NATURAL GROUND WATER SYSTEMS AND ASSOCIATED FRESHWATER CARBONATE DEPOSITS IN SOUTHERN OKLAHOMA

Ву

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Scope and Method of Study: The purpose of this investigation was to describe freshwater travertine deposits and to establish relationships between them and the carbonate rich ground water producing them. Two geographic areas, both with springs of Arbuckle Group origin were studied; Area A in the Arbuckle Mountains and Area B in the Slick Hills of Commache County. The samples were collected between May and July of 1984. The water samples were analyzed by standard techniques and the travertine deposits were examined using thin section analysis, scanning electron microscopy, xray diffraction, and chemical methods.

Findings and Conclusions: The travertines examined were texturally of two types; porous and banded. Scanning electron microscopy revealed the presence of algal tubules and diatoms. Needle shaped diatoms, possibly Synedra sp., were found only in Pleistocene travertines, whereas, boat shaped diatoms possibly Noviculla sp. were found in Pliestocene and Recent travertines. Turner Falls travertines were composed of bands of rosettes alternating with bands of algal tubules.

The precipitation of calcium carbonate results primarily because of ${\rm CO_2}$ loss. Water saturated with ${\rm CO_2}$ will lose ${\rm CO_2}$ to the atmosphere by a decrease in pressure and by agitation such as water flowing over rapids or waterfalls. romoval of water by evaporation changes the solubility product and also may lead to precipitation of carbonate. Plants may precipitate CaCO3 during photosynthesis by removing CO2 from the water or in the case of some algae, bicarbonate ions. Mosses have a symbiotic relationship with algae and act as excellant traps for calcium carbonate crystals.

ADVISER'S APPROVAL _

NATURAL GROUND WATER SYSTEMS AND ASSOCIATED FRESHWATER CARBONATE DEPOSITS IN SOUTHERN OKLAHOMA

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PREFACE

This study addresses the geochemical relationships between natural waters and the associated carbonate deposits. The Arbuckle Mountains and the Witichta Mountains, produces carbonate-rich water that under special conditions deposits freshwater carbonates at several locations in southern Oklahoma.

The completion and success of my graduate career would not have been possible without the assistance of several inportant people and the financial support of the University Center for Water Research. I would like to thank my thesis adviser, Dr. Arthur Hounslow, for his guidance, understanding and assistance throughout the past two years. Recognition and thanks to my thesis committee members for their support and help during my investigation; Dr. Nowell Donovan, helped in chosing carbonate deposit localities and review of the areas geology, Dr. Wayne Pettyjohn for keeping the "thumbs up" during the writing. Without the chemical background and laboratory expertise of Ray Powers this thesis and I would still be in the lab.

Special appreciation to those people who allowed me to obtain my samples and also to those that helped tote, carry, and pump water samples; Charlie and Dixie Oliver, property owners, Bert Speed, Chickasha National Refuge, Jim Blue,

Turner Falls Park, Debbie Ragland, field partner, and Steve and Kathy Bridges, field partners.

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CHAPTER I

INTRODUCTION

Objective and Scope

The primary objective of this investigation was to establish relationships between carbonate rich ground water, found locally in southern Oklahoma, and their associated carbonate deposits. A secondary objective was to use these relationships to determine the depositional environment of older freshwater carbonates.

Chemical analyses of spring, stream and well waters were used to determine if calcium carbonate precipitated or dissolved in four sample areas in southern Oklahoma. These areas were selected because, at one time or another, calcium carbonate was precipitated, and also because the Arbuckle Group was the source of the water. The Arbuckle Group is a combination of limestones, dolomites, and some sandstones of shallow water marine origin. The 6700 feet thick Arbuckle aquifer contains carbonate-rich water with abundant chemical analyses available. This prolific aquifer, characterized by solution openings and fractures does not exist outside the Arbuckle Mountain area, although the Arbuckle Group is reported to contain ground water in the Wichita Mountain area, (Havens, 1977). All the samples obtained for this

investigation where collected between May and July of 1984. During this time of year the region is arid and most of the springs and small streams have no flow, however, the stream water still available is base flow, or the contribution of ground water. The carbonate-rich ground water is assumed to have originated in the Arbuckle Formation.

For this investigation, the limited rock analysis, randomly sampled from outcrops of the Arbuckle Mountains are assumed to represent the entire formation. A comparison was made between the marine carbonates of the Arbuckle Formation and the freshwater carbonates deposited from this water.

Terminology

Freshwater carbonates are a varied group of deposits. Terminology is based on texture and mode of deposition rather than mineral composition. Europeans, particularly in Germany, have a very detailed classification that commonly overlaps. The present usage uses five terms: (Bates and Johnson, 1978)

- Hot Spring Deposits based on those carbonates found in thermal springs, highly mineralized,
- Speleothems carbonate deposits found in association with caves,
- Calcrete a pedogenic carbonate found in soil horizons,
- Travertine a hard dense carbonate, named for an extensive deposit near Tivoli, Italy,

Tufa - highly porous, spongy deposit, usually associated with plants.

The present trend is to identify as travertine all carbonate incrustation on plants without reference to density or pore volume, (Julia, 1984). Another term used more in European literature is sinter. In Julia's article this term is restricted to those deposits of abiotic origin, more dense and compact than tufa, also including speleothems and flow stones.

Computer Literature Searches

Three computer literature searches for this investigation were done by Oklahoma State University library personnel using two data banks, Water Resources Abstracts and GEOREF (American Geological Institute). The first search conducted in 1983, using the key words hydrology-Oklahoma, yielded two hundred titles. Two searches were conducted in 1984. One using keywords springs-Oklahoma, yielded fifty titles while the third search using key words geochemistry-Arbuckle Group-Oklahoma yielded only five titles, (see Appendix A).

Previous Works

Travertine investigations date back to the early nineteenth century in Europe. European published works include: Klahn (1928), Savelli and Wedepohl (1969), Muller (1969), Jacobson and Usdowski (1975), Flugel (1982), as well

as many others. Carbonate Sedimentology in Central Europe (Muller and Friedman, eds., 1968) is a collection of investigations by authors throughout Europe, which provides an extensive reference list. One investigation within this collection by Irion and Muller (1968) discusses the geochemistry of a German calcareous tufa, containing 89.4-100% CaCO3 that was reported to be a purely inorganic precipitate rather than biogenetic-inorganic one. One of the earliest works cited is Klahn's (1928) investigation of carbonate-rich waters and associated dolomite-rich spring tufas. Savelli and Wedepohi (1969) discuss the very sensitive conditions needed for travertine formation. study showed that travertine formation is related to bicarbonate spring waters which have circulated in faults where calcite solution from subsurface beds was present. investigation done by Jacobson and Usdowski (1975) reported a spring fed stream that precipitated calcite by inorganic processes in an irregular manner. Analyses of the waters at the spring head as well as downstream allowed the authors to reconstruct the origin of the spring. Many of the major available references such as Flugel (1982), Graf (1960), Kitano (1962), Chilingar and others (1967), and Bathhurst (1971) are primarily discussions of marine carbonate sediments with very little information on fresh water carbonates. An excellent recent resource is AAPG Memoir 33 (1983) "Carbonate Depositional Environments", which includes several sections on fresh water carbonate formation.

(1978) analyzed fresh water carbonate travertines found in Colorado using geochemical and petrographic techniques. He concluded that four of the travertine formations studied were an example of hydrothermal "freshwater" carbonate deposits and three factors that contribute to the character of the spring deposit; local topography, seasonal climatic change, and flow rate.

Travertine and tufa found in Oklahoma was first investigated by Emig (1917), who located the major deposits at Turner Falls and Price Falls. Where no geochemical data were mentioned in this initial report although Emig did recognize three periods of travertine deposition at Turner Falls as well as several modes of travertine deposition including the biogenetic contribution of mosses. Wilson and Guest (1961) reported not only the contributions of the mosses but also the association of diatoms in the formation of travertine. Ham (1980) and Donovan (1983) both mention the Turner Falls travertine deposit in discussing the geology of the Arbuckle Mountain area. Other modes of deposition of travertine and tufa have been cited, such as water mixing, which is reported to be responsible for the tufa deposits in Mono Lake, an alkaline environment (Dunn, 1953). Barnes (1965) investigated a travertine depositing creek in an arid climate and concluded that it was not evaporation but rather water lost through seepage and photosynthesis created the conditions for precipitation. There is a rapidly growing area of isotopic geochemistry

Mg, Sr, Na, and Fe in limestones and dolomites. He compares acetic acid and hydrochloric acid digesting. Weberling (1968) discusses mixed alkaline earth standards for several analytical methods with comparisons using carbonate samples.

CHAPTER II

CHEMICAL PROCEDURES

This investigation involved two different wet chemistry procedures; water analysis and rock analysis. Six parameters determined on each water sample but not on the rock were: temperature, pH, alkalinity, sulfate, chloride, and silica. Both water and rock samples were tested for fourteen elements using a Perkin-Elemer Atomic Absorption 403. The settings for each element analyzed were the manufacturers recommended values. The standards used for each element were purchased atomic absorption spectroscopy standards from Fisher Scientific. The detection limits, standards, sensitivity and absorbance values for each element are shown on Table 1. Two of the 14 elements, Al and Pb, were below the detection limits in all samples. Table 2 lists the standards used for each element analyzed.

Water Analysis

The water analyses began in the field with pH and temperature (OC) determinations and at a few sites specific conductivity. Two water samples were prepared at each site according to suggestions by EPA (1979), and stored in plastic five hundred milliliter bottles. These bottles had

Table I

WAVELENGTHS, CONCENTRATION RANGES, SENSITIVITIES FOR ELEMENTS
FOR DETERMINITATION BY ATOMIC ABSORPTION AND FLAME EMMISSION

Atomic Absorption* Wave-Optimum conc. range Detection Sensitivity length angstroms in solution limit 1% absorption Element Interferences _____ 3092.8 10 - 150 0.1 1.3 (1) A1 Ionization + 5515.5 100 - 1000 0.05 0.36(1)Ca,™ Ionization + Ba 1 - 10 0.09 4226.7 0.002 (2) POA, GAI, G SOA, G Ca Si,G 3247.5 2 - 200.005 0.15 (2) Cu 2 - 202483.3 0.005 0.15 (2) Fe HNO3, Ni, J SiO3 1 - 10 0.005 0.05(2)K 7664.9 Ionization + Li 6707.8 0.5 - 50.005 0.04(2)0.1 - 2AlG (high levels), Mg 2852.1 0.0003 0.01(2)SiG 2794.8 2 - 20 0.005 Mn 0.04(2)0.3 - 35890.0 0.002 0.015(2)Ionization + Na 4 - 400.03 0.7 (2) Pb 2833.1 2 - 20 Si,G Al,G PO,G Sr 4607.3 0.01 0.2 (2) Zn 2138.6 0.2 - 30.002 0.025(2)

(after Issac, 1973)

^{* (1)} Nitrous Oxide-acetylene (2) Air-acetylene

⁺ Ionization effects can be controlled by the addition of a large excess (1000 ppm) of an alkali metal salt such as KCl.

[►] Spectral interferences due to the CaOh absorption bandhead located at the Ba absorption. can be corrected for by subtracting the absorbance of a blank containing Ca.

G Can be controlled by the addition of lanthanum to the samplea (1%).

J Can be controlled by a very lean (hot) flame.

TABLE II

STANDARDS USED FOR AA ANALYSIS

- Al- The ions in the samples were lower than the detection limits. More than .2% HCl decreases the sensitivity. Standards were made of the following ppm 1, 3, 5, 7,
- Ba- Used a mixed standard (Weberling and others, 1968) diluted Ba standard with 1000 ppm potassium standard and .5 grams of KCl was added to all samples to prevent ionization. Standards were made of the following ppm 1, 3, 5, 10,
- Ca- Due to the amount of strontium present, a mixed standard was used (Weberling and others, 1968), 1% LaCl₂ was added to eliminate complexation interferences in both samples and standards, Standards were made of the following ppm-1, 3, 5, 7, 10. The extreme dilution used (1:2000) resulted in unreasonable reduction of accuracy for Ca amounts,
- Cr- Standards were made of the following ppm- .5, 1, 3,
- Cu- Standards were made of the following ppm- .25, .5,
- Fe- Standards were made of the following ppm- .5, 1, 5, 10
- Li- 1% LaCl₂ was added to both standards and samples Standards were made of the following ppm- .05, .125, .25, .5, 1
- K Standards were made of the following ppm- .5, 1, 3, 5
- Mg- Samples were diluted, but not to the extent of the Ca analyses
 1% LaCl₂ was added to both standards and samples Standards were made of the following ppm- 1, 3, 5,
- Mn- Standards were made of the following ppm- 1, 2, .5, 5, 10
- Na- Standards were made of the following ppm- 1, 3, 5, 7

Table II (continued)

- Pb- The ions in the samples were lower than the detection limits.
- Si- Analysis was conducted in the Water Quality Research Lab using a graphite furnace. Standards were made of the following ppm- .5, 1, 3, 5
- Sr- Mixed standards were used (Weberling and others, 1968) diluting the standards with 1000 ppm Ca standards also adding 1% LaCl₂ to standards and samples. Standards were made of the following ppm-1, 2, 3, 5
- Zn- Standards were made of the following ppm- .25, .5,
 1, 2

been rinsed with sample water three times before the actual sample was taken. The bottles were marked with location, pH, temperature, and time. One bottle was stored on ice to maintain 4°C. The other sample was treated by adding a few drops of 1:1 nitric acid to bring the pH below two. analyses for alkalinity, sulfate, and chloride were run on the samples within twenty-four hours. The titration used for alkalinity is based on EPA Standard Methods, (1979), using HCl for titration on the refrigerated samples. sulfate analysis was determined by turbidity, EPA (1979). Chloride determination was based on EPA (1979) mercuric chloride titration. Several other titrations were tried but their end point detection proved too difficult. procedures are included in Appendix B. Some of the water samples were filtered before analyses to eliminate suspended material. The nitric acid fixed samples were used in all atomic absorption spectrographic analyses. All analyses were completed within four months of sampling.

