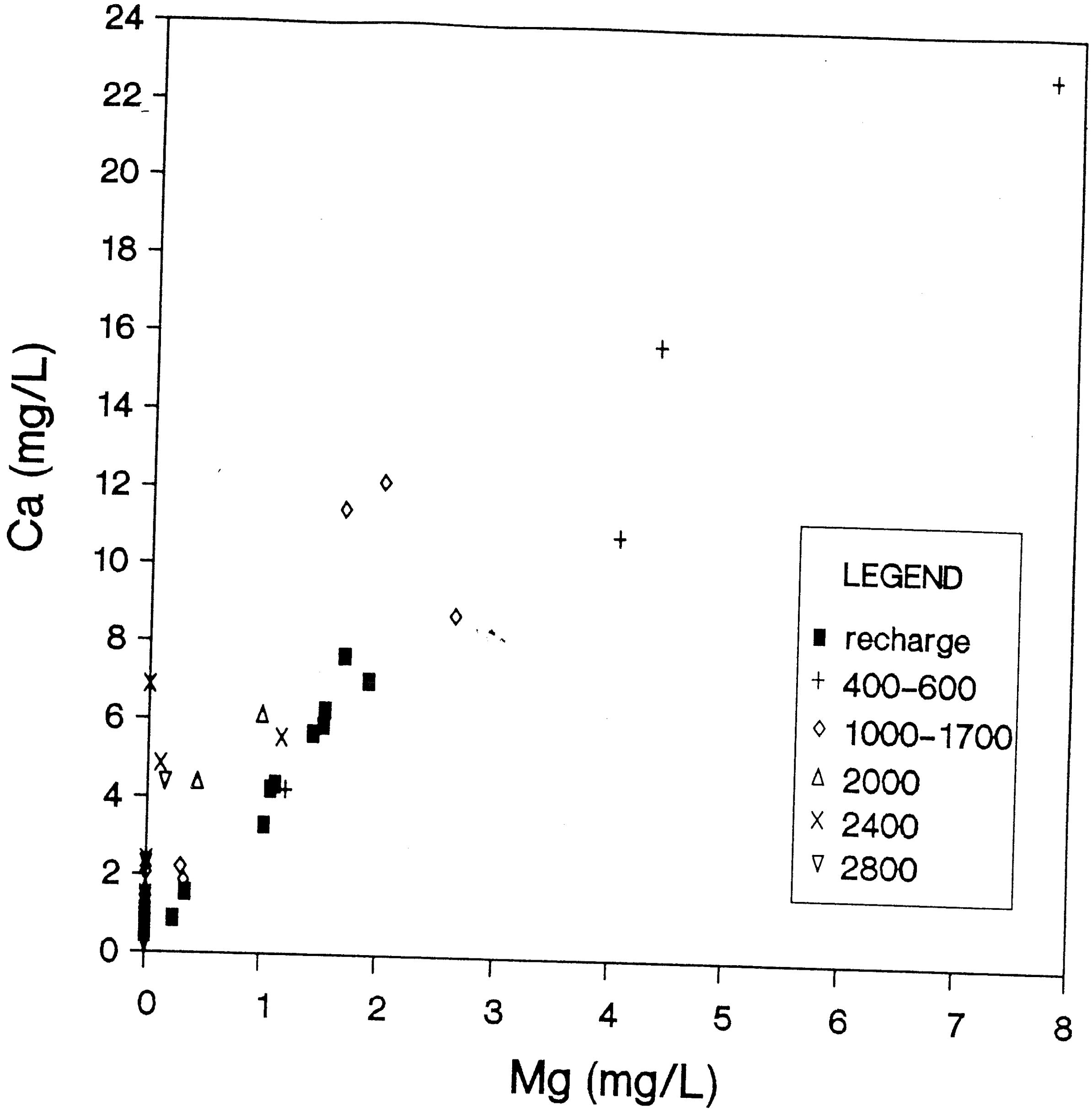

500
MSL
-500
-1000
-1500
-2000
-2500
-3000
Depth (ft. a/b MSL)
0
20
40
60
80
100
% calcite saturation

FIGURE 12



24
22
20
18
16
14
12
10
8
6
4
2
0
Ca (mg/L)
0
1
2
3
4
5
6
7
8
Mg (mg/L)
LEGEND
■ recharge
+ 400-600
◇ 1000-1700
△ 2000
X 2400
▽ 2800

FIGURE 13

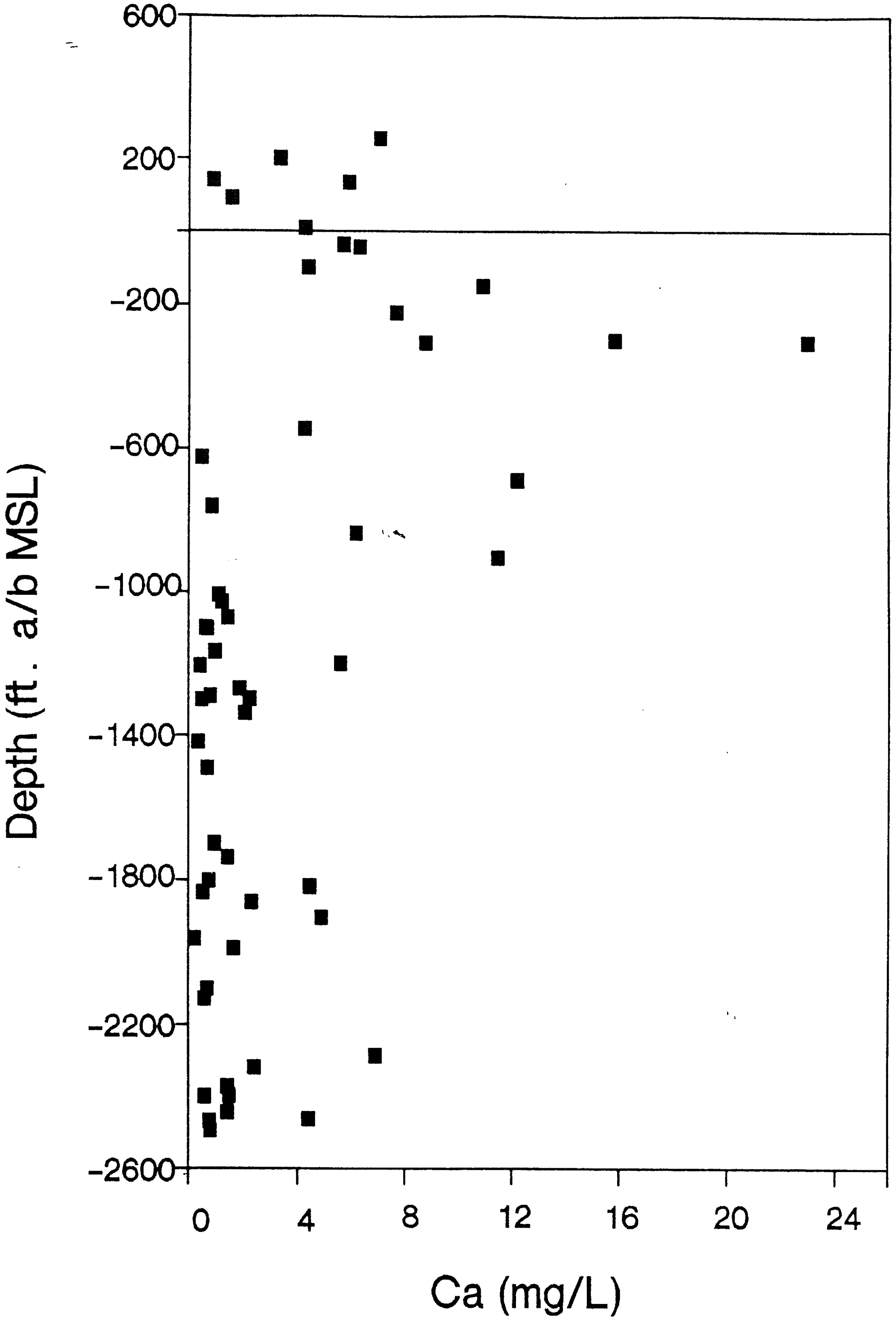

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
4
8
12
16
20
24
Ca (mg/L)

FIGURE 14

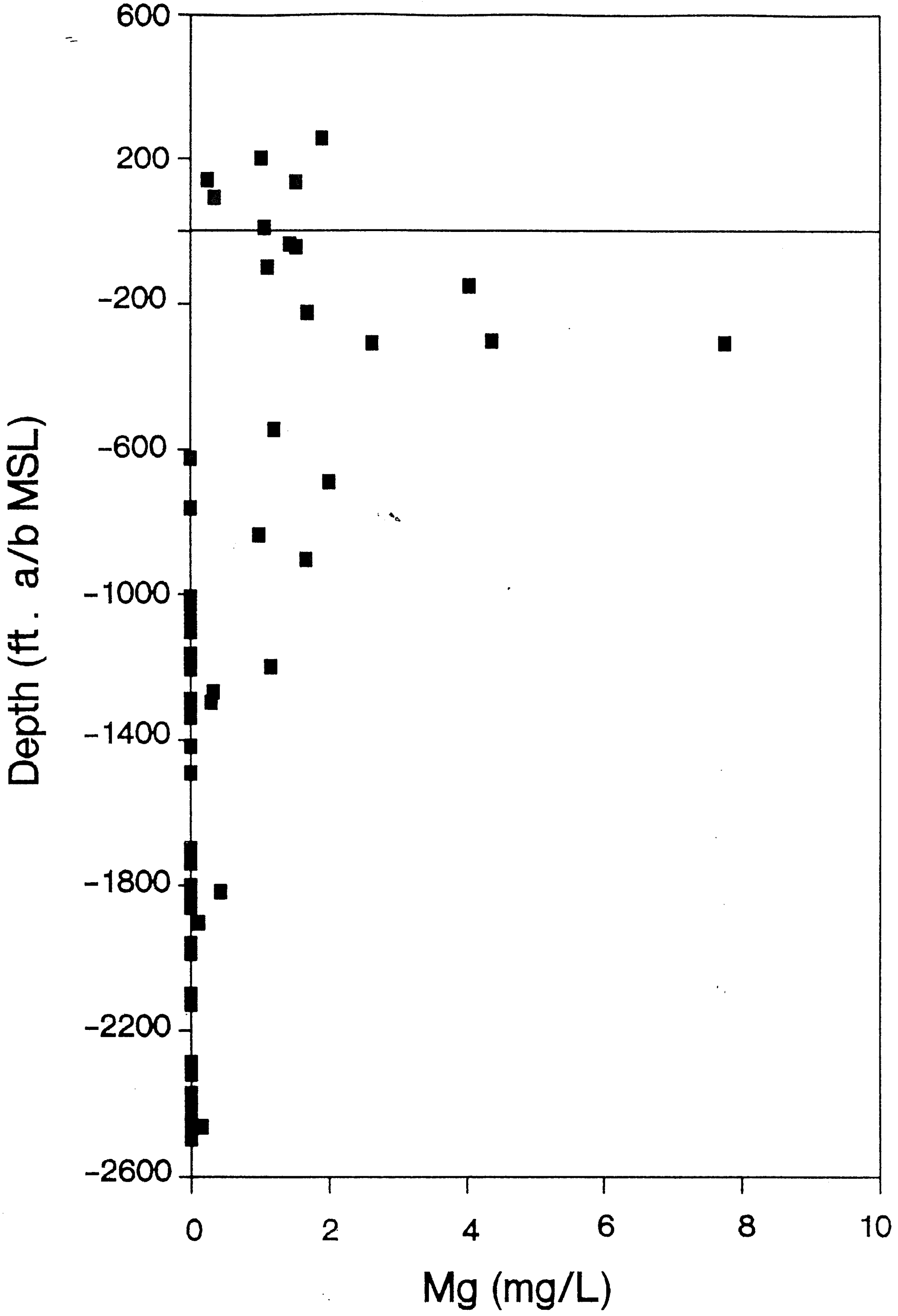

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
2
4
6
8
10
Mg (mg/L)

FIGURE 15

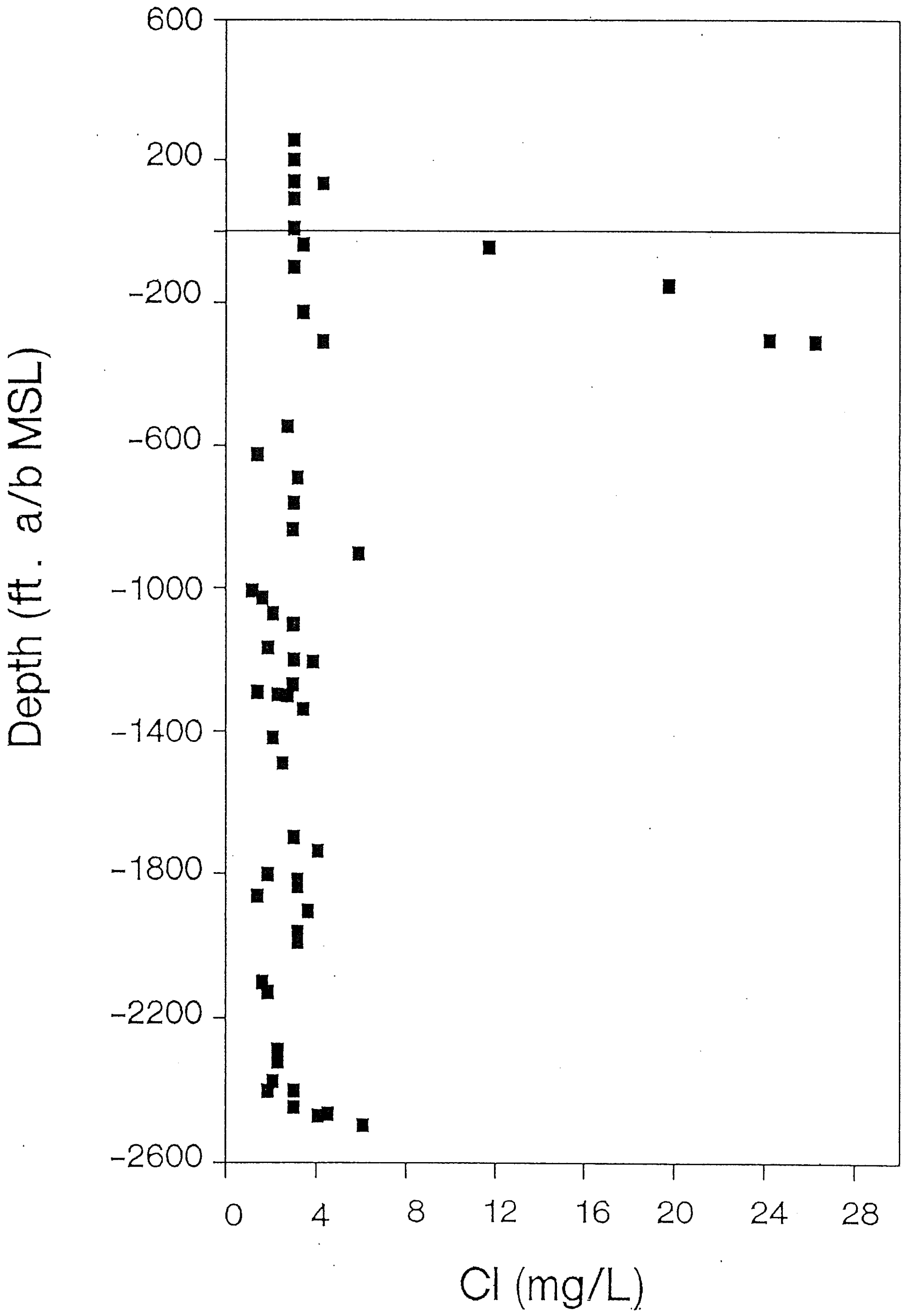

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
4
8
12
16
20
24
28
Cl (mg/L)

FIGURE 16

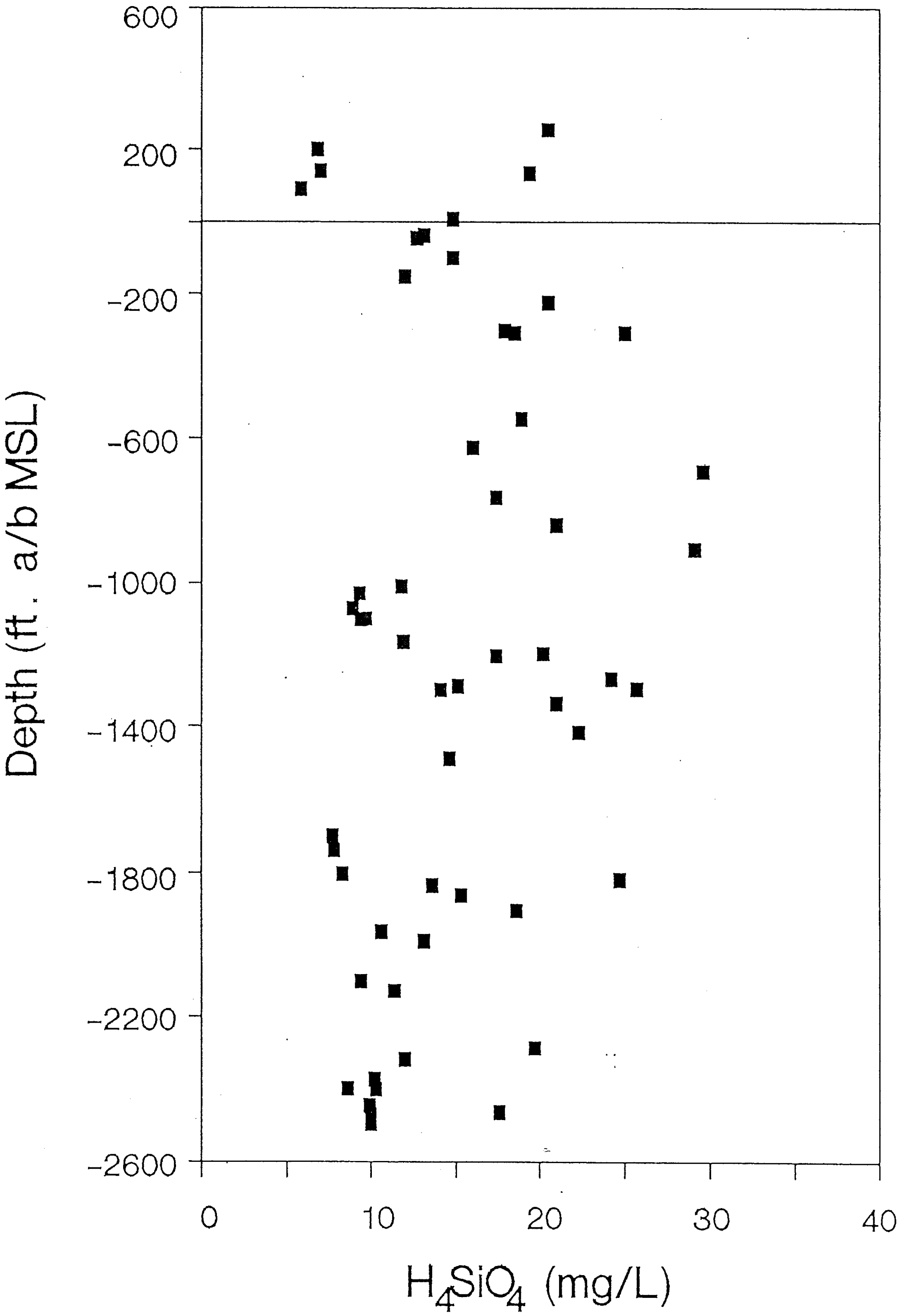
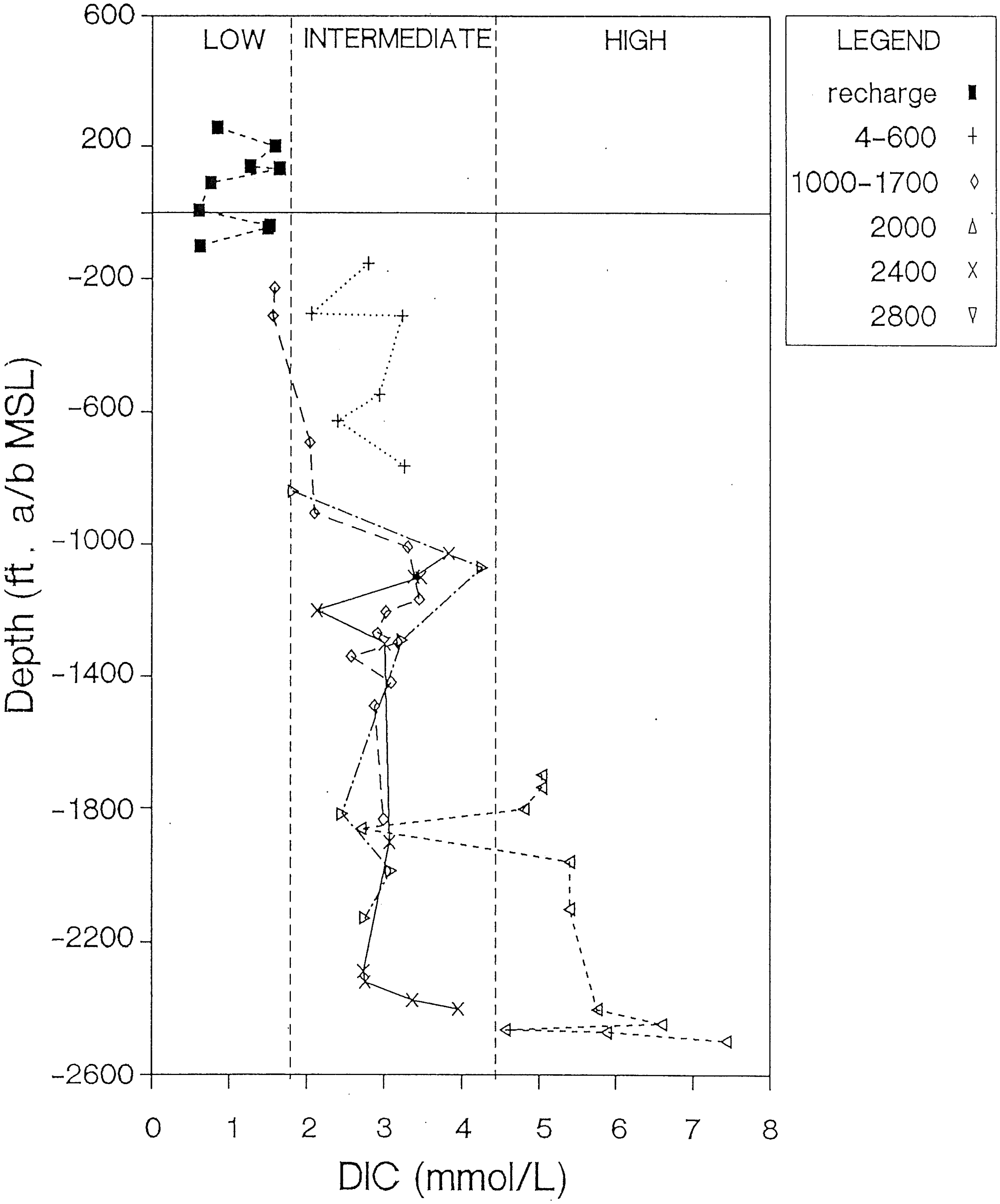
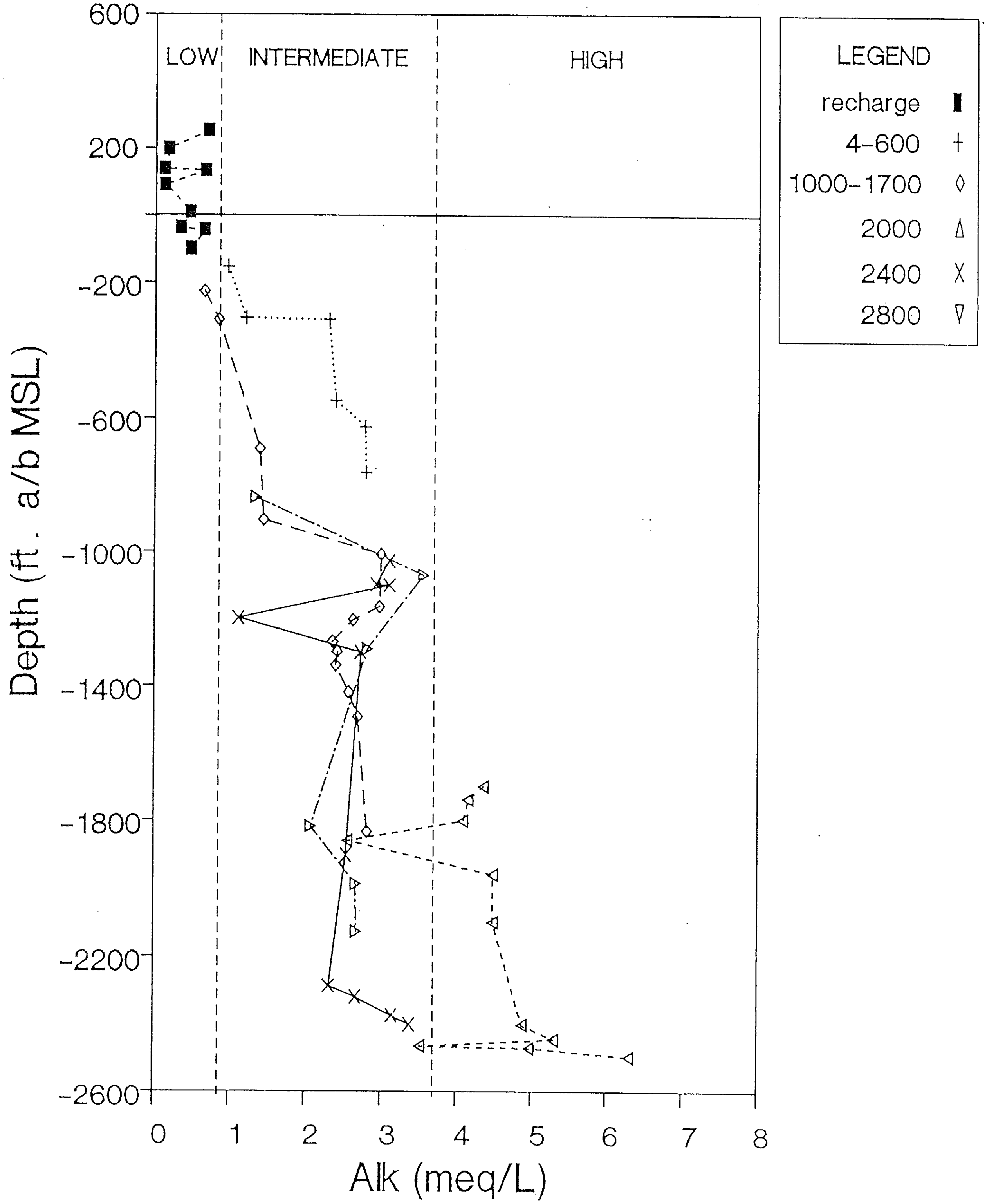

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
10
20
30
40
H_4SiO_4 (mg/L)

FIGURE 17



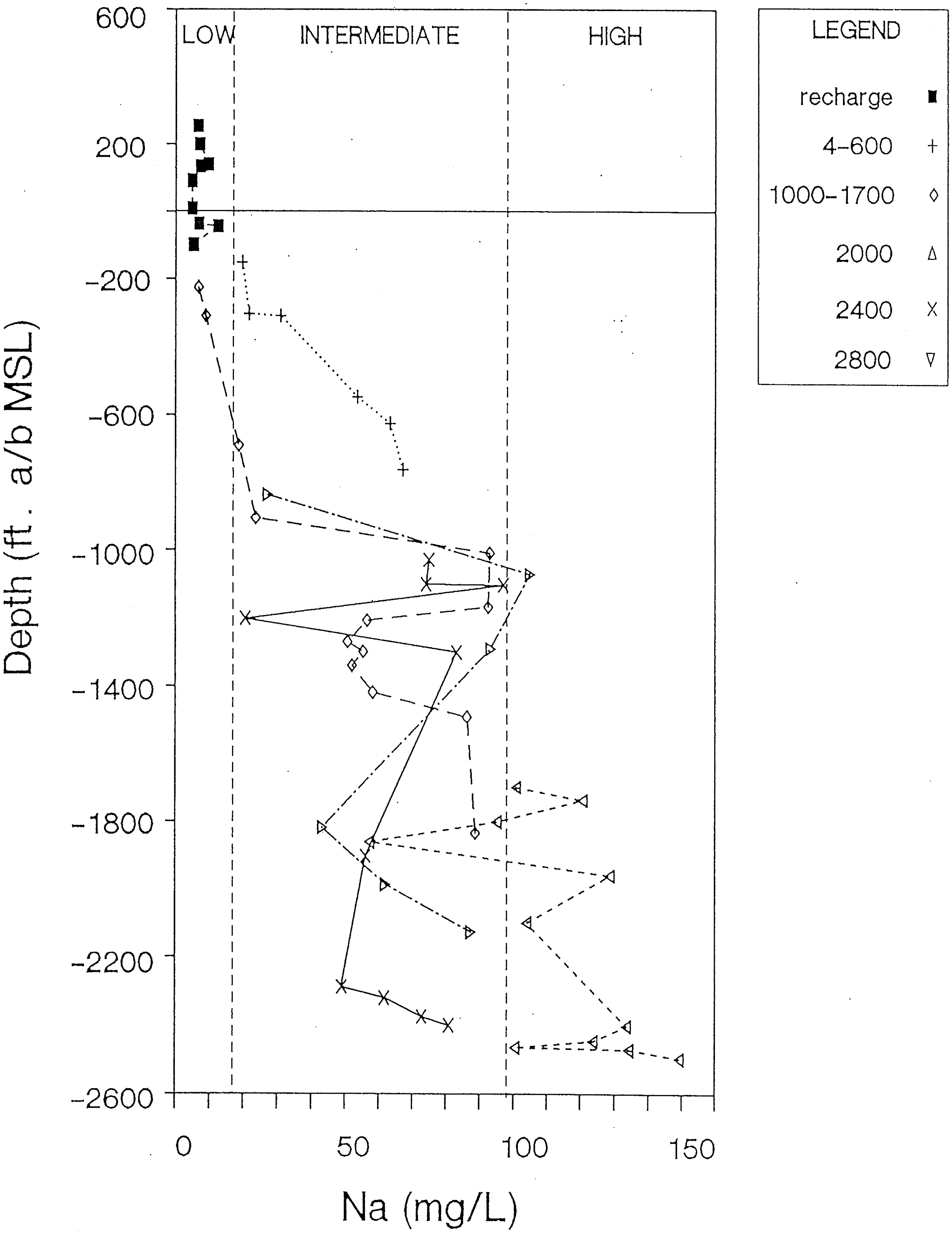
LOW
INTERMEDIATE
HIGH
LEGEND
recharge ■
4-600 +
1000-1700 ◊
2000 △
2400 X
2800 ▽
600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft . a/b MSL)
0
1
2
3
4
5
6
7
8
DIC (mmol/L)

FIGURE 18



LOW
INTERMEDIATE
HIGH
LEGEND
recharge ■
4-600 +
1000-1700 ◊
2000 △
2400 X
2800 ▽
600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
1
2
3
4
5
6
7
8
Alk (meq/L)

FIGURE 19



LOW
INTERMEDIATE
HIGH
LEGEND
recharge ▪
4-600 +
1000-1700 ◊
2000 Δ
2400 X
2800 ∇
600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
50
100
150
Na (mg/L)

FIGURE 20

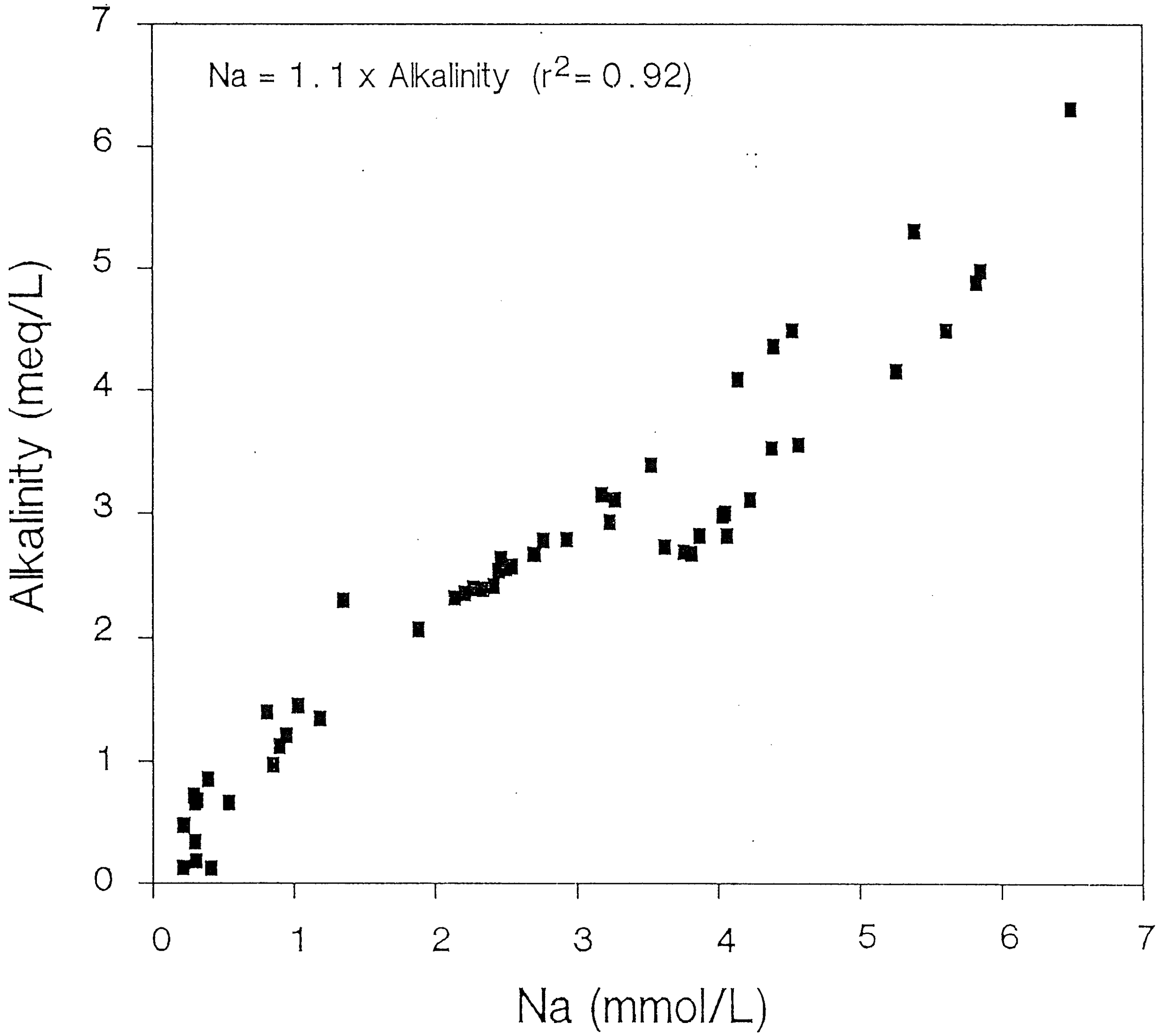

Na = 1.1 x Alkalinity (r^2= 0.92)
Alkalinity (meq/L)
Na (mmol/L)
0
1
2
3
4
5
6
7
0
1
2
3
4
5
6
7

FIGURE 21

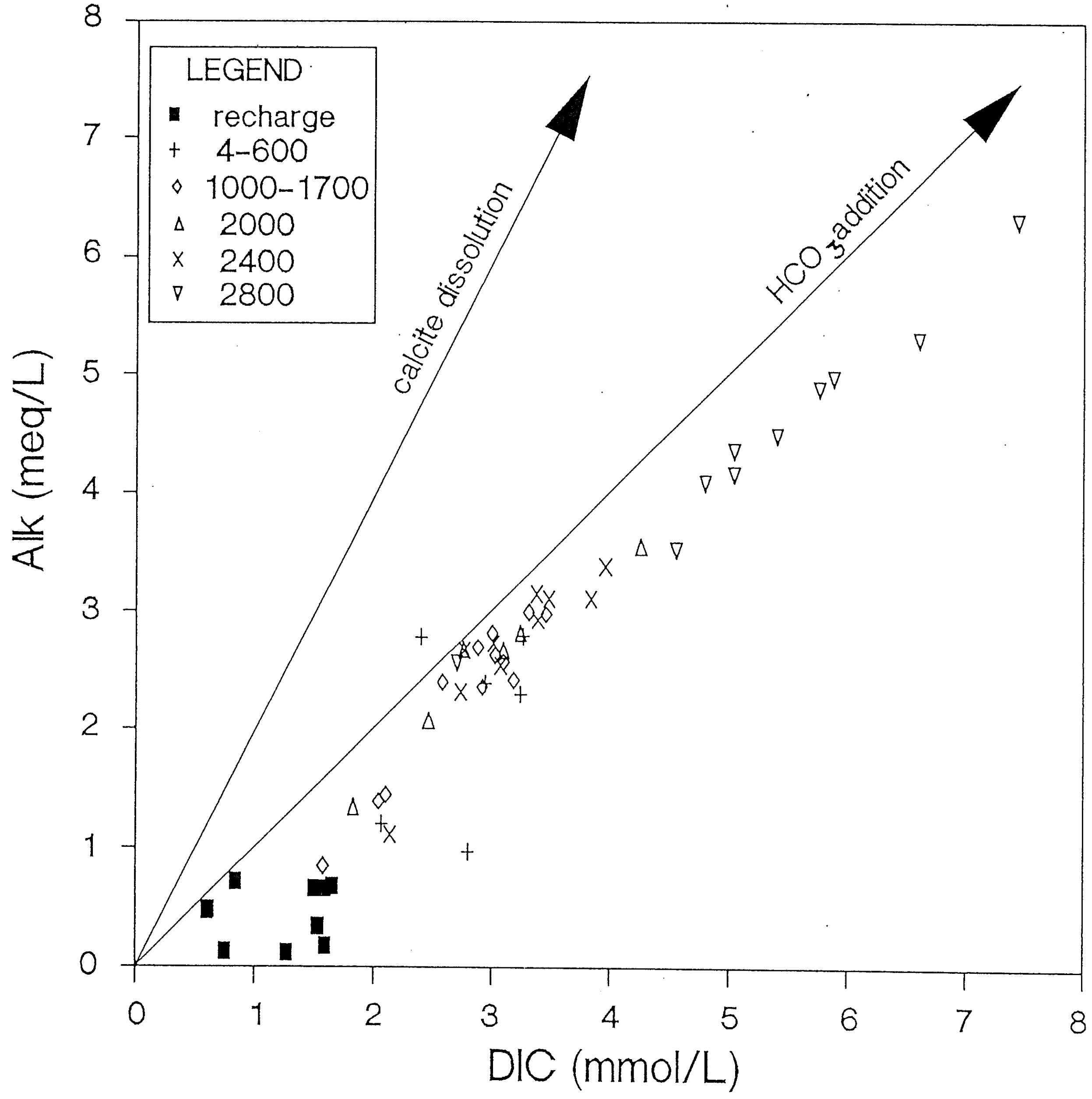
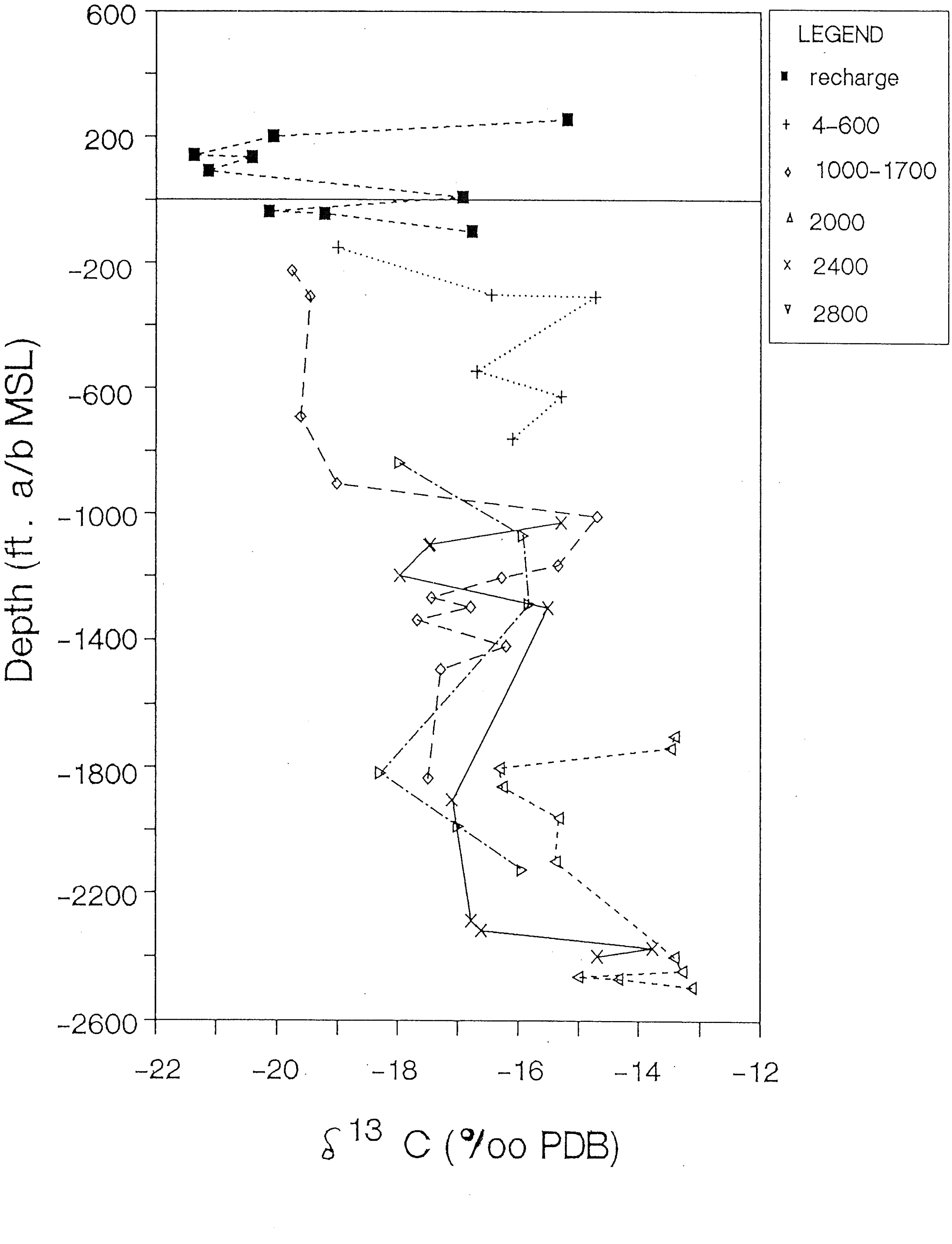