Rock Analysis

Three types of rocks were analyzed in this investigation. These included the Arbuckle Group, associated freshwater carbonate deposits found at water sample sites, and a group of miscellaneous freshwater carbonates.

All samples were crushed in a Spex Ball Mill using tungsten carbide balls and chamber for 2-4 minutes to

achieve a powder of -80 mesh. An approximate one gram sample was split out of twenty grams to obtain a representative sample. Between each sample the chamber and balls were washed, rinsed with 10% HCl, and rinsed again with distilled deionized water.

For quality control purposes, duplicates were run of each rock sample. If greater than 10% error was found the sample solute was redone. Approximately one gram of sample was weighed and recorded, and placed in a Teflon beaker. The sample was slightly wetted with deionized water and 40 ml of 10% HCl was added slowly. The beaker was covered with a watch glass and placed in a fume hood for 18 hours. covered beakers were then placeed in a boiling water bath or sand bath for an additional seven hours. While still warm, the samples were filtered through a .45 micron membrane filter. The beaker was rinsed with 10% HCl to remove the residue. An additional three washings of 10 ml. of 10% HCl followed. The filtrate was then diluted to 100 ml. with deionized water in a volumetric flask, then transferred and stored in an acid washed plastic bottle. Refer to Appendix B for actual lab procedures followed.

CHAPTER III

CARBONATE EQUILIBRIUM

The solution or precipitation of calcium carbonate in natural waters is dependent on various factors. A detailed investigation of the chemical systems involved in the carbonate cycle was done by Garrels (1960), Garrels and Christ (1965), and Krauskopf (1979). Many discussions of this model are available and will not be considered here.

A chemical reaction, such as the dissolution of calcium carbonate, is usually assumed to reach equilibrium (nothing added or removed). The Law of Mass Action states that if a system at equilibrium is disturbed by temperature, or pressure, or concentration, changes the system will tend to shift its equilibrium position so as to counteract the effect of the disturbance, (Brown and LeMay, 1981).

The carbonate system, assuming constant temperature (25°C) and constant pressure (1 atmosphere) can be modelled by the following five chemical reactions:

$$CaCO_3$$
 $Ca^{+2} + CO_3^{-2}$ (1)
 H_2CO_3 $H^+ + HCO_3^-$ (2)

$$HCO_3^ H^+ + CO_3^{-2}$$
 (3)

$$H_2O$$
 $H^+ + OH^-$ (4)

 CO_2 H_2CO_3 (5)

(Garrels and Christ, 1963)

In solutions that are sufficiently dilute the solute concentrations are nearly equal to their activities. Activity coefficient is merely an adjustment factor used to convert concentrations into a value used in thermodynamic equations, (Freeze and Cherry, 1979). A measure of the strength of electrostatic field caused by the ions usually is equal to the ionic strength, (Hem, 1970). At a low ionic strength of about $10^{-2.3}$ the Debeye-Huckel method was used to determine the activity coefficients.

Solubility is defined by Brown and LeMay (1981) as the amount of solute (CaCO₃) in a given quantity of solvent (natural waters) effected by temperature and pressure, and can change by adding some other substance to solution.

An equilibrium constant, (k), for a system at equilibrium is defined by Garrels and Christ (1965) as:

The product of the activities of the reaction products, each raised to the power indicated by its numerical coefficient, divided by the product of the activities of the reactants, each raised to a corresponding power, and is a constant at a given temperature, independent of total pressure. The equilibrium constants for equations 1 - 5 at 25°C, 1 atm. are:

(1)
$$[Ca+2]$$
 $[CO_3^{-2}]$ = k_{CaCO_3} = $10^{-8.3}$

(2)
$$[H^+] [HCO_3^-] = k_{H_2CO_3} = 10^{-6.4}$$

(3)
$$[H^{+}] [CO_{3}^{-2}] = k_{HCO_{3}^{-}} = 10^{-10.3}$$

(4)
$$[H^+]$$
 $[OH^-]$ $-\frac{1}{[H \ O]}$ $= K_{H_2O} = 10^{-14.0}$

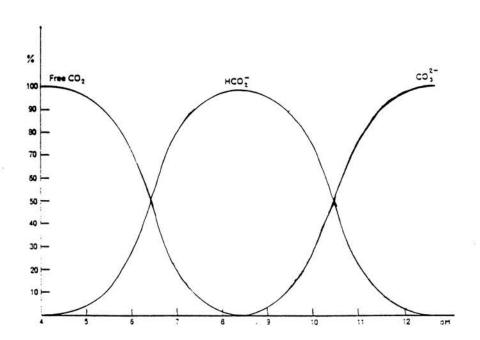
(5)
$$\frac{[H_2CO_3]}{-----} = K_{CO_2} = 10^{-1.47}$$

$$^{P}_{CO_{2q}}$$
[] = activity

If the ion activity product is equal to the equilibrium constant, then equilibrium exists and the solution is saturated. Theoretically if the ion product is greater than k then precipitation occurs until I = k, if I is less than k the solid dissolves until I = k, (Brown and LeMay, 1981).

If the solubility of Ca^{+2} were held constant at equilibrium there are three factors that would influence the chemical reaction to move left or right; pH, temperature, and the partial pressure of CO_2 . Assuming the same temperature and CO_2 the amount of $\operatorname{HCO}_3^{-1}$, $\operatorname{H}_2\operatorname{CO}_3$, and CO_3^{-2} present is controlled by the pH value. As the pH increases (OH is added) the [$\operatorname{H}_2\operatorname{CO}_3$] decreases while [HCO_3] increases, see Figure 1, (Equations 2, 3, and 4). $\operatorname{H}_2\operatorname{CO}_3$ has almost entirely dissociated to HCO_3 at pH 8.5. Increases pass pH 8.5 decreases [HCO_3] as [CO_3^{-2}] increases (see Figure 1).

According to LeChatelier's principle, when heat is added to an endothermic solution (natural waters) the equilibrium will shift in such a direction as to reverse the



Source: Golterman (1969).

Figure 1. Relation Between pH and % of Total "CO2" As Free CO2, $\rm HCO_3$, and $\rm CO_3$

effect of added heat, move the reaction to the right or increase solubility, (Brown and LeMay, 1981).

At 25°C and atmospheric CO_2 ($10^{-3.5}$ atm.) pure water saturated with calcite contains 20 mg/l Ca^{+2} and 61 mg/l HCO_3^- , whereas pure water saturated with calcite at $CO_2 = 10$ - 2.2 atm. will dissolve 58 mg/l Ca^{+2} and 177 mg/l HCO_3^- , (Jacobson, 1970). Jacobson and Langmuir (1970) also showed that the dissolved CO_2 changes the solubility of various ions. The amount of CO_2 is also controlled by biological systems such as photosythesis and evaporation which cause CO_2 to be removed and $CaCO_3$ to be precipitated.

CHAPTER IV

SAMPLE SITES

The sample sites for this investigation were chosen by using two criteria; the water was, or was thought to be of Arbuckle Group origin, and there was evidence of carbonate precipitation from this water at some time.

The best known travertine deposit in the state of Oklahoma, also a favorite tourist attraction, is Turner Falls, TlS, R01E, sec. 36, in Murray County. Another less well known travertine deposit is Price Falls, located south of Turner Falls, TlS, R02E, sec. 33. These two travertine falls and their associated streams are reported to have numerous travertine formations, (Emig, 1917). Fairchild, (1983) reported carbonate formation on many of the stream beds located throughout the Arbuckle Mountain area. This area overlying the Arbuckle aquifer in Murray County, designated Study Area A, (Figure 2) had numerous analyses of ground water, springs, and streams available.

The second area of study, Study Area B, is located in the northeastern corner of Commache County, T2N, R13W and T4N, R14W. This area was chosen because of the numerous springs and spring fed streams of Arbuckle Group origin. Carbonate precipitation had not been reported in the area

and chemical analyses of waters in the area were limited. Havens (1983) reported very limited success in drilling water wells in the Arbuckle of this area and and also that the resulting water was of variable quality.

The water samples obtained from the two study areas and the published Arbuckle aquifer data showed very similar water geochemistry. The water analyses graphically shown on a piper diagram, (Figure 3) are Ca-Mg bicarbonate rich water.

The geology of the two study areas is very complex, even though the major geologic formations are the same. Different geologic controls have produced different results. The areas are extensively folded and faulted by different systems and at different times.

The climate of the two study areas differs considerably. Study Area A is a moist, subhumid climate with an average rainfall of 35.9 in/yr. Study Area B is a drier, less humid climate with an approximate annual rainfall 28 in/yr, (Pettyjohn and others, 1983). Both areas of investigation have many intermittent streams and springs that flow only during, and shortly after periods of rain, (Fairchild, 1982). Well water levels at both Study Area A and Study Area B show a relativly quick response to precipitation. Spring and stream discharge is also responsive to the ground-water levels in Study Area A, there is no supportive evidence of the same in Study Area B.

The sampling scheme used in this investigation is based

on sample area and whether the sample was water or rock. In Sample Area A, all samples begin with an A followed by a letter, if water, or a number, if a rock sample. Sample Area B changes only the first letter to B, followed by a letter or number corresponding to water or rock sample. Four Arbuckle Group formation rock samples were used in this study and are designated by a C with a corresponding number; C! - Cool Creek, C2 - Fort Sill, C3 - McKenzie Hill, C4 - Royer. Any other analyses used from literature are labeled with a D followed by a corresponding letter or number.

Study Area A

The Arbuckle Mountain area is a moist, subhumid zone with precipitation consisting of rain with some light snow or sleet during the winter, (Fairchild, 1983). A weather station at Platt National Park records average rainfall of 35.9 in/yr with the average monthly rainfall being highest during April, May and June, (Figures 4 and 5). Recharge in the Arbuckle aquifer is by precipitation with natural recharge taking place by infilteration of precipitation into the ground or outcrops, and in some locations small sink holes or solution pipes. (Fairchild, 1983).

The occurence and movement of ground water is strongly controlled by lithology and structure in the Arbuckle aquifer because of extensive folding and faulting (Figure 6). Along with the major fault and fold systems are numerous associated minor faults, folds, and fractures which provide

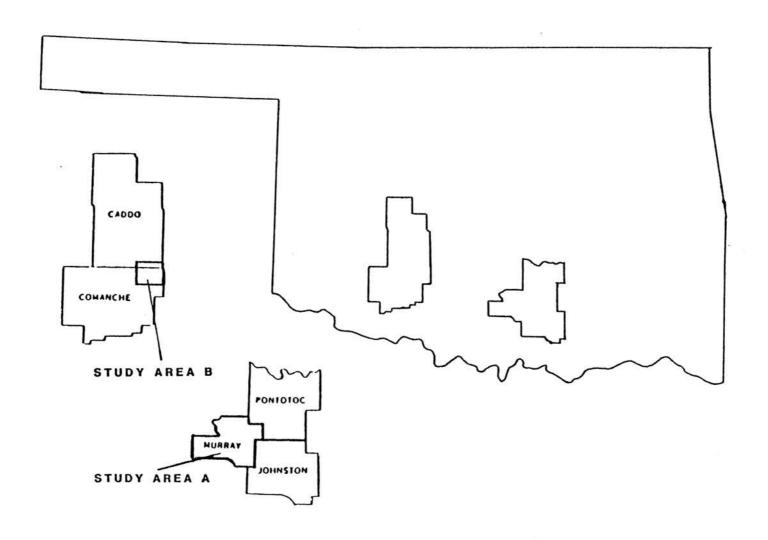
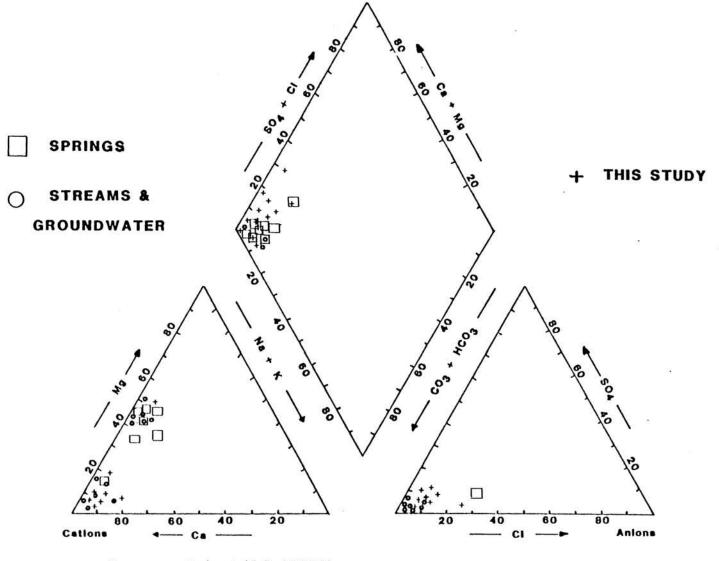
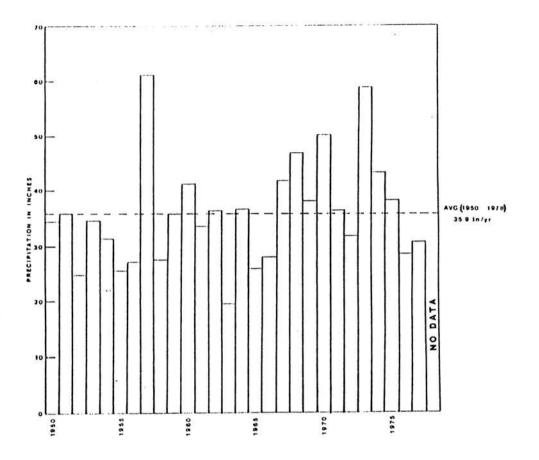


Figure 2. Location Map Showing Study Area A and B



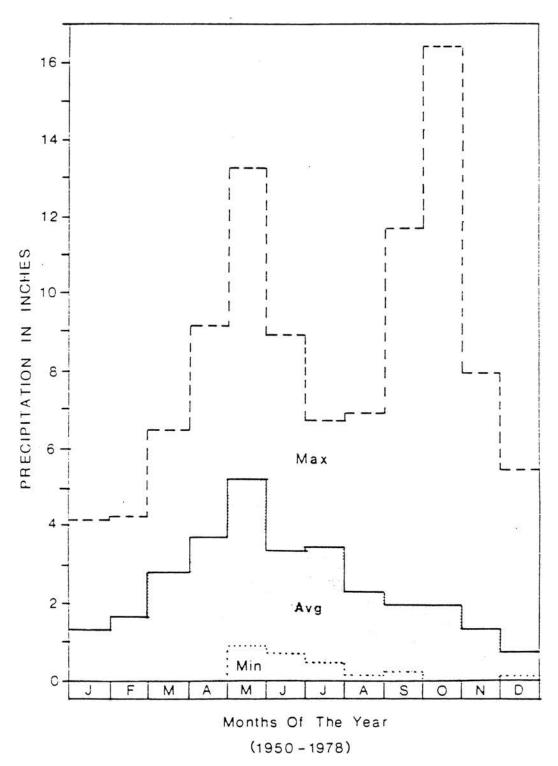
Source: Fairchild (1982)

Figure 3. Piper Diagram of Arbuckle Group Water



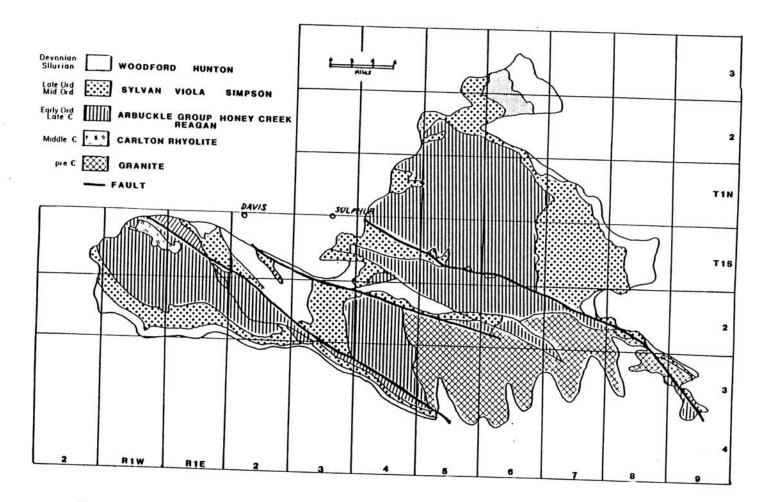
Data: NOAA

Figure 4. Average Yearly Precipitation for Platt National Park, Ok (1950 - 1977)



Data: NOAA

Figure 5. Maximum mean, and Maximum Monthly Precipitation For Platt National Park, Ok



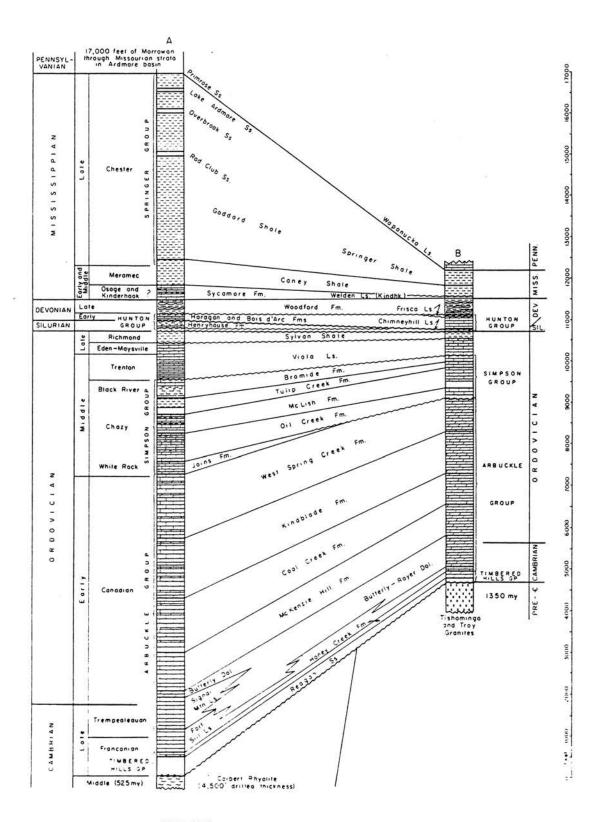
Source: Ham (1980)

Figure6. Geology Map of the Arbuckle Mountains (Study Area A)

ideal channels for ground-water movement. The rainwater, being a dilute acid enters the fractures, joints and bedding planes, enlarging them by dissolving the bedrock which results in an irregular network of openings that extend both vertically and laterally throughout the bedrock. Caliper logs from the area indicate possible openings as deep as 2,000 feet, although some of these could be drilling related. However, the assumption can be made that ground water circulation did or continues to occur at a depth of perhaps 2,000 feet. In addition, numerous cave systems are reported throughout the study area. Minor karst topography, streamline infilteration, and rock fractures all provide recharge to the aquifer. Hydrographs of the water levels in wells within the area indicate a fairly rapid response to changes in precipitation although the rate of recharge from the overall area varies because of differences in permeability of the subsurface formations, soil and vegetation, and evapotranspiration rates, (Fairchild, 1983).

The Arbuckle aquifer consists of several different geologic formations, each of which may have different hydrologic properties, but are still considered to be the Arbuckle aquifer based on stratigraphic correlations. The aquifer is composed of limestones, dolomites, and shale of shallow marine origin, (Figure 7).

The springs found in Study Area A by Fairchild (1984) are predominantly gravity springs occuring where the potentiometric surface intersects the land surface. Most of

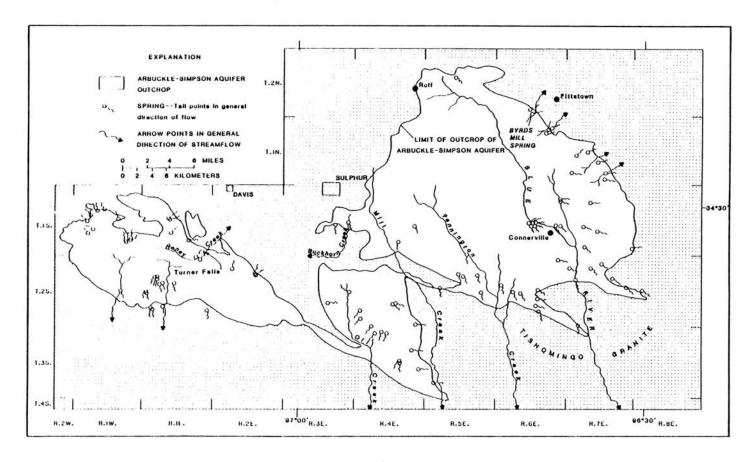


Source: Ham (1980)

Figure 7. Stratigraphic Column of the Arbuckle Mountains (Study Area A)

the springs are near faults or other fracture-like zones, that tend to be enlarged by carbonate solution. In the southeastern part of the area where faulting has brought the Precambrian age Tishmingo Granite of Precambrian age in contact with the Arbuckle Group, numerous springs and seeps are formed (see Figure 8). These springs are fault controlled, the granite acts as an impervious barrier to the ground water flow, and the spring is the natural release of the ground water, (Figure 9). Fairchild (1983) reports larger springs in the eastern part of the Arbuckle Mountain area, which is underlain primarily by dolomite in contrast to the western part of the area which is underlain primarily by limestone. The lithology is less likely to be responsible for this difference, then the size of drainage basin which is larger in the eastern part than the western part of the area.

Some springs that sustain enough discharge year round to produce perennial streams, such as Falls Creek and Honey Creek. Byrds Mill Spring near Fittstown is also a perennial spring. A 1958 hydrograph from a continuous paging station located at Byrds Mill Spring indicates that spring discharges vary with water levels, see Figure 10 (Fairchild, 1984). Fairchild (1984) reports that approximately 60% of the total runoff from the Arbuckle Mountain area is accounted for by the baseflow, or ground-water contribution, of the streams and springs. Tables 3 and 4 contain the chemical analyses for the rock and water samples found in



Source: Fairchild (1984)

Figure 8. Map of Arbuckle Mountain Area Showing Locations of Springs (Study Area A)

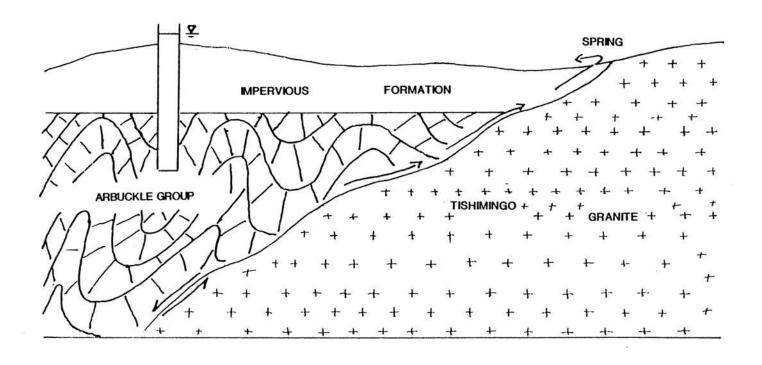
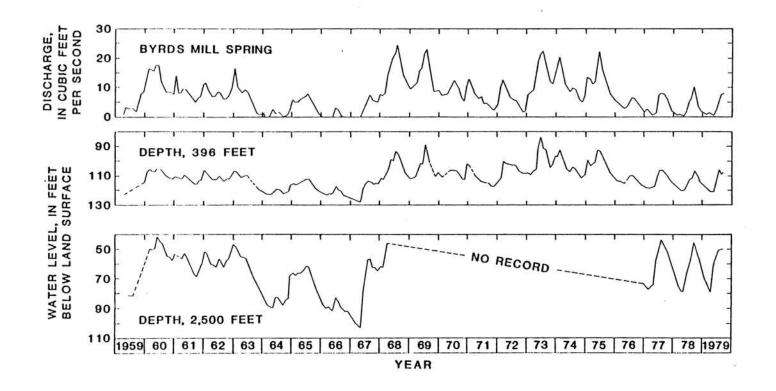


Figure 9. A Possible Hydrologic Mechanisim for Arbuckle Group Springs



Source: Fairchild (1984)

Figure 10. Hydrographs of Water Levels in Two Wells
That Tap the Arbuckle Aquifer and
Discharge From Byrds Mill Spring
(January 1959 - June 1979)

TABLE III

ROCK ANALYSIS FOR STUDY AREA A

Study Area A	Al T1NR3E s.1 Pleistocene?		A3 TISRIE s.36 Pleistocene Cave Deposit?	Permanent?	
 Isoluble					
Residue	5.3%	1.2%	12.3%	0.3%	0.3%
SiO ₂		_	_	_	=
CaO ²	43.2	48.8	60.4	47.6	48.5
K ₂ O	0.18	0.01	0.07	0.0	0.08
мģо	0.82	0.20	0.45	0.35	0.41
Ns ₂ O	0.25	0.29	0.29	0.11	0.14
mol Ca/Ca	a+Mg 0.97	0.99	0.99	0.99	0.99
nol Sr/Ca	3	0.24	0.27	= 34	0.51
Trace Ele (pph of m					
$A1^{+3}$	nd	nd	nd	nd	nd
Ba ⁺² Cr ⁺²	0.045	0.003	0.011	0.009	0.069
Cr^{+2}	0.002	0.003	0.003	0.002	0.003
Cu^{+2}	0.001	0.001	0.001	0.001	0.001
F6'4	0.479	0.072	0.233	0.029	0.110
Mn ⁺² Sr ⁺²	0.043	0.018	0.028	0.001	0.011
Sr ⁺²	nd	0.019	0.025	nd	0.039
z_n^{+2}		0.001	0.002	0.001	0.002
Pb ¹	nd	nd	0.039	0.020	nd