LEGEND
■ recharge
+ 4-600
◇ 1000-1700
△ 2000
× 2400
▽ 2800
calcite dissolution
HCO 3 addition
Alk (meq/L)
DIC (mmol/L)
0
1
2
3
4
5
6
7
8
0
1
2
3
4
5
6
7
8

FIGURE 22



LEGEND
■ recharge
+ 4-600
◊ 1000-1700
△ 2000
× 2400
▽ 2800
Depth (ft . a/b MSL)
600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
-22
-20
-18
-16
-14
-12
δ^{13} C (‰ PDB)

FIGURE 23 a

DIC (mmol/L)

Contour Interval = 0.5 mmol/L

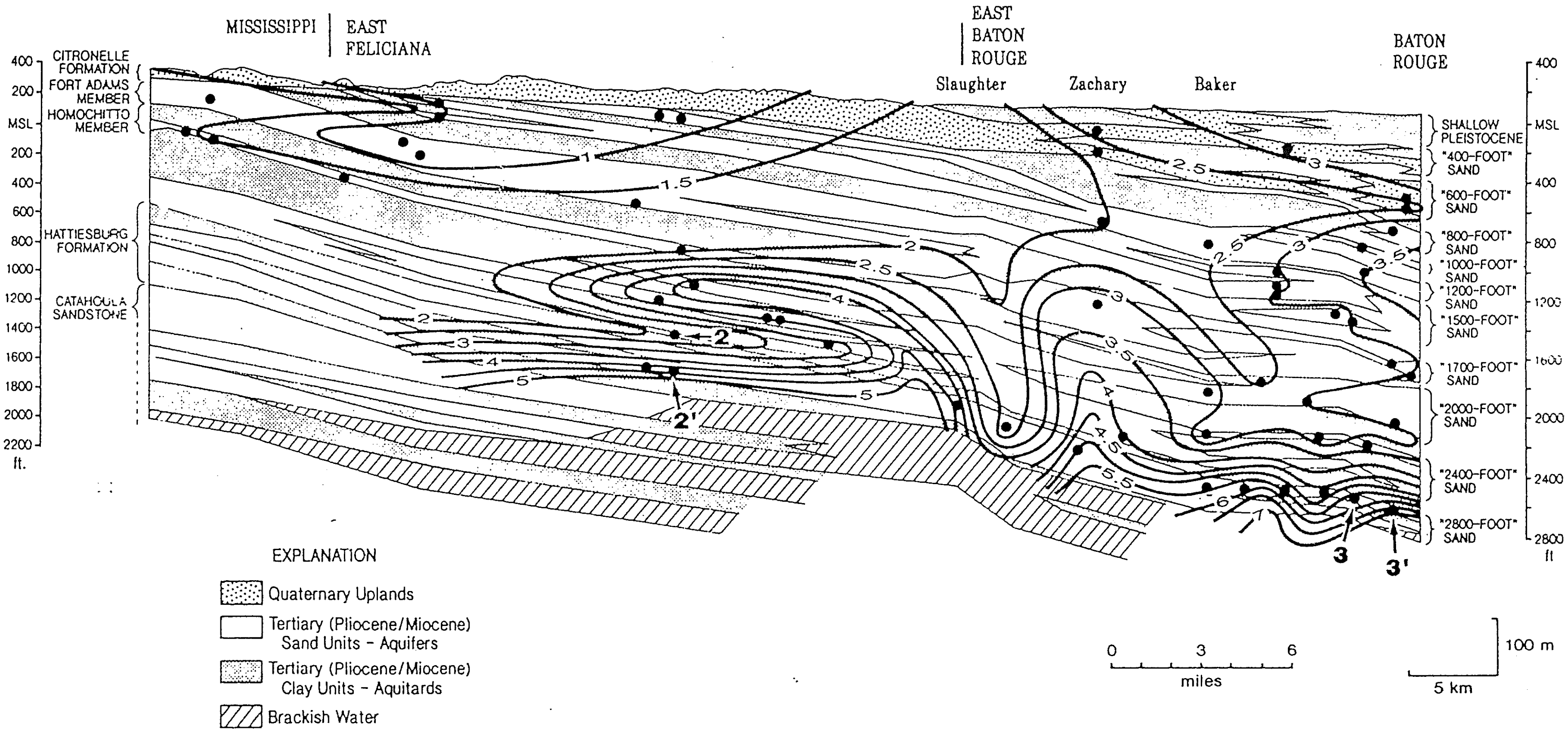


FIGURE 23 b

Alkalinity (meq/L)

Contour Interval = 0.5 meq/L

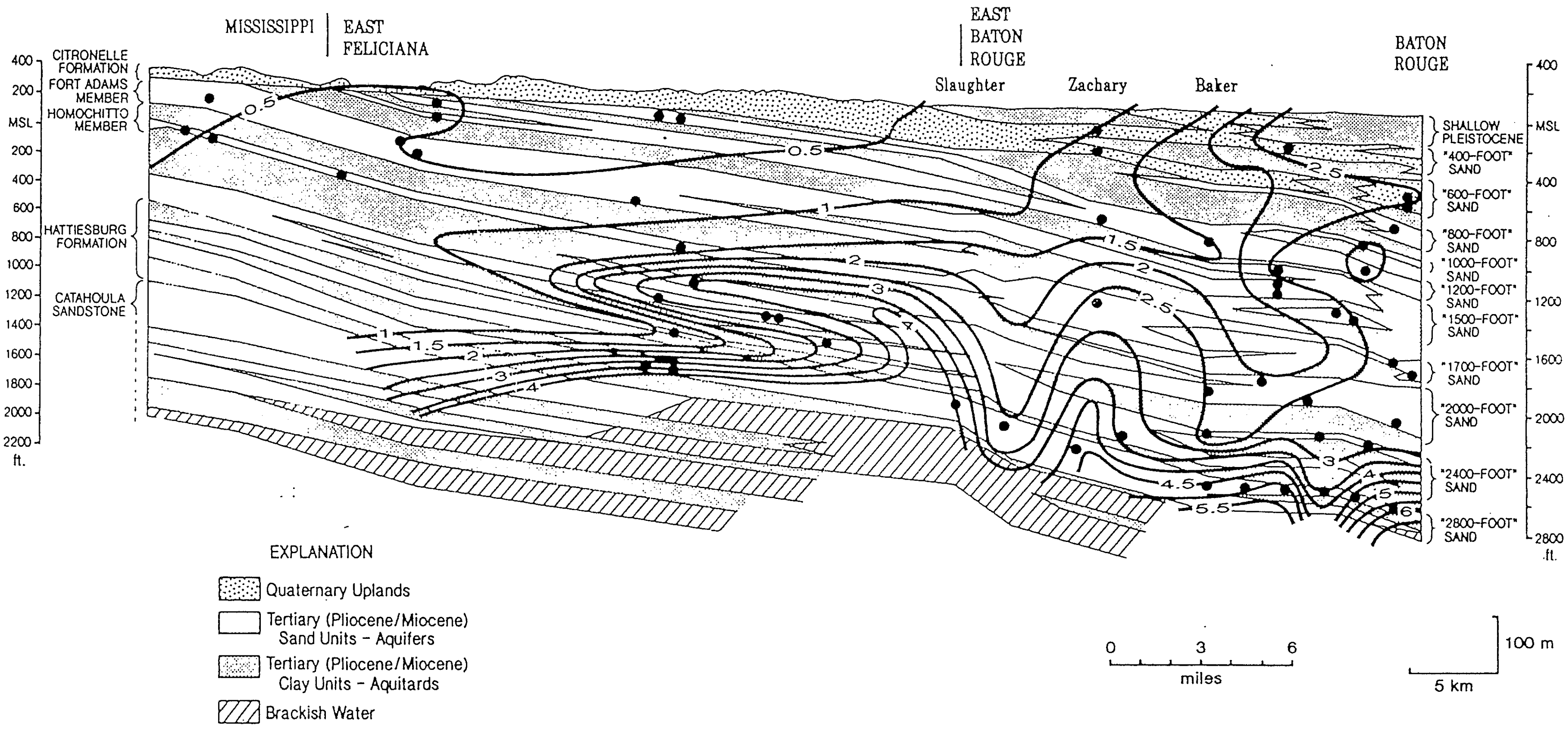


FIGURE 23 c

Na (ppm)

Contour Interval = 20 ppm

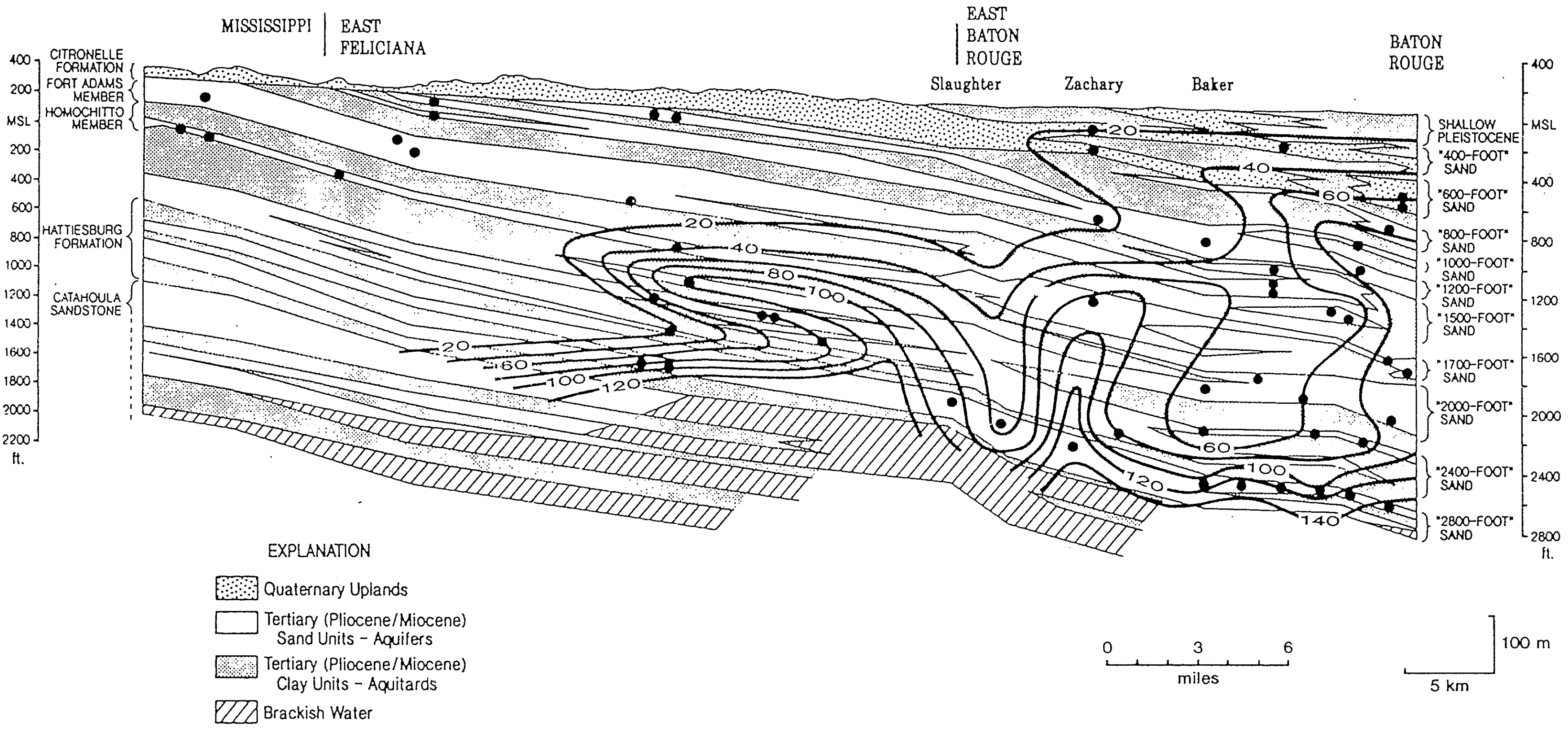


FIGURE 23 d

% Calcite Saturation

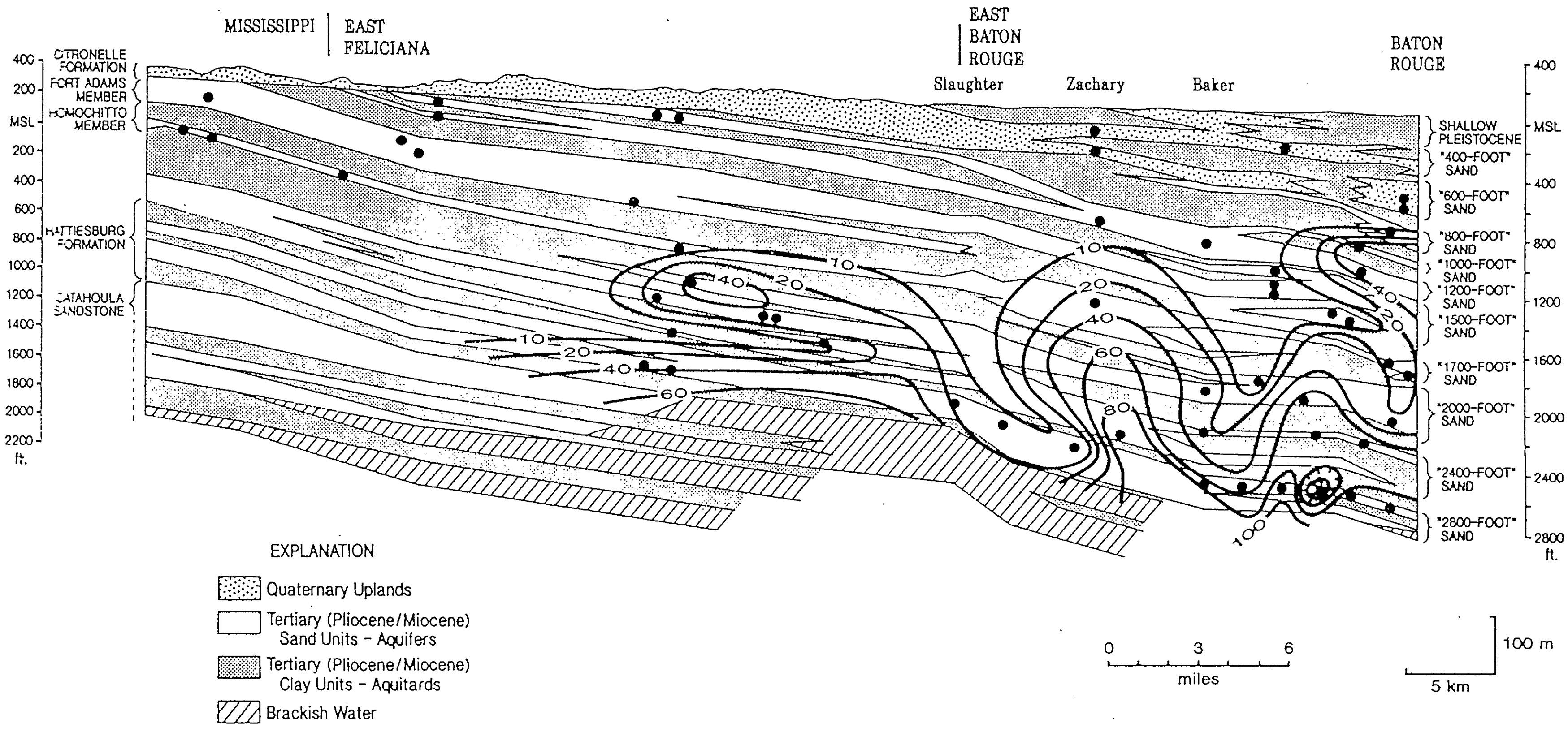


FIGURE 23 e

$\delta^{13}C$ (‰ PDB)

Contour Interval = 1‰

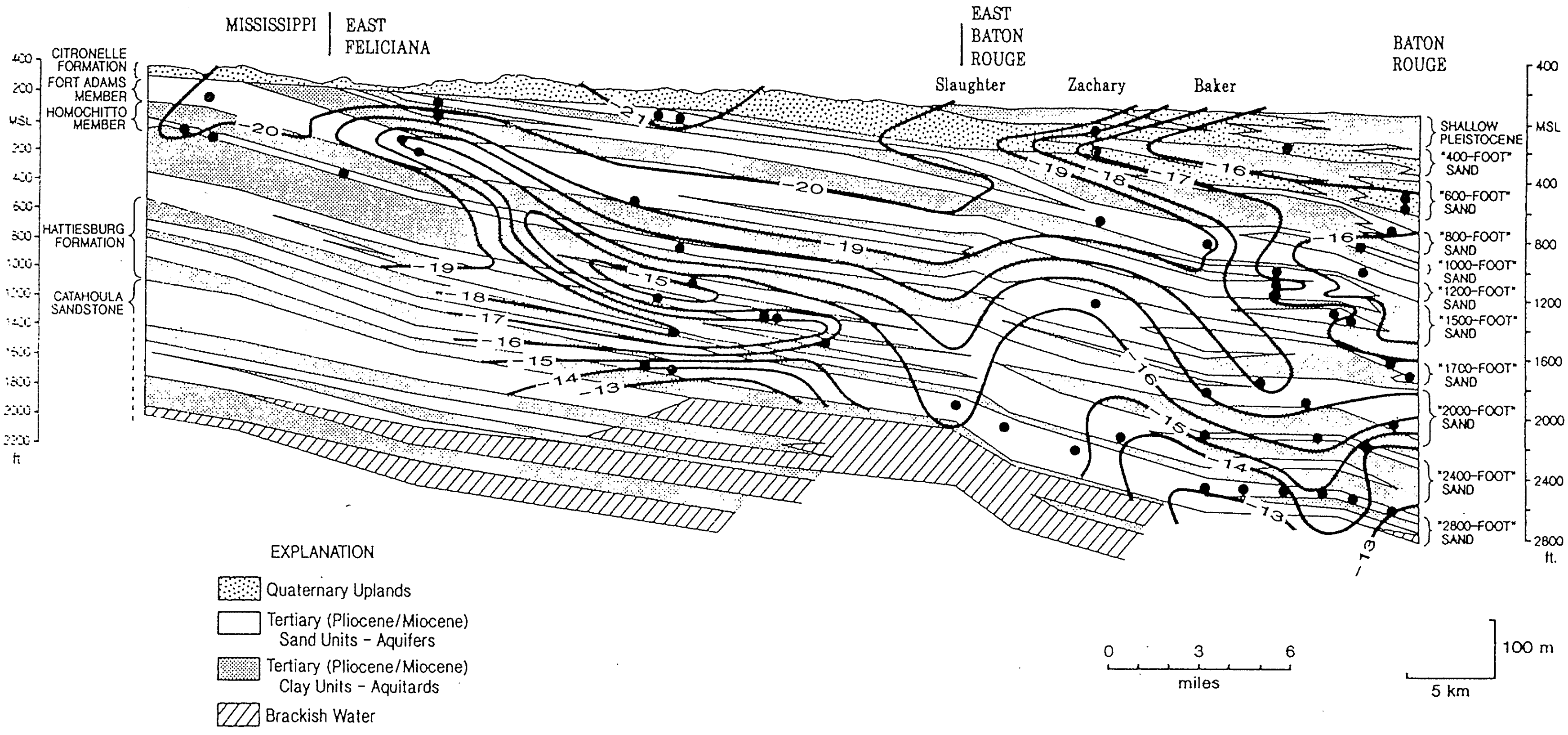


FIGURE 23 f

H_4SiO_4 (ppm)

Contour Interval = 4 ppm

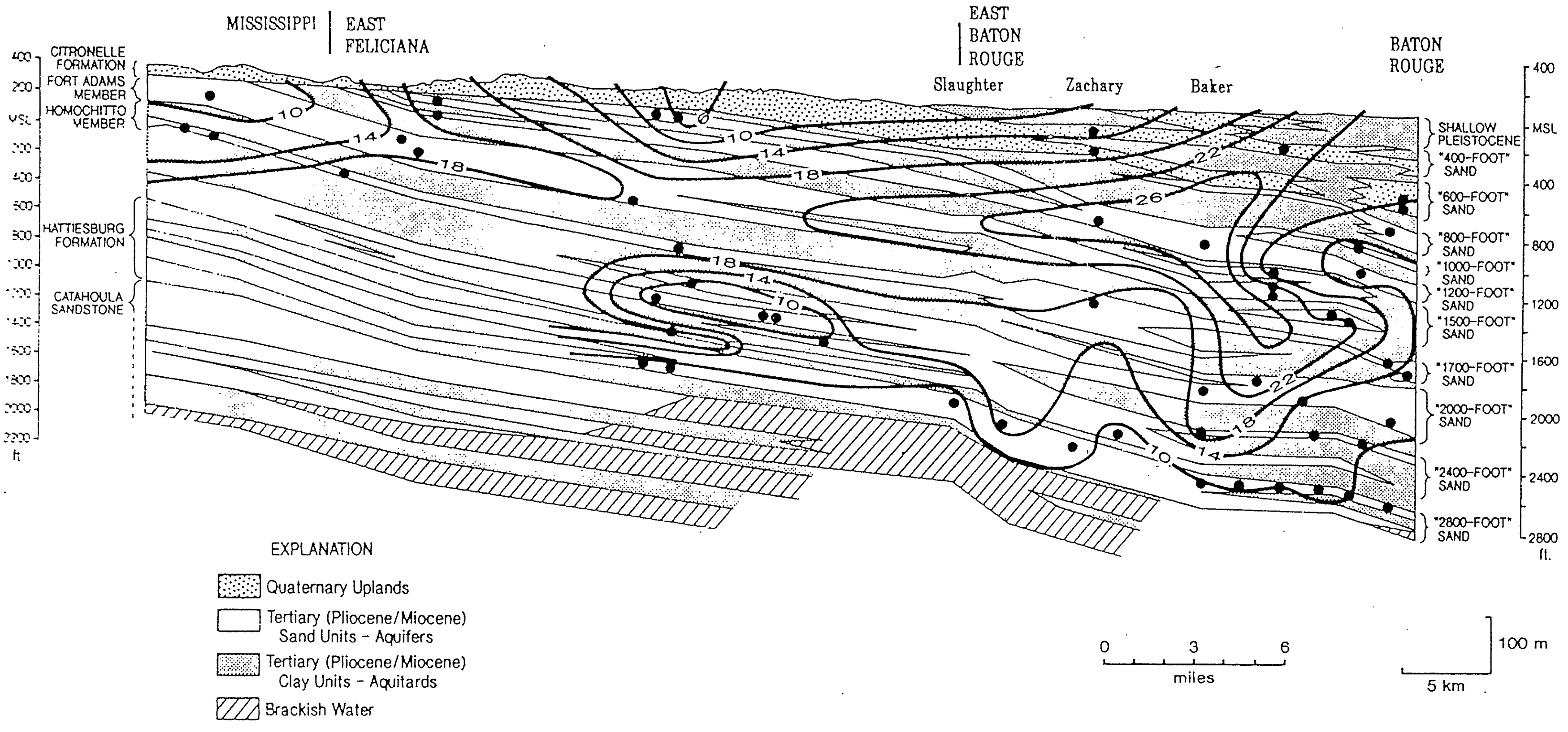


FIGURE 24

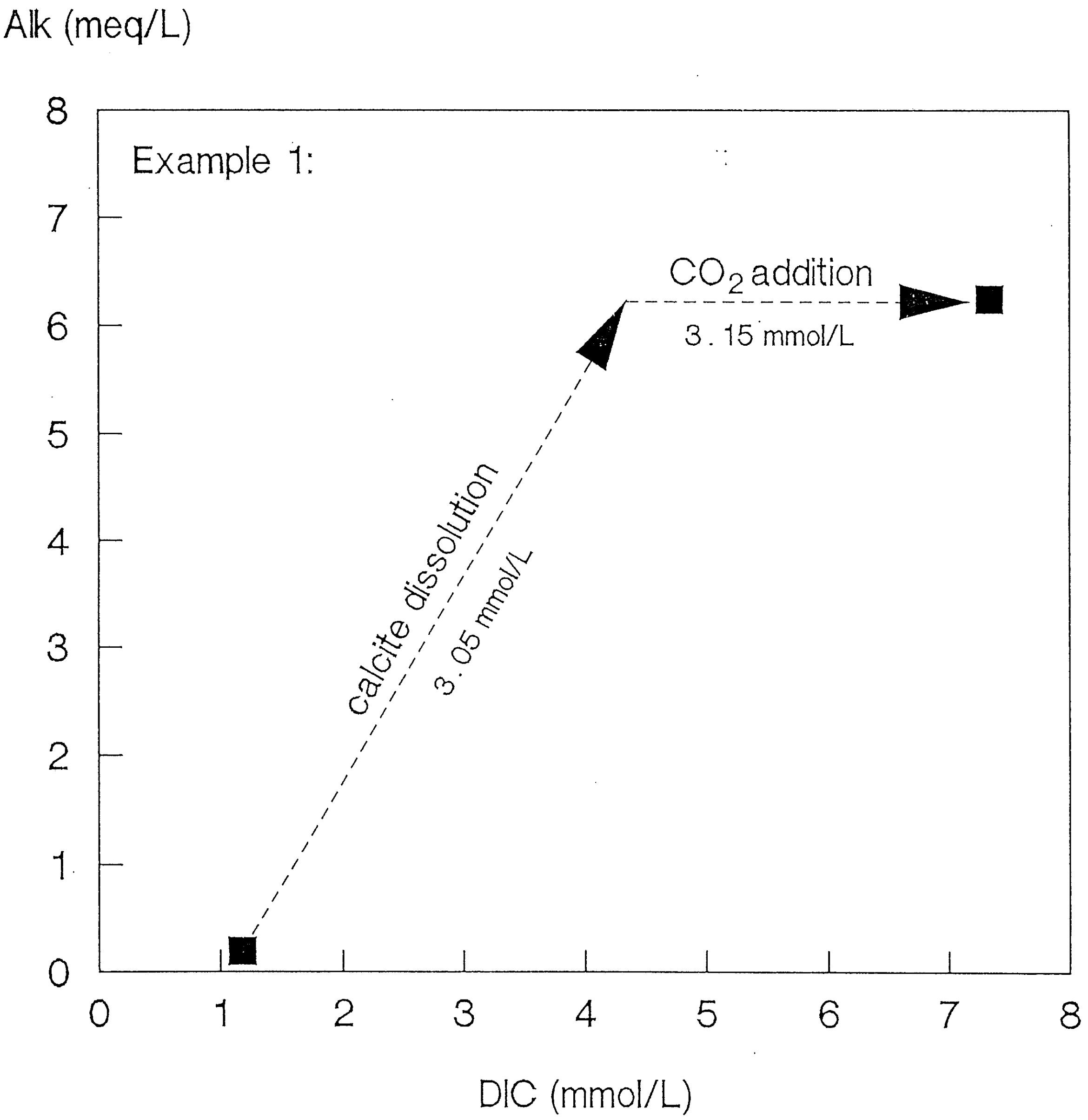
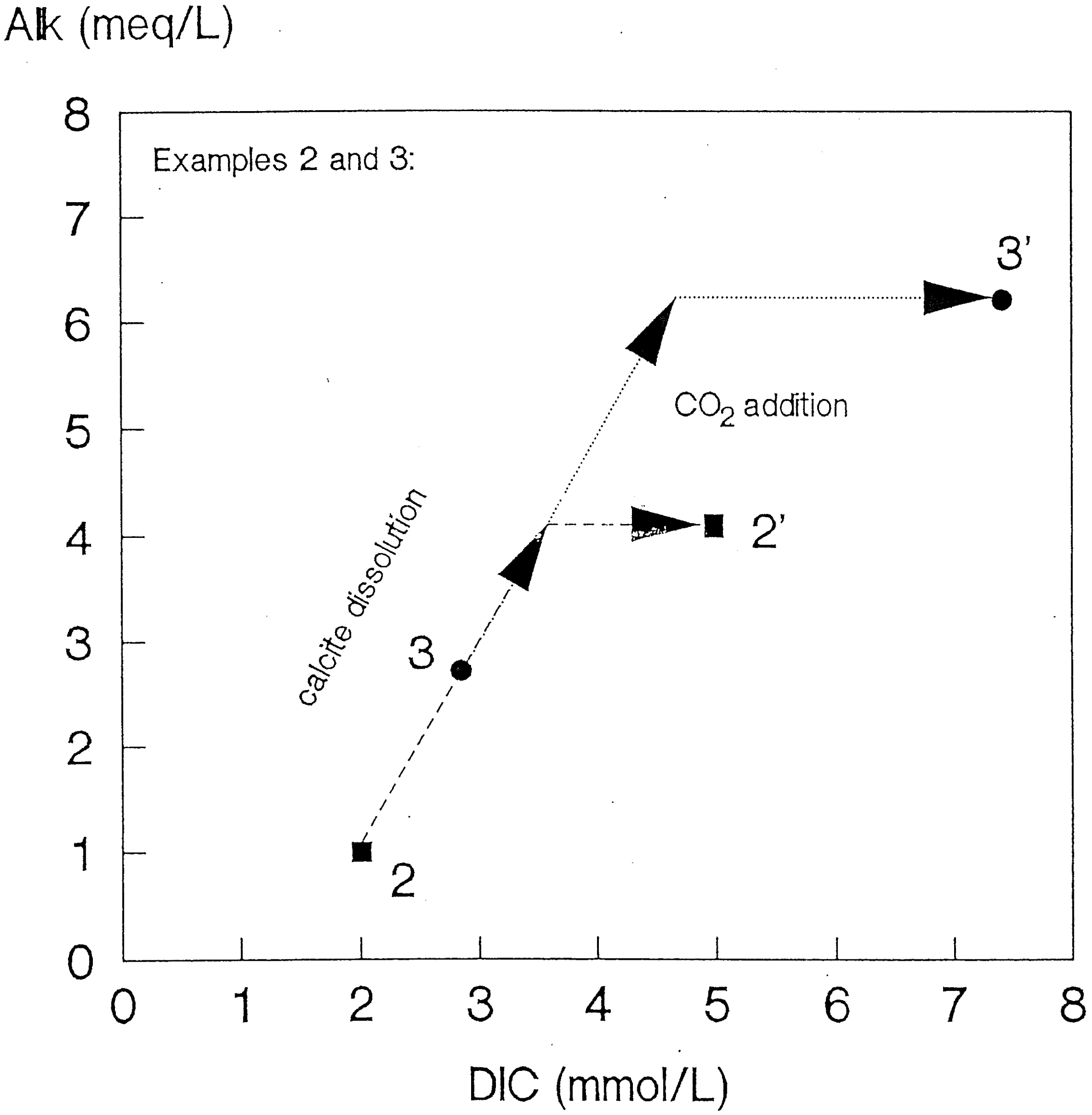

Alk (meq/L)
8
7
6
5
4
3
2
1
0
Example 1:
CO_2 addition
3.15 mmol/L
calcite dissolution
3.05 mmol/L
0
1
2
3
4
5
6
7
8
DIC (mmol/L)

FIGURE 25



2-2´ Lk.Istroma to EF251

				final-initial
DIC	2.1	5.0	(mmol/L)	2.9
Alk	1.1	4.2	(meq/L)	3.1
$\delta^{13}C$	-18	-13.5	(°/ooPDB)	

from diagram: CO_2 added = 1.4 mmol/L
HCO_3^- from calc. diss. = 1.55 mmol/L

using eqn. (1) from the text, $\delta^{13}C_{added}$ = -21.7°/oo

distance between wells: 2 miles
est. av. horizontal flow velocity (Buono, 1983): 0.07 mi/yr

using eqn. (2) from the text, CO_2 (PR) = 4.9×10^{-2} mmol/L/yr

---

3-3´ EB928 to EB700

			final-initial
DIC	2.8	7.4	3.6
Alk	2.7	6.3	3.8
$\delta^{13}C$	-16.6	-13.1	

from diagram: CO_2 added = 2.75 mmol/L
HCO_3^- from calc. diss. = 1.8 mmol/L

using eqn. (1) from the text, $\delta^{13}C_{added}$ = -18.1°/oo

distance between wells: 3 miles
est. av. horizontal flow velocity (Buono, 1983): 0.07 mi/yr

using eqn. (2) from the text, CO_2 (PR) = 6.4×10^{-2} mmol/L/yr

APPENDIX 1

SAMPLE	Aquifer Design.	Abs. depth (ft) GG	pH	Temp Celciu	Cl- (mg/L) GG	Na+ (mg/L) GG	Na (mmol/L)	K+ (mg/L)	Ca++ (mg/L)	Mg++ (mg/L)	H4SiO4 (mg/L)	H4SiO4 (mmol/L)	Al (mg/L)
EF175 (WhispPin	10	255	6.70	23	3.0	6.6	0.29	2.44	7.0	1.9	20.5	0.21	0.0
Centerville 1	10	-200	5.24	22	3.0	7.0	0.30	0.93	3.3	1.0	6.8	0.07	0.1
EF67 (Cobb/Rang	10	140	5.40	22	3.0	9.5	0.41	0.41	0.9	0.2	7.0	0.07	0.1
EF225 (Norwood)	10	134	6.50	22	4.3	7.2	0.31	2.1	5.9	1.5	19.4	0.20	0.0
Slaton's Store	10	90	5.40	23	3.0	4.8	0.21	0.74	1.6	0.3	5.8	0.06	0.0
EF57(Jack Jones	10	8	6.40	23	3.0	4.8	0.21	1.91	4.2	1.1	14.8	0.15	0.1
Centerville 2	10	-37	6.20	23	3.4	6.8	0.29	2.45	5.7	1.4	13.1	0.14	0.1
Centerville 3	10	-45	6.00	24	11.7	12.4	0.54	2.58	6.3	1.5	12.7	0.13	0.0
EF53(Ja.Jones)	10	-100	6.20	23	3.0	5.1	0.22	2	4.4	1.1	14.8	0.15	0.1
EB940 (GaPa-16)	400	-152	6.70	20	19.8	19.6	0.85	1.52	10.9	4.0	12.0	0.12	0.0
EB973 (GaPa-18)	600	-304	7.22	20	24.2	21.7	0.94	2.67	15.8	4.4	17.9	0.19	0.0
EB886 (Rollins)	600	-309	6.90	23	26.3	30.9	1.35	1.99	22.9	7.8	25.0	0.26	0.0
EB1132 (Parish)	400	-547	7.35	26	2.7	53.7	2.33	0.93	4.2	1.2	18.9	0.20	0.1
EB879 (Parish)	600	-626	8.25	24	1.4	63.5	2.76	0.09	0.5	0.0	16.0	0.17	0.0
EB1018 (Parish)	600	-763	8.30	24	3.0	67.2	2.92	0.25	0.8	0.0	17.4	0.18	0.3
EF221 (Wilson)	1500	-226	6.18	23	3.4	6.8	0.29	2.53	7.6	1.7	20.5	0.21	0.0
EF252 (High Est	1500	-310	7.08	22	4.3	8.9	0.39	2.62	8.8	2.6	18.5	0.19	0.0
EB840 (GaPa-7)	1200	-691	6.60	24	3.2	18.6	0.81	2.66	12.2	2.0	29.6	0.31	0.1
EB1153 (Rollins	1200	-905	7.20	25	5.9	23.6	1.03	2.64	11.5	1.7	29.1	0.30	0.1
EB632 (CW-1)	1200	-1009	8.82	26	1.2	93.0	4.05	0.28	1.1	0.0	11.8	0.12	0.0
EB772 (CW-2)	1200	-1166	8.89	27	1.8	92.6	4.03	0.09	1.0	0.0	11.9	0.12	0.1
EB403 (Exxon)	1200	-1206	8.50	27	3.8	56.7	2.46	0.24	0.4	0.0	17.4	0.18	0.0
EB977 (Allied)	1500	-1269	7.50	28	3.0	50.7	2.21	0.44	1.9	0.3	24.2	0.25	0.0
EB867 (Parish)	1500	-1298	7.25	27	2.3	55.5	2.41	0.81	2.2	0.3	25.7	0.27	0.2
EB905 (Parish)	1500	-1338	7.70	22	3.4	52.1	2.27	0.37	2.1	0.0	21.0	0.22	0.0
EB371B (Copoly)	1500	-1418	8.06	28	2.1	58.4	2.54	0.24	0.3	0.0	22.3	0.23	0.1
EB961 (CW-5)	1500	-1491	8.70	25	2.5	86.3	3.75	0.28	0.7	0.0	14.6	0.15	0.0
EB873 (CW-3)	1700	-1834	8.77	25	3.2	88.8	3.86	0.35	0.5	0.0	13.6	0.14	0.4
EF227 (Tigator)	2000	-838	6.75	24	3.0	27.1	1.18	2.3	6.2	1.0	21.0	0.22	0.1
EF262 (Jackson)	2000	-1072	8.65	26	2.1	104.9	4.56	0.76	1.4	0.0	8.9	0.09	0.0
EB837 (GaPa-5)	2000	-1291	8.90	26	1.4	93.3	4.06	0.51	0.8	0.0	15.1	0.16	0.1
EB904 (Parish)	2000	-1818	7.00	30	3.2	43.2	1.88	0.77	4.4	0.4	24.7	0.26	0.0
EB1030 (Copoly)	2000	-1988	8.80	29	3.2	62.0	2.70	0.31	1.7	0.0	13.1	0.14	0.2
EB878 (CW-4)	2000	-2128	8.83	27	1.8	87.5	3.81	0.35	0.6	0.0	11.4	0.12	0.2
EF258 (Jackson)	2400	-1028	8.50	26	1.6	75.0	3.26	0.81	1.2	0.0	9.3	0.10	0.1
EF273 (Veteran2	2400	-1100	8.80	27	3.0	74.2	3.23	0.49	0.6	0.0	9.7	0.10	0.0
EF272 (Veteran1	2400	-1102	8.75	27	3.0	97.1	4.22	0.34	0.7	0.0	9.4	0.10	0.1
Lake Istroma	2400	-1200	6.70	28	3.0	20.6	0.90	2.96	5.6	1.2	20.2	0.21	0.1
EF282 (Dixon)	2400	-1300	8.70	28	2.7	83.2	3.62	0.47	0.5	0.0	14.1	0.15	0.0
EB1031 (Parish)	2400	-1903	8.00	30	3.6	56.2	2.44	0.46	4.9	0.1	18.6	0.19	0.0
EB1032 (Parish)	2400	-2287	7.70	32	2.3	49.1	2.14	0.82	6.9	0.0	19.7	0.21	0.0
EB928 (Bk-7)	2400	-2319	8.58	33	2.3	61.9	2.69	0.43	2.4	0.0	12.0	0.12	0.0
EB351 (Exxon)	2400	-2374	8.70	34	2.05	72.9	3.17	0.34	1.4	0.0	10.2	0.11	0.1
*Well 21 (GaPa)	2400	-2400	8.80	34	3.0	80.9	3.52	0.38	1.5	0.0	8.6	0.09	0.0
EF?? (Clinton2)	2800	-1700	8.55	30	3.0	100.9	4.39	0.69	0.9	0.0	7.7	0.08	0.1
EF251 (Clinton1	2800	-1739	8.55	32	4.1	120.8	5.25	0.46	1.4	0.0	7.8	0.08	0.1
EB831 (Parish)	2800	-1803	8.49	30.5	1.8	95.1	4.14	0.31	0.8	0.0	8.3	0.09	0.0
EB829 (Parish)	2800	-1862	8.00	29	1.4	57.4	2.50	1.01	2.3	0.0	15.3	0.16	0.0
EB832 (Parish)	2800	-1961	8.79	30	3.2	128.8	5.60	0.34	0.2	0.0	10.6	0.11	0.1
EB830 (Parish)	2800	-2100	9.00	32.5	1.6	104.0	4.52	0.3	0.7	0.0	9.4	0.10	0.1
EB730 (Parish)	2800	-2401	8.86	29	1.8	133.7	5.82	0.4	0.6	0.0	10.3	0.11	0.4
EB922 (Parish)	2800	-2445	8.70	33.5	3.0	123.8	5.38	0.46	1.4	0.0	9.9	0.10	0.1
EB995 (Parish)	2800	-2463	7.80	32	4.5	100.6	4.38	0.67	4.4	0.2	17.6	0.18	0.0
EB978 (Allied)	2800	-2470	8.95	34	4.1	134.4	5.85	0.37	0.8	0.0	10.0	0.10	0.1
EB700 (Parish)	2800	-2495	8.80	35	6.1	149.3	6.49	0.57	0.8	0.0	10.0	0.10	0.1