Table III (Continued)

Study Area	Al TlNR3E s.l	A2 TISRIE s.36	A3 TISRIE s.36	A4 Blue Creek Can.	A5 T1SR2E s.33
A	Pleistocene?	Recent	Pleistocene Cave Deposit?	Permanent? Travertine	Price Falls
Tho	orium ^l nd anium ^l nd	nd	nd	nd	0.022
Ura	anium ¹ nd	nd	nd	nd	0.010
mol Mn/	'Fe 0.09	0.26	0.12	0.03	0.10

Table III (Continued)

Study	Cl	C2	C3	C4	
Area	Cool Creek	Fort Sill	McKenzie HIll	Royer	
Α	Farm	Farm	Farm	Farm	
Insoluble					
Residue	7.8%	6.3%	9.0%	6.2%	
SiO ₂	1 <u>122</u> 4 1 22 6	=		=	
CaO ²	36.8	48.9	28.5	46.0	
	0.03	0.01	0.00	0.00	
K ₂ MgO	3.9	0.88	1.4	3.6	
Na ₂ O	0.49	0.31	0.24	0.40	
mol Ca/Ca+Mo	g 0.87	0.98	0.96	0.93	
mol Sr/Ca	0.12	0.01	0.18		
Trace Elemen	nts				
(pph of rock	k)				
$A1_{+2}^{+3}$	nd	nd	nđ	nd	
Ba+2 Cr+2	0.011	0.015	0.007	0.002	
Cr^{+2}	0.002	0.002	0.002	0.002	
Cu+2	0.001	0.001	0.001	0.001	
Fo'2	0.110	0.300	0.418	0.312	
Mn ^{TZ}	0.029	0.010	0.042	0.023	
SrTZ	0.007	0.001	0.013	nd	
Zn ⁺² Pb 1	0.002	0.001	0.001	0.001	
Pb 1	-	3 - 3	1449	() <u></u> ()	

Table III (Continued)

Stud Area A	ly ı	Cl Cool Creek Farm	C2 Fort Sill Farm	C3 McKenzie HIll Farm	C 4 Royer Farm	
	Thorium Uranium	1 _ 1 _	- - -	_	- - -	
mol	Mn/Fe	0.26	0.03	0.10	0.07	

^{1 =} x-ray flourescent semi-qualitative pph
values are an average of duplicates

% by weight

nd = none detectable

TABLE IV

WATER ANALYSIS FOR STUDY AREA A **

STUDY AREA A	AA T1NR3E s.1 stream	AB TISRIE s.36 stream	AC TISRIE s.36 below falls	t T2NT6E s.34 spring	t T1NR7E s.19 spring	29
Cemp OC	21 7.5	26 6.8	30 6.4	10 7.9	18 7.3	
Cations						
Ca ⁺² Mg ⁺² Na ⁺¹ K ⁺¹	38.4 27.4 3.1 1.6	84.8 3.1 5.7 .65	67.8 3.2 2.8 .66	61.0 37.0 4.1 1.0	85.0 40.0 31.0 2.6	
nions						
$\begin{array}{c} \text{HCO}_{3}^{-1} \\ \text{CO}_{3}^{-2} \\ \text{SO}_{4}^{-2} \end{array}$	233.2 0 10.7 11.0	374.8 0 10.8 21.2	168.6 0 10.3 13.7	372.0 0 6.0 5.8	400.0 0 30.0 62.0	
nol Ca/Ca+	Mg .46 .25	.94 .25	.93	.50	•56 -	

TABLE IV (CONTINUED)

STUDY AREA A	AA T1NR3E s.1 stream	AB TISRIE s.36 stream	AC TISRIE s.36 below falls	t T2NT6E s.34 spring	t T1NR7E s.19 spring
Trace Elem					
	nents				
A1+3	nd	nd	nd	nd	.01
B 2+2	.23	nd	nd	nd	<u> </u>
Cr+2 Cu+2 Fe+2	nd	nd	nd	nd	,
Cu^{+2}	nd	nd	nd	nd	.01
Fe ⁺²	.20	.20	nd	nd	.03
Mn ^{T2}	.01	.06	.03	nd	nd
Sr ⁺²	nd	.15	.24	(4.7.4)()	
z_n+2	nd	nd	nd	nd	.50
mol Mn/Fe	.25	•25			

TABLE IV (CONTINUED)

STUDY AREA A	t TINR6E s.ll spring	t TISR4E s.27 spring	t TISR3E s.24 spring	t T1SR5E s.34 spring	t TlNR6E s.24 spring	
Temp ^O C pH	17 7.2	18 7.3	17 7.4	17 7.5	18 7.4	
Cations						
Ca ⁺² Mg ⁺² Na ⁺¹ K ⁺¹	75.0 38.0 2.0 1.0	80.0 27.0 4.4 1.3	73.0 36.0 8.8 1.5	72.0 39.0 2.5 .90	77.0 38.0 2.7 1.4	
Anions						
HCO CO3 SO4 C1	3 400.0 0 5.5 2.9	300.0 0 7.5 5.4	400.0 0 8.7 12.0	400.0 0 8.3 3.5	400.0 0 6.8 3.7	
mol Ca/Ca mol Sr/Ca		•55 -	.53	.64	•55	

TABLE IV (CONTINUED)

STUDY AREA A	t TlNR6E s.ll spring	t T1SR4E s.27 spring	t T1SR3E s.24 spring	t T1SR5E s.34 spring	t T1NR6E s.24 spring
Trace Ele	ments				
A1+3	nd	.03	.03	.03	.01
Ba ⁺²	=			=	-
Cr ⁺²	-	.01	nd	nd	nd
Cu^{+2}	nd	nd	.01	.01	.01
Fe ⁺²	.03	.02	.07	.05	.08
Mn^{+2}	.01	.01	nd	nd	.01
Sr ⁺²	# <u>[m.1]</u>	1 - 2			:
Ba+2 Cr+2 Cu+2 Fe+2 Mn+2 Sr+2 Zn+2	.03	.06	.20	.03	.80
mol Mn/Fe					1.0

^{** -} analyses reported in mg/l
 * - value calculated by difference
nd - none detectable
† - Fairchild, 1984

Study Area A, respectively.

Honey Creek

In this investigation Honey Creek and Turner Falls are considered to be representative of carbonate rich waters and associated freshwater carbonate deposits. Turner Falls is a unique situation in that it is a creation of Honey Creek and not the destruction (stream erosion) of more resistant rock layers. Honey Creek is a permanent stream of water supplied by numerous subsurface fault springs in the McKenzie Hill Limestone. The surrounding drainage area is primarily limestone terrain, with numerous intermittent springs and streams. Honey Creek flows in a northeasternly direction into the Washita River downstream.

The travertine deposit, Turner Falls, is situated on a cliff face of McKenzie Hill Limestone located in Murray County, TlS, RlE sec. 36. A fault trace parallels the valley of Honey Creek, downfaulting the Cool Creek Limestone on the northeast against the immediately underlying McKenzie Hill Limestone of the southwest. Flowing over the rapids and small waterfalls in the stream, it precipitates travertine throughout the length of the canyon until it plunges approximately 77 feet to the valley floor. Emig (1917) suggested that the valley was once filled with travertine and the falls had a maximum height of approximately 150 feet. His reconstruction of this event is shown in Figure 11. After the initial deposition during



Source: Emiq (1917)

Figure 11. Reconstruction of Turner Falls

the Pleistocene the travertine deposits were eroded, in some cases to a lower level than the original base. At Turner Falls this period of erosion produced a distinct gorge. Following this erosion period a second period of travertine deposition began, producing a second series of smaller waterfalls and rapids, which ended about 1850. Since this time a period of equilibrium has existed between erosion and deposition.

Emig (1917) identified three periods of travertine deposition at Turner Falls. The oldest period of formation is recorded in the large cliffs and caves above the level of Honey Creek above the falls. These deposits are approximately 60 feet thick immediately above the natural falls at the lower end of the gorge Extending upstream for a distance of 450 feet they gradually diminish to only a few feet in thickness. This travertine is cavernous and porous with a large amount of clays. A sample of travertine was taken from a cave located approximately 50 feet directly above the present falls, A2. Another travertine sample, taken from below the falls , consisted of travertine encrusting a branch, Al (see Figure 12). Calcium Carbonate precipitates on anything that falls into Honey Cree, an example of this is seen in Figure 13. Two water sample locations, AB and AC, were chosen to represent this area, see Figure 14. AB was taken above the falls near a small waterfall. the second was taken below the falls near the travertine sample site Al, also near small waterfalls.



Figure 12. Banded Travertine Deposit on a Branch, Honey Creek, Below Turner Falls



Figure 13. Calcium Carbonate Coating Leaves, Honey Creek



Figure 14. Honey Creek and Turner Falls

Fairchild (1982 and 1984) reported ground water, stream, and spring water chemistry throughout the Arbuckle Mountain area. His data was used throughout this investigation.

Falls Creek

Falls Creek and Price Falls are very similar to Honey Creek and Turner Falls. Emig (1917) identified many periods of deposition and erosion, including the formation of Table Mountain. Price Falls is divided into a Lower Falls and Upper Falls. The Upper Falls is approximately 19 feet high and is formed by a natural fall of Viola Limestone while the Lower Falls is a natural fall on the Chimneyhill Limestone, both fault controlled. Unlike Honey Creek, which is at equilibrium, Falls Creek is causing erosion of the travertine in this area. Falls Creek flows in a northeasternly direction into the Washita River and is fed by numerous fault controlled springs. The travertine sample taken from this area, A3, was a grab sample collected by Dr. Donovan. No water sample was obtained from this site.

Chickasha National Refuge

Chickasha National Refuge a very interesting site because of the complexity of the geology and the hydrology. Within the confines of this park there are numerous hydrogen sulfide flowing wells and springs as well as carbonate rich wells and springs. The geology has as yet to be fully understood. Travertine Creek begins at the eastern corner

of the park, fed by two springs, Buffalo and Antelope Springs, and flows westeardly meandering through the park. Travertine deposits begin approximately 0.25 miles from the springs. Several objects are shown in the visitor center coated with calcium carbonate, the visitor center is also constructed, in part, by travertine taken from the area. A water sample was taken approximately 100 feet from the dried up springs in Travertine Creek, AA. There appeared to be no carbonate precipitation occuring at this location. A travertine sample was taken 0.5 miles further downstream, approximately 8 feet above the present stream level, Al, (see Figure 15).

Study Area B

There are seven investigation sites located in the Slick Hills of Commache County, Study Area B. This area is geologically very complex with several major fault systems cutting across the region, specifically the Meers Fault, Blue Creek Canyon Fault Complex, and the Ketch Creek Fault, see Figure 16. The Stratigraphic section of the Slick Hills (Figure 17) shows that the Arbuckle Group is well represented. The fault systems are responsible for the discharge mechanism of the Arbuckle Group water, fault controlled springs and spring-fed streams, see Figures 18 and 19. Precipitation provides the only means for recharge into the Arbuckle Group. The water moves along the many exposed tilted bedding planes, fractures, and faults of the

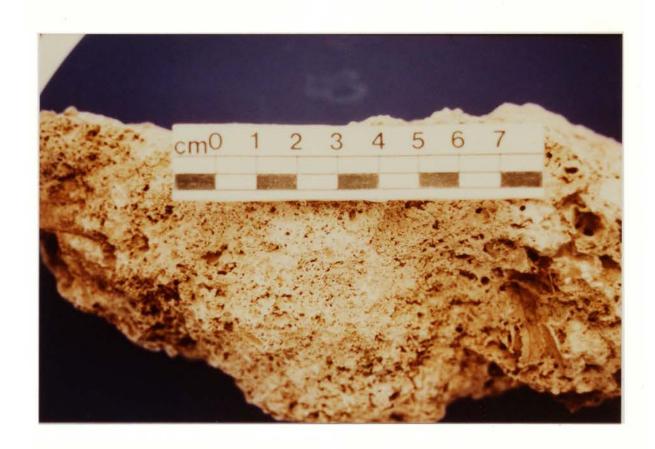


Figure 15. Pleistocene Age Travertine, Sample A

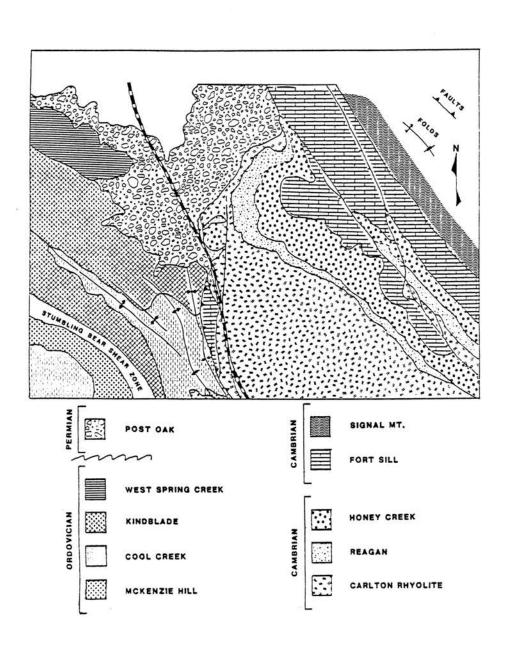


Figure 16. Geologic Map of Blue Creek Canyon, Study Area B

EKA	PERIOD	AGE	LITHOLGY	GENERAL STRAT. SLICK HILLS OF	IGRAPHIC LOG FOR TH SOUTHWESTERN OKLAHO	E MA	
			1 1	FORMATION	AVERAGE THICKNESS	GROUP	
Paleoz.	Permian	Wolf-		Wichita (Post Oak Member)	120 m (400 ft)	SHenne- Siser	
ue		Early Ordovician Canadian	Canadian		West Spring Creek	90 m (300 ft)	
	ian				Kindblade	425 m (1400 ft)	
eozoic	Early Ordovic			0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Cool Creek	425 m (1400 ft)	Upper Arbuckle
Early Paleozoic				McKenzie Hill	300 m (1000 ft)		
		1 =		Signal Mountain	150 m (500 ft)	Louer backle	
	ian		Croixian	20	Fort Sill	120 m (400 ft)	Lover
	Cambrian	! Š	弄	Honey Creek	90 m (300 ft)	Timbered	
i		ررا		Reagan Sandstone	45 m (150 ft)	==	