SAMPLE	(meq/L)	(mmol/L)	(PDB)	calcite	dolomite
EF175 (WhispPin	0.72	0.84	-15.2	0.5	0.0
Centerville 1	0.18	1.59	-20.1	0.0	0.0
EF67 (Cobb/Rang	0.12	1.27	-21.4	0.0	0.0
EF225 (Norwood)	0.68	1.65	-20.4	0.2	0.0
Slaton's Store	0.13	0.75	-21.1	0.0	0.0
EF57(Jack Jones	0.47	0.60	-16.9	0.1	0.0
Centerville 2	0.34	1.53	-20.1	0.1	0.0
Centerville 3	0.66	1.50	-19.2	0.1	0.0
EF53(Ja.Jones)	0.48	0.61	-16.8	0.1	0.0
EB940 (GaPa-16)	0.97	2.80	-19.0	0.8	0.0
EB973 (GaPa-18)	1.21	2.06	-16.5	4.8	0.3
EB886 (Rollins)	2.30	3.24	-14.7	7.0	0.5
EB1132 (Parish)	2.39	2.94	-16.7	4.6	0.2
EB879 (Parish)	2.78	2.40	-15.3	4.1	0.0
EB1018 (Parish)	2.79	3.26	-16.1	8.4	0.0
EF221 (Wilson)	0.66	1.59	-19.8	0.1	0.0
EF252 (High Est	0.85	1.57	-19.5	1.6	0.0
EB840 (GaPa-7)	1.40	2.04	-19.6	1.3	0.0
EB1153 (Rollins	1.45	2.10	-19.0	5.3	0.1
EB632 (CW-1)	3.00	3.31	-14.7	42.2	0.0
EB772 (CW-2)	2.98	3.46	-15.3	45.4	0.0
EB403 (Exxon)	2.63	3.02	-16.3	7.3	0.0
EB977 (Allied)	2.36	2.92	-17.4	3.1	0.0
EB867 (Parish)	2.42	3.18	-16.8	2.0	0.0
EB905 (Parish)	2.40	2.58	-17.7	4.2	0.0
EB371B (Copoly)	2.57	3.10	-16.2	2.2	0.0
EB961 (CW-5)	2.69	2.88	-17.3	17.6	0.0
EB873 (CW-3)	2.82	3.00	-17.5	16.2	0.0
EF227 (Tigator)	1.35	1.82	-18.0	0.9	0.0
EF262 (Jackson)	3.56	4.26	-15.9	43.5	0.0
EB837 (GaPa-5)	2.82	3.24	-15.8	34.7	0.0
EB904 (Parish)	2.07	2.46	-18.3	2.3	0.0
EB1030 (Copoly)	2.67	3.10	-17.0	64.1	0.0
EB878 (CW-4)	2.68	2.76	-15.9	21.7	0.0
EF258 (Jackson)	3.11	3.84	-15.3	23.9	0.0
EF273 (Veteran2	2.93	3.38	-17.5	23.5	0.0
EF272 (Veteran1	3.11	3.48	-17.5	24.2	0.0
Lake Istroma	1.12	2.14	-18.0	0.7	0.0
EF282 (Dixon)	2.73	3.01	-15.5	13.9	0.0
EB1031 (Parish)	2.54	3.07	-17.1	29.9	0.5
EB1032 (Parish)	2.32	2.74	-16.8	21.4	0.0
EB928 (Bk-7)	2.67	2.76	-16.6	67.4	0.0
EB351 (Exxon)	3.15	3.37	-13.8	63.5	0.0
#Well 21 (GaPa)	3.39	3.96	-14.7	89.8	0.0
EF?? (Clinton2)	4.36	5.04	-13.4	32.7	0.0
EF251 (Clinton1	4.16	5.04	-13.5	51.8	0.0
EB831 (Parish)	4.09	4.80	-16.3	22.2	0.0
EB829 (Parish)	2.56	2.70	-16.3	13.7	0.0
EB832 (Parish)	4.49	5.40	-15.3	12.3	0.0
EB830 (Parish)	4.49	5.40	-15.4	78.5	0.0
EB730 (Parish)	4.89	5.76	-13.4	43.2	0.0
EB922 (Parish)	5.31	6.60	-13.3	97.4	0.0
EB995 (Parish)	3.53	4.56	-15.0	24.5	0.4
EB978 (Allied)	4.98	5.88	-14.3	89.1	0.0
EB700 (Parish)	6.31	7.44	-13.1	84.4	0.0

APPENDIX 2

AN IMPROVED MICROEXTRACTION TECHNIQUE FOR MEASURING DISSOLVED INORGANIC CARBON (DIC), $\delta^{13}C_{DIC}$, AND $\delta^{18}O_{H_2O}$ FROM MILLILETER-SIZE WATER SAMPLES

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ABSTRACT

Dissolved inorganic carbon (DIC), $\delta^{13}C_{DIC}$, and $\delta^{18}O_{H2O}$ are traditionally measured using three different analytical techniques. The DIC-acid extraction method has been simplified, and a precise, accurate, and relatively simple technique for analyzing all three parameters from a single 2mL or smaller water sample has been developed.

Water samples are injected through a septum into a temperature controlled, water-jacketed, evacuated vessel containing approximately 0.3mL of orthophosphoric acid and a magnetic spinbar. The extraction line and vessel are coupled directly to the inlet of the mass spectrometer. Evolved CO_2 is drawn through two -90°C traps to separate water vapor and is condensed into a liquid nitrogen trap. Yields of 98 to 100% are achieved by using a capillary tube between the reaction vessel and traps, dynamic "cold" pumping with liquid nitrogen, acidification to less than 1pH unit, and vigorous stirring. DIC is measured as a function of the voltage produced by mass 44 of the CO_2 gas in a fixed volume, and the CO_2 is then analyzed for $\delta^{13}C_{DIC}$ and $\delta^{18}O_{H2O}$ using conventional mass spectrometry techniques.

The method is fast (45 min. per sample), reproducible (std. dev. DIC = +/- 0.1 mmol/L; std. dev. $\delta^{13}C_{DIC}$ = +/- 0.1°/oo; std. dev. $\delta^{18}O_{H2O}$ = +/- 0.1°/oo), and accurate. It represents a considerable refinement over existing methods, and is especially valuable for studies in which sample size is a limiting factor.

It can also replace the more cumbersome conventional methods where sample size is no object.

1. INTRODUCTION

The uses of dissolved inorganic carbon (DIC), carbon isotope, and oxygen isotope measurements for enhancing research in oceanography, hydrology, volcanology, and paleoclimatology are well known and diverse. Typically, each parameter requires a separate analytical technique for measurement. To reduce the number of techniques and amount of sample needed, an existing DIC extraction method was modified and a single, accurate, and precise means of analyzing DIC, $\delta^{13}C_{DIC}$ (Graber et al., 1990), and $\delta^{18}O_{H2O}$ on 2mL and smaller samples was developed.

Most methods now in use for extracting DIC for carbon isotope measurement involve acidifying the water sample and collecting the liberated CO_2 gas (e.g. Craig, 1954; Sackett and Moore, 1966; Tan et al., 1973). Commonly, CO_2 is stripped from the sample by bubbling the sample with nitrogen gas (Broecker et al., 1960; Deuser and Hunt, 1969; Kroopnick et al., 1970). In general, 50 to 100mL of sample are used. Sackett and Moore (1966) estimated they achieved a 90% yield, while Deuser and Hunt (1969) estimated yields greater than 99%. Tan et al. (1973), Sackett and Moore (1966), Deuser and Hunt (1969), and Herczeg and Fairbanks (1987) all achieved precisions of +/- 0.3°/oo, while Kroopnick et al. (1970) reported a precision better than +/- 0.1°/oo.

DIC has been measured gravimetrically (Broecker et al., 1960), by mercury manometer (Tan et al., 1973), by gas chromatograph (Kroopnick et al., 1970), and by coulometry

(Johnson et al., 1985). These methods all require additional sample (50-250mL) and have varying precisions partly dependent on the method used to extract CO_2. Except for coulometry, reported precisions are approximately equivalent to Tan et al.'s (1973) report of 2 to 4 ml/L; accuracies are approximately equal to Kroopnick et al.'s (1970) report of +/- 0.5%.

To analyze smaller samples, McCorkle et al. (1985) flushed ampules with nitrogen gas and transferred 3 mL of sample via syringe to the ampule. The ampule was broken under vacuum, the sample acidified, and the CO_2 stripped off with nitrogen gas. DIC was measured manometrically and transferred to another flask for isotopic analysis. DIC of standard solutions always measured several percent higher than the value calculated, but precision of replicate analyses was +/- 0.1°/oo.

Oxygen isotope composition of water is most commonly measured using the CO_2-H_2O equilibration method described by Epstein and Mayeda (1953). It requires an additional 5 to 20 mL of sample, and achieves a precision of +/- 0.1°/oo. Minute samples of water can also be analyzed using guanadine hydrochloride (cite) or bromine pentafluoride (O'Neil and Epstein, 1966; Blattner, 1973), but these extraction methods are complex and tedious.

The techniques each suffer from one or more flaws; they need too much sample, require expensive equipment, are too cumbersome, or are insufficiently documented. We thus embarked on a series of experiments designed to fully test the range, precision, and accuracy of a combined method which would deliver DIC, $\delta^{13}C_{DIC}$, and $\delta^{18}O_{H_2O}$ from a single 2 mL sample. The method has a precision and accuracy of +/- 0.1°/oo for both $\delta^{13}C$ and $\delta^{18}O$, and a precision and accuracy of +/- 0.1 mmol/L for DIC. Herein we describe in detail the technique, limits, and pitfalls. The results of our 150 determinations suggest to us that previous techniques may have been insufficiently tested and may not yield results with as high accuracies as formerly supposed.

2. METHODS

2.1 Reaction Technique

The reaction vessel is a small, water-jacketed, glass bottle with an arm fitted with a three-layer rubber septa (Figure 1). It connects via O-ring and clamp to a glass tube with a valve. The glass tube is ´corked´ with a three-layer rubber septa that is pierced by a thin needle. The needle acts as a capillary tube, keeping water inside the vessel while allowing CO_2 to escape. A removable U-trap is attached to an elbow joint, and then clamped to the reaction vessel and valve piece. These four pieces make up a removable assembly which is clamped onto a permanent microextraction line coupled directly to the inlet of the mass spectrometer (Figure 2). The assembly can be removed, cleaned, and dried when necessary.

Approximately 0.3mL of anhydrous orthophosphoric acid and a magnetic spinbar are placed in the reaction vessel, and the whole assembly is clamped onto the line and evacuated. The vessel is kept at a 25°C +/- 0.1°C by circulating water through the glass water jacket using a circulating water pump. Once the line is fully evacuated by the diffusion pump, valves to the pumps and mass spectrometer are closed (valves 3 and 4 in Figure 2), trap C is immersed in liquid nitrogen, and trap A is immersed in a dry ice-ethyl alcohol mixture. Trap B is kept at -90°C using an electric immersion cooler. Two mL of water sample, drawn into a syringe, is added through the reaction vessel septum and expelled, and the needle is immediately removed. The acidified solution is stirred vigorously by a magnetic stirrer for a total of thirty (30) minutes.

Several aspects of the evacuation are important. First, the valves between the reaction vessel and the traps must be open while injecting the water in order to draw CO_2 immediately to the liquid nitrogen-cooled trap. If the valves are not open, fractionation results. Second, much experimentation has shown that the optimum inner diameter for the needle valve (capillary) is 0.016 mm. A needle with a larger diameter allows much water to escape, while too narrow a diameter blocks the passage of CO_2 and causes fractionation. The needle is imbedded in a septum in the glass stem and extends only a few millimeters into the bowl. This eliminates blockage of the needle by sprayed water droplets. Third, after fifteen (15) minutes, the first dry ice/ethyl alcohol bath (Trap A) must be lowered by an inch or so. The water frozen in the trap slowly refreezes at the new dry ice/alcohol level and CO_2 physically trapped beneath the ice is liberated without oxygen re-equilibration.

The residual uncondensable gases are pumped away and the CO_2 is isolated in trap C. The liquid nitrogen is replaced by a dry ice/ethyl alcohol mixture, and the CO_2 is transferred to a freezing finger immersed in liquid nitrogen. The CO_2 is again isolated, dry ice/alcohol is exchanged for liquid nitrogen, and CO_2 is transferred to the inlet system of the mass spectrometer. The gas is allowed to sublimate into a portion of the inlet system with a fixed volume and connected to the source through the capillary leaks, and the voltage produced by mass 44 of that volume of gas is measured and recorded. This is the measurement of DIC. The isotope ratio of the gas is then analyzed against a machine standard.

Once the reaction is complete and the CO_2 is isolated, the assembly can be removed, cleaned, replaced with another, and dried. Three reaction vessels and U-tubes, two needle stems, and one elbow joint are enough to run all day. The permanent -90°C trap, trap B, should be pumped dry every four samples or so; failure to do so will eventually result in spurious results. The U-trap and reaction vessel are changed for each sample; the needle valve can usually be used all day but occasionally must be replaced.

2.2 Standardizing Techniques

$NaHCO_3$ solutions were used to calibrate the voltage generated by mass 44 versus umoles of CO_2 measured. $NaHCO_3$ must be vacuum roasted at approximately 200°C for 4 hours in order to drive off adsorbed CO_2. If not freshly heated and cooled completely under vacuum, the results will be spurious and yield inaccurate and imprecise measurements.

Several standard solutions ranging in concentration from 0.5 to 8.3 mmole/L were prepared from $NaHCO_3$ using CO_2-free distilled water (boiled 15 minutes, cooled through a drying tube) and stored in 100mL bottles sealed with septa and aluminum seals.

For measuring DIC, several $NaHCO_3$ solutions of known molarities were prepared, and an equation which relates the voltage of mass 44 of the gas in a fixed volume versus umoles of DIC in the sample was calibrated. The equation is used to translate voltage of unknowns into mmol/L DIC. The fixed volume we use for most of our samples is the inlet system itself, isolated from the bellows (Figure 3). To handle samples containing more than 24 umoles (12 mmol/L for 2mL sample), a second equation relating mass 44 voltage in the fixed volume to mass 44 voltage of a larger, ´bellows-open´ volume was also calibrated. For our mass spectrometer, the equations are as follows:

(i) umol = 0.24 x Voltage of mass 44 of fixed volume

$r^2 = 1.0$

(ii) Voltage of mass 44 of fixed volume = 6.31 x Voltage of mass 44 of ´bellows-open´ volume +8.28

$r^2 = 1.0$

Although we usually use 2 mL water samples, our equations compare mass 44 voltage with the total umoles of DIC measured. Mmol/L is then calculated by dividing umoles of sample by volume of the sample (mL). This makes it possible to vary sample size without recalibrating a new equation.

The oxygen isotope composition of CO_2 aqueous (measured by this method) is 1.07°/oo heavier than CO_2 vapor (measured by the Epstein and Mayeda method) at 25°C (Vogel et al., 1970). In order to directly compare results between this method and the traditional equilibration method, the measured values are corrected for this fractionation. No other oxygen correction is needed, as the oxygen of the CO_2-H_2O system is completely water-dominated.

Three CO_2 samples were prepared to monitor and correct for mass spectrometer and tuning changes over time. The voltage of mass 44 in the fixed volume was measured daily, weekly, biweekly, and then monthly, and always measured within the precision reported. It is suggested that a known volume of gas is measured biweekly or monthly, after any major changes to the mass spectrometer, or after a long lapse of time in order to monitor and correct for long-term changes in mass spectrometer calibration.

Solutions with high molar DIC concentrations (~8 mmol/L) last for at least 6 months and probably much longer. We used an 8.3mmolar solution as a daily standard. Low molar solutions are diluted by air from the needle and/or by atmospheric invasion through the cap and last only a few weeks, depending on the number of aliquots removed and the molarity.

3. RESULTS

3.1 Accuracy and Precision

Five samples of solid $NaHCO_3$ were dissolved in 100% phosphoric acid and analyzed. Their average $\delta^{13}C$ value was $-1.54^{o}/oo$ with a standard deviation of $0.08^{o}/oo$ (Table 1). Ten analyses of a water standard prepared from the same $NaHCO_3$ yielded an average $\delta^{13}C$ of $-1.56^{o}/oo$ with a standard deviation of 0.03o/oo (Table 2). Precision was 0.1o/oo or better for every concentration measured, including 0.5mmol/L. Accuracy, however, declined as molarity decreased. At a concentration of 1.0mmol/L, the accuracy was off by 0.2o/oo.

Ten replicate analyses of a standard had an average mass 44 voltage of 69.5 volts using a resistor of 10^{10} ohms with a standard deviation of 1.0 volts. This translates to an average of 8.3mmol/L with a standard deviation of 0.1mmol/L (Table 1). Thirty nine analyses of seven standards of differing molarities had an average (predicted minus actual) DIC of 0.0 mmol/L with a standard deviation of 0.1 mmol/L. The equation is thus an accurate predictor of the actual DIC content, as suggested by the correlation coefficient of 1.0.

Ten replicate analyses of the same standard had an average $\delta^{18}O$ value of -10.10o/oo with a precision of 0.08o/oo (Table 1).

A comparison of oxygen isotope measurements obtained using the Epstein and Mayeda (1953) technique and this technique is presented in Table 2. Three different waters with $\delta^{18}O$ values ranging between +0.4 and -40.3o/oo were measured multiple times by both methods. The mean values and standard deviations are essentially equal for each of the three waters.

3.2 Limits

For both $\delta^{13}C$ and $\delta^{18}O$, the accuracy of the analysis declines when the molarity decreases. A 1.5mmolar solution is accurate within 0.1o/oo, but a 1.0mmolar solution is depleted in both carbon and oxygen by approximately 0.2o/oo compared with the correct value. Thus, we consider 1.0 mmol/L to be the limit of resolution. Increasing the sample size in order to increase the total umoles analyzed does not improve the situation. This suggests to us that either a fixed, minute percentage of CO_2 cannot be driven out of the sample, or that a finite amount of CO_2 is adsorbed on the glass and O-ring fittings and cannot be collected. This fraction only becomes significant when the molar DIC content of the solution is very low. Most lake and groundwaters, and all seawater and brines meet and exceed this threshold (Stumm and Morgan 1981).

The precision and accuracy of 0.1 mmol/L for DIC measurements is equal to or better than measurements made manometrically, but is inferior to that of coulometry. However, in most waters, variations are many times larger than 0.1mmol/L, and this method is sufficient.

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FIGURE CAPTIONS

Figure 1. Reaction vessel for extracting DIC from water samples.

Figure 2. Reaction vessel and extraction line.

Figure 3. Calibration between DIC and voltage produced by the mass 44 across a 10^{10} ohm resistor of a known CO_2 sample in a fixed volume of the inlet system.

TABLE 1: Carbon isotope composition ($\delta^{13}C$) of solid $NaHCO_3$ compared with $\delta^{13}C_{DIC}$, $\delta^{18}O_{H2O}$, and DIC measured on replicate samples using the new technique.

	Solid $NaHCO_3$	Dissolved $NaHCO_3$		
	$\delta^{13}C$ (°/oo PDB)	$\delta^{13}C$ (°/oo PDB)	$\delta^{18}O$ (°/oo PDB)	DIC (mmol/L)
	-1.55	-1.49	-10.11	8.21
	-1.60	-1.58	-10.08	8.16
	-1.48	-1.60	-9.99	8.40
	-1.44	-1.55	-10.12	8.46
	-1.63	-1.59	-10.10	8.40
		-1.58	-10.09	8.22
		-1.56	-9.94	8.46
		-1.61	-10.23	8.34
		-1.53	-10.16	8.40
		-1.51	-10.17	8.34
Mean	-1.54	-1.56	-10.10	8.34
STD.	0.08	0.03	0.08	0.10

TABLE 2: $\delta^{18}O$ of three different water samples measured using the Epstein and Mayeda (1953) method compared with the $\delta^{18}O_{H_2O}$, $\delta^{13}C_{DIC}$, and DIC results using this technique.

Sample	CO_2-H_2O method	This technique		
	$\delta^{18}O$ (o/ooSMOW)	$\delta^{18}O$ (o/ooSMOW)	$\delta^{13}C$ (o/ooPDB)	DIC (mmol/L)
EB730	-4.7	-4.7	-13.4	5.8
	-4.8	-4.6	-13.4	5.8
	-4.6	-4.4	-13.4	5.8
	-4.5	-4.5	-13.4	5.8
	-4.5	-4.6	-13.4	5.9
Mean	-4.6	-4.6	-13.4	5.8
STD.	0.1	0.1	0.0	0.1
VH-A	-40.4	-40.3	-15.9	2.3
	-40.5	-40.4	-16.0	2.3
	-40.0	-40.4	-16.0	2.3
Mean	-40.3	-40.4	-16.0	2.3
STD.	0.3	0.1	0.1	0.0
Gulf Net	0.4	0.5	0.7	2.5
	0.3	0.6	0.7	2.6
	0.9	0.7	0.8	2.7
	0.4	0.5	0.7	2.7
	0.2	0.4	0.7	2.7
	0.5			
Mean	0.4	0.5	0.7	2.6
STD.	0.2	0.1	0.0	0.1

EB730 is a fresh groundwater from the Baton Rouge aquifer system;
VH-A is melted ´blue ice´ from Vestfolol Hills, Antartica;
Gulf Net is sea water sampled from the Gulf of Mexico.

FIGURE 1

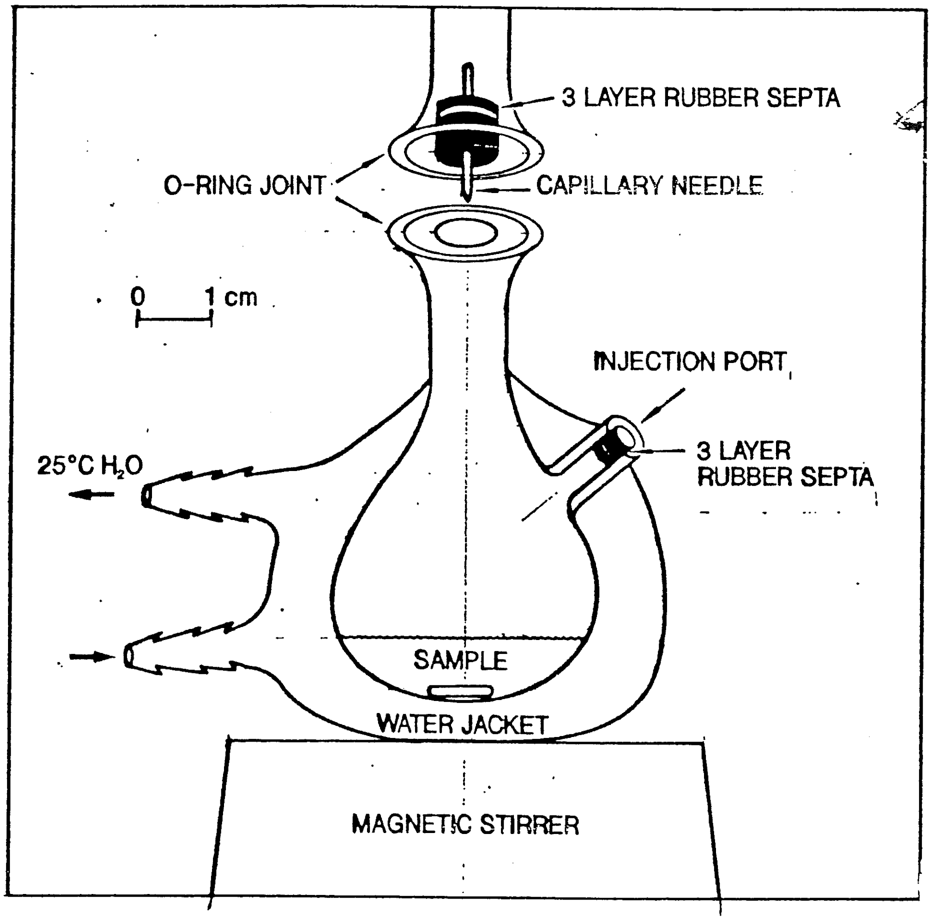

3 LAYER RUBBER SEPTA
O-RING JOINT
CAPILLARY NEEDLE
0 1 cm
INJECTION PORT
3 LAYER RUBBER SEPTA
25°C H2O
SAMPLE
WATER JACKET
MAGNETIC STIRRER

FIGURE 2

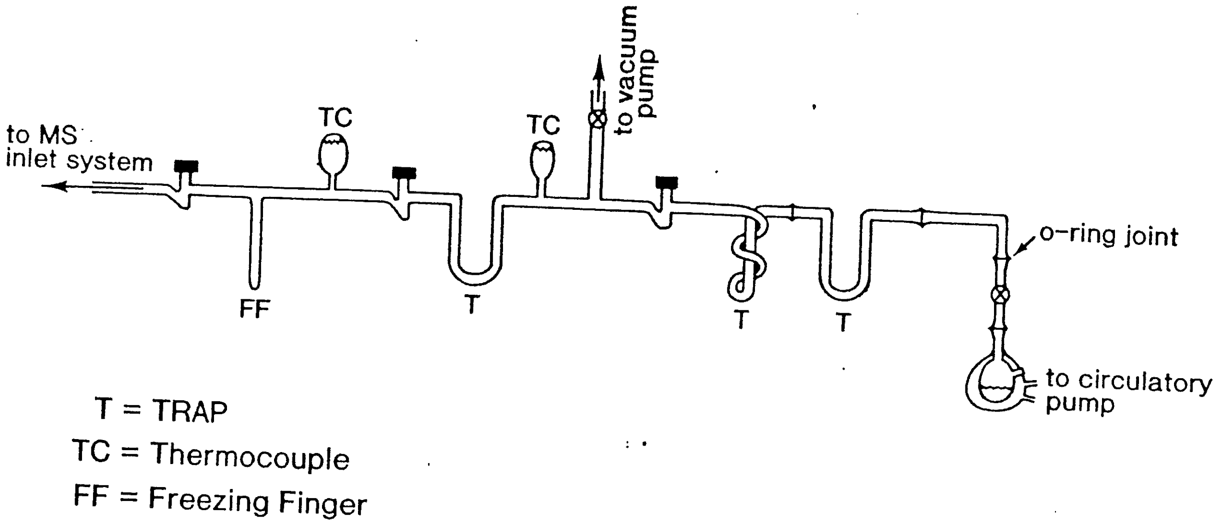
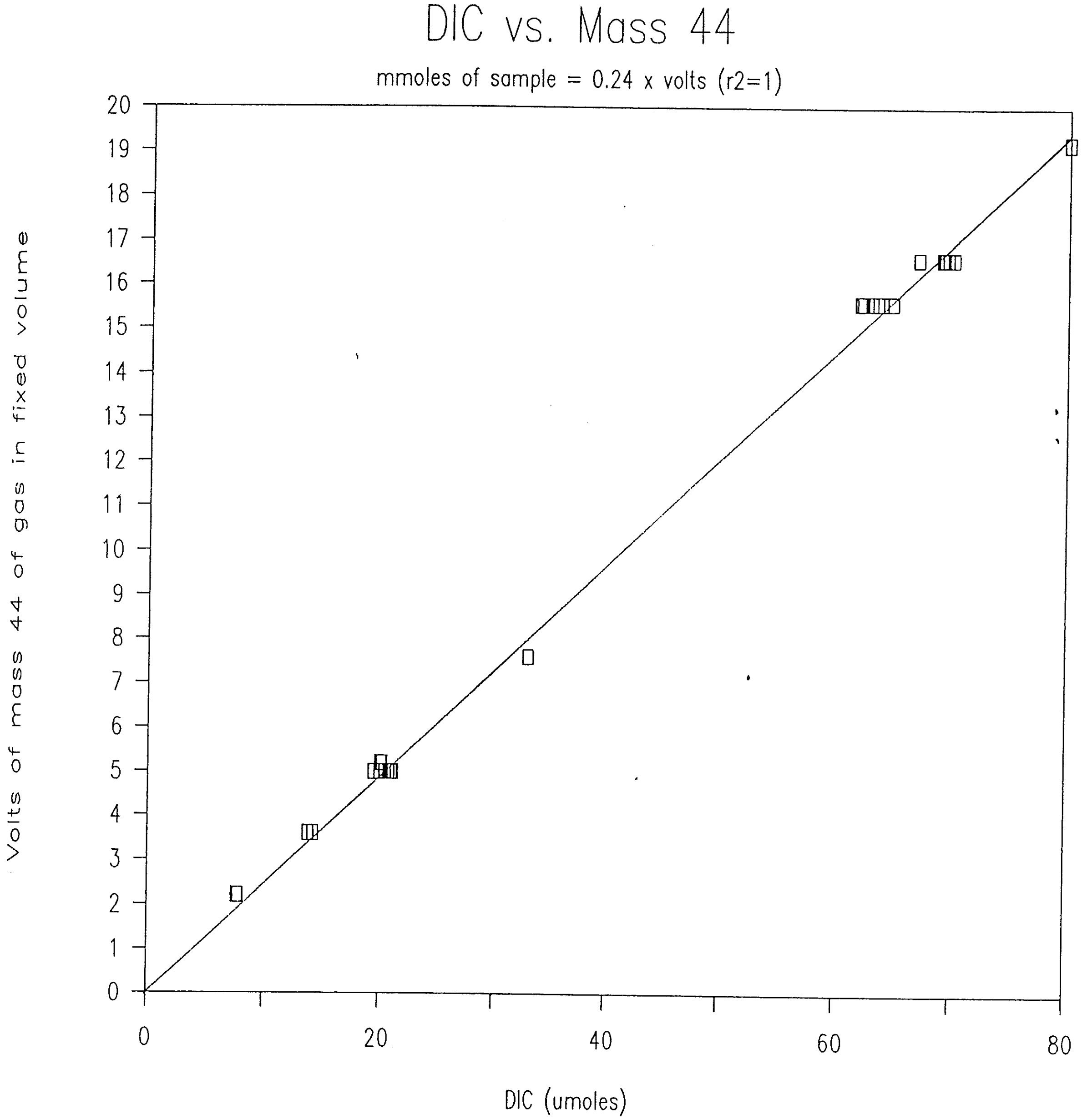

to MS inlet system
TC
TC
to vacuum pump
o-ring joint
FF
T
T
T
to circulatory pump
T = TRAP
TC = Thermocouple
FF = Freezing Finger

FIGURE 3



DIC vs. Mass 44

mmoles of sample = 0.24 x volts (r2=1)

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16. Abstract

High $Na\text{-}HCO_3$ water in the stacked sand and clay aquifer system of Southeastern Louisiana was found to be caused by a combination of bacterial oxidation of organic matter, ion exchange, and calcite dissolution. Dissolution of feldspar had little impact on water chemistry. Na and alkalinity are highly correlated as a result of calcite dissolution and subsequent exchange by clays of 2 Na ions for each Ca ion. Na content is a good indicator of the amount of calcite dissolved.

The contribution to the carbon budget by bacterially-mediated organic degradation is substantial and coequal to the contribution by calcite dissolution. Microbial activity is dominated by aerobic bacteria, and there is little or no contribution by either sulfate-reducers or methanogens.

Bacterial activity is concentrated within the deeper aquifers, and is much less important in the shallow and intermediate sands. The average rate of CO_2 production is estimated to be 5.4×10^{-3} $mmolL^{-1}yr^{-1}$, while in high CO_2 productivity areas, rates are more than ten times greater (6.4×10^{-2} $mmolL^{-1}yr^{-1}$).

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PROJECT COMPLETION REPORT

Nature and Rates of Bacterial Metabolism in the Aquifers of Southeastern Louisiana

By

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and
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LOUISIANA WATER RESOURCES
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Louisiana State University
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NATURE AND RATES OF BACTERIAL METABOLISM IN THE AQUIFERS OF SOUTHEAST LOUISIANA

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Baton Rouge, LA 70803

Final Report submitted to Director, LWRRI
September 15, 1990

SYNOPSIS

Project-Number: 127-90-5157

Start: 09-01-89
End: 08-31-90

Title: Nature and Rates of Bacterial Metabolism in the Aquifers of Southeast Louisiana

Investigators: Dr. Ellen R. Graber
Prof. Paul Aharon
Dept. of Geology and Geophysics, LSU

COWRR: 05B

Congressional District: 6th

Key Words: Groundwater hydrology (97), Bacteria (19), Isotopes (33)

Problem and Research Objectives:

This study addresses three problems relevant to the southeast Louisiana aquifers. The first is concerned with the rates and spatial distribution of excess CO_2 production. The second concerns whether CO_2 is derived from bacterially-oxidized organic matter. The final is to understand the origin and evolution of the groundwater major element chemistry and its high Na-HCO_3 levels. The specific objectives were:

1. To determine the in situ rate of CO_2 production.

2. To establish the effect of viable bacterial activity on groundwater chemistry, and to test the hypothesis that high bicarbonate levels are the result of deep seated bacterial metabolism.

3. To ascertain the distribution of bacteria in the subsurface, and to improve understanding of processes which lead to mineralization or corrosive development of secondary porosity in clastic sediment aquifers.

4. To distinguish between aerobic, sulfate-reducing, and methanogenic microbial metabolism.

5. To evaluate the relative roles of calcite dissolution, silicate dissolution, and ion exchange in modifying groundwater chemistry.

Methodology:

Carbon Sources in Groundwaters:

Stable carbon isotopes, ^{13}C and ^{12}C, occur in natural carbon compounds at about 1 and 99% abundance, respectively. Isotope ratios of $^{13}C/^{12}C$ in natural carbon-bearing compounds vary considerably with the source of the carbon and the pathway of carbon fixation during metabolic processes. Hence it is possible to use carbon isotope ratios to study both the source of the carbon and the biota affecting it.

During rainfall in recharge areas, CO_2-charged precipitation introduces carbon dioxide with atmospheric values of -6 to -7°/oo into the aquifer system. As the waters percolate through the unsaturated zone, CO_2 derived from aerobic bacterial oxidation of organic material in the soil zone is added. The isotopic composition of the resultant CO_2 is substantially more depleted in ^{13}C relative to the atmospheric value because organic matter and its oxidation products preferentially sequester the ^{12}C isotope. An increase in CO_2 resulting from bacterial respiration in the soil or aquifer leads to the dissolution of carbonate and silicate minerals, thus adding excess bicarbonate to the groundwater. In the case of carbonate dissolution, the $\delta^{13}C$ composition of DIC is expected to yield intermediate values between those of CO_2 released from bacterial respiration, and those of the dissolved carbonate with typical values of 2 to -5°/oo. In the case of silicate dissolution, DIC $\delta^{13}C$ is expected to remain unchanged, as no new carbon is added to the system.

Mass balance calculations using measured values of $\delta^{13}C$, DIC, alkalinity, sodium, and H_4SiO_4 can be used to evaluate chemical changes occurring between points along a groundwater flow path. The isotope composition of the added CO_2 can be calculated in order to determine its source using the mass balance equation below:

$$\delta^{13}C_f = (\delta^{13}C_i)(m_i) + (\delta^{13}C_a)(m_a) + (\delta^{13}C_c)(m_c)/m_i+m_a+m_c$$

$\delta^{13}C_f$ is the measured (final) isotope composition of the sample, $\delta^{13}C_i$ is the isotope composition of the original DIC, m_i is the number of moles of original DIC, $\delta^{13}C_a$ is the isotopic composition of the added CO_2, m_a is the number of moles of added CO_2, $\delta^{13}C_c$ is the isotopic composition of the dissolved carbonate mineral, and m_c is the number of moles of carbonate mineral dissolved.

Rates of excess CO_2 production along groundwater flow paths can be estimated by applying another mass balance equation:

$$CO_2\ (PR) = (R)(m_a)/L$$

where CO_2 (PR) is the production rate of CO_2 averaged over a flow path segment, m_a is the moles of CO_2 added, L is the length of the flow path, and R is the rate of groundwater flow.

Alkalinity and Total Dissolved Inorganic Carbon (DIC):

An important concept in the study of waters is *alkalinity*, defined as the hypothetical amount of strong base that must be neutralized in order to reach a pH corresponding to a solution of pure CO_2 and water. In a simple system, consisting of only NaOH and CO_2, alkalinity is given by:

$$A = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

In dilute natural waters, total alkalinity is generally taken to be equal to carbonate alkalinity. Between a pH of 5 and 9, bicarbonate is the dominant carbon-bearing species, and the bicarbonate concentration is essentially equal to the alkalinity.

Total dissolved inorganic carbon (DIC) is the amount of carbon in both charged and uncharged species in solution, and is represented by a mass balance on carbon:

$$DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

An important property of alkalinity is that it does not change when CO_2 is added to or withdrawn from the solution. Altering the amount of CO_2 in solution does change the total dissolved inorganic carbon (DIC). Adding or removing bicarbonate (HCO_3^-) changes both DIC and alkalinity in a one-to-one ratio, while adding or removing CO_3^{2-} changes alkalinity by two units and DIC by one unit.

A graphic technique developed by Deffeyes using alkalinity as the ordinate and DIC as the abscissa has a number of useful characteristics. Changes in solution chemistry move the point representing the solution on the diagram in definite directions depending on the reaction stoichiometry. Since reactions such as calcite dissolution and CO_2 addition alter the solution according to definite stoichiometries, the change in solution chemistry can be split into component vectors representing a calcite component and a CO_2 component. In this way, contributions to the carbon budget by various processes can be assessed and distinguished.

Principal Findings and Significance:

The primary goal of this study was to evaluate the contribution of bacterial metabolism to the development of high Na-HCO_3 waters in the Baton Rouge aquifer system. In so doing, the nature and rates of bacterial activity were explored, and the relative roles of ion exchange, silicate dissolution, calcite dissolution, and bacterial oxidation of organic material were elucidated.

The impact of silicate reactions on groundwater chemistry was found to be negligible, while the impacts of bacterial production of CO_2, calcite dissolution, and ion exchange on major element and isotope chemistry were found to be profound. Sodium, derived by a two-for-one ion exchange with calcium, was found to be a good predictor of the amount of calcite dissolved.

The contribution to the carbon dioxide budget by bacteria oxidizing organic matter deep in the aquifers was substantial (3.15 mmol/L), and coequal to the contribution by calcite dissolution (3.05 mmol/L). These contributions can be differentiated by plotting DIC versus alkalinity on a Deffeyes diagram, and by dividing them into their component vectors.

There is no evidence for methanogenic microbial activity on the basis of carbon isotope values. There is also little or no evidence for sulfate reducing bacteria, which can be distinguished from aerobic bacteria on the basis of their byproducts and on the sodium content of the waters. Aerobic bacteria produce CO_2, which causes calcite dissolution and ion exchange with sodium, while sulfate-reducers produce HCO_3^- and no subsequent calcite dissolution and sodium release. Sulfate-reduction can be detected by a sodium deficiency compared with HCO_3^- (alkalinity). In this aquifer system, sulfate-reduction occurs only in the deepest part of the 2800 foot aquifer, and its contribution to the total bacterial carbon budget is insignificant.

Bacterial activity is concentrated at particular zones in the deeper aquifers, and is minimal in the rest of the system. In those areas of high productivity ($6.4x10^{-2}$ versus an average productivity of $5.4x10^{-3}$), it is expected that porosity has been corrosively enhanced. The hydraulic conductivities of the 2000 and 2800 foot aquifers, are, in fact, higher than those of the shallower aquifers. Due to calcium uptake on clays, all the waters are undersaturated with respect to calcite, although saturation is approached in the deeper sand units. Local microenvironments may develop in which saturation or oversaturation is achieved, and in which calcite may precipitate. However, calcite cementation should be minimal overall.

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DISCLAIMER

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ABSTRACT

High Na-HCO$_3$ water in the stacked sand and clay aquifer system of Southeastern Louisiana was found to be caused by a combination of bacterial oxidation of organic matter, ion exchange, and calcite dissolution. Dissolution of feldspar had little impact on water chemistry. Na and alkalinity are highly correlated as a result of calcite dissolution and subsequent exchnage by clays of 2 Na ions for each Ca ion. Na content is a good indicator of the amount of calcite dissolved.

The contribution to the carbon budget by bacterially-mediated organic degradation is substantial and coequal to the contribution by calcite dissolution. Microbial activity is dominated by aerobic bacteria, and there is little or no contribution by either sulfate-reducers or methanogens.

Bacterial activity is concentrated within the deeper aquifers, and is much less important in the shallow and intermediate sands. The average rate of CO$_2$ production is estimated to be $5.4\text{x}10^{-3}$ mmolL^{-1}yr^{-1}, while in high CO$_2$ productivity areas, rates are more than ten times greater ($6.4\text{x}10^{-2}$ mmolL^{-1}yr^{-1}).

TABLE OF CONTENTS

11.0 Appendix 2: An Improved Microextraction Technique for Measuring Dissolved Inorganic Carbon (DIC), $\delta^{13}C_{DIC}$, and $\delta^{18}O_{H_2O}$ From Milliliter-Size Water Samples

1.0 DEFINITION OF THE PROBLEM

Oxidation of soil organic matter to CO_2 by shallow-seated bacteria is a well-known phenomenon, and, accompanied by dissolution of calcite, constitutes a dominant control over carbonate chemistry of groundwaters (Freeze and Cherry, 1979). In a number of aquifer systems consisting of stacked and stratified sands and clays, however, there is excess bicarbonate which cannot be attributed to soil gas and calcite dissolution. It was suggested, therefore, that deep-seated degradation of organic matter within the confined aquifers was responsible for the excess bicarbonate (Foster, 1950).

Until recently, there was no proof that viable bacterial populations existed deep within aquifers. However, a number of studies have now documented the presence of bacteria in deep, confined, clastic and carbonate aquifers from a variety of geographic locations (Dockins et al., 1980; Olson et al., 1981; Chapelle et al., 1987; Chapelle et al., 1988; Grossman et al., 1989; Fliermans, 1989). The proposed relationship between excess bicarbonate and bacterial degradation of organic matter (Foster, 1950) can be tested using carbon isotopes to trace the source of carbon (e.g. Pearson and Friedman, 1970; Rightmire and Hanshaw, 1973; Winograd and Farlekas, 1974; Chapelle et al., 1989; Grossman et al., 1989).

The freshwaters of the Southern Hills Regional Aquifer System of Louisiana have high sodium and high bicarbonate levels. Morgan and Winner (1962) and Khan et al. (1972) cited bacterial processes and ion exchange as the most likely controls over the water chemistry. This was challenged by Hanor (1980) on the basis of thermodynamic considerations; he suggested that feldspar dissolution and clay formation could explain the observed major element chemistry.

This study addresses three problems relevant to the southeastern Louisiana aquifers. The first is concerned with the rates and spatial distribution of excess CO_2 production. The second concerns whether CO_2 is derived from bacterially-oxidized organic material. The final is to understand the origin and evolution of the groundwater major element chemistry and its high Na-HCO_3 levels. The specific objectives were:

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4. To distinguish between aerobic, sulfate-reducing, and methanogenic microbial metabolism.

5. To evaluate the relative roles of calcite dissolution, silicate dissolution, and ion exchange in modifying groundwater chemistry.

2.0 BACKGROUND INFORMATION

2.1 The Aquifer System

The Southern Hills Regional Aquifer System (named by Buono, 1983) of southeastern Louisiana and southwestern Mississippi consists of a series of gulfward dipping, east-west trending, alternating sand aquifers and clay aquitards of Miocene to Pleistocene age (Figure 1). These are overlain by shallow Pleistocene upland deposits and Mississippi River alluvial deposits. The system is bounded hydraulically to the west by the Mississippi River, to the north by the outcrop limit, to the south by the Baton Rouge Fault Zone, and to the east by the Amite River, a groundwater divide (Figure 2). Discharge occurs in the southern-most part of the system, while recharge by rain and leakage from overlying aquifers occurs in the northern four-fifths of the region (Figure 2). The study area includes Amite County (Mississippi), East Feliciana Parish (Louisiana), and East Baton Rouge Parish (Louisiana) (Figure 3).

Tertiary and Lower Pleistocene sand and clay sediments were deposited during repeated transgressions and regressions of the Gulf of Mexico (Sellards et al., 1932; Dixon, 1963). Flood plain, deltaic, and fluvial sediments were deposited during the dominant regressive intervals, with thin interfingering marine clays and marls deposited during transgressions. As a result, beds are discontinuous over the area and many of the sand units are hydraulically connected (Morgan, 1963; Khan et al., 1972; Buono, 1983). In the study area, the sands are informally named according to their depth of occurrence at the Baton Rouge Fault Zone, a leaky hydrologic barrier (Figure 1) (Buono, 1983). Groundwater is salty on the downthrown (south) side of the fault.

Sand units south of the Baton Rouge fault are saturated with brackish connate waters; on the north side of the fault, the sands have been flushed with freshwater (Rollo, 1969; Whiteman, 1979). As a result of incomplete flushing, the deepest "2800 foot sand" (Whiteman, 1979) unit contains remnant connate water for several miles north of the fault (Whiteman, 1979). Saltwater encroachment through the barrier has also occurred to a limited extent in the upper sand units (Rollo, 1969; Whiteman, 1979).

Aquifer sands are dominated by quartz with subordinate amounts of feldspar some of which has been altered to clay (Meyer and Turcan, 1955; Hanor, 1980). Calcium carbonate is locally abundant. Aquitard sediments consist of a mixture of sand, silt, and clay minerals; the fine-grained layered silicates are in exchange equilibrium with the nearby aquifer waters. Organic carbon in the aquicludes comprises between 0.1 and 3 wt% of the bulk sediment (Hanor, 1980).

Recharge rates, established from tritium isotope profiles (Aharon, unpubl. data), vary from 0.3 to 0.6 meters per year. Groundwater generally flows southerly in response to topographic gradients from north to south, with an estimated horizontal flow velocity of 78m/yr and 200 m/yr in the shallow (400-600 foot sands) and deeper (2000 foot sands) aquifers, respectively (Buono, 1983). Upward flow and discharge from the system occur at lower elevations near the Baton Rouge fault zone. Accelerated whose experiments showed that waters in contact with lignite, calcite, and ion exchange material became similar in composition to the natural waters occurring in coastal plains aquifers. Foster hypothesized that oxidation of organic material was the source of excess CO_2 in the system, and that subsequent dissolution of calcium carbonate was accompanied by base exchange of sodium for calcium on clays.

Hanor (1980) rejected the role of ion exchange in forming $Na\text{-}HCO_3$ rich waters, and instead invoked silicate breakdown reactions with subsequent incorporation of Ca and Mg on newly formed clay lattice sites. Excess Na was produced by the breakdown of Na-bearing smectite and feldspar. He suggested that *in situ* bacterial alteration of organic matter during earliest clay diagenesis produced bicarbonate that migrated outward into the sands. Ion exchange was rejected on the basis that connate waters were riverine and were therefore already in exchange equilibrium with the sediments.

Isotopic studies of the total dissolved carbon phase in groundwaters from other aquifer systems tend to support Foster's model (Pearson and Friedman, 1970; Winograd and Farlekas, 1974; Rightmire and Hanshaw, 1973). The $\delta^{13}C$ composition of the excess dissolved carbon phases generally indicates an organic source. Thus far, little work has been done to delineate the relative roles of ion exchange, carbonate dissolution, and silicate dissolution, and few attempts have been made to distinguish between possible bacterial pathways (e.g., aerobic oxidation and sulfate reduction).

withdrawal rates, however, have resulted in a cone of depression centered at the Baton Rouge industrial complex. This cone of depression has disrupted natural flow patterns. The age of the oldest fresh water in the system was calculated from Darcy's law to lie between 4000 and 8000 years, indicating that most of the groundwater postdates both glacial precipitation and glacial melt (Gonthier, 1989).

Bicarbonate content was computed on the basis of mass and charge balance by Khan et al. (1972), and was used to divide the freshwater into three zones: (1) shallow, unconfined aquifers containing approximately 2 mmol/L of bicarbonate; (2) transition zone between zones 1 and 3 in the "400", "600", and "800 foot sands;" and (3) "1000" to "2800 foot sands" with increasing Na and HCO_3 contents with depth.

2.2 Previous Work

The groundwater hydrology of Southeast Louisiana has been comprehensively studied over the previous fifty years (e.g. Cushing and Jones, 1945; Meyer and Turcan, 1955; Morgan, 1961, 1963; Morgan and Winner, 1962; Smith, 1969; Kazmann, 1970; Rollo, 1969; Khan et al., 1972; Nyman and Fayard, 1978; Martin and Whiteman, 1989). Geochemistry of the waters has been studied by Meyer and Turcan (1955), Morgan (1961), Morgan and Winner (1962), Khan et al. (1972), Hanor (1980), and Gonthier (1989).

Several different hypotheses have been developed to explain the origin of elevated $Na-HCO_3$ contents in the Southern Hills Regional Aquifer complex. The classic work was by Foster (1950), Although Foster (1950) speculated that bacterial oxidation of organic material occurs deep within aquifers, until recently, most evidence of bacterial activity was indirect. Several studies have now documented the presence of bacteria in shallow and deep groundwaters by enumeration and incubation. Aerobic, sulfate-reducing, methanogenic, and facultatively anaerobic bacteria have each been identified from different sites and depths (Olson et al., 1981, Chapelle et al., 1987, Chapelle et al., 1988, Grossman et al., 1989, Fliermans, 1989). The occurrence of viable bacterial assemblages as deep as 1800 meters (Olson et al., 1981) supports the feasibility of Foster's model.

3.0 METHODS

Groundwater samples from fifty-four (54) active freshwater wells in East Baton Rouge Parish, East Feliciana Parish, and Amite County (Figure 3) were collected at the well heads between January and June of 1990. Collection sites were selected to achieve reasonable coverage of each of the major sands from the recharge area to the discharge area. Active wells were sparse in the area between the recharge zone (towns of Norwood, Clinton, Wilson, Jackson, Centerville), and the discharge zone (Zachary, Baker, Baton Rouge).

Temperature (+/- 0.5°C) and pH (+/- 0.01 standard pH unit) were measured on-site, and tightly sealed 100 mL bottles were removed to the laboratory. A few grains of mercuric chloride were added to each bottle before sealing in order to prevent subsequent bacterial activity. In most cases, alkalinity titrations were performed within twenty-four hours. Dilute hydrochloric acid (0.01N) was used to titrate 5 to 10 mls of water in a covered, stirred beaker using an Orion pH meter and combination pH electrode. The equivalence point was determined using Gran calculations (Gran, 1952). The reproducibility of the alkalinity measurements was +/-0.1 meq/L.

Total dissolved inorganic carbon (DIC) and $\delta^{13}C$ were determined within a week of collection using the technique described in Graber and Aharon (in prep; Appendix 2). In this method, 2 ml samples are injected into a temperature-controlled, evacuated reaction vessel containing phosphoric acid. The evolved CO_2 is removed from the solution by stirring and dynamic cold pumping using a series of dry ice/alcohol and liquid nitrogen-cooled traps. The amount of CO_2 is measured with the mass spectrometer and the gas is analyzed for its isotopic composition. Accuracy and precision for DIC measurements were both within 0.1 mmol/L, and for $\delta^{13}C$, were within 0.1°/oo. Results are reported in the delta notation ($\delta^{13}C = ({}^{13}C/{}^{12}C_{(sample)} - {}^{13}C/{}^{12}C_{(standard)})/{}^{13}C/{}^{12}C_{(standard)}) \times 1000$ in parts per thousand (°/oo) with respect to the Peedee Belemnite Standard (PDB). Mass spectrometer corrections as reported by Craig (1954) were followed.

$\delta^{18}O$, Na content, and Cl content were analyzed by Gonthier (1989) from water samples collected from these same wells in 1987. $\delta^{18}O$ was determined using the Epstein and Mayeda (1953) equilibration method with a reproducibility of 0.1°/oo. Chloride was determined by the Mohr titration method with a reproducibility of +/- 1ppm. Ca, Mg, Na, and H_4SiO_4 contents of the 1990 samples were determined by inductively coupled plasma (ICP) analysis (std. dev.: H_4SiO_4 = +/- 2%, Na = +/- 2%, Ca = +/- 2%, Mg = +/- 2%).

Calcite and dolomite saturation states (defined as the free energy of dissolution) were computed using the collected data and temperature dependent equilibrium constants reported by Butler (1982). For saturation calculations, sulfate (not measured) concentrations were taken to be 8 mg/L, the average value reported by Khan et al. (1972) for Baton Rouge waters. The calculations were also performed using values ranging between 2 and 14 ppm (2 standard deviations). The difference in computed saturations was less than 2 percentage points.

The data generated for this report is tabulated in Appendix 1. Data from Gonthier's (1989) study is also presented in Appendix 1.

4.0 THEORY AND METHODOLOGY

4.1 Carbon Sources in Groundwaters

Stable carbon isotopes, ^{13}C and ^{12}C, occur in natural carbon compounds at about 1 and 99% abundance, respectively. Isotope ratios of $^{13}C/^{12}C$ in natural carbon-bearing compounds vary considerably with the source of the carbon and the pathway of carbon fixation during metabolic processes. Hence it is possible to use carbon isotope ratios to study both the source of the carbon and the biota affecting it. Carbon sources in groundwater, bacterially-mediated chemical reactions, and the effects of bacterial activity on $\delta^{13}C$, carbonate alkalinity, and DIC, are summarized in Table 1.

During rainfall in recharge areas, CO_2-charged precipitation introduces carbon dioxide with atmospheric values of -6 to -7°/oo into the aquifer system (Keeling et al., 1979). As the waters percolate through the unsaturated zone, CO_2 derived from aerobic bacterial oxidation of organic material in the soil zone is added. The isotopic composition of the resultant CO_2 is substantially more depleted in ^{13}C relative to the atmospheric value because organic matter and its oxidation products preferentially sequester the ^{12}C isotope (Deines, 1980). An increase in CO_2 resulting from bacterial respiration in the soil or aquifer leads to the dissolution of carbonate and silicate minerals, thus adding excess bicarbonate to the groundwater. In the case of carbonate dissolution, the $\delta^{13}C$ composition of DIC is expected to yield intermediate values between those of CO_2 released from bacterial respiration, and those of the dissolved carbonate with typical values of 2 to -5°/oo (Milliman, 1974). In the case of silicate dissolution, $\delta^{13}C_{DIC}$ is expected to remain unchanged, as no new carbon is added to the system.

Mass balance calculations using measured values of $\delta^{13}C$, DIC, alkalinity, sodium, and H_4SiO_4 can be used to evaluate chemical changes occurring between points along a groundwater flow path. The isotope composition of the added CO_2 can be calculated in order to determine its source using the mass balance equation below (Chapelle et al., 1987):

$$\delta^{13}C_f = (\delta^{13}C_i)(m_i) + (\delta^{13}C_a)(m_a) + (\delta^{13}C_c)(m_c)/m_i+m_a+m_c \quad (1)$$

$\delta^{13}C_f$ is the measured (final) isotope composition of the sample, $\delta^{13}C_i$ is the isotope composition of the original DIC, m_i is the number of moles of original DIC, $\delta^{13}C_a$ is the isotopic composition of the added CO_2, m_a is the number of moles of added CO_2, $\delta^{13}C_c$ is the isotopic composition of the dissolved carbonate mineral, and m_c is the number of moles of carbonate mineral dissolved.

Rates of excess CO_2 production along groundwater flow paths can be estimated by applying another mass balance equation (Chapelle et al., 1987):

$$CO_2\ (PR) = (R)(m_a)/L \quad (2)$$

where CO_2 (PR) is the production rate of CO_2 averaged over a flow path segment, m_a is the moles of CO_2 added, L is the length of the flow path, and R is the rate of groundwater flow.

4.2 Alkalinity and Total Dissolved Inorganic Carbon (DIC)

An important concept in the study of waters is *alkalinity*, defined as the hypothetical amount of strong base that must be neutralized in order to reach a pH corresponding to a solution of pure CO_2 and water (Butler, 1982). In a simple system, consisting of only NaOH and dissolved carbon species, alkalinity is given by:

$$A = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (3)$$

The operational definition (titrate the sample with standard HCl to the methyl orange endpoint) applied to a natural water may also include other weak acids and bases such as borate, ammonia, hydrolized ferric ion, or organic acid anions, and is called total alkalinity. In dilute natural waters, total alkalinity is generally taken to be equal to carbonate alkalinity (Butler, 1982). Between a pH of 5 and 9, bicarbonate is the dominant carbon-bearing species, and the bicarbonate concentration is essentially equal to the alkalinity.

Total dissolved inorganic carbon (DIC) is the inventory of carbon in both charged and uncharged species in solution, and is represented by a mass balance of carbon:

$$DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \quad (4)$$

An important property of alkalinity is that it does not change when CO_2 is added to or withdrawn from solution, because the combination of charged concentrations given by Eq. (3) are unaffected. Altering the amount of CO_2 in solution does change tha total dissolved inorganic carbon (DIC). Adding or removing bicarbonate (HCO_3^-) changes both DIC and alkalinity in a one-to-one ratio, while adding or removing CO_3^{2-} changes alkalinity by two units and DIC by one unit.

A graphic technique developed by Deffeyes (1965) using alkalinity as the ordinate and DIC as the abscissa has a number of useful characteristics. Changes in solution chemistry move the point representing the solution on the diagram in definite directions depending on the reaction stoichiometry. For example, in Figure 4a, adding CO_2 changes only the concentration of DIC, and thus the initial solution moves from point 1 to point 2. Addition of OH- increases only alkalinity, and moves the solution from point 2 to point 3. As depicted in Figure 4b, the dissolution of calcite contributes 2 units to alkalinity for each additional unit of DIC. Since reactions such as calcite dissolution and CO_2 addition alter the solution according to definite stoichiometries, the change in solution chemistry can be split into component vectors representing a calcite component and a CO_2 component. In this way, contributions to the carbon budget by various processes can be assessed and distinguished.

5.0 RESULTS

A number of the measured chemical parameters display a general increase with depth. Water temperature measured at the well head increases from approximately 20°C in the shallow recharge zone to 35°C in the discharge zone (Figure 5). This represents a minimum geothermal gradient of 15°C/km. Other parameters which generally increase with depth include pH (5 to 9 standard pH units) (Figure 6), DIC (0.7 to 7.5 mmol/L) (Figure 7), alkalinity (0.1 to 6.5 meq/L) (Figure 8), $\delta^{13}C$ (-22 to -13°/oo) (Figure 9), Na (5 to 150 mg/L) (Figure 10), and calcite saturation (0% to 97%) (Figure 11). All the waters were found to be completely undersaturated with repect to dolomite (Appendix 1).

Calcium and magnesium are highly positively correlated (Figure 12), and display substantial, though non-linear, decreases with depth (Figures 13 and 14). Chloride is invariant and low, except for four shallow (400-600 foot aquifer) wells with elevated contents (Figure 15). Although the 400-600 foot aquifers suffer from saltwater intrusion (Whiteman, 1979), the absence of corresponding elevated Na contents suggests an anthropogenic source for the chloride (Gonthier and Aharon, 1990). Except for low values in the shallowest recharge wells, silica content of the waters seems to decrease with depth, albeit with large scatter, from a maximum of 30 ppm to a minimum of 10 ppm (Figure 16).

Although DIC, alkalinity, and sodium generally increase with depth, their behavior within each sand unit is complex and non-linear (Figures 17, 18, and 19). In each case, the recharge zone is impoverished and the 2800 foot aquifer is enriched. All the intervening sands (400, 600, 1000, 1200, 1500, 1700, 2000, and 2400 foot) have intermediate and variable compositions unrelated to absolute depth. This zonation varies markedly from that reported by Khan et al. (1972) (Section 2.1). The discrepancy is probably due to the fact that Khan et al. did not measure alkalinity, but computed it from a charge balance. Their empirical method of alkalinity estimate is deficient because values incorporate the measurement errors of all the parameters.

Sodium and alkalinity display a marked linear covariance with depth (Figure 20). This correlation can also be seen within each sand unit by comparing trends along lithologic layers (Figures 18 and 19). Importantly, although DIC and alkalinity are also highly correlated ($r^2=0.93$) (Figure 21), Na tracks DIC much less well than it tracks alkalinity (compare Figures 17 and 19 with Figures 18 and 19).

$\delta^{13}C$ is quite variable at all depths, and can be relatively high even in the recharge zone (Figure 22). This is because at low DIC levels, $\delta^{13}C$ is very sensitive to additions of carbon which can make up a large percentage of the total. Overall, there is a ^{13}C enrichment with increasing depth from approximately -22°/oo to -13°/oo.

Chemical patterns are contoured on projections (Figure 1) along a north-south cross-section line (Figure 23a-f). Several trends common to the measured parameters are noted. First, chemical gradients are gentle over most of the cross sectional area, both along recharge flow paths from the north to the south, and along discharge flow paths from deep to shallow aquifers. Second, there are steep chemical gradients at intermediate depths in the 1700, 2000, 2400, and 2800 foot aquifers. Third, steep gradients in the 2400 and 2800 foot aquifer occur in the deepest portion of the sands and are nearly horizontal. Because the wells are projected into a single plane, steep contoured gradients do not necessarily represent changes parallel to flow.

The patterns for DIC, alkalinity, Na, and calcite saturation are very similar (Figure 23a-d). In the discharge area, the gradients are small until the 2400 and 2800 foot sands are reached. Further north, there are steep chemical gradients in the 1700, 2000, 2400, and 2800 foot sands. In the discharge area and deep aquifers, $\delta^{13}C$ (Figure 23e) contours are similar to DIC, alkalinity, Na, and % calcite saturation. In the recharge area and shallow aquifers, however, the pattern of ^{13}C-enrichment differs because $\delta^{13}C$ is more sensitive to small changes in DIC and alkalinity when the initial DIC content is low. The chemical contours of H_4SiO_4 (Figure 23f) are quite different from the others in two ways: (i) where all the other parameters increase, H_4SiO_4 decreases; and (ii) H_4SiO_4 content is variable in the shallow aquifers throughout the whole area. This suggests that local mineralogy may more impact on H_4SiO_4 concentrations than does overall, downflow, chemical change.

6.0 DISCUSSION

6.1 The Rejected Model - Sodium-rich Silicate Dissolution

There are a number of lines of evidence suggesting that feldspar dissolution is not responsible for downflow increases in sodium as suggested by Hanor (1980). First, incongruent dissolution reactions involving a sodium-rich silicate such as albite and a clay such as kaolinite, would release approximately twice as much silicic acid to solution as Na:

$$NaAlSi_3O_8\ (ab) + H_2CO_3^* + 9/2H_2O \ - \ Na^+ + HCO_3^- + 2H_4SiO_4 + 1/2Al_2Si_2O_5(OH)_4\ (kaol) \quad (5)$$

However, Na content of the waters varies from 0.5 to 7 mmol/L while H_4SiO_4 content varies only 0.1 to 0.35 mmol/L, a twentyfold increase of Na over H_4SiO_4.

Second, feldspar dissolution does not contribute new carbon atoms to the DIC system, and $\delta^{13}C_{DIC}$ should remain unchanged. In fact, though, $\delta^{13}C_{DIC}$ increases from $-22^{o}/_{oo}$ to $-13^{o}/_{oo}$ from the recharge area to the deepest part of the aquifer complex.

Third, during the breakdown of feldspar to clay, dissolved CO_2 is converted to HCO_3^-, thus the overall amount of DIC remains fixed while alkalinity increases. On a Deffeyes plot of DIC versus alkalinity (Figure 4), the point representing the solution will move up parallel to the alkalinity axis during feldspar dissolution. In an actual groundwater system, where CO_2 is also being added, the samples will plot in the field above the bicarbonate line marked in Figure 21. In this study, the samples plot well below the bicarbonate line.

Fourth, if feldspar dissolution is the source of sodium, the observed increase in sodium with depth should be accompanied by an increase in silicic acid. However, silicic acid concentrations in the groundwaters generally decrease in concentration with depth in the intermediate and deep aquifers (Figure 16).

Based on the evidence above, feldspar dissolution cannot account for the chemical changes observed in these waters. The hypothesis suggested by Hanor (1980) is insupportable and is thus rejected.

6.2 The Accepted Model - Calcite Dissolution, Ion Exchange, and Bacterial CO_2 Production

All the evidence suggests that the processes of calcite dissolution, ion exchange, and bacterial CO_2 production combine to result in the observed water chemistry.

6.2.1 Calcite Dissolution

One way to explain the increase of $\delta^{13}C_{DIC}$ with depth (Figure 22) is by dissolution of calcite with an average carbon isotope composition of 0°/oo. The increase in bicarbonate concentration downflow can also be attributed to calcite dissolution, a process which increases DIC by one unit and alkalinity by two on a Deffeyes diagram. Groundwater samples should and do plot in the field below the bicarbonate line marked in Figure 21 when the combined processes of calcite dissolution and CO_2 addition occur. The amount of CO_2 added versus the amount of calcite dissolved can be resolved by plotting the solution compositions on a Deffeyes diagram and by dividing the components into their respective vectors (Figure 4b). This has been discussed Section 4.2.

There is an increase in calcite saturation with depth, from 0% saturated to nearly 100% saturated (Figure 11). The increase corresponds to that of alkalinity through the section (Figure 23b and d), suggesting a relationship between the two.

One parameter which should increase as calcite is dissolved is calcium. However, calcium decreases downflow (Figure 13). This can be explained by calcium uptake on clays with the concommitant release of ions such as sodium. If ion exchange is occuring, sodium would increase downflow, as is observed in Figures 10 and 23c.

6.2.2 Ion Exchange

In rejecting ion exchange of Ca for Na on clays in the aquifers and aquitards, Hanor (1980) assumed that the initial connate waters were riverine and are still extant in the aquifer system. This means that the water and sediments would have been in exchange equilibrium at the time of deposition, and that there would have been no thermodynamic drive for ion exchange. However, initial connate waters were brackish (Rollo, 1969; Whiteman, 1979), and have been subsequently flushed by fresh water recharge (Morgan, 1961; Buono, 1983; Gonthier, 1989). Using Darcy's law, Gonthier (1989) calculated the age of the oldest fresh water in the system to be only 8000 years.

The cation exchange capacity (CEC) of the bulk clay, a mixture of kaolinite, illite, and montmorillonite (Hanor, 1980), ranges from 36 to 76 meq/100 grams, and for bulk sediment, from 13 to 53 meq/100 grams (Hanor, 1980). These sodium-saturated clays (originally in equilibrium with brackish connate waters) were thus the most probable source of Na for exchange with Ca brought into the system by recharge waters and by calcite dissolution.

In addition to providing a source of Na and a sink for Ca, ion exchange drives calcite dissolution forward beyond its natural equilibrium and causes undersaturated conditions to linger. The amount of calcite dissolved can be determined by the stoichiometry of calcite dissolution, which requires that moles of calcite dissolved are equal to the moles of calcium and half the moles of HCO_3^- in solution.

$$CaCO_3 + H_2CO_3^* \quad - \quad Ca^+ + 2HCO_3^- \qquad (6)$$

If ion exchange results in a 2:1 substitution of Na for Ca (Stumm and Morgan, 1981, p. 643), then moles of calcite dissolved should also equal half the moles of Na in solution. The good correlation observed between Na and alkalinity (Figure 20) supports this relationship.

Mass balances computed using both Na and alkalinity can provide a test of the importance of ion exchange in controlling groundwater chemistry. Na can also be used to evaluate minor contributions by feldspar dissolution. For example, excess Na over alkalinity may be ascribed to feldspar contributions. Similarly, excess alkalinity over Na can be used to differentiate between bicarbonate derived from calcite dissolution and bicarbonate derived via sulfate reduction. This will be discussed in a later section.

6.2.3 Sources and Rates of CO_2 Production Across the Aquifer System

A single mass balance calculation based on initial and final water compositions can serve to preface the following discussion of sources and rates of CO_2 generation in the subsurface. Equation (1), presented earlier and reproduced below, will be used. This equation has terms for the initial DIC, an addition of CO_2, and an addition of dissolved calcite. Using this equation, the isotopic composition of the added CO_2 will be computed.

Recharge waters are best represented by an initial DIC content of 1.2 mmol/L and HCO_3^- of 0.2 mmol/L; the oldest (deepest) water contains 7.4 mmol/L DIC and 6.3 mmol/L HCO_3^-. Na content of the recharge waters is approximately 0.4 mmol/L; Na content of the deepest water is 6.5 mmol/L. $\delta^{13}C_i$ (initial) is -22°/oo; $\delta^{13}C_f$ (final) is -13°/oo. H_4SiO_4 remains nearly unchanged at approximately 0.1 mmol/L. The dissolved calcite (moles of dissolved calcite = m_c) is assumed to have a $\delta^{13}C$ ($\delta^{13}C_c$) value of 0°/oo (marine carbonate generally varies between -5 to +2°/oo, with 0°/oo being a reasonable average value).

In order to determine the molar contributions of calcite and CO_2, the initial and ending DIC and alkalinity contents are plotted on a Deffeyes diagram (Figure 24). The calcite and CO_2 are broken into component vectors and their respective contributions are read from the plot. In this case, 3.15 mmol/L of CO_2 are added, and 3.05 mmol/L of calcite are dissolved.

We wish to solve for $\delta^{13}C_a$, the carbon isotope composition of the added CO_2:

$$\delta^{13}C_f = (\delta^{13}C_i)(m_i) + (\delta^{13}C_a)(m_a) + (\delta^{13}C_c)(m_c)/(m_i+m_a+m_c)$$

$$-13 = (-22)(1.2) + (\delta^{13}C_a)(3.15) + (0)(3.05)/1.2 + 3.15 + 3.05$$

hence: $\delta^{13}C_a = -22.16$

Using a calcite of $\delta^{13}C$ equal to -5°/oo instead of 0°/oo yields -17.3°/oo for the incoming CO_2.

Sediment samples were unavailable for this study, and thus neither organic matter nor carbonate were measured directly for $\delta^{13}C$. It is assumed that the organic material of the aquifers and aquitards consists of a mixture of C3 and C4 terrestrial plants, marine plankton, and marine plants. The more labile organic components of these are enriched in ^{13}C (Deines, 1981; Degens, 1969), but bacteria selectively use ^{12}C-enriched functional groups (Rosenfield and Silverman, 1959; Kaplan and Rittenberg, 1964). Based on probable sources, organic matter may vary in composition between -15 to -30°/oo. The average $\delta^{13}C$ of organic matter among all marine sediments is -23°/oo (Anderson and Arthur, 1982). This value is certainly in good agreement with the $\delta^{13}C$ values of -22.2 and -17.3 calculated above for the incoming CO_2.

In this instance, the change in sodium content is exactly equal to the change in alkalinity. Thus sodium content could also be used to indicate how much calcite was dissolved. This demonstrates the importance of ion exchange in controlling groundwater chemistry.

A similar general calculation can be made to ascertain the average rate of CO_2 production from the surface to the deepest point in the aquifer using equation (2). The total distance between these two points is approximately 41 miles. An average horizontal flow velocity is taken to be 0.07miles/yr, which is an average of the velocities in the 2400 and 2800 foot sands (Buono, 1983). Simply regarded, the CO_2 production rate can be calculated as the flow rate multiplied by the amount of CO_2 added, all divided by the length of the flow path:

CO_2 (PR) = Rma/L

CO_2 (PR) = (0.07) x (3.15)/41

CO_2 (PR) = $5.4\text{x}10^{-3}$ $\text{mmolL}^{-1}\text{yr}^{-1}$

The calculated average production rate (using 3.15 mmol/L of added CO_2 as determined from the Deffeyes diagram in Figure 24) is $5.4\text{x}10^{-3}$ $\text{mmolL}^{-1}\text{yr}^{-1}$.

6.2.4 Sources and Rates of CO_2 Production in High Productivity Zones

The rate of CO_2 production is not uniform across the aquifer system, but is concentrated in particular zones: at intermediate depths in the 1700, 2000, 2400, and 2800 foot aquifers, and at the deepest reaches of the 2400 and 2800 foot aquifers (Figure 23). Two additional mass balance calculations in high productivity areas are shown in Figure 25. In the first area, labeled 2-2′ on Figure 23a, the carbon isotope composition of the incoming CO_2 is calculated to be -21.7°/oo, and in the second, labeled 3-3′, -18.1°/oo. Again, these values indicate an organic source of carbon. The rates of CO_2 production were calculated to be $4.9\text{x}10^{-2}$ and $6.4\text{x}10^{-2}$ $\text{mmolL}^{-1}\text{yr}^{-1}$, respectively. This is more than a tenfold increase over the average production rate.

The results of all these calculations indicate that the source of additional CO_2 is in situ bacterial alteration of organic matter. The rates of CO_2 production vary throughout the system, and production is concentrated in the lower sand units. The amount of bacterially-generated CO_2 is substantial, and is overall slightly higher than the amount of bicarbonate contributed to the system by calcite dissolution.

6.3 Nature of Bacterial Activity

The computed carbon isotope values for incoming CO_2 of -17 to -22°/oo preclude contributions from methane oxidation or methanogenesis. This is because methanogenesis causes intense fractionation of carbon isotopes between the two products, CO_2 and methane (CH_4). CO_2 produced during methanogenesis will be very enriched in ^{13}C, and will have a carbon isotope composition of +10 to +30°/oo. The mass balances above, however, indicate that the composition of the incoming CO_2 was only -22 to -17°/oo. $\delta^{13}C_{DIC}$ from other aquifers in which methanogenesis occurs is as heavy as 0°/oo, and mass balances clearly identify the heavy CO_2 source (Grossman et al., 1989).

There is also little or no evidence for substantial contributions by sulfate-reducing bacteria. In all but 5 wells from the deepest portion of the 2800 foot aquifer, no H_2S was detected by smell, indicating less than 25 ppb H_2S (Standard Methods, 1985). Second, the SO_4^{--} content is essentially invariant throughout the section (Khan et al. 1972). If sulfate-reducing bacteria were active, H_2S would be more prevalent, and sulfate levels would decrease downflow (Foster, 1950).

In the deepest wells, a faint H_2S odor indicated that sulfate reduction was occurring. Significant contributions by sulfate-reducers can, in this system, be determined on the basis of HCO_3^- and Na contents. The reduction of sulfate to sulfide and the oxidation of organic matter liberates HCO_3^-, not CO_2. If sulfate-reduction is considerable, some of the excess alkalinity will be derived from sulfate reduction, and only some from calcite dissolution. The change in Na, as the calcite dissolution index, would be less than the change in alkalinity, and the difference between Na and alkalinity would be a measure of the amount of sulfate reduction. In the 2800 foot sand, sodium is essentially equal to the alkalinity (Appendix 2), indicating that no significant contribution to the carbon budget was made by sulfate-reducers.

Thus we conclude that the vast majority of the bacterial activity in this aquifer is aerobic in origin.

7.0 CONCLUSIONS

The primary goal of this study was to evaluate the contribution of bacterial metabolism to the development of high $Na-HCO_3$ waters in the Baton Rouge aquifer system. In so doing, the nature and rates of bacterial activity were explored, and the relative roles of ion exchange, silicate dissolution, calcite dissolution, and bacterial oxidation of organic material were elucidated.

The impact of silicate reactions on groundwater chemistry was found to be negligible, while the impacts of bacterial oxidation of organic matter, calcite dissolution, and ion exchange on major element and isotope chemistry were found to be profound. Sodium, derived by a two-for-one ion exchange with calcium, was found to be a good predictor of the amount of calcite dissolved.

The contribution to the carbon dioxide budget by bacteria oxidizing organic matter deep in the aquifers was substantial (3.15 mmol/L), and coequal to the contribution by calcite dissolution (3.05 mmol/L). These contributions can be differentiated by plotting DIC versus alkalinity on a Deffeyes diagram, and by breaking them into their component vectors.

There is no evidence for methanogenic microbial activity on the basis of carbon isotope values. There is also little or no evidence for sulfate reducing bacteria, which can be distinguished from aerobic bacteria on the basis of their byproducts and on the sodium content of the waters. Aerobic bacteria produce CO_2, which causes calcite dissolution and ion exchange with sodium, while sulfate-reducers produce HCO_3^- and no subsequent calcite dissolution and sodium release. Sulfate-reduction can be detected by a sodium deficiency compared with HCO_3^- (alkalinity). In this aquifer system, sulfate-reduction probably occurs only in the deepest part of the 2800 foot aquifer, and its contribution to the total bacterial carbon budget is insignificant.

Bacterial activity is concentrated at particular zones in the deeper aquifers, and is minimal in the rest of the system. In those areas of high productivity (6.4×10^{-2} versus an average productivity of 5.4×10^{-3}), it is expected that porosity has been corrosively enhanced. The hydraulic conductivities of the 2000 and 2800 foot aquifers, are, in fact, higher than those of the shallower aquifers (Buono, 1983). Due to calcium uptake on clays, all the waters are undersaturated with respect to calcite, although saturation is approached in the deeper sand units. Local microenvironments may develop in which saturation or oversaturation is achieved, and in which calcite may precipitate. However, calcite cementation should be minimal overall.

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9.0 FIGURE CAPTIONS

Figure 1. Hydrogeologic section showing the freshwater bearing units in East Feliciana and East Baton Rouge Parishes (from Morgan, 1963). The numbers represent the locations of the wells sampled in this study projected into the field of view.

Figure 2. Map view of study area (hatched) and the regional groundwater system.

Figure 3. Map showing sample locations and cross section line of Figure 1.

Figure 4. DIC plotted versus alkalinity in Deffeyes (1965) diagrams. (A) Reactions cause solutions to change according to a definite stoichiometry. In this case, the addition of CO_2 causes DIC to increase and alkalinity to remain the same. Similarly, addition of a strong base will increase the alkalinity without changing DIC. (B) Calcite dissolution causes alkalinity to increase by two units and DIC to increase by one unit. Since the total change in DIC can be split into component vectors representing a calcite dissolution component and a CO_2 addition component, the amount that each has contributed to the carbon budget can be read from the plot.

Figure 5. Water temperature versus depth of well. Temperature increases with depth from approximately 20°C in the shallow recharge zone to 35°C in the discharge zone.

Figure 6. Hydrogen ion concentration in pH units versus depth of well. Note that pH increases with depth from 5.2 to 8.9 pH units.

Figure 7. Total dissolved inorganic carbon (DIC) versus depth of well. DIC increases with depth from 0.7 mmol/L to 7.5 mmol/L.

Figure 8. Alkalinity versus depth of well. Alkalinity increases with depth from 0.2 meq/L to 6.5 meq/L.

Figure 9. $\delta^{13}C_{DIC}$ versus depth of well. $\delta^{13}C$ is variable, but becomes more enriched with increasing depth. At low DIC concentrations, $\delta^{13}C$ is sensitive to additions to the carbon budget and is therefore more variable at shallow depths where DIC is low overall, than at deeper depths where DIC is considerably higher.

Figure 10. Sodium ion concentration versus depth of well (some data is from Gonthier, 1989). Note that Na increases overall from 5 mg/L to 150 mg/L with increasing depth.

Figure 11. Percent calcite saturation versus depth of well. There is a general increase in calcite saturation with increasing depth.

Figure 12. Crossplot depicting the linear correlation ($r^2 = 0.93$) between calcium and magnesium in mg/L.

Figure 13. Calcium ion concentration versus depth of well. Calcium concentrations are highest in the shallow aquifers, and decrease non-linearly to nearly constant and low values in the deeper aquifers. Recharge waters are also low in calcium.

Figure 14. Magnesium ion concentration versus depth of well. Magnesium concentrations are highest in the shallow aquifers, and decrease non-linearly to essentially zero in the deeper aquifers. Recharge waters are also low in magnesium.

Figure 15. Chloride ion concentration versus depth of well (data from Gonthier, 1989). Chloride is invariant and low, except for four shallow (400-600 foot aquifer) wells with elevated contents . Although the 400-600 foot aquifers suffer from saltwater intrusion (Whiteman, 1979), the absence of corresponding elevated Na contents suggests an anthropogenic source (Gonthier and Aharon, 1990).