Figure 17. Stratigraphic Log of the Slick Hills, Study Area B

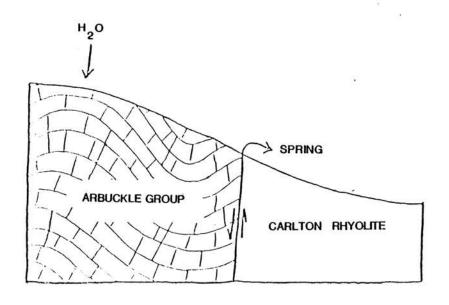


Figure 18. The Hydrologic Mechanisım for Ketch Creek Spring

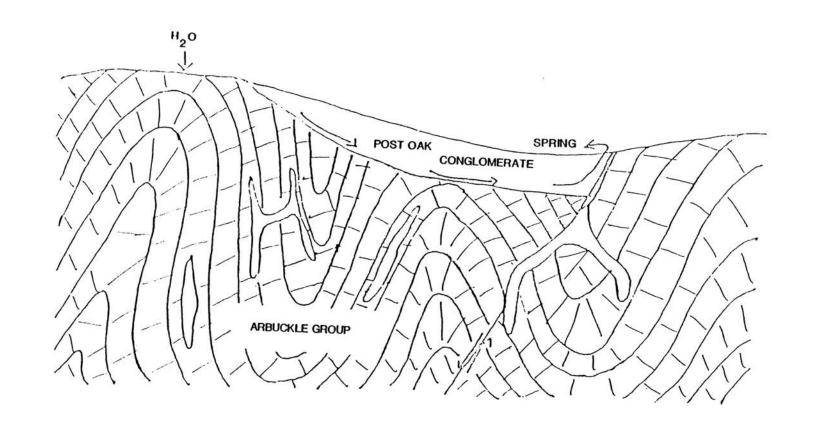


Figure 19. A Possible Hydrologic Mechanism for Jimmy Creek

predominately limestone, dolomite, and shale formation, ultimately reaching the regional water table. The geologic complexity of the area creates problems in water well drilling. Many times a dry hole is encountered at 600 or more feet. On the other hand, many wells and springs flow under artesian conditions. The springs found in this study area, as well as many of the small spring-fed streams, are ephermal, in that they flow only during, and for a short time after, a recharge event.

Tables 5 and 6 contain the chemical analyses of Study Area B rock and water samples, respectively. The sample site descriptions follow.

Ketch Creek Area

Ketch Creek spring also an example of a fault controlled spring, (Figure 18) is located at TIS, R14E, sec. 8. Several other springs along the same fault plane have been reported. The spring, in May, was reduced to a seep with all the other springs dry. The water sample, BE, unlike any of the other water samples, reacted immediately to the addition of 1:1 nitric acid, used as a preserving agent, indicating an abundance of carbonate. There were some green mosses still present along the damp spring path as well as a soft "chalky" deposit, precipitated on clumps of grass, see Figure 20. These deposits were found along the edge of what appeared to be the creek bed, and occured in scattered deposits approximately 10 feet downstream from

TABLE V

ROCK ANALYSIS FOR STUDY AREA B

		B2 T4NR12W s. 7 Recent stream		B4 T4NR13W s. 8 near waterfall	
Isoluble Residue	28.6%	3.0%	6.4%	25.8%	
$\begin{array}{c} \mathrm{SiO_2} \\ \mathrm{CaO} \\ \mathrm{K_2O} \\ \mathrm{MgO} \\ \mathrm{Na_2O} \end{array}$	30.2 0.04 0.30	42.2 5.2 0.47	48.5 1.2 0.60	36.5 1.2 0.92	- 4
mol Sr/Ca		0.80 0.04	0.98 0.17	0.97 1.35	
Trace Ele					
A1+3 Ba+2 Cr+2 Cu+2 Fe+2 Mn+2 Sr+2 Zn+2 Pb	nd 0.049 0.003 0.001 0.360 0.050 0.012 0.002	nd 0.016 0.003 0.001 0.078 0.004 0.003 0.001 0.020	nd 0.030 0.003 0.001 0.314 0.010 0.013	nd 0.017 0.002 0.001 0.324 0.030 0.077 0.002	

Table V (Continued)

Stud	ły	Bl	B2	В3	B4	
Area	T4 NF	R13W s. 2	T4NR12W s. 7	T4NR12W s. 8	T4NR13W s. 8	
В	Recer	t stream	Recent stream	Float sample	near waterfall	
	Thorium 1	_	nd	_		260
	Thorium ¹ Uranium ¹	-	nd nd	=		:40

Table V (Continued)

Study Area B	B5 T4NR13W s. 8 Recent travertine		B7 T4NR13W s. 8 Recent travertine	B8 T4NR13W s. 8 Pleistocene travertine	
Insoluble					
Residue	1.2%	3.8%	4.9%	4.3%	
SiO ₂	_	()	=	-	
CaO ²	44.2	49.2	45.9	45.0	
K ₂ O	6.9	1.0	0.83	2.3	
мĝО	0.43	0.43	0.46	0.54	
Na ₂ O	0.18	0.15	0.28	0.18	
mol Ca/Ca+	Mg 0.99	0.99	0.99	0.98	
mol Sr/Ca		0.52	0.72	0.61	
Trace Elem					
$A1^{+3}$	nd	nd	nd	nd	
Ra ⁺²	0.041	0.031	0.004	0.041	
Cr+2 Cu+2 Fe+2 Mn+2	0.003	0.003	0.003	0.003	
Cu ⁺²	0.001	0.001	0.001	0.001	
Fe ⁺²	0.111	0.142	0.196	0.137	
$Mn_{\perp 2}^{\perp 2}$	0.015	0.018	0.016	0.014	
Sr ⁺²	0.052	0.040	0.052	0.043	
Z_n^{+2}	0.001	0.005	0.002	0.001	
Pb 1	<u>-</u>	S	-	0.059	

Table V (Continued)

Study		B5	В6	В7	В8	
Area	T4NR	13W s. 8	T4NR13W s. 8	T4NR13W s. 8	T4NR13W s. 8	
В	Recent		Recent travertine	Recent travertine	Pleistocene travertine	
	travertine					
Thor	ium 1		-			
	nium ¹	-		500 500	-	
nol Mn/F	°e		0.14	0.13	0.08	0.10

^{1 =} x-ray flourescent semi-qualitative pph
values are an average of duplicates

% by weight

nd = none detectable

TABLE VI

WATER ANALYSIS FOR STUDY AREA B **

Study Area Area	BA T4NR13W s. 2 stream	BB T4NR12W s. 7 stream	BC T4NR13W s. 8 pond	BD T4NR13W s. 8 well	
Temp ^O C pH	8.0	18 7.8	18 6.9	15 7 .4	
Cations					
Ca ⁺² Mg+2 Na+1 K ⁺ 1	85.0 6.0 5.1 1.0	91.0 7.0 5.1 1.3	87.0 8.0 1.4 0.51	47.0 4.0 8.5 2.0	
Anions					
нсо-3 со-3 so-4 с14	1 284.0 0 25.22 14.61	264.0 0 25.62 18.70	232.0 0 17.38 32.86	160.0 0 21.82 7.30	
mol Ca/Ca-mol Sr/Ca		0.89	0.87	0.88	

TABLE VI (CONTINUED)

Study	BA	BB	BC	BD	
Area	T4NR13W s. 2	T4NR12W s. 7	T4NR13W s. 8	T4NR13W s. 8	
Area	stream	stream	pond 	well	
Trace Ele	ements				
A1+3 Ba+2 Cr+2 Cu+2 Fe+2 Mn+2 Sr+2 Zn+2	nd	nd	nd	nd	
Ba ⁺²	nd	0.98	nd	nd	
Cr ⁺²	nd	nd	nd	nd	
Cu^{+2}	nd	nd	nd	nd	
Fe ⁺²	nd	nd	nd	nd	
Mn^{+2}	0.06	0.01	0.06	0.01	
Sr ⁺²	nd	nd	nd	nd	
Z n ⁺²	nd	nd	nd	nd	
mol Mn/Fe	-	_			

TABLE VI (CONTINUED)

Study Area B	BE TO4NT12W s. spring	BF 7 TO4NR12W s. 7 stream	BG TO4NR13W s. 8 stream	BH TO4NR13W s. stream	8
Temp OC	27 7.1	19 7.6	23 8.2	24 7.6	
Cations					
Ca ⁺ Mg ⁺ Na ⁺ K ⁺ 1	2 59.0 2 9.0 1 3.3 2.5	60.0 1.7 0.92 1.0	75.0 12.0 1.2 0.63	67.0 5.1 1.8 0.61	
Anions					
HCO CO3 SO4 C1	$ \frac{1}{2} $ * 250.0 0 2 18.82 7.30	* 146.0 0 3.26 33.67	* 259.0 0 28.19 4.78	* 166.0 0 15.10 28.68	Si di
mol Ca/C mol Sr/C		0.00	0.00 0.04	0.00	

TABLE VI (CONTINUED)

Study Area	B5 T4NR13W s. 8	B6 T4NR13W s. 8	B7 T4NR13W s. 8	B8 T4NRl3W s. 8	
В	Recent travertine	Recent travertine	Recent travertine	Pleistocene travertine	
Trace El	ements				
Al ⁺ Ba ⁺ Cr ⁺ Cu ⁺ Fe ⁺ Mn ⁺ Sr ⁺	3 nd	nd	nd	nd	
Ba [†]	2 nd	nd	nd	nd	
Cr ⁺	0.41	nd	nd	nd	
Cu [†]	0.13	nd	nd	nd	
Fe [†]	2.60	0.64	nd	nd	
Mn ⁺	0.63	0.51	nd	nd	
Sr [†]	2 1.27	nd	0.73	nd	
Z n ⁺	2 0.06	nd	nd	nd	
mol Mn/F	e 0.22	0.96			

^{** -} analyses reported in mg/l
 * - value calculated by difference
nd - none detectable

t - Fairchild, 1984



Figure 20. Ketch Creek Calcium Carbonate Spring Deposit, Sample B

the spring head. This deposit was labeled B2 and contained an unusual amount of trace elements, similar to the associated water sample BE.

Another water sample was obtained from a small stream located 25 miles away. This stream appeared to be springfed because of the amount of flow and no appearence of ever being dry, BF. There was no evidence of carbonate deposits at this site.

Blue Creek Area

The Blue Creek Canyon Fault system is most likely responsible for controlling the springs of this area. Water samples were taken along Hwy. 58, T4N, R13W, sec. 2. A pond on the west side of the road was formed by the intersection of several faults. This pond is reported to be spring fed but at the sampling times no springs were noticed, and the level of the water appeared to stay constant throughout the year, BC. On the opposite side of the road an ephemeral stream flows across Carlton Rhyolite. Two water samples were taken one week apart, BA and BB. It appeared that there was a decrease in stream flow between the time BA was taken and BB water was sampled. Evaporation appeared to be the mechanisim responsible for a white, soluble deposit on the rhyolite at the water's edge. This deposit never had any degree of build-up, nor were there any carbonate deposits found along the stream site. A shallow alluvial domestic well, approximately 30 feet in depth was sampled and



Figure 21. Water Sample BC, Taken at Jimmy Creek near Meer's Fault



Figure 22. Small Travertine Waterfall Along Jimmy Creek

falls, and contained a leaf impression similar to the leaves found along the stream edge, (Figure 23).



Figure 23. Leaf Impression in Pleistocene Age Travertine, Sample B

CHAPTER V

TEXTURAL DESCRIPTIONS

Travertine textures are varied as the environments in which they can be found. Porous, massive, plant impressions, crystalline, and banded are only a few of the descriptive terms that may be applied to them. Colors are generally white to light brown, with crystalline travertines having a wider variety of colors.