Figure 16. Silicic acid content versus depth of well. Silicic acid content of the waters appears to decrease (albeit with considerable scatter) with depth in the deeper aquifers, and is variable in the recharge and shallow aquifer zones.

Figure 17. Changes in DIC content of the waters within each aquifer sand unit. Water from the recharge zone has a low DIC content while the deepest "2800-foot" sand has the highest overall DIC content. All of the intermediate aquifers have intermediate values. The variability within each sand unit reflects their heterogeneity and also indicates that the sampled wells are not always aligned along flow paths.

Figure 18. Changes in the alkalinity content of the waters within each aquifer sand unit. Water from the recharge zone has a low alkalinity content while the deepest "2800-foot" sand has the highest overall alkalinity content. All of the intermediate aquifers have intermediate values. The variability within each sand unit reflects their heterogeneity and also indicates that the sampled wells are not always aligned along flow paths.

Figure 19. Changes in Na content of the waters within each aquifer sand unit. Water from the recharge zone has a low Na content while the deepest "2800-foot" sand has the highest overall Na content. All of the intermediate aquifers have intermediate values. The variability within each sand unit reflects their heterogeneity and also indicates that the sampled wells are not aligned along flow paths. The patterns for Na match those for alkalinity very well; the match between Na and DIC is less good.

Figure 20. Linear correlation between Na and alkalinity. There is nearly a 1:1 relationship between these two parameters.

Figure 21. DIC versus alkalinity for the water samples. Note that DIC and alkalinity are linearly correlated. The departure of the points from the "bicarbonate" line suggests the presence of excess CO_2 (see text).

Figure 22. Changes in $\delta^{13}C$ composition of DIC within each aquifer sand unit. $\delta^{13}C$ is quite variable at all depths, and can be relatively heavy even in the recharge zone. Overall, there is a ^{13}C enrichment with increasing depth from approximately -22°/oo to -13°/oo. $\delta^{13}C$ is very sensitive to small changes in DIC or alkalinity at low concentrations overall, and thus shows irregular responses down flow.

Figure 23. Contours of chemical parameters across a north-south section of the Southeast Louisiana aquifer system. Well locations were projected onto a general cross section line running from Amite County, Mississippi to East Baton Rouge Parish, Louisiana (Figures 1 and 3). Concentrations of various parameters have been plotted and contoured on the general cross section. The patterns for each parameter are similar, but vary in distinctive ways. (a) DIC (mmol/L), (b) alkalinity (meq/L), (c) Na (mg/L), (d) % calcite saturation, (e) $\delta^{13}C$ (°/ooPDB), (f) H_4SiO_4 (mg/L). Generally, in the discharge area, the gradients are low until the 2400 and 2800 foot sands are reached. Further north, however, there

are steep chemical gradients in the 1700, 2000, 2400, and 2800 foot sands. In the discharge area and deep aquifers, $\delta^{13}C$ (e) contours are similar to DIC, alkalinity, NA, and % saturation (a-d). In the recharge area and shallow aquifers, the pattern of $\delta^{13}C$ enrichment is different, because $\delta^{13}C$ is more sensitive to small changes in DIC and alkalinity when the initial DIC content is low overall. The chemical contours of H_4SiO_4 (f) differ from the others in two significant ways: (1) where (a) through (e) increase, (f) decreases; and (2) H_4SiO_4 content is very variable in the shallow aquifers throughout the whole area. This suggests that local mineralogy and other conditions have more impact on H_4SiO_4 concentrations than does overall, downflow, chemical change. All the waters plot in the kaolinite stability field.

Figure 24. Deffeyes plot of DIC versus alkalinity used to determine the relative proportions of CO_2 added by organic degradation versus bicarbonate added via calcite dissolution. In this example, the amount of additional CO_2 brought into the system is 3.15 mmol/L and the amount of HCO_3^- derived from calcite dissolution is 3.05 mmol/L. The $\delta^{13}C$ value of the incoming CO_2 is calculated to be -22.2.

Figure 25. Deffeyes plot of DIC versus alkalinity used to determine the relative proportions of organically-derived CO_2 versus HCO_3^- from calcite dissolution in two high productivity areas marked on Figure 23a as 2-2′ and 3-3′.

Table 1: Bacterially-mediated processes and resultant carbon isotope ($\delta^{13}C$), total dissolved inorganic carbon (DIC), and alkalinity (Alk.) changes.

CO_2 Source	Reaction Type	$\delta^{13}C$ (°/oo PDB)	DIC	Alk.
Rainwater infiltration	$CO_2+H_2O \rightarrow H_2CO_3*$	-6:-7	inc.	dec.
Bacterial oxidation	$CH_2O+O_2 \rightarrow CO_2+H_2O$	-12:-26	inc.	dec.
Carbonate dissolution	$CaCO_3+H_2CO_3* \rightarrow 2HCO_3^-+Ca^{++}$	2:-5	inc.	inc.
Sulfate reduction	$2CH_2O+SO_4^{--} \rightarrow H_2S+2HCO_3^-$	-12:-26	inc.	inc.
Anaerobic fermentation	$CH_3COOH \rightarrow CH_4+CO_2$	10:30	inc.	dec.
Aerobic methane oxidation	$CH_4+2O_2 \rightarrow CO_2+2H_2O$	-30:-60	inc.	dec.

FIGURE 1

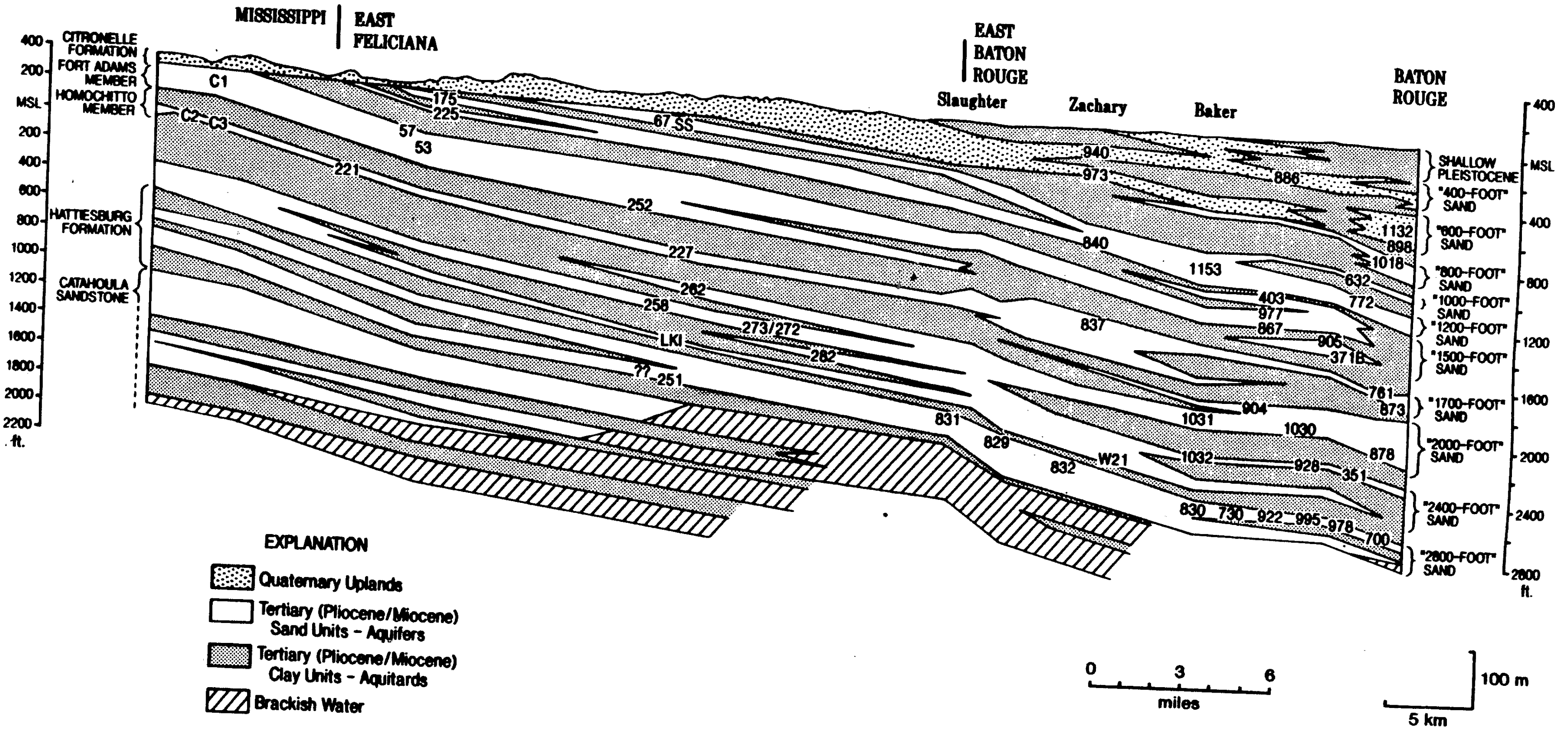

MISSISSIPPI
EAST FELICIANA
EAST BATON ROUGE
Slaughter
Zachary
Baker
BATON ROUGE
400
200
MSL
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
ft.
CITRONELLE FORMATION
FORT ADAMS MEMBER
HOMOCHITTO MEMBER
HATTIESBURG FORMATION
CATAHOULA SANDSTONE
C1
C2
C3
175
225
57
53
67 SS
221
252
227
262
258
LKI
273/272
282
??
251
940
973
840
837
831
829
832
W21
886
1132
898
1018
1153
632
403
977
867
772
905
371B
761
873
904
1031
1030
1032
928
351
878
830
730
922
995
978
700
SHALLOW PLEISTOCENE
"400-FOOT" SAND
"600-FOOT" SAND
"800-FOOT" SAND
"1000-FOOT" SAND
"1200-FOOT" SAND
"1500-FOOT" SAND
"1700-FOOT" SAND
"2000-FOOT" SAND
"2400-FOOT" SAND
"2800-FOOT" SAND
400
MSL
400
800
1200
1600
2000
2400
2800
ft.
EXPLANATION
Quaternary Uplands
Tertiary (Pliocene/Miocene) Sand Units - Aquifers
Tertiary (Pliocene/Miocene) Clay Units - Aquitards
Brackish Water
0
3
6
miles
100 m
5 km

FIGURE 2

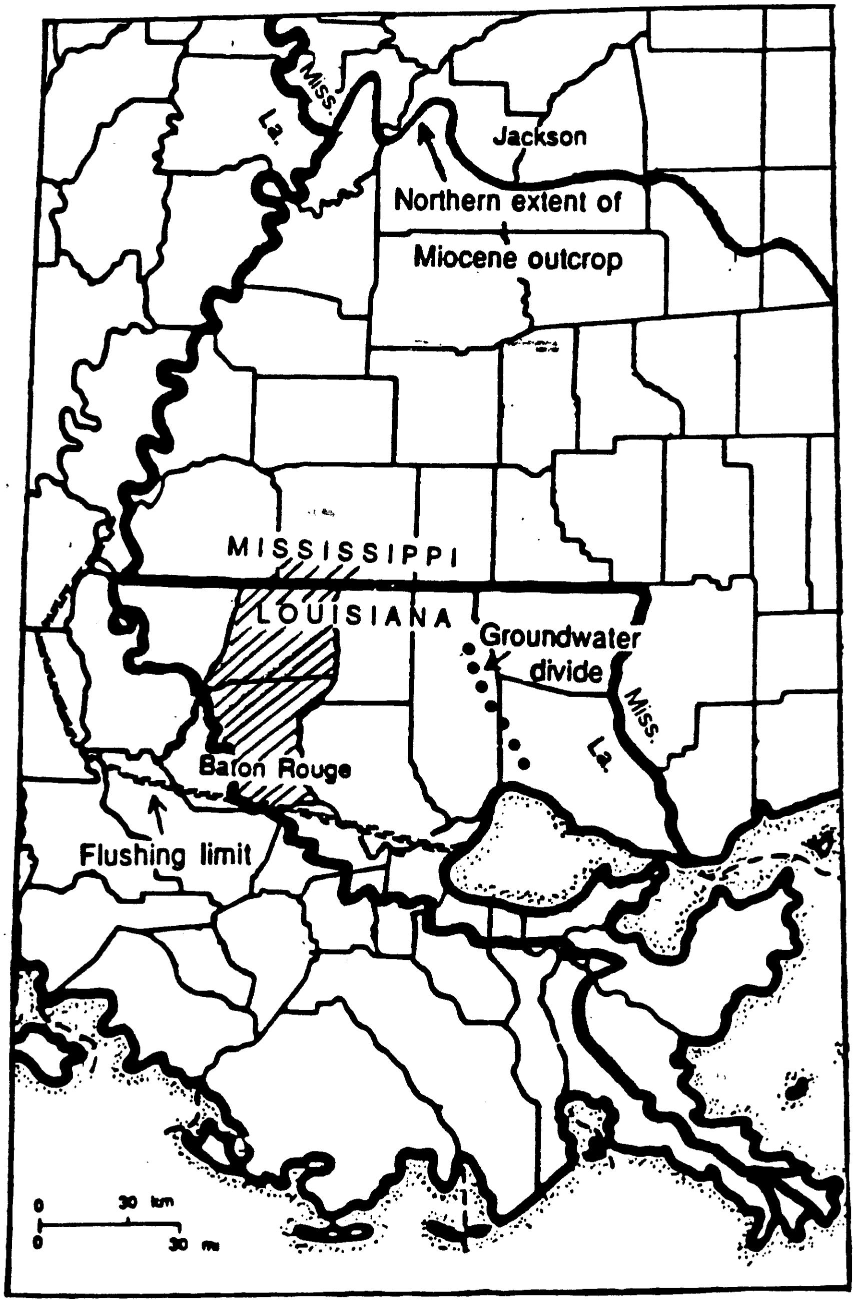
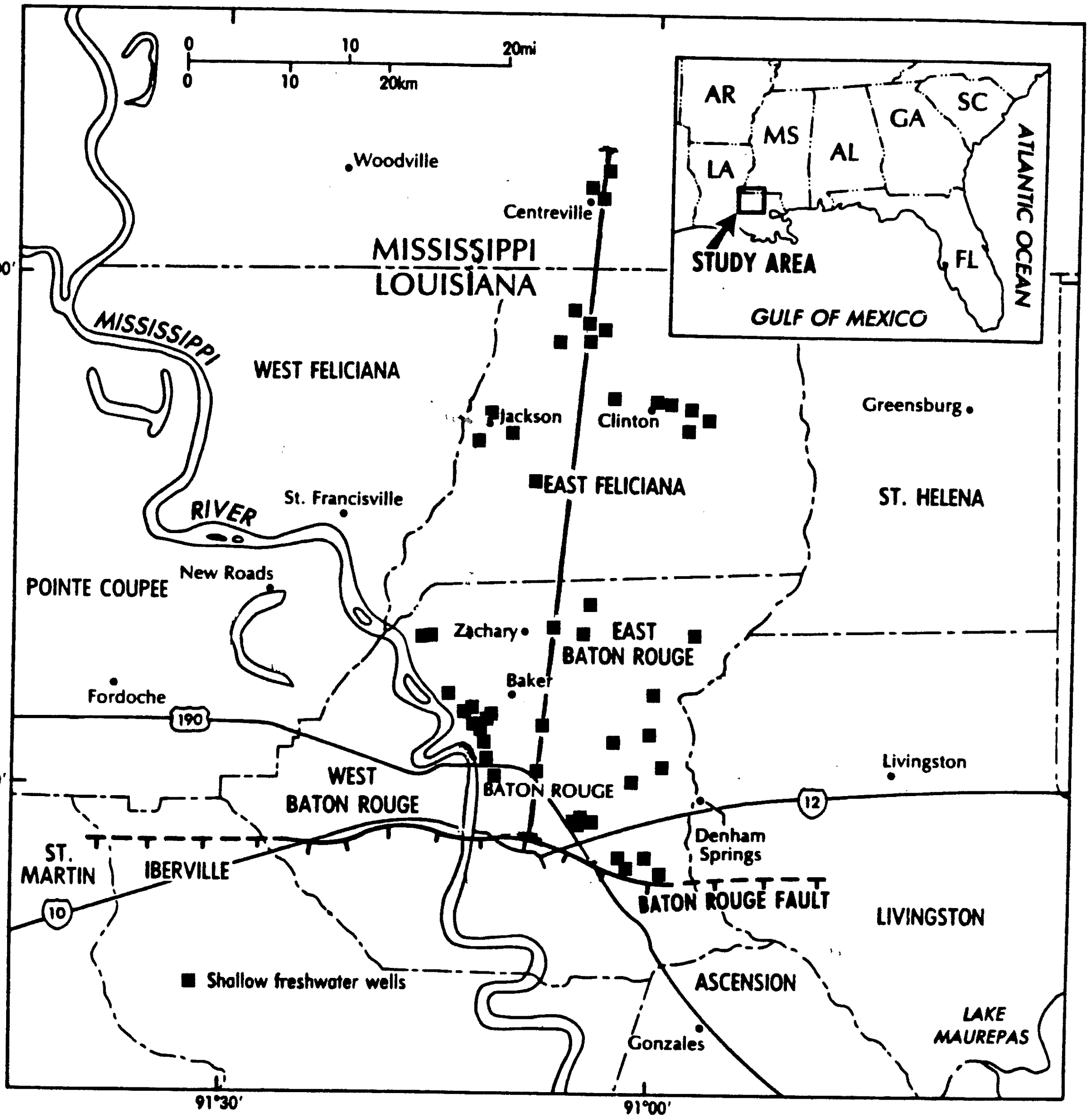

Miss.
La.
Jackson
Northern extent of
Miocene outcrop
MISSISSIPPI
LOUISIANA
Groundwater
divide
Miss.
La.
Baton Rouge
Flushing limit
0 30 km
0 30 mi

FIGURE 3



0 10 20mi
0 10 20km
Woodville
Centreville
MISSISSIPPI
LOUISIANA
31°00′
MISSISSIPPI
RIVER
WEST FELICIANA
Jackson
Clinton
Greensburg
EAST FELICIANA
ST. HELENA
St. Francisville
POINTE COUPEE
New Roads
Zachary
EAST BATON ROUGE
Baker
Fordoche
190
30°30′
WEST BATON ROUGE
BATON ROUGE
Livingston
12
Denham Springs
ST. MARTIN
IBERVILLE
10
BATON ROUGE FAULT
LIVINGSTON
■ Shallow freshwater wells
ASCENSION
LAKE MAUREPAS
Gonzales
91°30′
91°00′
AR
MS
AL
GA
SC
LA
FL
STUDY AREA
GULF OF MEXICO
ATLANTIC OCEAN

FIGURE 4

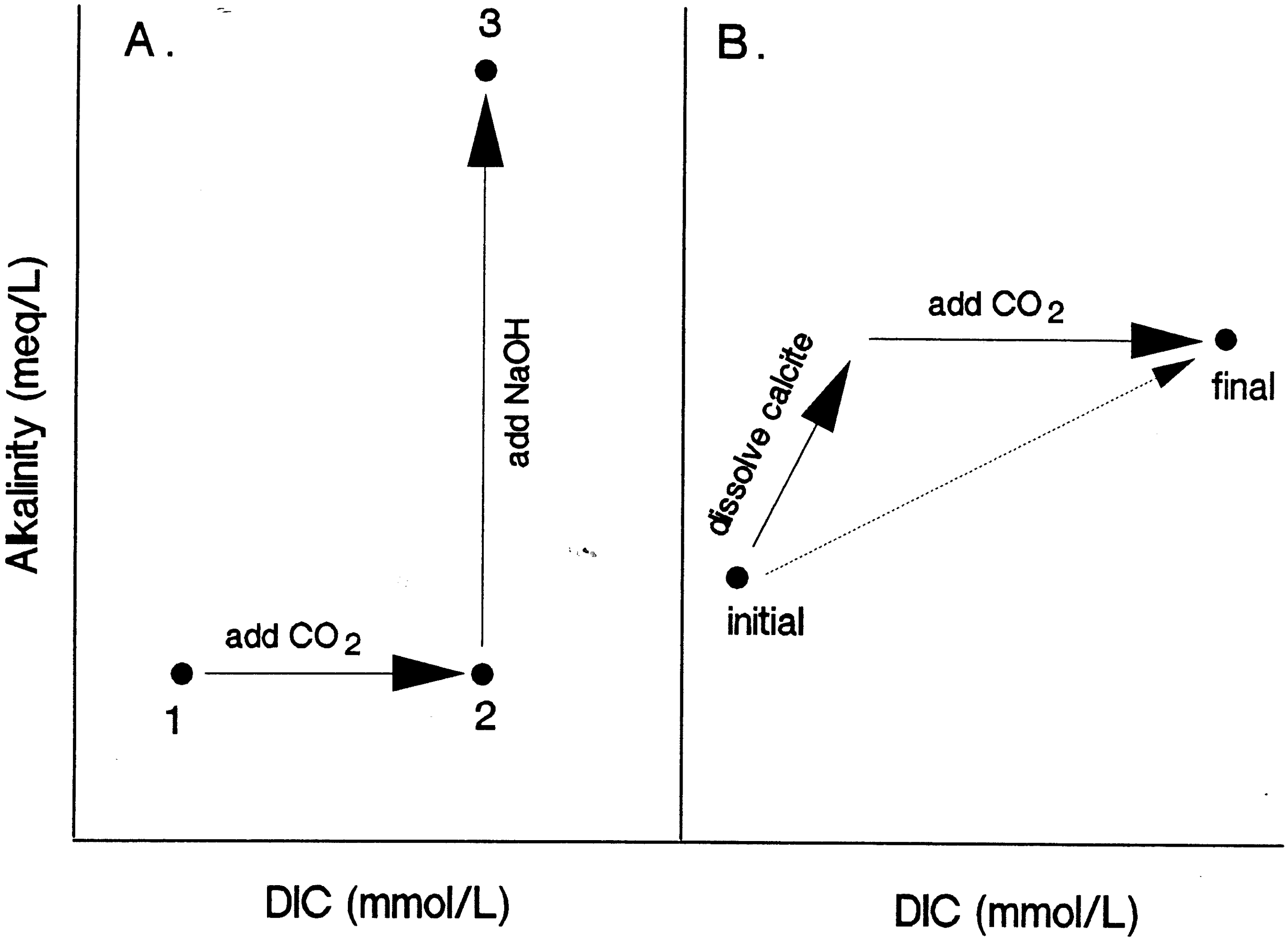

A.
B.
Alkalinity (meq/L)
1
2
3
add CO2
add NaOH
initial
final
dissolve calcite
add CO2
DIC (mmol/L)
DIC (mmol/L)

FIGURE 5

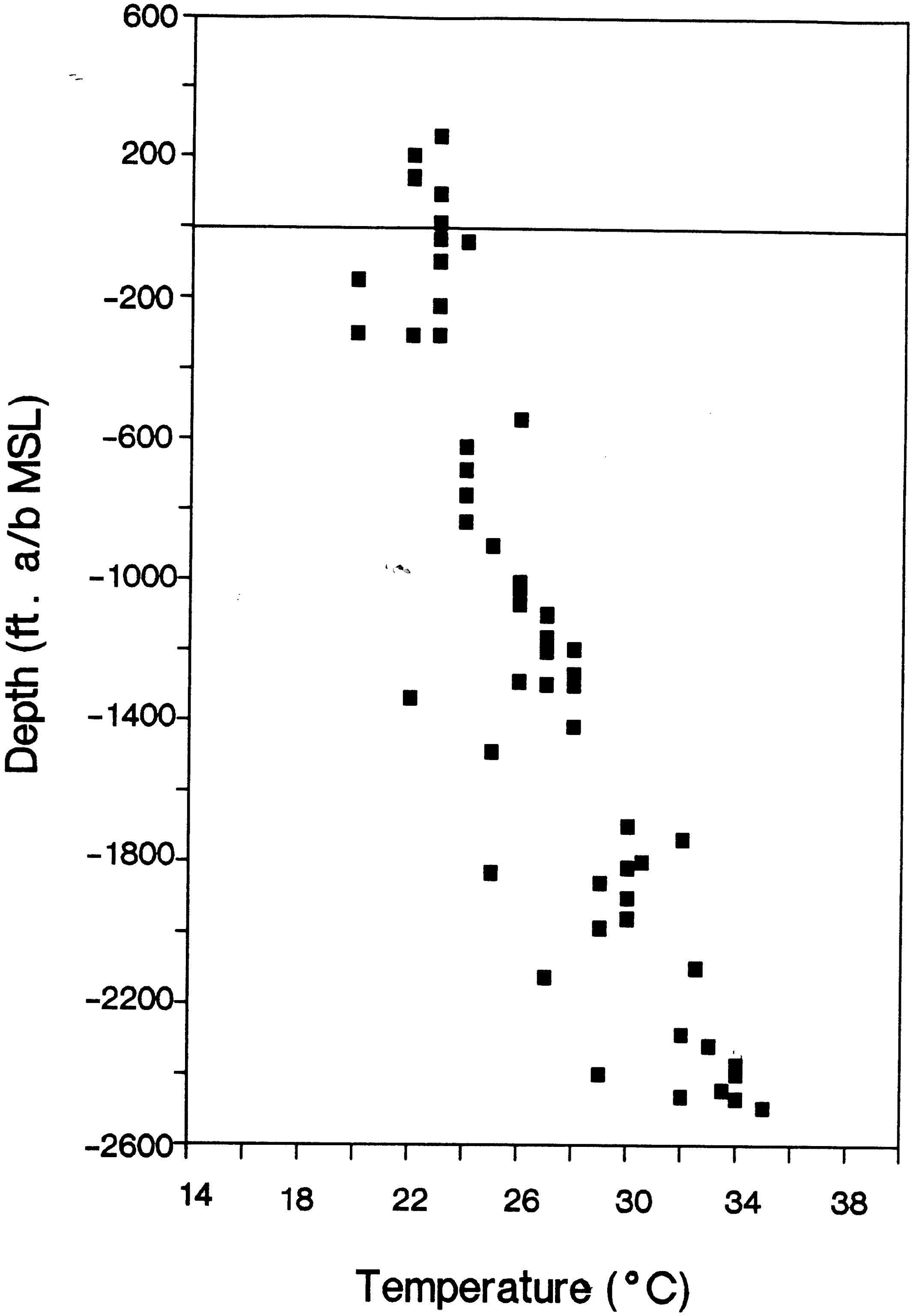

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
14
18
22
26
30
34
38
Temperature (°C)

FIGURE 6

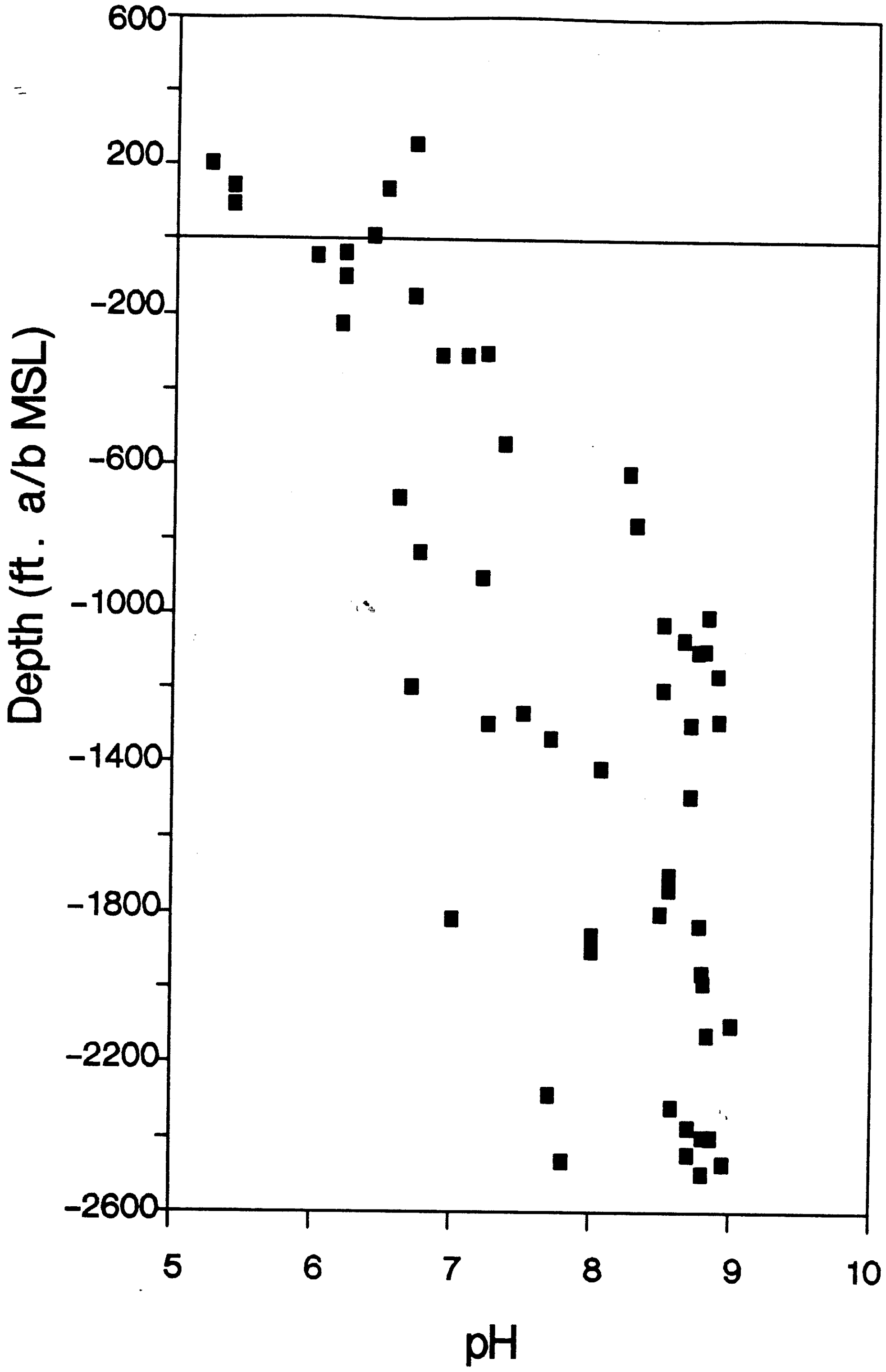

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
5
6
7
8
9
10
pH

FIGURE 7

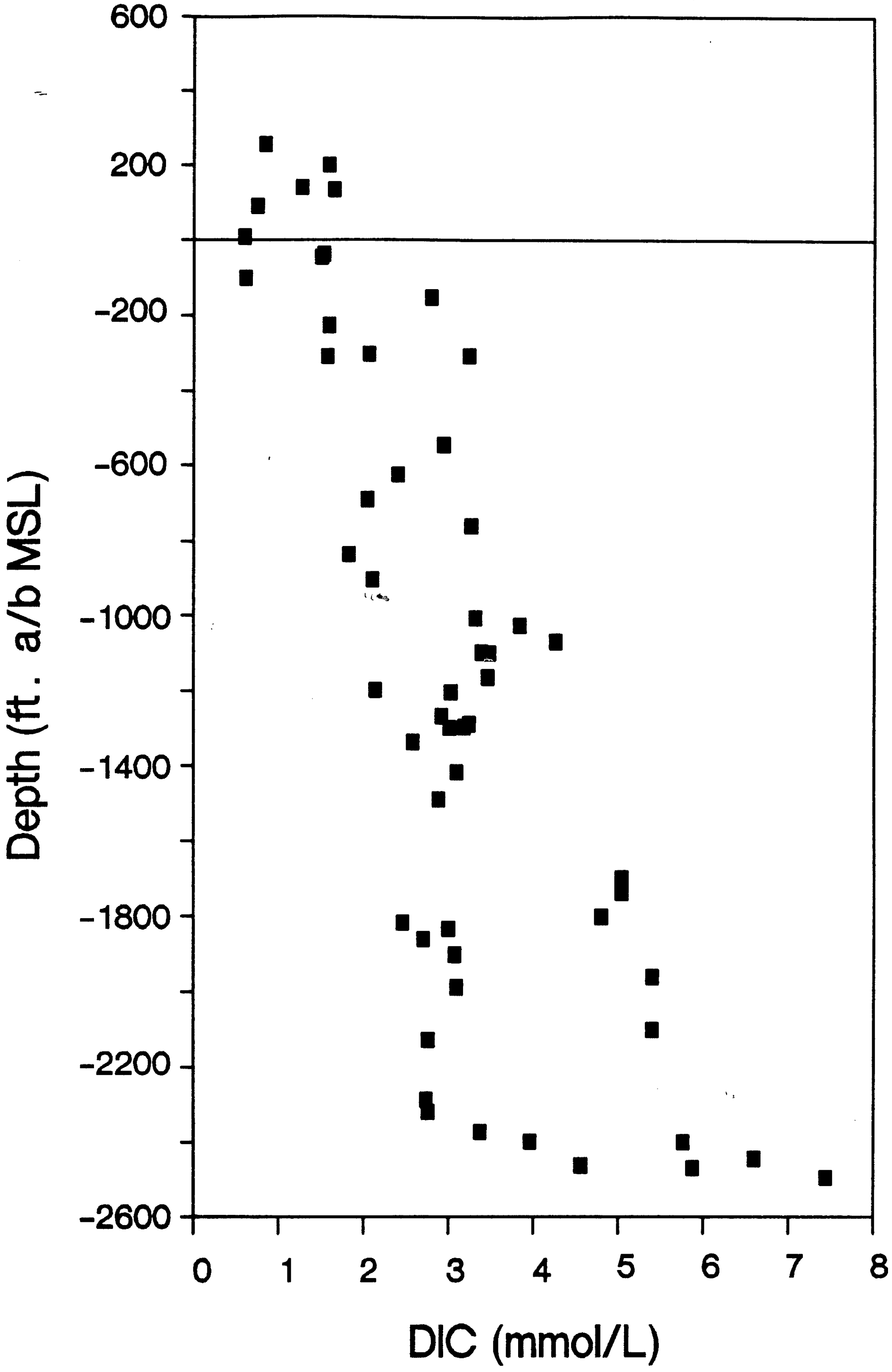

Depth (ft. a/b MSL)
600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
0
1
2
3
4
5
6
7
8
DIC (mmol/L)

FIGURE 8

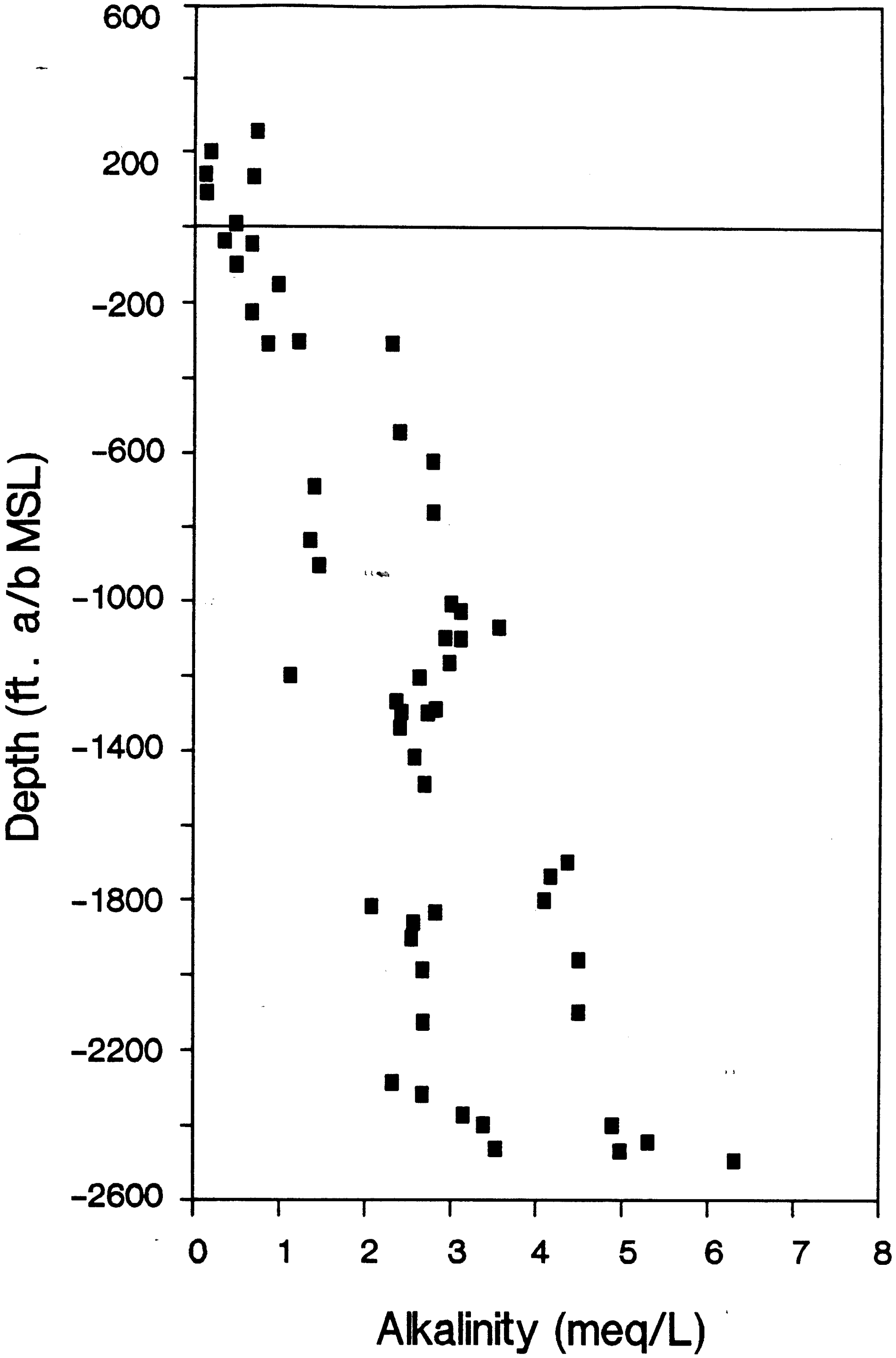

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
0
1
2
3
4
5
6
7
8
Depth (ft. a/b MSL)
Alkalinity (meq/L)