The travertines in this investigation are predominately of two textural types in hand sample; banded and porous. These travertines of Pleistocene through present age do not have any crystalline textures as do some Permian travertines seen elsewhere in Oklahoma. The textural descriptions given below are based on hand sample descriptions, thin section analysis, and scanning electron microscope interpretations of selective travertine samples. Both Study Area A and Study Area B were described using thes three methods.

Study Area A

Banded and porous travertines of Pleistocene and Recent age are found in Study Area A. The Recent travertines of Falls Creek and Honey Creek have banded textures. A Pleistocene age cave deposit from Turner Falls and a

Pleistocene age travertine from Travertine Creek have a porous texture.

The banded travertine, from Turner Falls, sample Al, taken from an encrusted travertine stick showed alternate bands of calcium carbonate varying in texture and color. White, dense, striated bands, with what appeared to be growth layers of 0.5 to 4 mm. in thickness alternated with a light brown layer. This light brown layer contained various fragments of plant pieces with a very dense, porous texture. A thin section was not made of this sample because of its friability. A scanning electron microscope examination of these bands showed completly different textures. The light brown bands, at a magnification of 206x, appear as algal tubules, similar to those described by Scholle (1984), (Figure 24). The dense white bands appear as fields of rosettes at 206x magnification, (Figure 25a). At 845x these rosettes appear dense and admixed with small crystals of calcite, (Figure 25b).

The other banded travertine sample, A5, located at Price Falls, had a similar texture in hand sample although the banding was not as prominent as in sample A4. A thin section of sample A5 showed fibrous calcite with several growth bands, (Figures 26 and 27).

Sample A3, a travertine cave deposit obtained from the Turner Falls area, has a reddish-brown color and a porous texture. X-ray analysis of the sample showed it to be a low-magnesium calcite. Electron microscope analysis showed

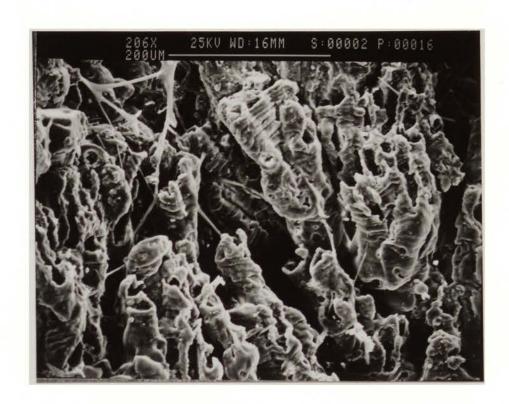


Figure 24. SEM Photograph of a Recent Banded Travertine From Turner Falls, light brown band, algal tubules. Magnification 206x

286X 25KU WD:16MM \$:88802 P:88804

a.

b



Figure 25. SEM Photographs of a Recent
Banded Travertine From Turner
Falls, White Band,
a) Magnification 206x

a) Magnification 206xb) Magnification 845x

a.





Photomicrograph of a Recent banded Travertine From Price Falls. Magnification 40x. a) Plane Polarized light b) Crossed Polars Figure 27.

that the sample containes an amorphous algal material with a few microscopic crystals, (Figure 28). At a higher magnification (4000x) needle like shapes were seen. Based on the literature example Allanson (1973), identification of these needles indicates they are the diatom, Synedra sp..

Sample A4, also a Pleistocene age travertine, was obtained from Chickasha National Refuge and is a very porous, dark beige, travertine with numerous plant impressions. X-ray diffraction analyses of the sample showed it to be a low-magnesium calcite. A thin section of this sample showed calcified plant parts, (Figure 29). There were very small calcite crystals forming along the inside edges of the pore spaces, (Figure 30). The electron microscopic analysis (magnification 1040x) showed algal material and the needle like shapes seen in sample A3, possibly Synedra sp., (Allanson, 1973), (Figure 31).

Study Area B

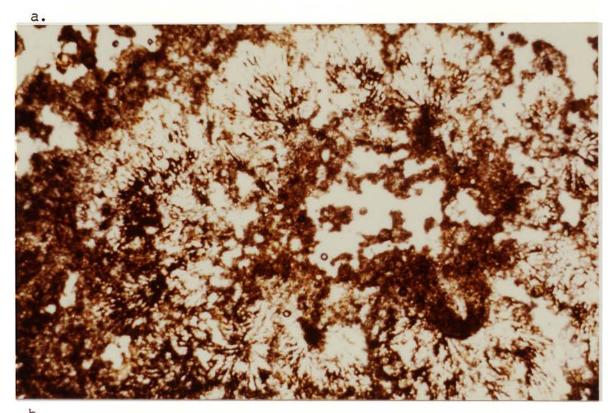
Travertines found in Study Area B are porous in texture, with on exception; the Ketch Creek spring deposit, which has a spongy amorphous texture deposited on grass.

A Pleistocene age travertine sample from Jimmy Creek, sample B7, was porous, light brown travertine and contained numerous plant impressions and a variety of pore sizes and shapes. There appeared to be a white, dense layer around some non-carbonate pebbles, and some pores had a smooth, darker brown surface. X-ray analysis of the sample showed a





SEM photographs of a Pleistocene cave deposit From Turner Falls a) Magnification 1740x and b) Magnification 4000x Figure 28.



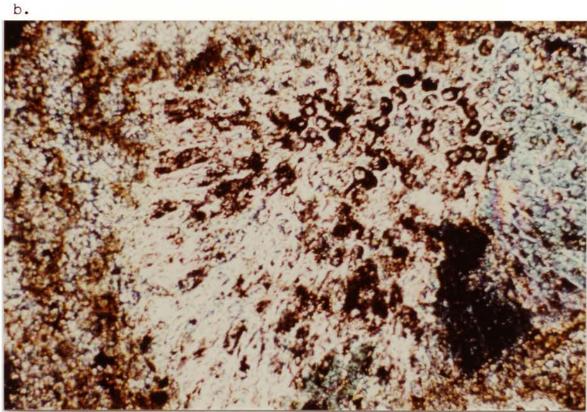


Figure 29. Photomicrograph of a Pleistocene Travertine From Chickasha National Refuge. Crossed Polars a) Magnification 40x b) Magnification 200x

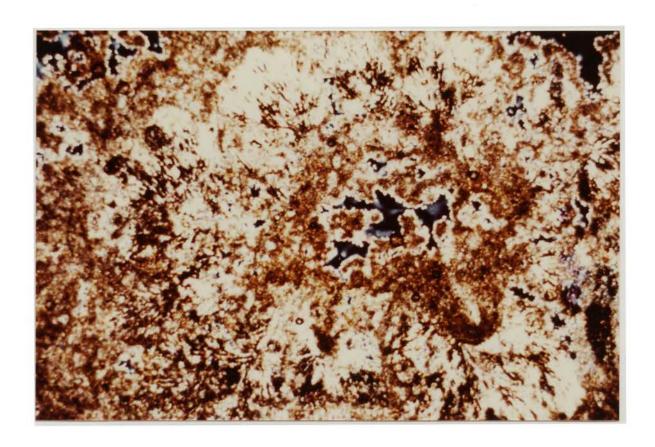


Figure 30. Photomicrograph of a Pleistocene Travertine From Chickasha National Refuge Showing Calcite Crystals Fringing the Pore Spaces.

Crossed Polars. Magnification 40x



Figure 31. SEM Photomicrograph of a Pleistocene Travertine From Chickasha National Refuge.

Magnification 40x

low-magnesium calcite. Electron microscopic interpretations showed algal material with very few crystals present, (Figure 32). The Recent travertine samples from Jimmy Creek were all similar in hand sample. Mosses made up the surface layer, which was a light brown cellular textured layer. Indistinct banding could be seen in the samples B2, B4, and B5. Thin section analysis showed calcified plant pieces at 40x magnification, with lime mud coating the edges, (Figure 33). Small calcite crystals were also found growing along the lime mud edge into the pore spaces in this sample. Electron microscopic examination at a magnification of 1090x showed boat shaped diatoms, perhaps Novicula sp., (Figure The Ketch Creek spring deposit was unique in both texture and location. Found on small clumps of grass a short distance from the spring head, this deposit was a moist, off-white, amorphous calcium carbonate precipitate. X-ray examination of this sample showed it to be a lowmagnesium calcite. Microscopically at a magnification of 1790x, diatoms, algal material, and very small crystals of less than 10 um are seen, (Figures 35 and 36). These boat shaped diatoms are perhaps Novicula sp.



Figure 32. SEM Photograph of a Pleistocene Travertine From Jimmy Creek Magnification 1090x

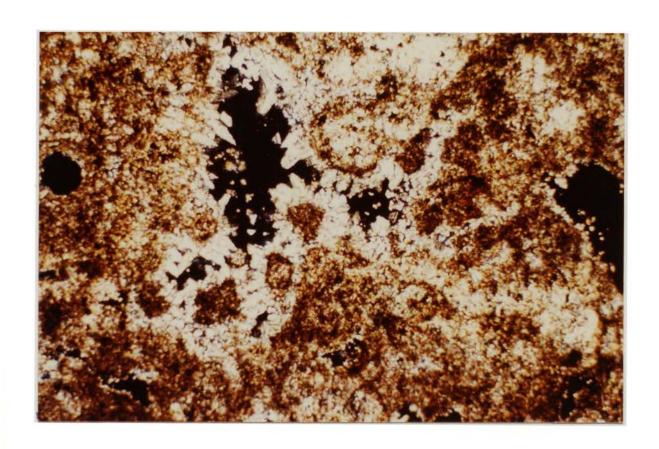


Figure 33. Photomicrograph of a Recent Travertine From Jimmy Creek Showing Calcite Crystals Fringing the Pore Spaces Crossed Polars. Magnification 40x



Figure 34. SEM Photograph of a Recent Travertine From Jimmy Creek Showing Novicula sp. Diatoms Magnification 1090x



Figure 35. SEM photograph of a Spring
Deposit From Ketch Creek
Spring
Magnification 1760x



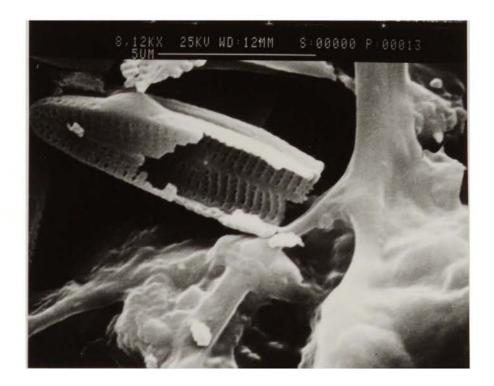


Figure 36. SEM Photographs of a Spring
Deposit From Ketch Creek
Spring Showing Novicula
sp. Diatoms

- a) Magnification 1790x
- b) Magnification 8120x

a.

b.

CHAPTER VI

ROCK-WATER RELATIONSHIPS

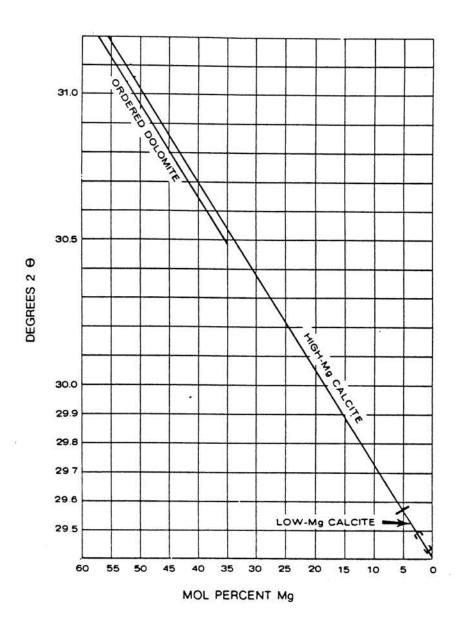
The three groups of samples being considered are 1) freshwater deposits (travertines and tufas), 2) carbonaterich springs, streams, and ground water, and 3) freshwater carbonates which have natural waters still associated with A Ca/Mg or Mg/Ca ratio was used in water and rock interpretations as a determination of the degree of limestone of dolomite present. Two other ratios associated primarily with marine rock geochemistry are a Sr/Ca (Graf, 1960, and others) and Mn/Fe (Trent, 1978). Friedman (1969) reported the use of trace elements (barium, manganese and iron) as indicators of environments. There was little published material found by this author that describes the possible relationships between freshwater carbonates and the associated natural waters, such as carbonate-rich springs. In the present study, Ca/Ca+Mg has been used, as well as, (when data are available) Sr/Ca and Mn/Fe for both water and rocks. Electron Microscopy was also used to determine relationships between travertine deposits and associated waters. In this study, however, electron microscope examination was conducted only on the travertine samples and not the waters, producing very interesting results.

Carbonate Rocks

Published data describing the elemental content and geochemical relationships of carbonate rocks is abundant, however little deals specifically with freshwater carbonates. The geochemistry of fresh water differs considerably from that of sea water, therefore the geochemistry of fresh water carbonates is different in many aspects from carbonate rocks of marine origin.

The data analyzed in this investigation is reported as percent by weight whole rock (having used 10% HCl acid for digestion), Tables 3 and 5.