FIGURE 9

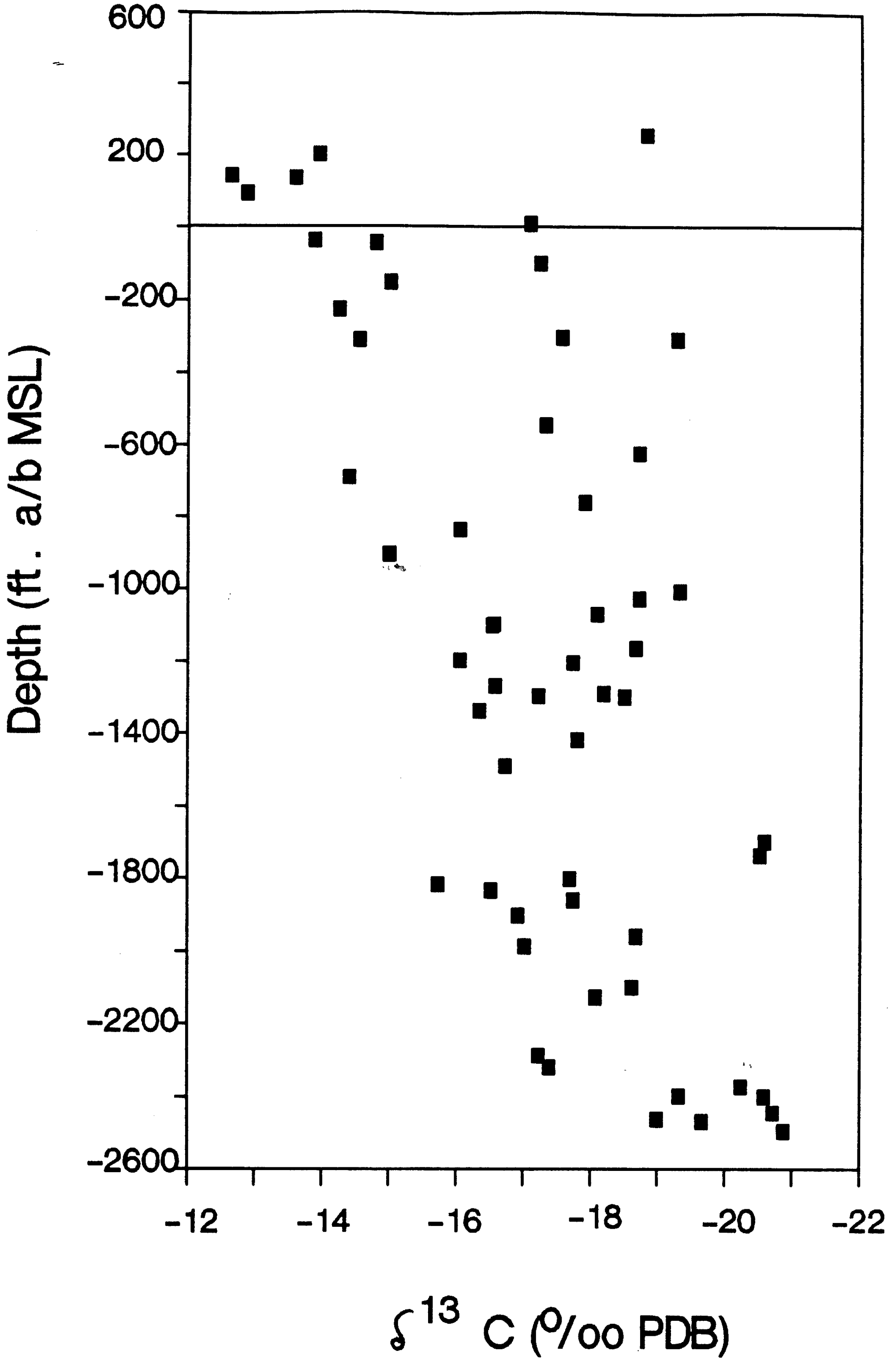
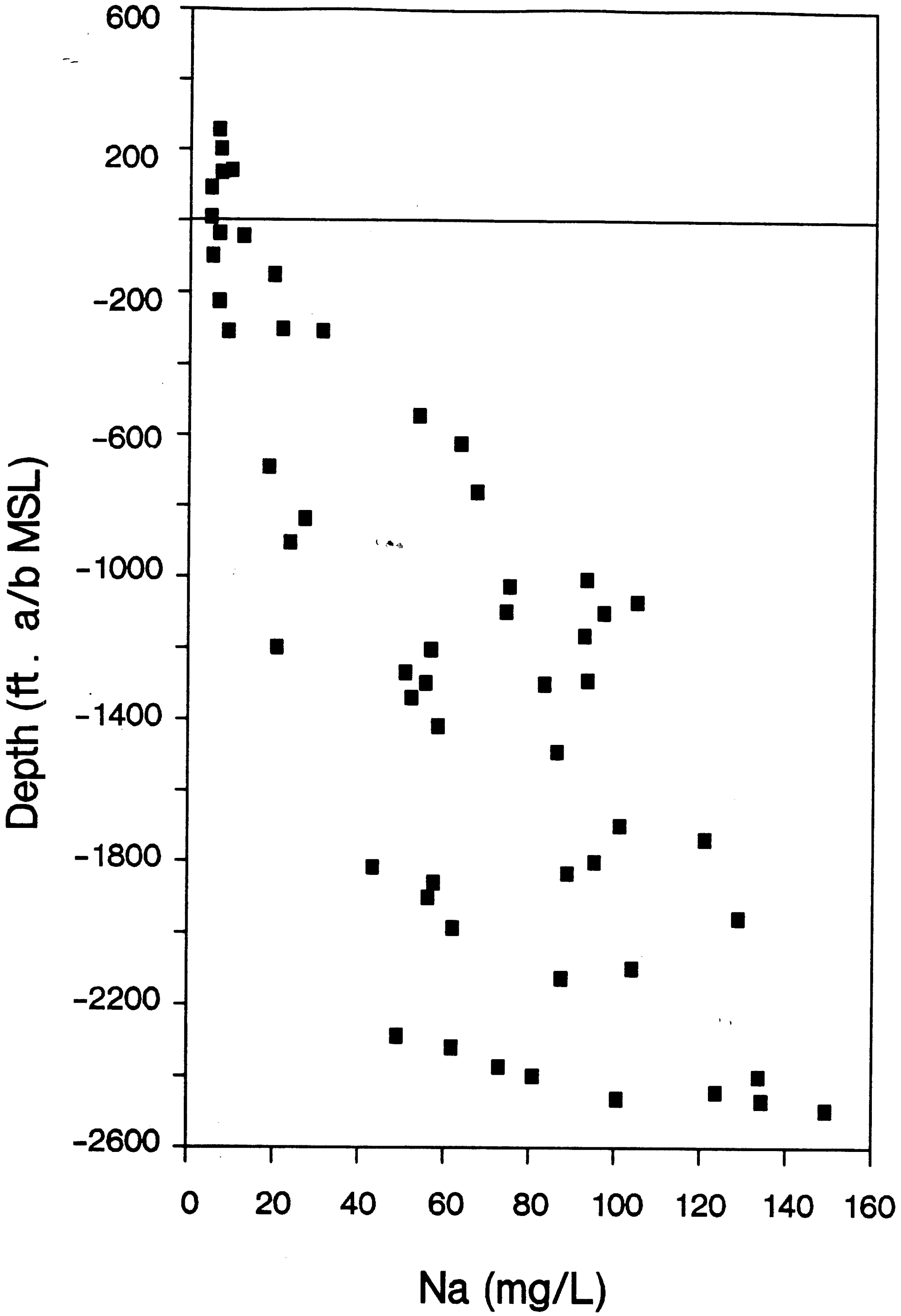

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
-12
-14
-16
-18
-20
-22
δ13 C (0/oo PDB)

FIGURE 10



600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
20
40
60
80
100
120
140
160
Na (mg/L)

FIGURE 11

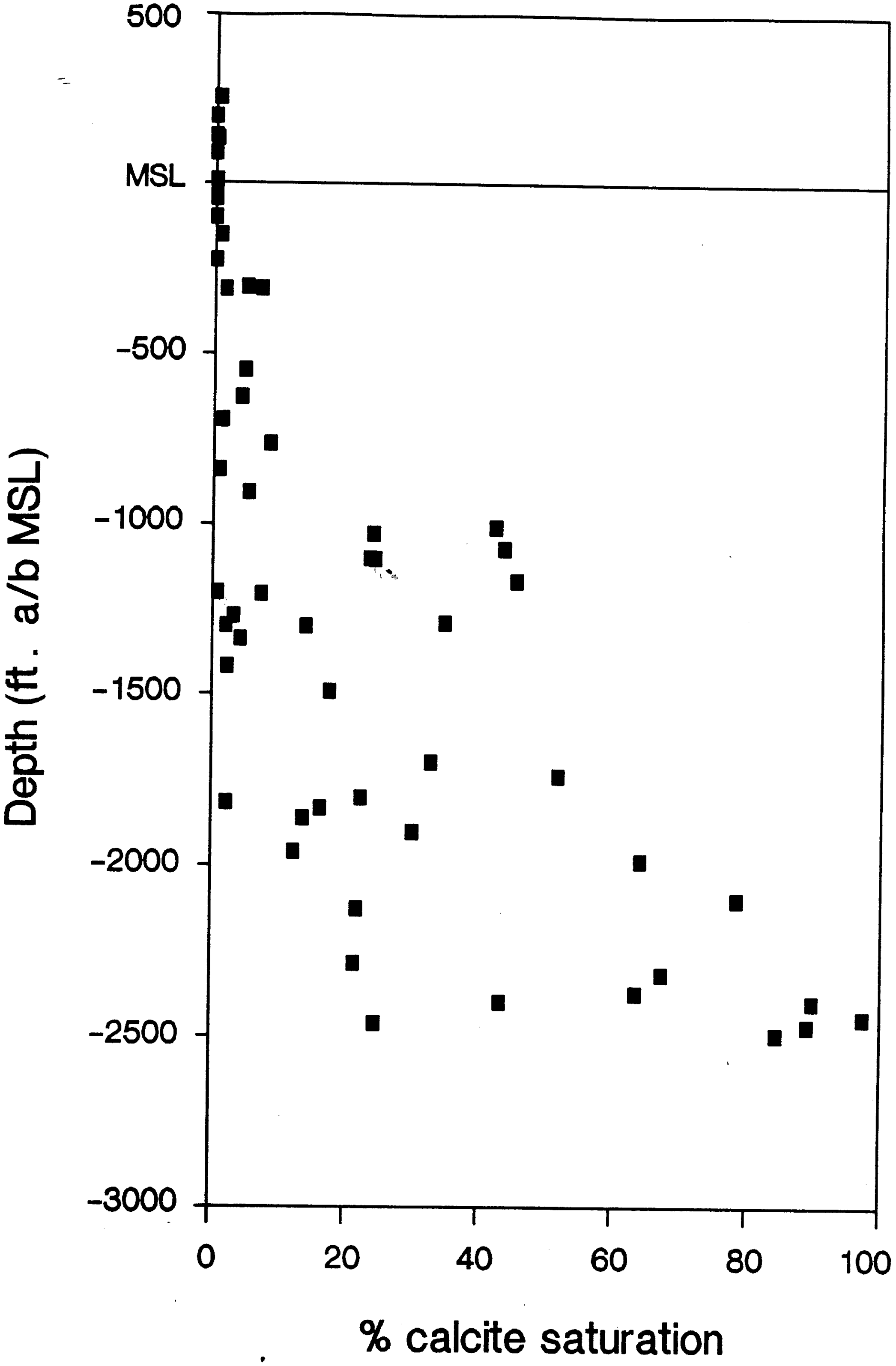
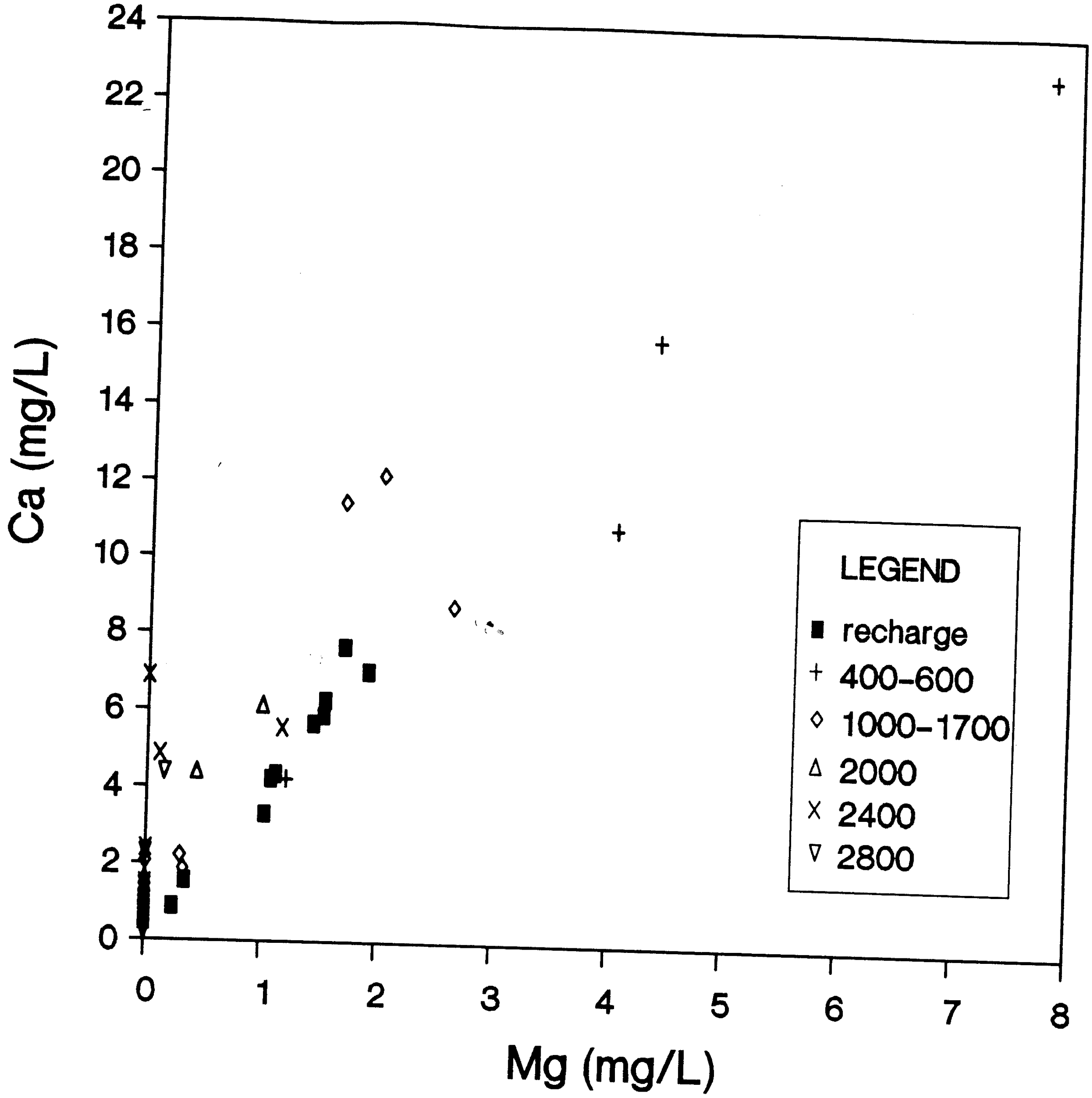

500
MSL
-500
-1000
-1500
-2000
-2500
-3000
Depth (ft. a/b MSL)
0
20
40
60
80
100
% calcite saturation

FIGURE 12



24
22
20
18
16
14
12
10
8
6
4
2
0
Ca (mg/L)
0
1
2
3
4
5
6
7
8
Mg (mg/L)
LEGEND
■ recharge
+ 400-600
◇ 1000-1700
△ 2000
× 2400
▽ 2800

FIGURE 13

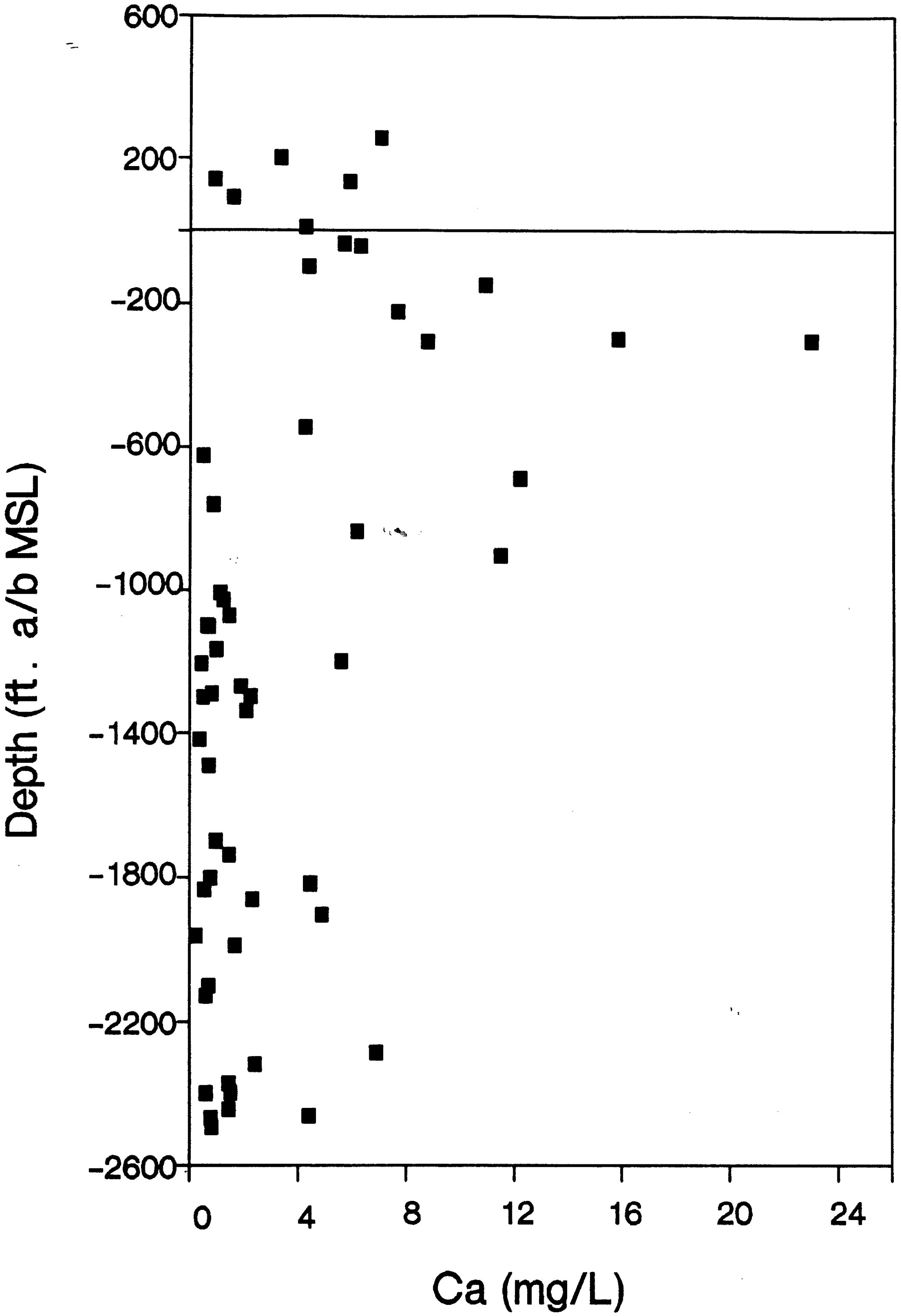

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft . a/b MSL)
0
4
8
12
16
20
24
Ca (mg/L)

FIGURE 14

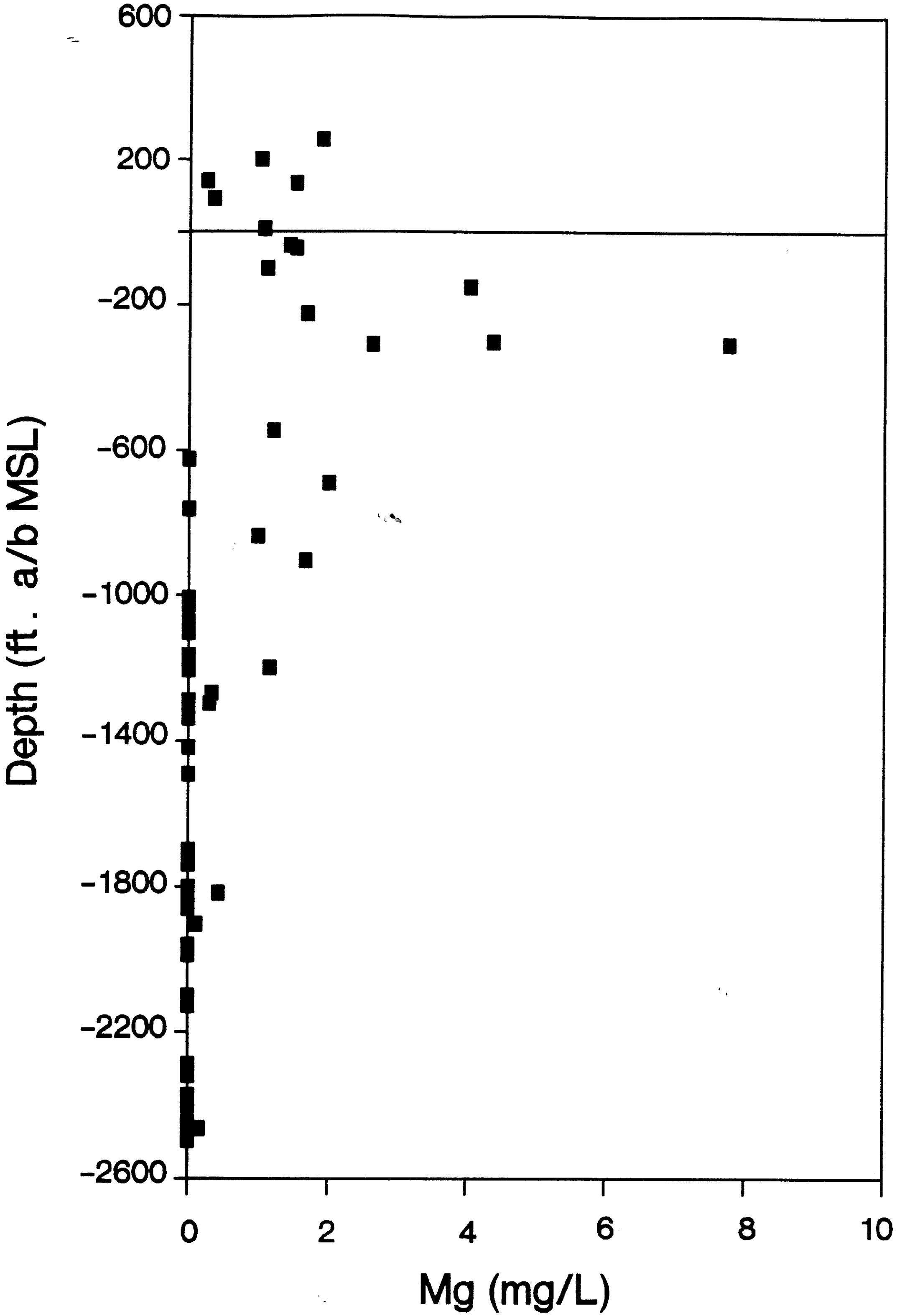
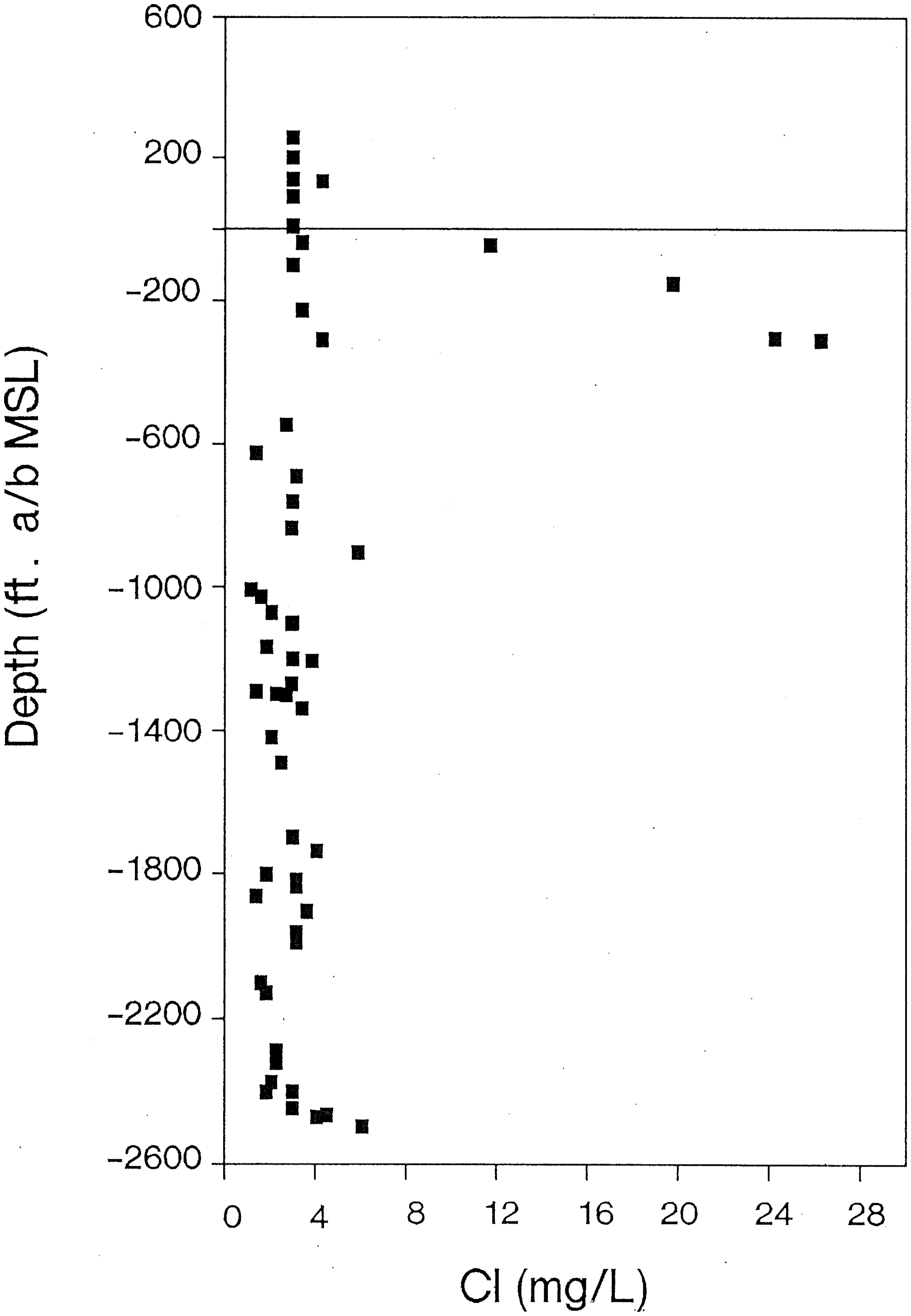

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
2
4
6
8
10
Mg (mg/L)

FIGURE 15



600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
4
8
12
16
20
24
28
Cl (mg/L)

FIGURE 16

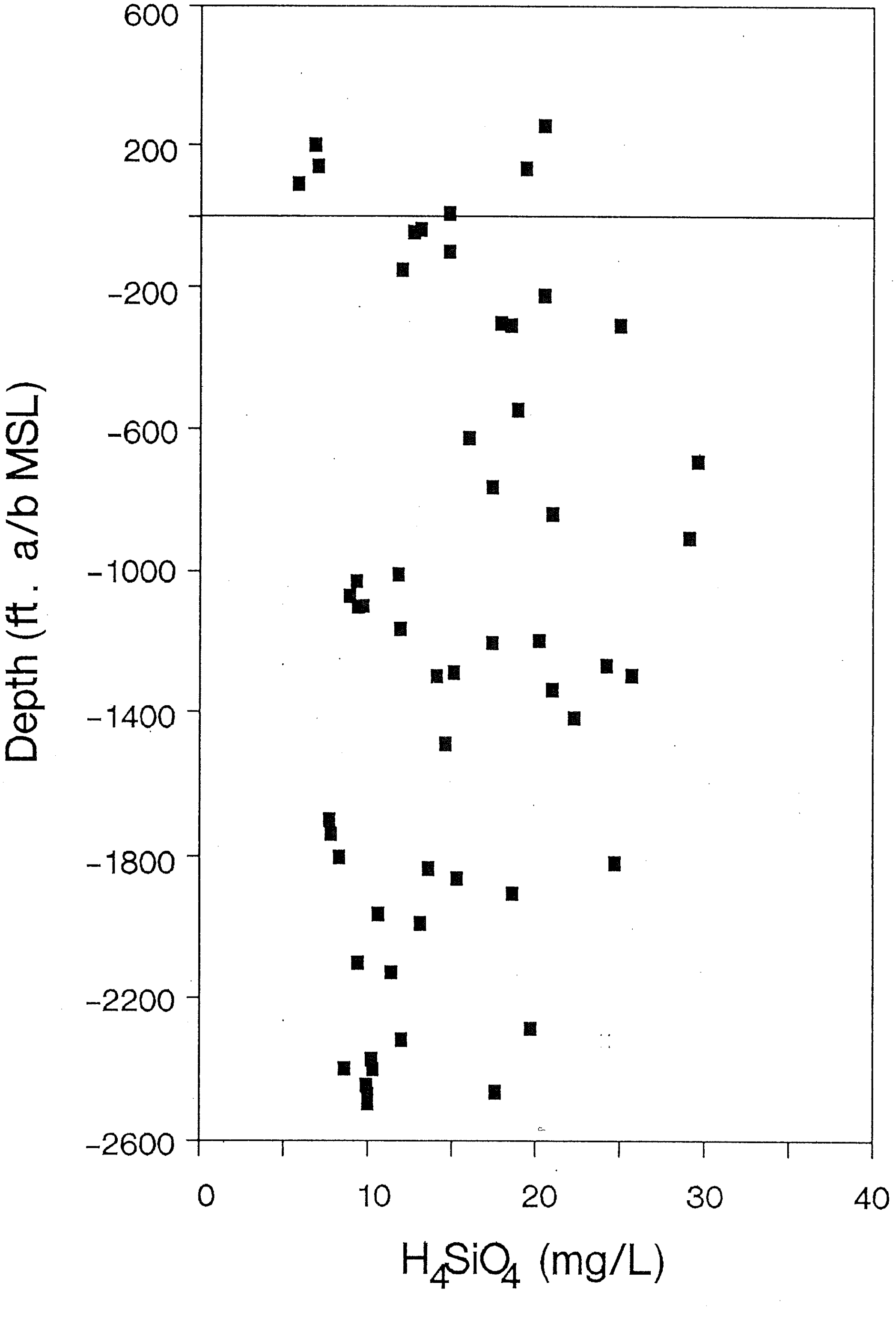
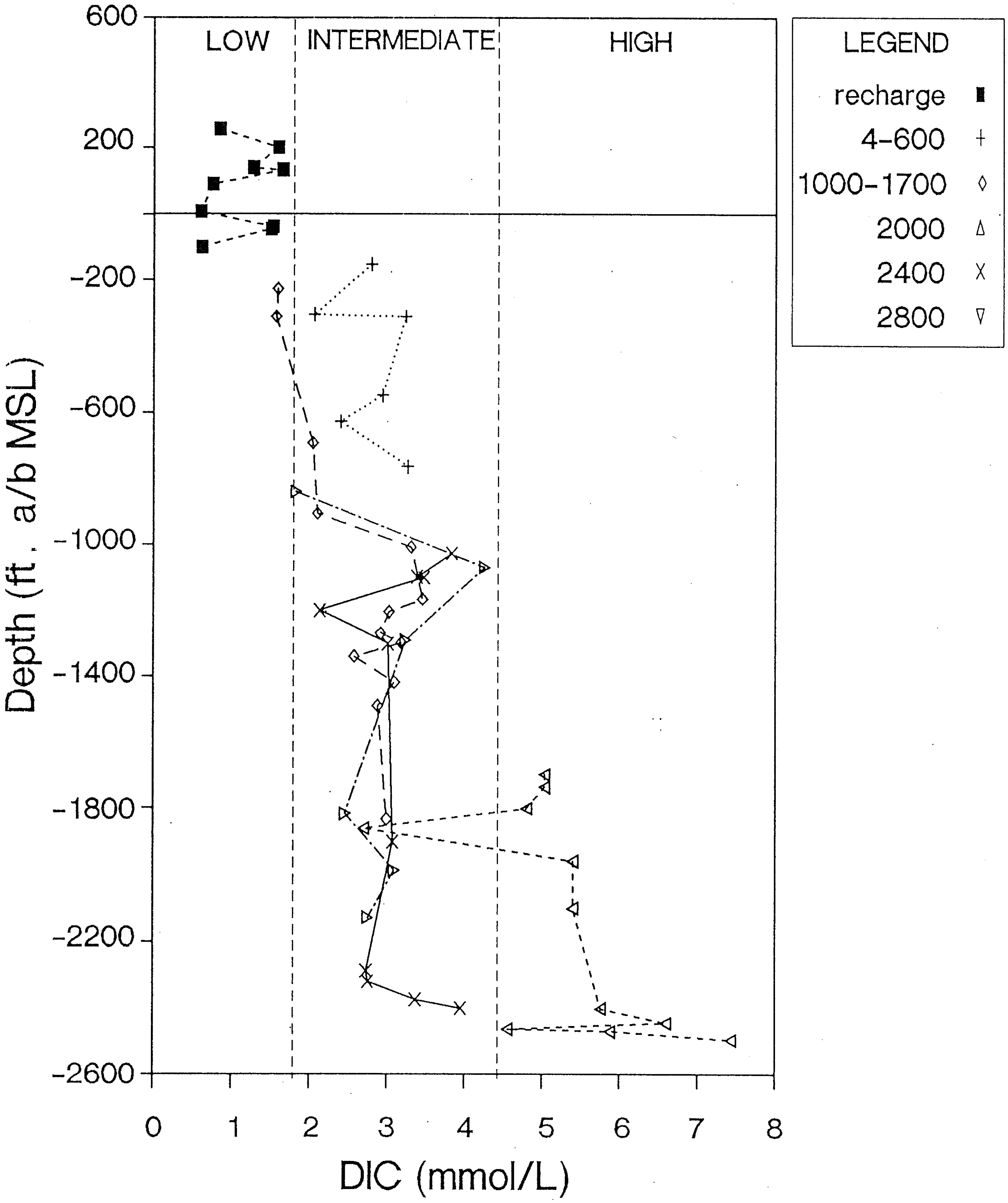
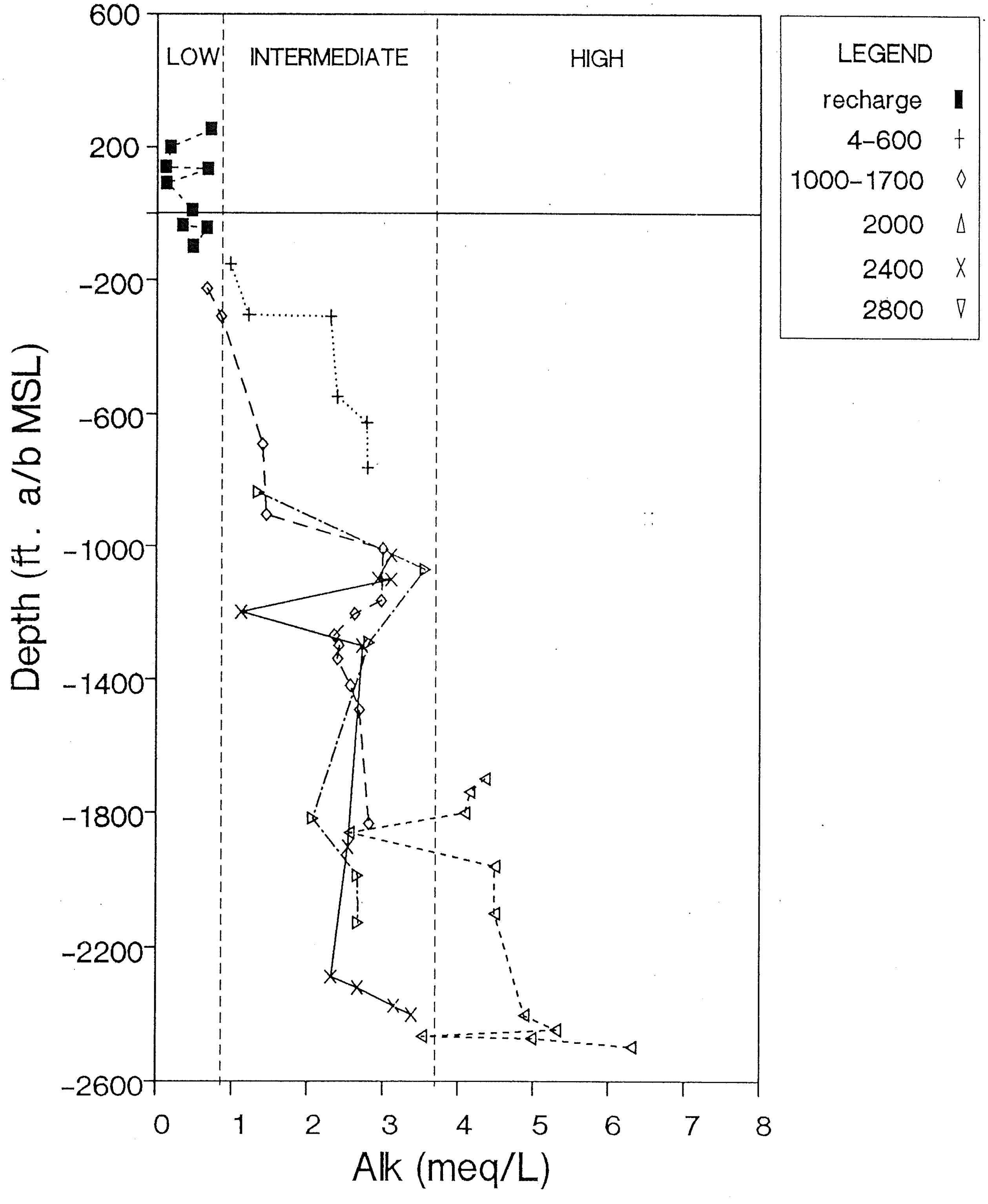

600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
10
20
30
40
H_4SiO_4 (mg/L)

FIGURE 17



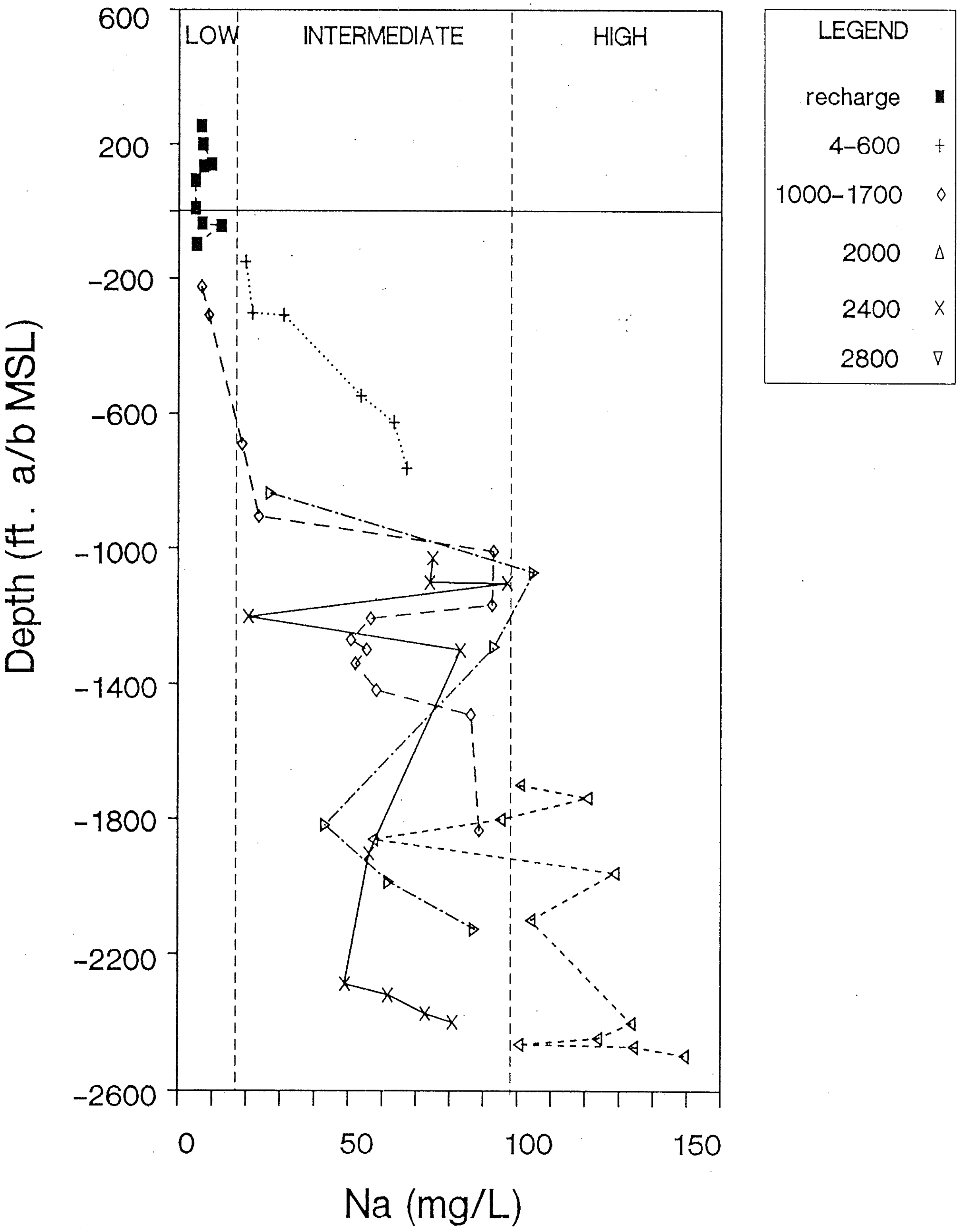
LOW
INTERMEDIATE
HIGH
LEGEND
recharge ■
4-600 +
1000-1700 ◊
2000 ◁
2400 X
2800 ▽
600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft . a/b MSL)
0
1
2
3
4
5
6
7
8
DIC (mmol/L)

FIGURE 18



LOW
INTERMEDIATE
HIGH
LEGEND
recharge ▮
4-600 +
1000-1700 ◊
2000 △
2400 X
2800 ▽
600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
1
2
3
4
5
6
7
8
Alk (meq/L)

FIGURE 19



LOW
INTERMEDIATE
HIGH
LEGEND
recharge
4-600
1000-1700
2000
2400
2800
600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft. a/b MSL)
0
50
100
150
Na (mg/L)