The mineralogical composition of five travertines was determined by x-ray diffraction. The magnesium within the calcite lattice was found by measuring the (112) peak of calcite using quartz as an internal standard. All samples showed a low-magnesium calcite according to Schollo's classification (Figure 37). Trent (1978) using the same classification showing that three travertine samples from Colorado were high-magnesium calcite/argonite. The trace element contents of the seven powdered travertine samples was accomplished by semi-quantitative analysis using x-ray fluorescent spectrography (done by FLUO-X-SPEC analytical laboratory); see Appendix C for the analyses. Three analyses showed varying amounts of columbium, rubidium, yttrium, and zirconium. One sample, A2, contained 100 ppm



Source: Scholle, 1984

Figure 37. Plot of Degrees 20

Versus Mol % Mg.

Graph Based on (112)

Peak Shift in

Carbonate Rocks.

Data Obtained From

This Study Plot

Along a Line Between

Parantheses.

of titanium, 220 ppm thorium, and 95 ppm uranium.

The electron microscopic examination provided further differentiation between travertine deposits by showing different microscopic textures. Algal material, diatoms, and rosettes of unknown origin were found in the travertines sampled.

Calcium Content

The small insoluble residue and large calcium content of most of the travertines investigated indicated a relatively pur e form of calcium carbonate (found to be calcite by x-ray differaction) for the freshwater limestones associated with the Arbuckle Group waters. Trent (1978) also found high calcium content and low insoluble residues for the various freshwater travertine samples in Colorado. He did not look at the chemistry of any of the associated waters.

Magnesium Content

The magnesium content is proportionally lower than calcium. All the travertines sampled except A4 showed an average of 2966 ppm of magnesium. Using Scholle's classification and corrected 20 values from x-ray analysis the freshwater travertines sampled are low-magnesium calcite, as are Armstrong's (unpubl. thesis) travertines. Irion and Muller (1968) reported low magnesium contents in German travertines. However, Klahn (1928) reported an occurrence

of dolomitic tufas associated with magnesium rich waters in Germany.

Iron Content

The iron content of freshwater carbonates is extremely variable within the study areas. Irion and Muller (1968) reported iron contents from 46 to 3900 ppm in German travertines. Trent (1978) reported iron contents as high as 10% by weight in Colorado deposits. This investigation resulted in iron contents ranging from none detectable to 2.6 ppm in waters and from 200 to 4787 ppm in the travertines.

Manganese Content

Manganese content in freshwater carbonates is als extremely variable. However the content of manganese in this study of freshwater carbonates is swell below the average for sedimentary carbonate rocks, (Graf, 1960).

Strontium and Barium Content

The average Sr/Ca ratio of limestone is 0.71, derivied primarily from marine limestones in waters of high strontium, sea water, (Armstrong, unpubl. thesis).

Literature does report a definite decrease in strontium content with increasing age, (Graf, 1960). Strontium content does seem to decrease with a decrease in Ca/Ca+Mg content as shown in Figure 38. The use of strontium to

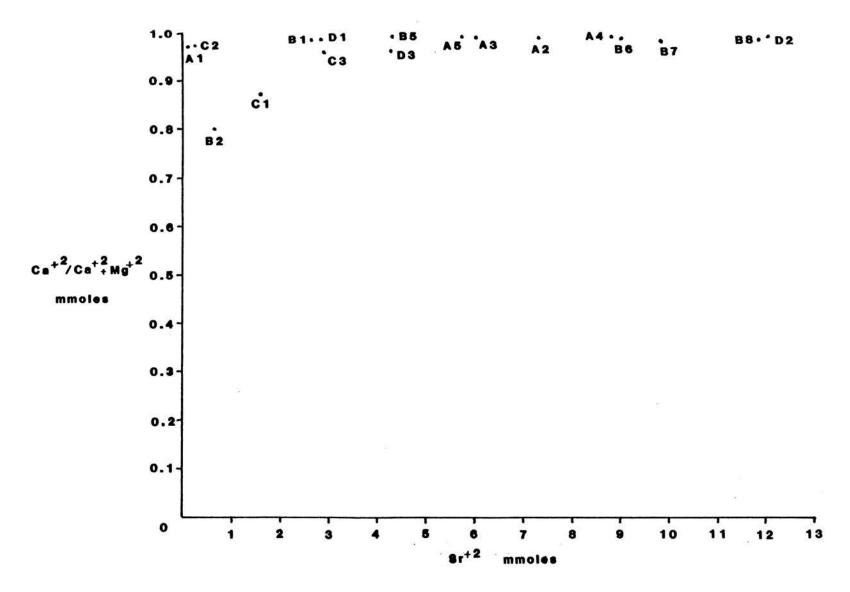


Figure 38. Graph of $Ca^{+2}/Ca^{+2}+Mg^{+2}$ vs. Sr^{+2} Using Samples In This Study

distinguish between recent and Pleistocene deposits was not possible because of the lack of significant variability. The strontium range found in this investigation was 1 ppm to 77 ppm with barium ranging between 2ppm and 69 ppm.

Water

The Arbuckle aquifer is a limestone-dolomite aquifer, recharged primarily by precipitation. In the Arbuckle Mountain area approximately 78% of annual precipitation is lost through evapotranspiration. The Slick Hills in Commache County lose even more precipitation to evapotranspiration, approximately 93%.

The magnesium content of the water from the Arbuckle Group varies depending on bedrock. Nearly all of the Arbuckle Group formations are limestone in the western half of the Arbuckle Mountains (Study Area A) grading into dolomites, sandstone, and shales to the east. The chemistry of the water directly reflects this transition. Magnesiumpoor water is seen in the Piper diagram of Murray County, limestone dominat, Figure 39, and magnesium-rich waters in the Piper diagrams of Pontotoc and Johnson Counties, predominantly dolomite, Figures 40 and 41, (Hart, 1974). Fairchild (1984) analyzed the springs located in the eastern part of the Arbuckle Mountains, Figure 42. The majority of the springs he sampled contained a higher content of magnesium than the springs sampled in this investigation, because of hte primary dolomitic lithology. Study Area B

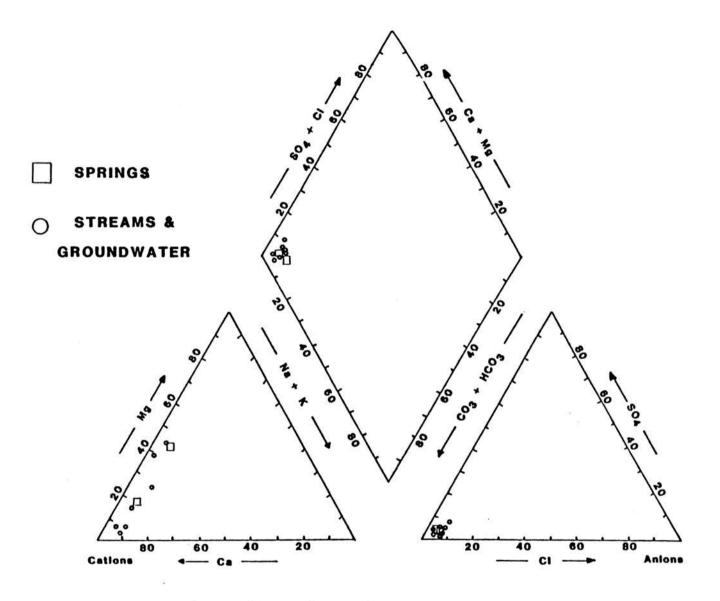


Figure 39. Piper Diagram of Murray County

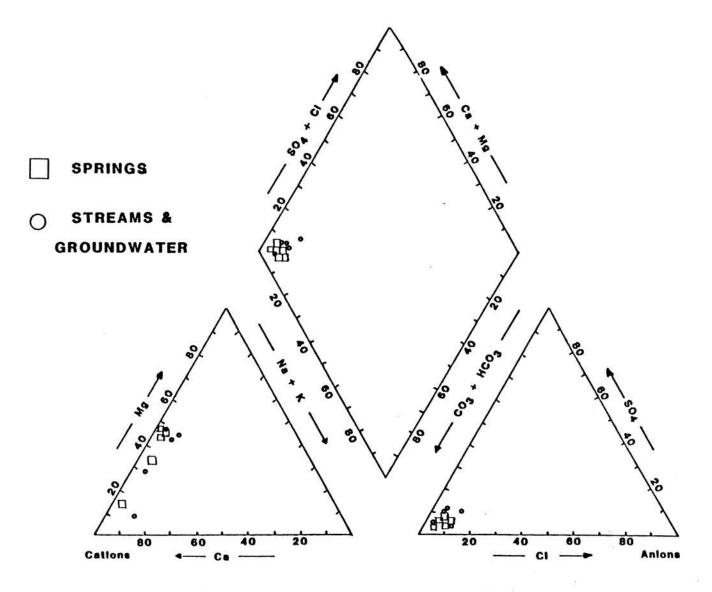
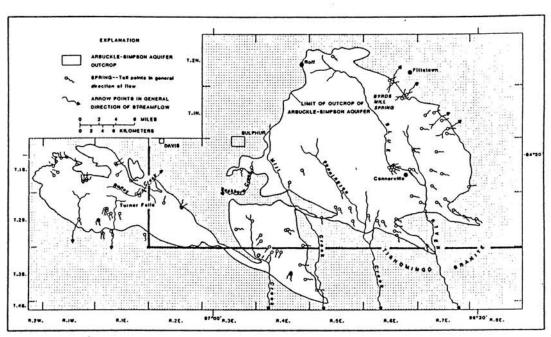


Figure 41. Piper Diagram of Johnson County



LMST.RICH DOLO.RICH

Source: Fairchild, 1984

Figure 42. Location of Limestone Rich and Dolomite Rich Springs in the Arbuckle Mountain Area

showed similar low magnesium waters typical of the limestone rich western half of Study Area A.

Chickasha National Refuge, in Study Area A, is a complex problem. Fairchild (1983) reported various wells being shut down due to an oily residue of various amounts appearing on the surface of the water. The water sample, A, analyzed from Travertine Creek in Chickasha County showed an above normal amount of sulfate and chloride present. Except for this area around Sulfur, Ok., which lies in the north part of the Arbuckles, the sodium, potassium, chloride, and sulfate content of the ground water are low and exhibit little variation. It may be assumed therefore that these anomalous values could be the result of deeper subsurface brines mixing with the Arbuckle aquifer water. Ther does not hawever seem to be a corresponding increase in sodium and chloride as one would expect.

The bicarbonate ion concentrations from the waters in this investigation, though relatively high are typical for limestone aquifers of various ages, see Table 7. The concentration found in this study does not seem to be unusually high. Several travertine producing waters reported by White and others (1969) had a much higher bicarbonate ion concentration.

Trace elements analyzed in the Arbuckle Group waters were: Al, Ba, Cr, Cu, Fe, Mn, Sr, and Zn, see Tables 4 and 5. Most of these trace elements were not detectable except for manganese and iron which had maximum concentrations of

TABLE VII

Bicarbonate Ion Levels in Selected Waters

Locality	This invest- igation	нсо ₃ -2 meq/1	TDS	Ca Ca+Mg	Aquifer Type	Age	Prod. Trav. Y/N
Iceland, warmspring (White, 1963)		24.91	_	0.89	basalt- rhyolite	Quat.	+
KeeneWonder, CA spring (White, 1963)		19.8	3630	0.56	_	Paleo.	+
Lebanon Lmst., TN well (White, 1963)	58.1	7.5	720	0.73	Lmst.	Ord.	?
Austrian Spring (Clarke, 1924)		6.6	_	0.67	?	?	+
Arbuckle Group Ground Water (Avg.) (Fairchild, 1982)	*	6.0	=	0.65	Lmst.	Ord.	+
AL well (310 ft. deep) (White, 1963)		4.8	722	0.62	Lmst.	Camb.	?

TABLE VII (continued)

Locality	This invest- igation	нсо ₃ -2 meq/1	TDS	Ca Ca+Mg	Aquifer Type	Age	Prod. Trav. Y/N
Study Area B Hwy. 58, stream	*	4.6	-	0.89	Lmst.	Ord.	+
Jimmy Creek upstream Study Area B	*	4.2	-	0.89	Lmst.	Ord.	+
Texas, well (White, 1963)		4.5	450	0.82	Lmst.	Cret.	?
New Mexico, well (White, 1963)		3.9	823	0.67	Lmst.	Per.	?
Travertine Creek Study Area A	*	3.8	-	0.46	?Lmst.	?Ord.	_
Florida, well (White, 1963		3.2	297	0.61	Lmst.	Eoc.	?
Jimmy Creek downstream Study Area B	*	2.7	-	0.79	Lmst.	Ord.	_
Honey Creek Study Area A	*	2.7	2 2	0.94	Lmst.	Ord.	+
Alaska, spring		2.6	230	0.59	Dolo.	Camb.	?

6300 ppm and 2600 ppm respectively. The water sample, BE, from Ketch Creek spring contained more of a variety of trace elements than any of the other water samples. The variety could indicate a deeper water mixing or a lithologic change in the subsurface.