FIGURE 20

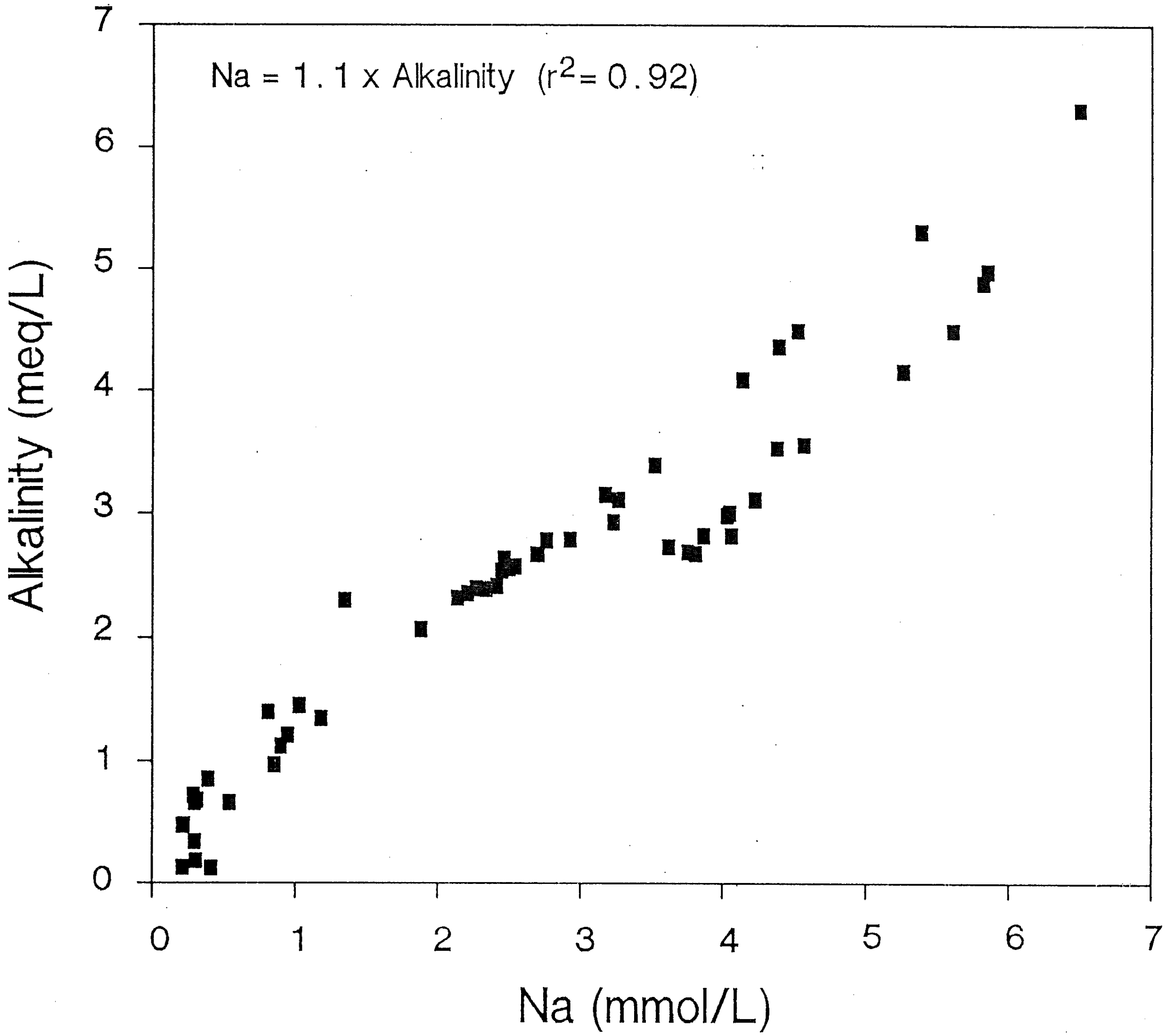

Na = 1.1 x Alkalinity (r^2= 0.92)
Alkalinity (meq/L)
Na (mmol/L)
0
1
2
3
4
5
6
7
0
1
2
3
4
5
6
7

FIGURE 21

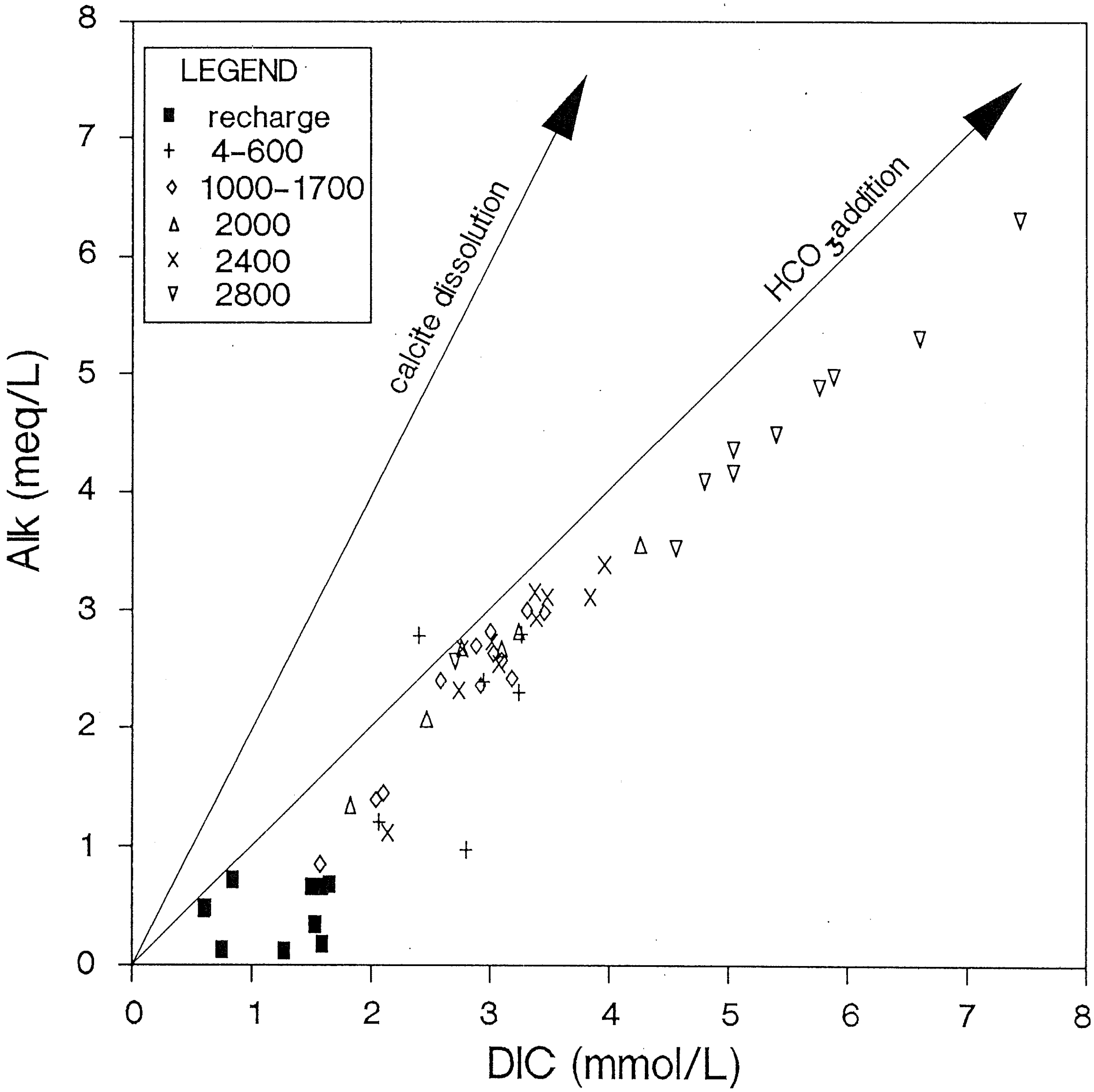
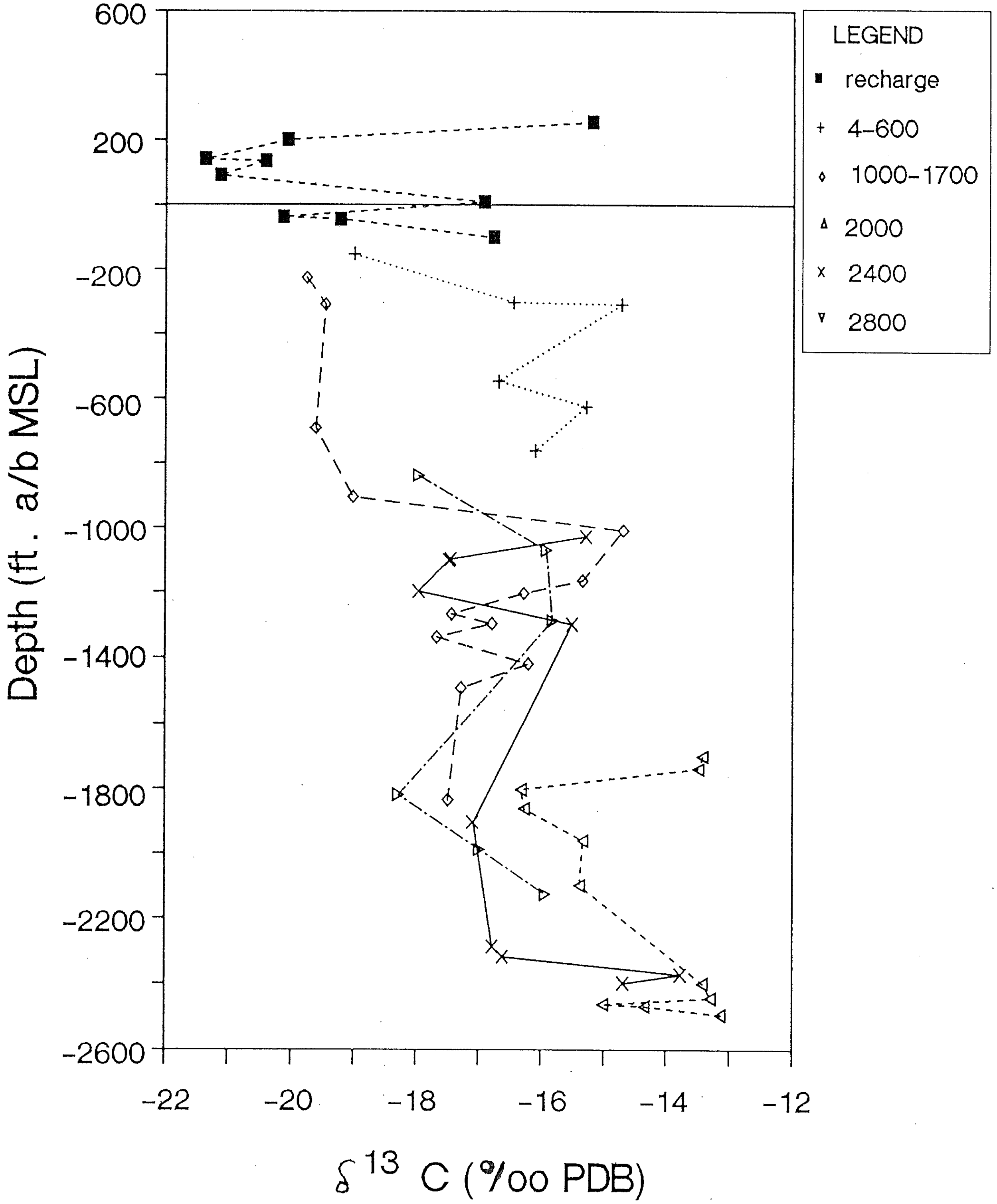

LEGEND
■ recharge
+ 4-600
◊ 1000-1700
△ 2000
× 2400
▽ 2800
calcite dissolution
HCO_3 addition
Alk (meq/L)
DIC (mmol/L)
0
1
2
3
4
5
6
7
8

FIGURE 22



LEGEND
recharge
4-600
1000-1700
2000
2400
2800
600
200
-200
-600
-1000
-1400
-1800
-2200
-2600
Depth (ft . a/b MSL)
-22
-20
-18
-16
-14
-12
δ 13 C (‰ PDB)

FIGURE 23 a

DIC (mmol/L)

Contour Interval = 0.5 mmol/L

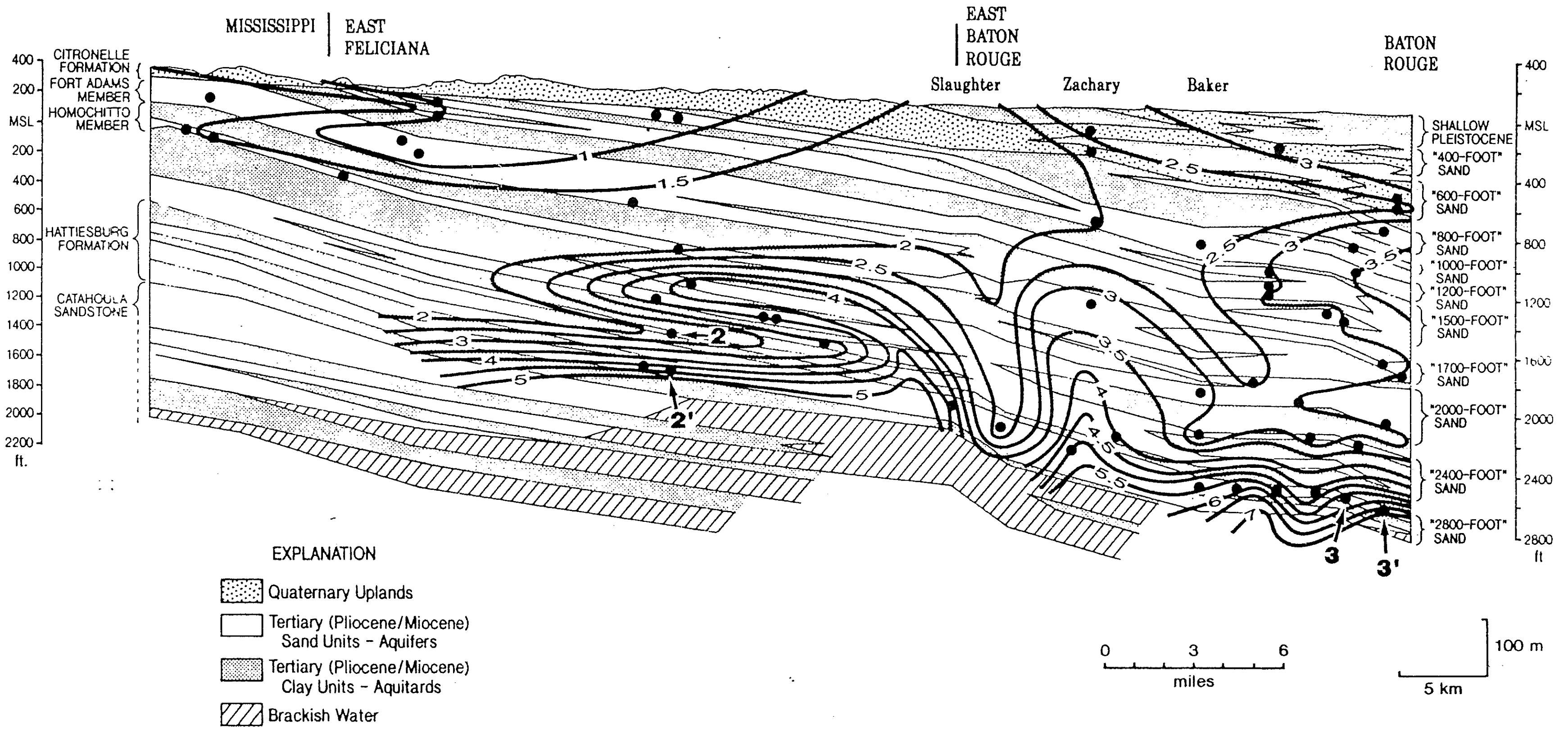


FIGURE 23 b

Alkalinity (meq/L)

Contour Interval = 0.5 meq/L

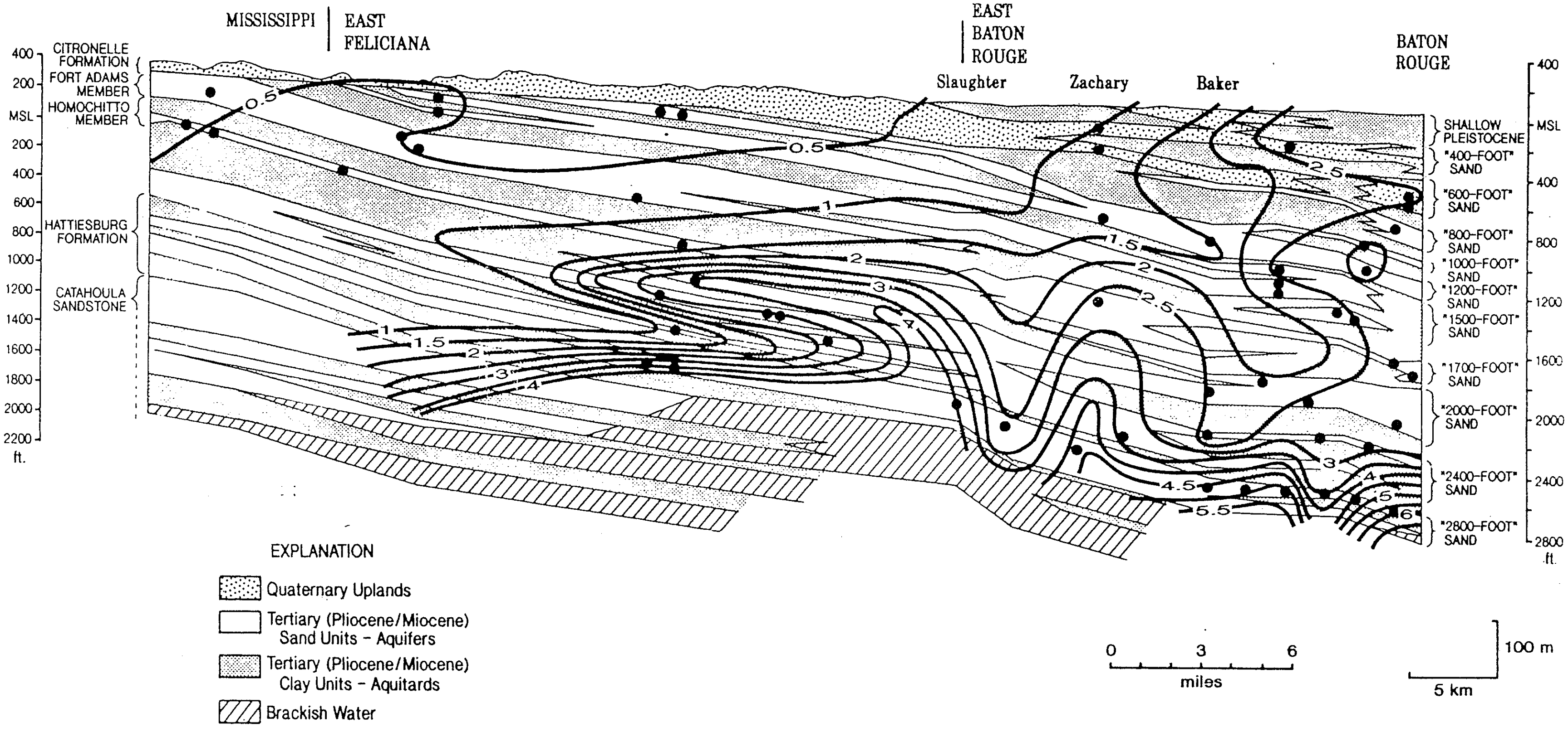


FIGURE 23 c

Na (ppm)

Contour Interval = 20 ppm

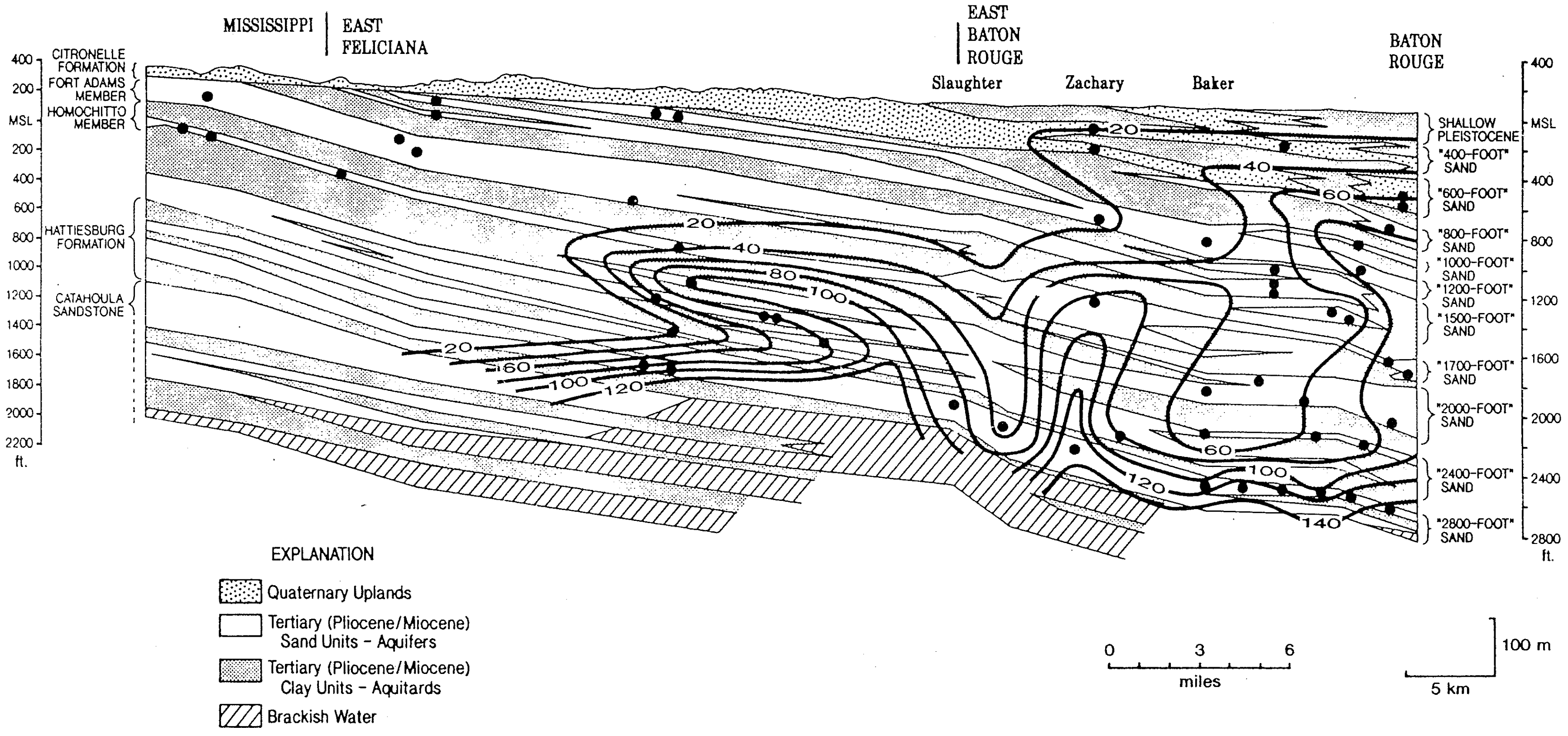


FIGURE 23 d

% Calcite Saturation

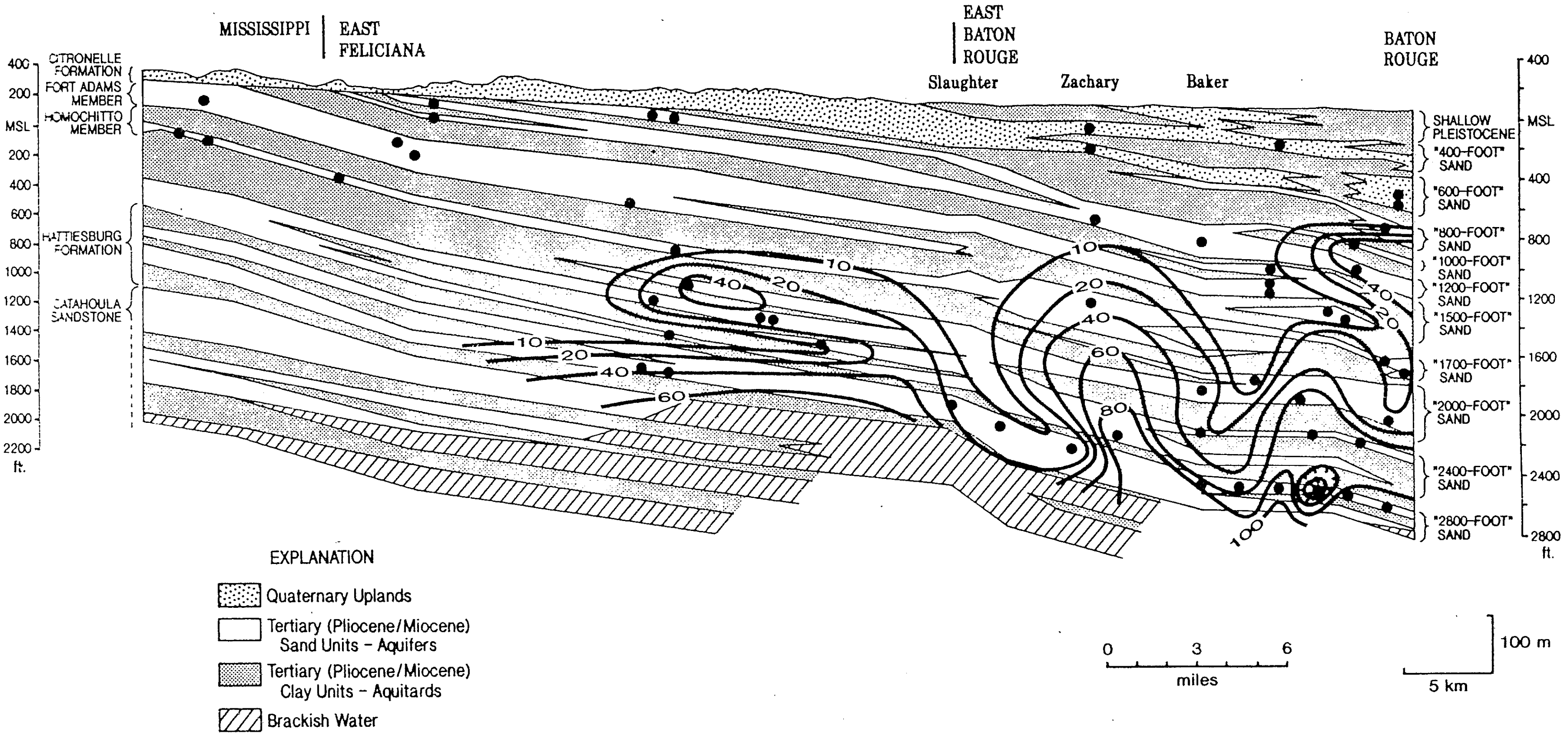


FIGURE 23 e

$\delta^{13}C$ (‰ PDB)

Contour Interval = 1‰

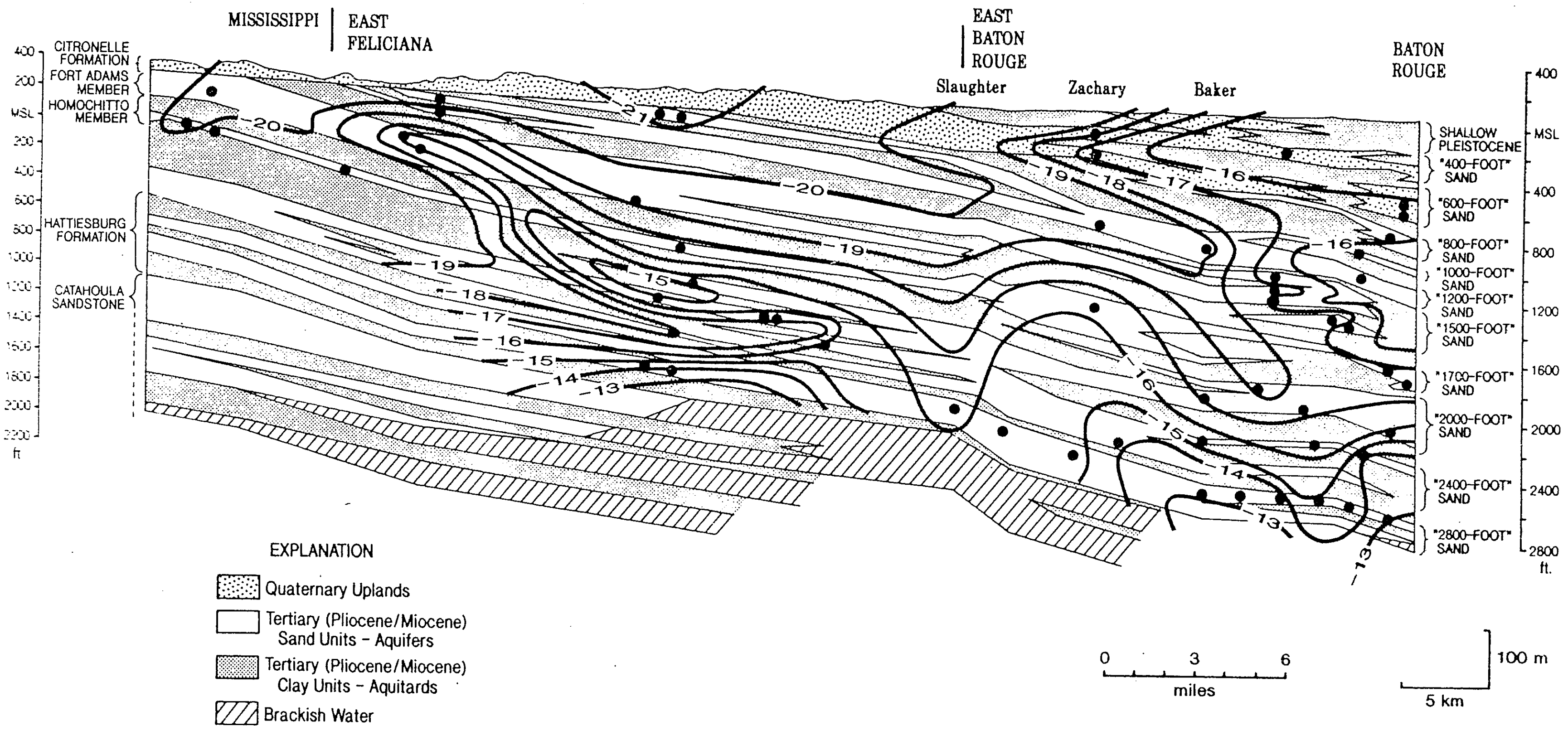


FIGURE 23 f

H_4SiO_4 (ppm)

Contour Interval = 4 ppm

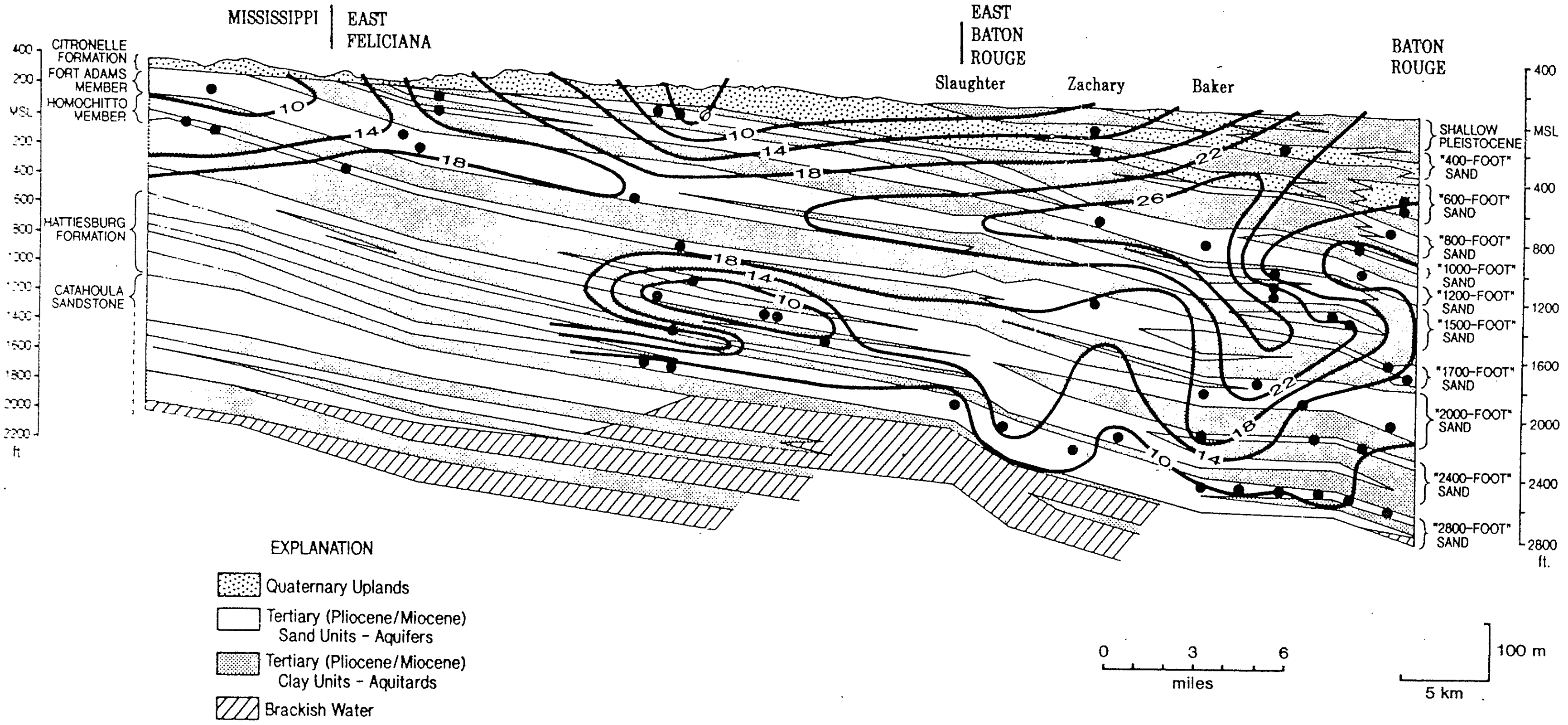


FIGURE 24

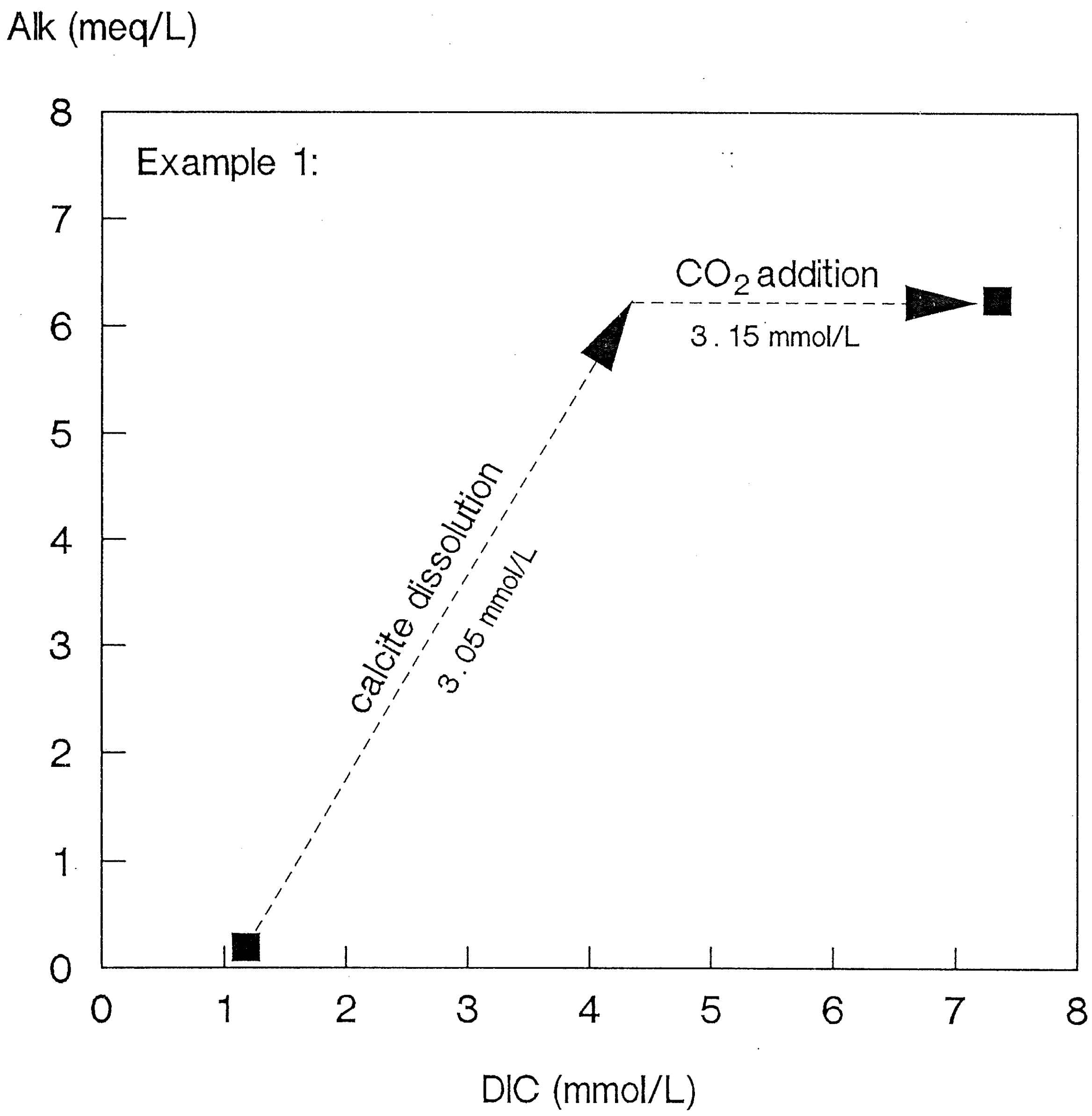
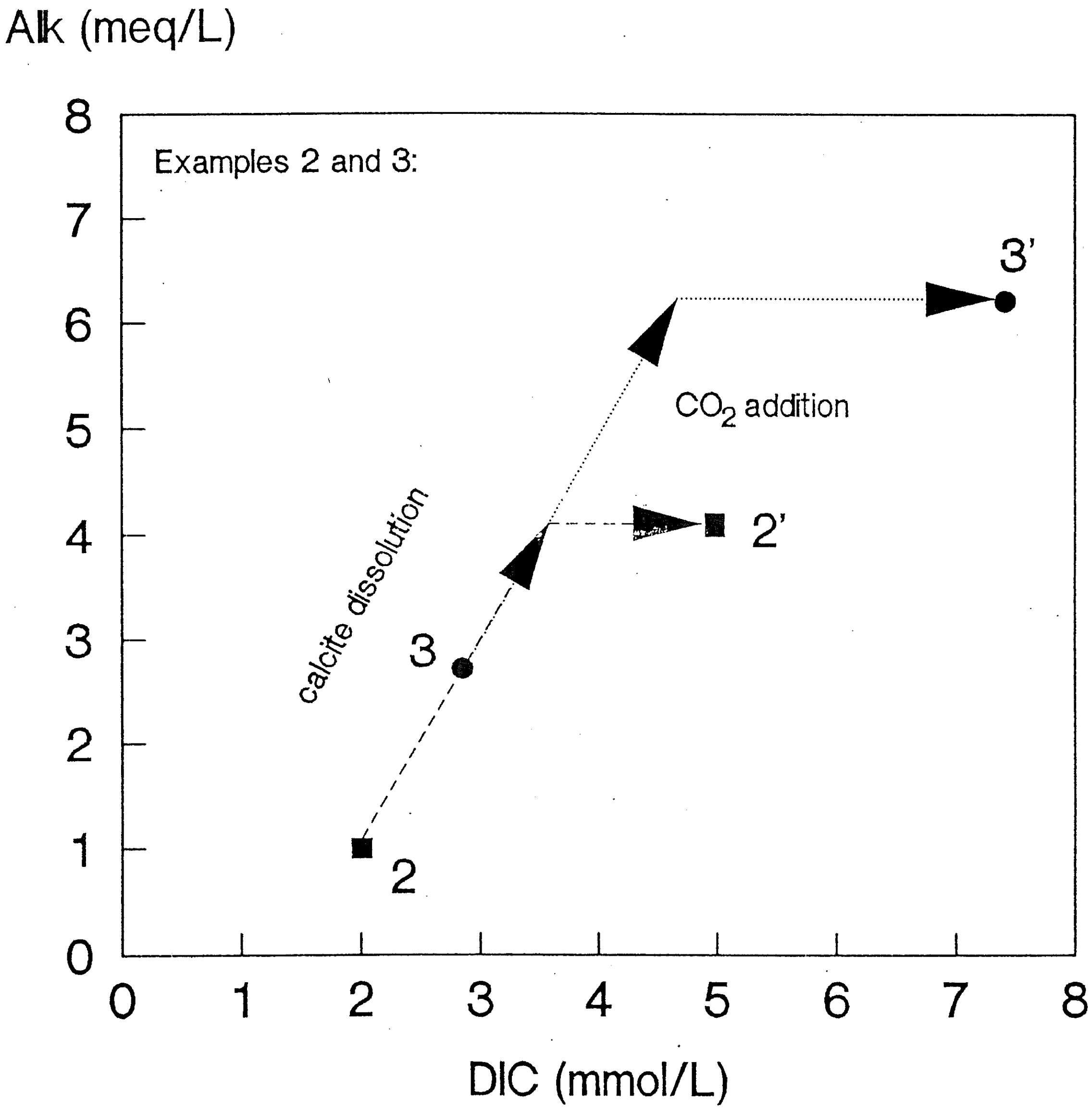

Alk (meq/L)
8
7
6
5
4
3
2
1
0
Example 1:
CO2 addition
3.15 mmol/L
calcite dissolution
3.05 mmol/L
0
1
2
3
4
5
6
7
8
DIC (mmol/L)

FIGURE 25



<u>2-2′</u> Lk.Istroma to EF251				final-initial
DIC	2.1	5.0	(mmol/L)	2.9
Alk	1.1	4.2	(meq/L)	3.1
$\delta^{13}C$	-18	-13.5	($^{o}/_{oo}$PDB)	

from diagram: CO$_2$ added = 1.4 mmol/L
HCO$_3^-$ from calc. diss. = 1.55 mmol/L

using eqn. (1) from the text, $\delta^{13}C_{added} = -21.7\,^{o}/_{oo}$

distance between wells: 2 miles
est. av. horizontal flow velocity (Buono, 1983): 0.07 mi/yr

using eqn. (2) from the text, CO$_2$ (PR) = $4.9\mathrm{x}10^{-2}$ mmol/L/yr

---

<u>3-3′</u> EB928 to EB700			final-initial
DIC	2.8	7.4	3.6
Alk	2.7	6.3	3.8
$\delta^{13}C$	-16.6	-13.1	

from diagram: CO$_2$ added = 2.75 mmol/L
HCO$_3^-$ from calc. diss. = 1.8 mmol/L

using eqn. (1) from the text, $\delta^{13}C_{added} = -18.1\,^{o}/_{oo}$

distance between wells: 3 miles
est. av. horizontal flow velocity (Buono, 1983): 0.07 mi/yr

using eqn. (2) from the text, CO$_2$ (PR) = $6.4\mathrm{x}10^{-2}$ mmol/L/yr

APPENDIX 1

SAMPLE	Aquifer Design.	Abs. depth (ft) GG	pH	Temp Celciu	Cl- (mg/L) GG	Na+ (mg/L) GG	Na (mmol/L)	K+ (mg/L)	Ca++ (mg/L)	Mg++ (mg/L)	H4SiO4 (mg/L)	H4SiO4 (mmol/L)	Al (mg/L)
EF175 (WhispPin	10	255	6.70	23	3.0	6.6	0.29	2.44	7.0	1.9	20.5	0.21	0.0
Centerville 1	10	-200	5.24	22	3.0	7.0	0.30	0.93	3.3	1.0	6.8	0.07	0.1
EF67 (Cobb/Rang	10	140	5.40	22	3.0	9.5	0.41	0.41	0.9	0.2	7.0	0.07	0.1
EF225 (Norwood)	10	134	6.50	22	4.3	7.2	0.31	2.1	5.9	1.5	19.4	0.20	0.0
Slaton's Store	10	90	5.40	23	3.0	4.8	0.21	0.74	1.6	0.3	5.8	0.06	0.0
EF57(Jack Jones	10	8	6.40	23	3.0	4.8	0.21	1.91	4.2	1.1	14.8	0.15	0.1
Centerville 2	10	-37	6.20	23	3.4	6.8	0.29	2.45	5.7	1.4	13.1	0.14	0.1
Centerville 3	10	-45	6.00	24	11.7	12.4	0.54	2.58	6.3	1.5	12.7	0.13	0.0
EF53(Ja.Jones)	10	-100	6.20	23	3.0	5.1	0.22	2	4.4	1.1	14.8	0.15	0.1
EB940 (GaPa-16)	400	-152	6.70	20	19.8	19.6	0.85	1.52	10.9	4.0	12.0	0.12	0.0
EB973 (GaPa-18)	600	-304	7.22	20	24.2	21.7	0.94	2.67	15.8	4.4	17.9	0.19	0.0
EB886 (Rollins)	600	-309	6.90	23	26.3	30.9	1.35	1.99	22.9	7.8	25.0	0.26	0.0
EB1132 (Parish)	400	-547	7.35	26	2.7	53.7	2.33	0.93	4.2	1.2	18.9	0.20	0.1
EB879 (Parish)	600	-626	8.25	24	1.4	63.5	2.76	0.09	0.5	0.0	16.0	0.17	0.0
EB1018 (Parish)	600	-763	8.30	24	3.0	67.2	2.92	0.25	0.8	0.0	17.4	0.18	0.3
EF221 (Wilson)	1500	-226	6.18	23	3.4	6.8	0.29	2.53	7.6	1.7	20.5	0.21	0.0
EF252 (High Est	1500	-310	7.08	22	4.3	8.9	0.39	2.62	8.8	2.6	18.5	0.19	0.0
EB840 (GaPa-7)	1200	-691	6.60	24	3.2	18.6	0.81	2.66	12.2	2.0	29.6	0.31	0.1
EB1153 (Rollins	1200	-905	7.20	25	5.9	23.6	1.03	2.64	11.5	1.7	29.1	0.30	0.1
EB632 (CW-1)	1200	-1009	8.82	26	1.2	93.0	4.05	0.28	1.1	0.0	11.8	0.12	0.0
EB772 (CW-2)	1200	-1166	8.89	27	1.8	92.6	4.03	0.09	1.0	0.0	11.9	0.12	0.1
EB403 (Exxon)	1200	-1206	8.50	27	3.8	56.7	2.46	0.24	0.4	0.0	17.4	0.18	0.0
EB977 (Allied)	1500	-1269	7.50	28	3.0	50.7	2.21	0.44	1.9	0.3	24.2	0.25	0.0
EB867 (Parish)	1500	-1298	7.25	27	2.3	55.5	2.41	0.81	2.2	0.3	25.7	0.27	0.2
EB905 (Parish)	1500	-1338	7.70	22	3.4	52.1	2.27	0.37	2.1	0.0	21.0	0.22	0.0
EB371B (Copoly)	1500	-1418	8.06	28	2.1	58.4	2.54	0.24	0.3	0.0	22.3	0.23	0.1
EB961 (CW-5)	1500	-1491	8.70	25	2.5	86.3	3.75	0.28	0.7	0.0	14.6	0.15	0.0
EB873 (CW-3)	1700	-1834	8.77	25	3.2	88.8	3.86	0.35	0.5	0.0	13.6	0.14	0.4
EF227 (Tigator)	2000	-838	6.75	24	3.0	27.1	1.18	2.3	6.2	1.0	21.0	0.22	0.1
EF262 (Jackson)	2000	-1072	8.65	26	2.1	104.9	4.56	0.76	1.4	0.0	8.9	0.09	0.0
EB837 (GaPa-5)	2000	-1291	8.90	26	1.4	93.3	4.06	0.51	0.8	0.0	15.1	0.16	0.1
EB904 (Parish)	2000	-1818	7.00	30	3.2	43.2	1.88	0.77	4.4	0.4	24.7	0.26	0.0
EB1030 (Copoly)	2000	-1988	8.80	29	3.2	62.0	2.70	0.31	1.7	0.0	13.1	0.14	0.2
EB878 (CW-4)	2000	-2128	8.83	27	1.8	87.5	3.81	0.35	0.6	0.0	11.4	0.12	0.2
EF258 (Jackson)	2400	-1028	8.50	26	1.6	75.0	3.26	0.81	1.2	0.0	9.3	0.10	0.1
EF273 (Veteran2	2400	-1100	8.80	27	3.0	74.2	3.23	0.49	0.6	0.0	9.7	0.10	0.0
EF272 (Veteran1	2400	-1102	8.75	27	3.0	97.1	4.22	0.34	0.7	0.0	9.4	0.10	0.1
Lake Istroma	2400	-1200	6.70	28	3.0	20.6	0.90	2.96	5.6	1.2	20.2	0.21	0.1
EF282 (Dixon)	2400	-1300	8.70	28	2.7	83.2	3.62	0.47	0.5	0.0	14.1	0.15	0.0
EB1031 (Parish)	2400	-1903	8.00	30	3.6	56.2	2.44	0.46	4.9	0.1	18.6	0.19	0.0
EB1032 (Parish)	2400	-2287	7.70	32	2.3	49.1	2.14	0.82	6.9	0.0	19.7	0.21	0.0
EB928 (Bk-7)	2400	-2319	8.58	33	2.3	61.9	2.69	0.43	2.4	0.0	12.0	0.12	0.0
EB351 (Exxon)	2400	-2374	8.70	34	2.05	72.9	3.17	0.34	1.4	0.0	10.2	0.11	0.1
*Well 21 (GaPa)	2400	-2400	8.80	34	3.0	80.9	3.52	0.38	1.5	0.0	8.6	0.09	0.0
EF?? (Clinton2)	2800	-1700	8.55	30	3.0	100.9	4.39	0.69	0.9	0.0	7.7	0.08	0.1
EF251 (Clinton1	2800	-1739	8.55	32	4.1	120.8	5.25	0.46	1.4	0.0	7.8	0.08	0.1
EB831 (Parish)	2800	-1803	8.49	30.5	1.8	95.1	4.14	0.31	0.8	0.0	8.3	0.09	0.0
EB829 (Parish)	2800	-1862	8.00	29	1.4	57.4	2.50	1.01	2.3	0.0	15.3	0.16	0.0
EB832 (Parish)	2800	-1961	8.79	30	3.2	128.8	5.60	0.34	0.2	0.0	10.6	0.11	0.1
EB830 (Parish)	2800	-2100	9.00	32.5	1.6	104.0	4.52	0.3	0.7	0.0	9.4	0.10	0.1
EB730 (Parish)	2800	-2401	8.86	29	1.8	133.7	5.82	0.4	0.6	0.0	10.3	0.11	0.4
EB922 (Parish)	2800	-2445	8.70	33.5	3.0	123.8	5.38	0.46	1.4	0.0	9.9	0.10	0.1
EB995 (Parish)	2800	-2463	7.80	32	4.5	100.6	4.38	0.67	4.4	0.2	17.6	0.18	0.0
EB978 (Allied)	2800	-2470	8.95	34	4.1	134.4	5.85	0.37	0.8	0.0	10.0	0.10	0.1
EB700 (Parish)	2800	-2495	8.80	35	6.1	149.3	6.49	0.57	0.8	0.0	10.0	0.10	0.1

*GG = data from Gonthier, 1989

SAMPLE	(meq/L)	(mmol/L)	(PDB)	calcite	dolomite
EF175 (WhispPin	0.72	0.84	-15.2	0.5	0.0
Centerville 1	0.18	1.59	-20.1	0.0	0.0
EF67 (Cobb/Rang	0.12	1.27	-21.4	0.0	0.0
EF225 (Norwood)	0.68	1.65	-20.4	0.2	0.0
Slaton's Store	0.13	0.75	-21.1	0.0	0.0
EF57(Jack Jones	0.47	0.60	-16.9	0.1	0.0
Centerville 2	0.34	1.53	-20.1	0.1	0.0
Centerville 3	0.66	1.50	-19.2	0.1	0.0
EF53(Ja.Jones)	0.48	0.61	-16.8	0.1	0.0
EB940 (GaPa-16)	0.97	2.80	-19.0	0.8	0.0
EB973 (GaPa-18)	1.21	2.06	-16.5	4.8	0.3
EB886 (Rollins)	2.30	3.24	-14.7	7.0	0.5
EB1132 (Parish)	2.39	2.94	-16.7	4.6	0.2
EB879 (Parish)	2.78	2.40	-15.3	4.1	0.0
EB1018 (Parish)	2.79	3.26	-16.1	8.4	0.0
EF221 (Wilson)	0.66	1.59	-19.8	0.1	0.0
EF252 (High Est	0.85	1.57	-19.5	1.6	0.0
EB840 (GaPa-7)	1.40	2.04	-19.6	1.3	0.0
EB1153 (Rollins	1.45	2.10	-19.0	5.3	0.1
EB632 (CW-1)	3.00	3.31	-14.7	42.2	0.0
EB772 (CW-2)	2.98	3.46	-15.3	45.4	0.0
EB403 (Exxon)	2.63	3.02	-16.3	7.3	0.0
EB977 (Allied)	2.36	2.92	-17.4	3.1	0.0
EB867 (Parish)	2.42	3.18	-16.8	2.0	0.0
EB905 (Parish)	2.40	2.58	-17.7	4.2	0.0
EB371B (Copoly)	2.57	3.10	-16.2	2.2	0.0
EB961 (CW-5)	2.69	2.88	-17.3	17.6	0.0
EB873 (CW-3)	2.82	3.00	-17.5	16.2	0.0
EF227 (Tigator)	1.35	1.82	-18.0	0.9	0.0
EF262 (Jackson)	3.56	4.26	-15.9	43.5	0.0
EB837 (GaPa-5)	2.82	3.24	-15.8	34.7	0.0
EB904 (Parish)	2.07	2.46	-18.3	2.3	0.0
EB1030 (Copoly)	2.67	3.10	-17.0	64.1	0.0
EB878 (CW-4)	2.68	2.76	-15.9	21.7	0.0
EF258 (Jackson)	3.11	3.84	-15.3	23.9	0.0
EF273 (Veteran2	2.93	3.38	-17.5	23.5	0.0
EF272 (Veteran1	3.11	3.48	-17.5	24.2	0.0
Lake Istroma	1.12	2.14	-18.0	0.7	0.0
EF282 (Dixon)	2.73	3.01	-15.5	13.9	0.0
EB1031 (Parish)	2.54	3.07	-17.1	29.9	0.5
EB1032 (Parish)	2.32	2.74	-16.8	21.4	0.0
EB928 (Bk-7)	2.67	2.76	-16.6	67.4	0.0
EB351 (Exxon)	3.15	3.37	-13.8	63.5	0.0
#Well 21 (GaPa)	3.39	3.96	-14.7	89.8	0.0
EF?? (Clinton2)	4.36	5.04	-13.4	32.7	0.0
EF251 (Clinton1	4.16	5.04	-13.5	51.8	0.0
EB831 (Parish)	4.09	4.80	-16.3	22.2	0.0
EB829 (Parish)	2.56	2.70	-16.3	13.7	0.0
EB832 (Parish)	4.49	5.40	-15.3	12.3	0.0
EB830 (Parish)	4.49	5.40	-15.4	78.5	0.0
EB730 (Parish)	4.89	5.76	-13.4	43.2	0.0
EB922 (Parish)	5.31	6.60	-13.3	97.4	0.0
EB995 (Parish)	3.53	4.56	-15.0	24.5	0.4
EB978 (Allied)	4.98	5.88	-14.3	89.1	0.0
EB700 (Parish)	6.31	7.44	-13.1	84.4	0.0

APPENDIX 2

AN IMPROVED MICROEXTRACTION TECHNIQUE FOR MEASURING DISSOLVED INORGANIC CARBON (DIC), $\delta^{13}C_{DIC}$, AND $\delta^{18}O_{H2O}$ FROM MILLILETER-SIZE WATER SAMPLES

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ABSTRACT

Dissolved inorganic carbon (DIC), $\delta^{13}C_{DIC}$, and $\delta^{18}O_{H2O}$ are traditionally measured using three different analytical techniques. The DIC-acid extraction method has been simplified, and a precise, accurate, and relatively simple technique for analyzing all three parameters from a single 2mL or smaller water sample has been developed.

Water samples are injected through a septum into a temperature controlled, water-jacketed, evacuated vessel containing approximately 0.3mL of orthophosphoric acid and a magnetic spinbar. The extraction line and vessel are coupled directly to the inlet of the mass spectrometer. Evolved CO_2 is drawn through two -90°C traps to separate water vapor and is condensed into a liquid nitrogen trap. Yields of 98 to 100% are achieved by using a capillary tube between the reaction vessel and traps, dynamic "cold" pumping with liquid nitrogen, acidification to less than 1pH unit, and vigorous stirring. DIC is measured as a function of the voltage produced by mass 44 of the CO_2 gas in a fixed volume, and the CO_2 is then analyzed for $\delta^{13}C_{DIC}$ and $\delta^{18}O_{H2O}$ using conventional mass spectrometry techniques.

The method is fast (45 min. per sample), reproducible (std. dev. DIC = +/- 0.1 mmol/L; std. dev. $\delta^{13}C_{DIC}$ = +/- 0.1°/oo; std. dev. $\delta^{18}O_{H2O}$ = +/- 0.1°/oo), and accurate. It represents a considerable refinement over existing methods, and is especially valuable for studies in which sample size is a limiting factor.

It can also replace the more cumbersome conventional methods where sample size is no object.

1. INTRODUCTION

The uses of dissolved inorganic carbon (DIC), carbon isotope, and oxygen isotope measurements for enhancing research in oceanography, hydrology, volcanology, and paleoclimatology are well known and diverse. Typically, each parameter requires a separate analytical technique for measurement. To reduce the number of techniques and amount of sample needed, an existing DIC extraction method was modified and a single, accurate, and precise means of analyzing DIC, $\delta^{13}C_{DIC}$ (Graber et al., 1990), and $\delta^{18}O_{H2O}$ on 2mL and smaller samples was developed.

Most methods now in use for extracting DIC for carbon isotope measurement involve acidifying the water sample and collecting the liberated CO_2 gas (e.g. Craig, 1954; Sackett and Moore, 1966; Tan et al., 1973). Commonly, CO_2 is stripped from the sample by bubbling the sample with nitrogen gas (Broecker et al., 1960; Deuser and Hunt, 1969; Kroopnick et al., 1970). In general, 50 to 100mL of sample are used. Sackett and Moore (1966) estimated they achieved a 90% yield, while Deuser and Hunt (1969) estimated yields greater than 99%. Tan et al. (1973), Sackett and Moore (1966), Deuser and Hunt (1969), and Herczeg and Fairbanks (1987) all achieved precisions of +/- 0.3°/oo, while Kroopnick et al. (1970) reported a precision better than +/- 0.1°/oo.

DIC has been measured gravimetrically (Broecker et al., 1960), by mercury manometer (Tan et al., 1973), by gas chromatograph (Kroopnick et al., 1970), and by coulometry

(Johnson et al., 1985). These methods all require additional sample (50-250mL) and have varying precisions partly dependent on the method used to extract CO_2. Except for coulometry, reported precisions are approximately equivalent to Tan et al.´s (1973) report of 2 to 4 ml/L; accuracies are approximately equal to Kroopnick et al.´s (1970) report of +/- 0.5%.

To analyze smaller samples, McCorkle et al. (1985) flushed ampules with nitrogen gas and transferred 3 mL of sample via syringe to the ampule. The ampule was broken under vacuum, the sample acidified, and the CO_2 stripped off with nitrogen gas. DIC was measured manometrically and transferred to another flask for isotopic analysis. DIC of standard solutions always measured several percent higher than the value calculated, but precision of replicate analyses was +/- 0.1°/oo.

Oxygen isotope composition of water is most commonly measured using the CO_2-H_2O equilibration method described by Epstein and Mayeda (1953). It requires an additional 5 to 20 mL of sample, and achieves a precision of +/- 0.1°/oo. Minute samples of water can also be analyzed using guanadine hydrochloride (cite) or bromine pentafluoride (O´Neil and Epstein, 1966; Blattner, 1973), but these extraction methods are complex and tedious.

The techniques each suffer from one or more flaws; they need too much sample, require expensive equipment, are too cumbersome, or are insufficiently documented. We thus embarked on a series of experiments designed to fully test the range, precision, and accuracy of a combined method which would deliver DIC, $\delta^{13}C_{DIC}$, and $\delta^{18}O_{H_2O}$ from a single 2 mL sample. The method has a precision and accuracy of +/- 0.1°/oo for both $\delta^{13}C$ and $\delta^{18}O$, and a precision and accuracy of +/- 0.1 mmol/L for DIC. Herein we describe in detail the technique, limits, and pitfalls. The results of our 150 determinations suggest to us that previous techniques may have been insufficiently tested and may not yield results with as high accuracies as formerly supposed.

2. METHODS

2.1 Reaction Technique

The reaction vessel is a small, water-jacketed, glass bottle with an arm fitted with a three-layer rubber septa (Figure 1). It connects via O-ring and clamp to a glass tube with a valve. The glass tube is ´corked´ with a three-layer rubber septa that is pierced by a thin needle. The needle acts as a capillary tube, keeping water inside the vessel while allowing CO_2 to escape. A removable U-trap is attached to an elbow joint, and then clamped to the reaction vessel and valve piece. These four pieces make up a removable assembly which is clamped onto a permanent microextraction line coupled directly to the inlet of the mass spectrometer (Figure 2). The assembly can be removed, cleaned, and dried when necessary.

Approximately 0.3mL of anhydrous orthophosphoric acid and a magnetic spinbar are placed in the reaction vessel, and the whole assembly is clamped onto the line and evacuated. The vessel is kept at a 25°C +/- 0.1°C by circulating water through the glass water jacket using a circulating water pump. Once the line is fully evacuated by the diffusion pump, valves to the pumps and mass spectrometer are closed (valves 3 and 4 in Figure 2), trap C is immersed in liquid nitrogen, and trap A is immersed in a dry ice-ethyl alcohol mixture. Trap B is kept at -90°C using an electric immersion cooler. Two mL of water sample, drawn into a syringe, is added through the reaction vessel septum and expelled, and the needle is immediately removed. The acidified solution is stirred vigorously by a magnetic stirrer for a total of thirty (30) minutes.

Several aspects of the evacuation are important. First, the valves between the reaction vessel and the traps must be open while injecting the water in order to draw CO_2 immediately to the liquid nitrogen-cooled trap. If the valves are not open, fractionation results. Second, much experimentation has shown that the optimum inner diameter for the needle valve (capillary) is 0.016 mm. A needle with a larger diameter allows much water to escape, while too narrow a diameter blocks the passage of CO_2 and causes fractionation. The needle is imbedded in a septum in the glass stem and extends only a few millimeters into the bowl. This eliminates blockage of the needle by sprayed water droplets. Third, after fifteen (15) minutes, the first dry ice/ethyl alcohol bath (Trap A) must be lowered by an inch or so. The water frozen in the trap slowly refreezes at the new dry ice/alcohol level and CO_2 physically trapped beneath the ice is liberated without oxygen re-equilibration.

The residual uncondensable gases are pumped away and the CO_2 is isolated in trap C. The liquid nitrogen is replaced by a dry ice/ethyl alcohol mixture, and the CO_2 is transferred to a freezing finger immersed in liquid nitrogen. The CO_2 is again isolated, dry ice/alcohol is exchanged for liquid nitrogen, and CO_2 is transferred to the inlet system of the mass spectrometer. The gas is allowed to sublimate into a portion of the inlet system with a fixed volume and connected to the source through the capillary leaks, and the voltage produced by mass 44 of that volume of gas is measured and recorded. This is the measurement of DIC. The isotope ratio of the gas is then analyzed against a machine standard.

Once the reaction is complete and the CO_2 is isolated, the assembly can be removed, cleaned, replaced with another, and dried. Three reaction vessels and U-tubes, two needle stems, and one elbow joint are enough to run all day. The permanent -90°C trap, trap B, should be pumped dry every four samples or so; failure to do so will eventually result in spurious results. The U-trap and reaction vessel are changed for each sample; the needle valve can usually be used all day but occasionally must be replaced.

2.2 Standardizing Techniques

$NaHCO_3$ solutions were used to calibrate the voltage generated by mass 44 versus umoles of CO_2 measured. $NaHCO_3$ must be vacuum roasted at approximately 200°C for 4 hours in order to drive off adsorbed CO_2. If not freshly heated and cooled completely under vacuum, the results will be spurious and yield inaccurate and imprecise measurements.

Several standard solutions ranging in concentration from 0.5 to 8.3 mmole/L were prepared from $NaHCO_3$ using CO_2-free distilled water (boiled 15 minutes, cooled through a drying tube) and stored in 100mL bottles sealed with septa and aluminum seals.

For measuring DIC, several $NaHCO_3$ solutions of known molarities were prepared, and an equation which relates the voltage of mass 44 of the gas in a fixed volume versus umoles of DIC in the sample was calibrated. The equation is used to translate voltage of unknowns into mmol/L DIC. The fixed volume we use for most of our samples is the inlet system itself, isolated from the bellows (Figure 3). To handle samples containing more than 24 umoles (12 mmol/L for 2mL sample), a second equation relating mass 44 voltage in the fixed volume to mass 44 voltage of a larger, ´bellows-open´ volume was also calibrated. For our mass spectrometer, the equations are as follows:

(i) umol = 0.24 x Voltage of mass 44 of fixed volume

$r^2 = 1.0$

(ii) Voltage of mass 44 of fixed volume = 6.31 x Voltage of mass 44 of ´bellows-open´ volume +8.28

$r^2 = 1.0$

Although we usually use 2 mL water samples, our equations compare mass 44 voltage with the total umoles of DIC measured. Mmol/L is then calculated by dividing umoles of sample by volume of the sample (mL). This makes it possible to vary sample size without recalibrating a new equation.

The oxygen isotope composition of CO_2 aqueous (measured by this method) is 1.07‰ heavier than CO_2 vapor (measured by the Epstein and Mayeda method) at 25°C (Vogel et al., 1970). In order to directly compare results between this method and the traditional equilibration method, the measured values are corrected for this fractionation. No other oxygen correction is needed, as the oxygen of the CO_2-H_2O system is completely water-dominated.

Three CO_2 samples were prepared to monitor and correct for mass spectrometer and tuning changes over time. The voltage of mass 44 in the fixed volume was measured daily, weekly, biweekly, and then monthly, and always measured within the precision reported. It is suggested that a known volume of gas is measured biweekly or monthly, after any major changes to the mass spectrometer, or after a long lapse of time in order to monitor and correct for long-term changes in mass spectrometer calibration.

Solutions with high molar DIC concentrations (~8 mmol/L) last for at least 6 months and probably much longer. We used an 8.3mmolar solution as a daily standard. Low molar solutions are diluted by air from the needle and/or by atmospheric invasion through the cap and last only a few weeks, depending on the number of aliquots removed and the molarity.

3. RESULTS

3.1 Accuracy and Precision

Five samples of solid $NaHCO_3$ were dissolved in 100% phosphoric acid and analyzed. Their average $\delta^{13}C$ value was -1.54°/oo with a standard deviation of 0.08°/oo (Table 1). Ten analyses of a water standard prepared from the same $NaHCO_3$ yielded an average $\delta^{13}C$ of -1.56°/oo with a standard deviation of 0.03°/oo (Table 2). Precision was 0.1°/oo or better for every concentration measured, including 0.5mmol/L. Accuracy, however, declined as molarity decreased. At a concentration of 1.0mmol/L, the accuracy was off by 0.2°/oo.

Ten replicate analyses of a standard had an average mass 44 voltage of 69.5 volts using a resistor of 10^{10} ohms with a standard deviation of 1.0 volts. This translates to an average of 8.3mmol/L with a standard deviation of 0.1mmol/L (Table 1). Thirty nine analyses of seven standards of differing molarities had an average (predicted minus actual) DIC of 0.0 mmol/L with a standard deviation of 0.1 mmol/L. The equation is thus an accurate predictor of the actual DIC content, as suggested by the correlation coefficient of 1.0.

Ten replicate analyses of the same standard had an average $\delta^{18}O$ value of -10.10°/oo with a precision of 0.08°/oo (Table 1).

A comparison of oxygen isotope measurements obtained using the Epstein and Mayeda (1953) technique and this technique is presented in Table 2. Three different waters with $\delta^{18}O$ values ranging between +0.4 and -40.3°/oo were measured multiple times by both methods. The mean values and standard deviations are essentially equal for each of the three waters.

3.2 Limits

For both $\delta^{13}C$ and $\delta^{18}O$, the accuracy of the analysis declines when the molarity decreases. A 1.5mmolar solution is accurate within 0.1°/oo, but a 1.0mmolar solution is depleted in both carbon and oxygen by approximately 0.2°/oo compared with the correct value. Thus, we consider 1.0 mmol/L to be the limit of resolution. Increasing the sample size in order to increase the total umoles analyzed does not improve the situation. This suggests to us that either a fixed, minute percentage of CO_2 cannot be driven out of the sample, or that a finite amount of CO_2 is adsorbed on the glass and O-ring fittings and cannot be collected. This fraction only becomes significant when the molar DIC content of the solution is very low. Most lake and groundwaters, and all seawater and brines meet and exceed this threshold (Stumm and Morgan 1981).

The precision and accuracy of 0.1 mmol/L for DIC measurements is equal to or better than measurements made manometrically, but is inferior to that of coulometry. However, in most waters, variations are many times larger than 0.1mmol/L, and this method is sufficient.

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FIGURE CAPTIONS

Figure 1. Reaction vessel for extracting DIC from water samples.

Figure 2. Reaction vessel and extraction line.

Figure 3. Calibration between DIC and voltage produced by the mass 44 across a 10^{10} ohm resistor of a known CO_2 sample in a fixed volume of the inlet system.

TABLE 1: Carbon isotope composition ($\delta^{13}C$) of solid $NaHCO_3$ compared with $\delta^{13}C_{DIC}$, $\delta^{18}O_{H_2O}$, and DIC measured on replicate samples using the new technique.

	Solid $NaHCO_3$	Dissolved $NaHCO_3$		
	$\delta^{13}C$ (°/ooPDB)	$\delta^{13}C$ (°/ooPDB)	$\delta^{18}O$ (°/ooPDB)	DIC (mmol/L)
	-1.55	-1.49	-10.11	8.21
	-1.60	-1.58	-10.08	8.16
	-1.48	-1.60	-9.99	8.40
	-1.44	-1.55	-10.12	8.46
	-1.63	-1.59	-10.10	8.40
		-1.58	-10.09	8.22
		-1.56	-9.94	8.46
		-1.61	-10.23	8.34
		-1.53	-10.16	8.40
		-1.51	-10.17	8.34
Mean	-1.54	-1.56	-10.10	8.34
STD.	0.08	0.03	0.08	0.10

TABLE 2: $\delta^{18}O$ of three different water samples measured using the Epstein and Mayeda (1953) method compared with the $\delta^{18}O_{H_2O}$, $\delta^{13}C_{DIC}$, and DIC results using this technique.

Sample	CO_2-H_2O method	This technique		
	$\delta^{18}O$ (°/ooSMOW)	$\delta^{18}O$ (°/ooSMOW)	$\delta^{13}C$ (°/ooPDB)	DIC (mmol/L)
EB730	-4.7	-4.7	-13.4	5.8
	-4.8	-4.6	-13.4	5.8
	-4.6	-4.4	-13.4	5.8
	-4.5	-4.5	-13.4	5.8
	-4.5	-4.6	-13.4	5.9
Mean	-4.6	-4.6	-13.4	5.8
STD.	0.1	0.1	0.0	0.1
VH-A	-40.4	-40.3	-15.9	2.3
	-40.5	-40.4	-16.0	2.3
	-40.0	-40.4	-16.0	2.3
Mean	-40.3	-40.4	-16.0	2.3
STD.	0.3	0.1	0.1	0.0
Gulf Net	0.4	0.5	0.7	2.5
	0.3	0.6	0.7	2.6
	0.9	0.7	0.8	2.7
	0.4	0.5	0.7	2.7
	0.2	0.4	0.7	2.7
	0.5			
Mean	0.4	0.5	0.7	2.6
STD.	0.2	0.1	0.0	0.1

EB730 is a fresh groundwater from the Baton Rouge aquifer system; VH-A is melted ´blue ice´ from Vestfolol Hills, Antartica; Gulf Net is sea water sampled from the Gulf of Mexico.

FIGURE 1

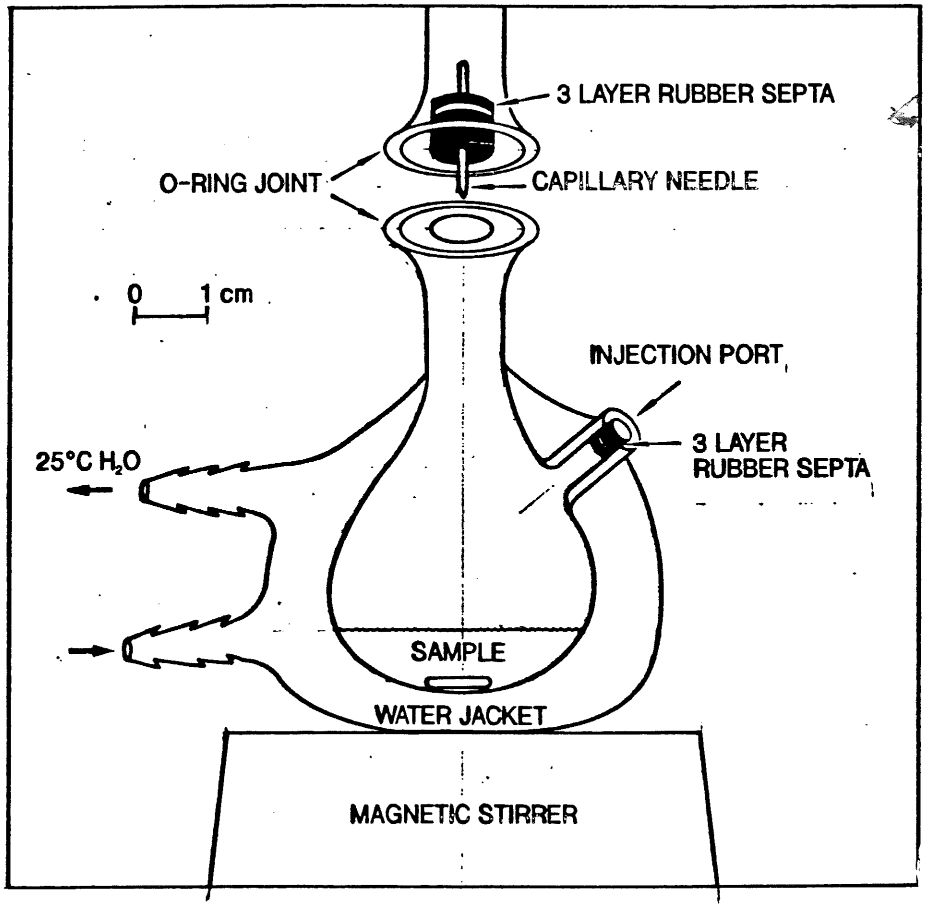
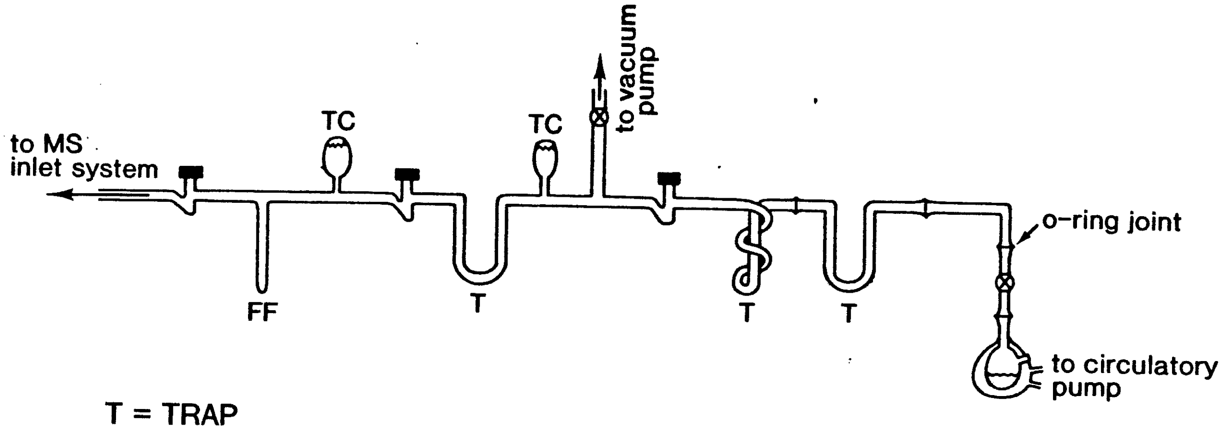
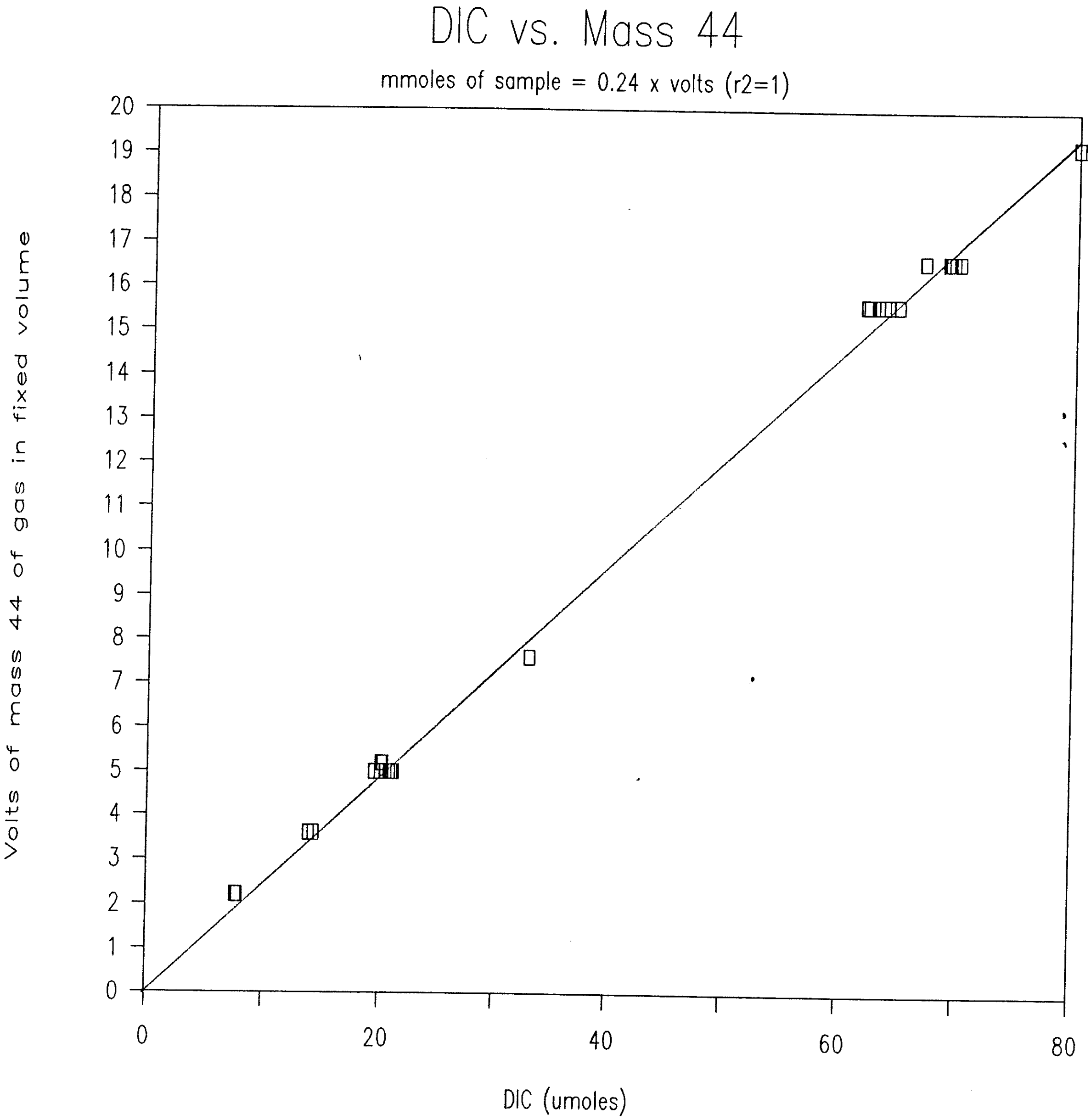

3 LAYER RUBBER SEPTA
O-RING JOINT
CAPILLARY NEEDLE
0
1 cm
INJECTION PORT
3 LAYER RUBBER SEPTA
25°C H₂O
SAMPLE
WATER JACKET
MAGNETIC STIRRER

FIGURE 2



T = TRAP
TC = Thermocouple
FF = Freezing Finger

FIGURE 3


DIC vs. Mass 44
mmoles of sample = 0.24 x volts (r2=1)
Volts of mass 44 of gas in fixed volume
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
0
20
40
60
80
DIC (umoles)