Rock and Associated Waters

The chemical process for dissolving calcium carbonate, CaCo3, within the bedrock requires the addition of CO2 to the ground water, thus moving the equilibrium equation to the left dissolving $CaCO_3$. Addition of CO_2 could be the result of O2 brought into the subsurface through rain combining with the organic matter present in the carbonate rock. As the water moves deeper into the bedrock, there is a decrease in the amount of O_2 , with a corresponding increase in CO2, producing an increase in HCO3, Ca+2, and Mg^{+2} in the water, Figure 43. When this water is discharged at the surface it will precipitate calcium carbonate only if it is supersaturated with respect ot CaCO3, and other conditions are appropriate. The precipitation of calcium carbonate is primarily the result of CO2 removal from the There are three major ways, by which, CO2 is removed from water; 1) a change in chemical parameters, pH, ionic strength, pressure, 2) a change in physical conditions of hte water such as pressure, aeration, and evaporation and 3) biological systems. There is frequently disagreement in the literature as to the method of CO2 removal. Many

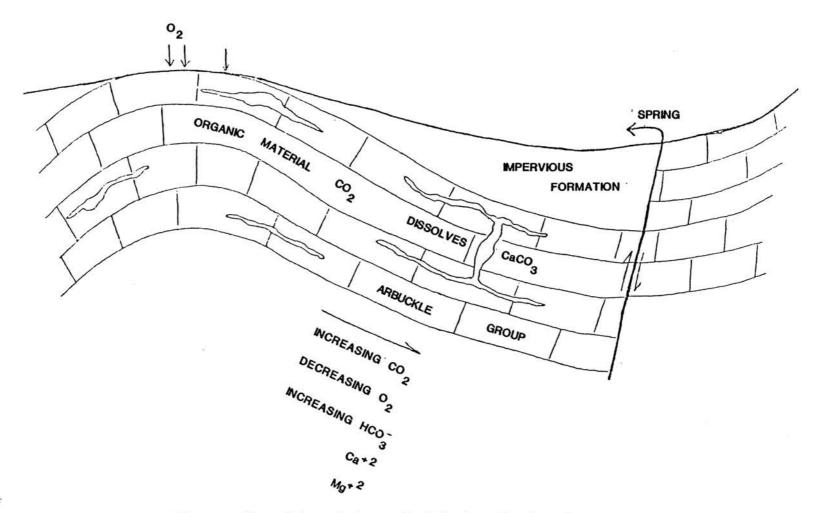


Figure 43. Dissolving of Calcium Carbonate

freshwater carbonate deposits are the combination of several methods of ${\rm CO}_2$ removal, combined together, or acting seperately, for example the result of environmental changes (such as seasonal changes).

The terminology of freshwater carbonates frequently reflects this classification, for example, tufa used to decribe CaCO₃ associated with plant life, travertines are dense, sometimes banded CaCO₃ deposits associated with physio-chemical CO₂ removal, and a very slow physio-chemical removal of CO₂ produces speleothem deposits.

Physical methods of CO2 removal are: changes in air temperature, aeration or removal of CO2. Evaporation of the surface water can also occur but this method does not lead to major calcium carbonate deposits, but is responsible for the deposits along the stream edge during hot weather. These deposits are removed with the increase in stream flow, Ketch Creek spring deposit, sample BE, and deposits found along the stream at Highway 58, smaple BD, are examples of this method of ${\rm CO}_2$ removal. The cooling of geothermal waters, specifically around Yellowstone National Park, is another way of removing CO₂ from the water. Trent (1978) suggested several of the travertines he sampled were of this type. Aeration is probably the most familiar method of removing CO2 from water. Emig (1917) tested several objects under Turner Falls for calcium carbonate build-upd. All of the objects were coated to some degree with calcium carbonate after three weeks. Jimmy Creek and Turner Falls

are the products, in part, of CO_2 removal by aeration. Jacobson and Usdowski (1975) found travertine deposits caused by water running over uneven stream beds.

Chemical removal of CO₂ is basically the removal of CO₂ through changes in pH, ionic strength, and pressure. Mixing of dissimilar waters either in the subsurface, an example is the stream studied by Barnes and O'Neil (1971) in the Coast Range, or changes at the surface with springs mixing with alkaline lakes. Mono Lake and Pyramid Lake are examples of springs mixing with lake water to form large deposits of calcium carbonate. Another example is the degassing of supersaturated CO₂ waters upon reaching the surface and mixing with stream waters at atmospheric pressure. Savelli and Wedepohl (1969) and Shuster and White (1971) investigated the CO₂ change from ground water to surface water and the resultant precipitation of calcium carbonate.

Biochemical removal of CO_2 is the result of plant life found in, and around, natural waters. Photosynthesis as a biochemical method has been investigated by Jones (1914), Emig (1917), and Wilson (1963). It is the algae that, even in microenvironments, chemically change the equilibrium of the surrounding water by absorbing HCO_3 for photosynthesis. Mosses and bacteria are unable to use HCO_3 for photosynthesis and thus it is the symbiotic relationship between mosses and algae, plus the filamentous structure of the mosses, that give the appearence that the mosses were instrumental in the precipitation of calcium carbonate.

Most water plants use the ${\rm CO}_2$ dissolved in the water for photosynthesis, however if the carbon is present mostly as bicarbonate only some varieties of plants can utilize it, primarily the algae.

Irion and Muller (1968) make the statement that, biogenetic-inorganic formation of CaCO3 is only of a slight importance and may be neglected as compared against the purely inorganic precipitation. This may not hold true if we consider that the microenvironments created by algae can drastically change the water chemistry in their immediate vicinity.

CHAPTER VII

RESULTS AND CONCLUSIONS

The following principal conclusions may be drawn from this investigation:

- 1) The waters sampled in this investigation are a calcium bicarbonate water with varying amounts of magnesium. Changes in bedrock cause a distinct change in water chemistry. As the limestone formations of the Arbuckle Mountain grade into dolomite to the east the water becomes more magnesium rich.
- 2) An increase in SO₄ and Cl is noticed to the north, in Study Area A, especially around Sulfur, Oklahoma. This increase of sulfate and chloride could be associated with deep brine water mixing however there was not an associated increase in sodium or potassium.
- 3) Generally, the chemistry of the water was influenced by a) whether the bedrock was limestone or dolomite dominant, b) length of residence, the longer time the greater the degree of saturation, c) flow path; fault controlled waters can introduce deep subsurface brines and

water mixing from outside the regional water table.

- 4) The chemistry of the recent carbonate deposits were influenced by the depositing waters, as demonstrated by trace element comparisons. Unfortunately published studies seldom contain analyses of carbonate deposits and associated waters which thus limits direct comparisons with those of this investigation.
- 5) Freshwater carbonate deposits can be classified according to the method of CO₂ removal from the precipitating waters. Physical removal is the release of CO₂ from the water by evaporation, cooling, or turbulence. Chemical precipitation of CaCO₃ can result from a change in ionic strength and pH by the mixing of dissimilar waters or the change in pressure from saturated waters reaching the surface. Removal of CO₂ by biochemical means is accomplished by the absorption of CO₂ during photosynthesis or in the case of some algae the removal of bicarbonate ions during photosynthesis or the vegetal activity of calcareous algae.
- 6) The textural description in hand sample of the travertine samples ranged from porous to banded. Porous texture was evident in both Recent and Pleistocene age travertines. Banded texture was only seen in Recent travertines.

- 7) The electron microscopic textures of the travertines varied considerably. Algal material was identified in many of the travertines, independent of age and hand sample texture. A banded travertine from Turner Falls showed bands of algal tubules with alternating bands of rosettes, origin unknown. Diatoms, possibly Novicula sp., were present in travertines of Recent and Pleistocene age. Needle-like diatoms, possibly Synedra sp., were found in travertine samples from Jimmy Creek and Turner Falls, both of Pleistocene age.
- 8) The microenvironment revealed by the scanning electron microscope is a delicate and complex system that suggests many further facets of research that could help solve some of the questions concerning freshwater travertine deposits.
- 9) Chemical parameters such as temperature, pH, and alkalinity need to be field calculated due to the changes caused by time and temperature.
- 10) Due to the lack of significant samples no relationship could be established to distinguish between Pleistocene age travertines and Recent deposits.
 - 11) More emphasis on lab techniques and quality

control could reduce the substantial error in reported geochemical data.

12) A definite need for standards (in nomenclature, analysis procedures, and reporting of data) was seen throughout this investigation.

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APPENDIX A

COMPUTER LITERATURE SEARCHES

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File89:GEOREF - 29-84-May
(Copr. American Geological Institute).
          Set . Items . Description
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   39- . .
           1982
   180 REFS.
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   DOC .TYPES .REPURTS MAP
                             Bibliographic Level: MONDGRAPHIC
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 United States
   Note: National Uranium Resource Evaluation Programs; includes microfiches
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7/3/2
  895668
          78-28878
  Petroleum, source-rack patential, of, Arbuckle, and Ellenburger groups.
southern mid-continent; United States
  Candwells, A. L.
  Union Dil Co: Calif.; Midland, Tex:, USA
  Colo: Sch. Mines: Q. 72: 3: 134m.: 1977.
  CODEN: QCSMAC . 78 REFS ..
  Subfile: B
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7/3/3
  811476
         76-377.22
  Chemical
            and, isotopic, investigation of stratignaphic, and tectonic
dolomites in Arbuckle Group, Arbuckle Mountains, South-central Oklahoma
  Sargent, K. A.
  Furman Univ., Der. Geol., Greenville, S.C., USA
  Am. Assoc. Pet. Geol., Bull. 60: 4: AAPS-SERM annual meeting,
                                                                     719e. .
1976
  CODEM: AARGES
  Subfile: B
  DOC . Type: SERIAL
                     Bibliographic Level: ANALYTIC
  Languages: English
7 TYPE 9/3/1-2 .
9/3/1
  97.0320 80-09983
  Petrology and seochemistry of the Carlton Rhyalite; southern Oklahoma
  Hanson, R. E.
  Oklahoma State Univ., Stillwater, Okla., USA
   161e. 1977.
   Subfile: B
   Degree Level: Master's
  Country of Public United States
  Doc Type: THESIS Bibliographic Level: MONDGRAPHIC
  Languages: English
 3/3/2
   865628
          77-47795
   Geochemistry of Wichita Mountain igneous nocks as related to copper and
 unanium mineralizations in southwestern Oklahoma
   Al-Shareby Z.; Hansony R. E.; Adamsy S. R.
   Okla: State Univ., Stillwater, Okla., USA
   The Geological Society of America: 89th annual meeting:
                                                           Denuer; Colo.,
 United States. Nov. 8-11, 1976
   Seol. Soc. Am., Abstr. Programs 8: 6. 752R/s.
                                                   1976
   CODEN: GAAPBC
   Subfile: B
   Country of Public United States
   Doc Type: SERIAL; CONFERENCE PURLICATION Bibliographic Level: AMALYTIC
   Languages: English
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A FDIALCO SEARCH FROM THE GEOREF DATABASE

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SAMPLE RECORD

The positions of the key fields are shown in the following sample record.

AN	1012344 80-48454
TI	Manganese and copper geochemistry of interstitial fluids from manganese nodule-rich pelagic sediments of the northeastern equatorial Pacific Ocean
AU	Callender, E.; Bowser, C. J.
CS	U. S. Geol. Surv., Reston, Va., USA; Univ. Wis., USA
JN PY	Am. J. Sci. 280: 10, 1063-1096p., 1980
CO SN	
SF	Subfile: B
CP	Country of Publ.: United States
DT BL	Doc Type: SERIAL Bibliographic Level: ANALYTIC
LA	Languages: English
LT LN	Latitude: N000000; N200000 Longitude: W1800000;
12.66	E1400000
DE	Descriptors: *Pacific Ocean; *nodules; *manganese;
	*diagenesis; *metals; *sediments; *copper ;
1 %	4. LUNGH-700 M MARANA LUNGH MARANA
	secondary structures; sedimentary structures;
or rore es	Equatorial Pacific: Northeast Pacific: remobilization
	; solubility; description; precipitation
SH	Section Headings: 07 .(MARINE GEOLOGY AND
10770	OCEANOGRAPHY)
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36	1982.)

Key to Data Fields

	AB	Abstract	JN	Journal Name	
	AN	GEOREF Accession Number	LA	Language	
	AU	Author	LN	Long I tude	
:	BL	Bibliographic Level	LT	Latitude	
	BN	ISBN	PU	Publisher	
	CL	Conference Location	PY	Publication Year	
	CO	CODEN	RN	Report Number	
7	CP	Country of Publication	SF	Subfile	
	CS	Corporate Source	SH	Section Heading Code	
	CT	Conference Title	SL	Summary Language	
	CY	Conference Year	SN	ISSN	
	DE	Descriptor	TI	Title	
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Data present in record depends on output format requested and type of record.

2680 SPRINGS Searcher BREWER Requestor SMITH-PATTERSON
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User 4939 Date: 16dec83 Time: 14:29:10 File: 89 Set Items Description
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O TUFA AND OKLAHOMA Print 5/3/1-45 Search Time: 0.183 Prints: 45

1184380 83-38283

An evaluation of water resources for enhanced oil recovery operations, Cement Field, Caddo and Grady counties, Oklahoma Preston, D. A.; Harrison, W. E.; Luza, K. V.; Prater, L.; Reddy, R.
Okla, Geol. Surv., Norman, Ok, USA
Special Publication - Oklahoma Geological Survey 82-5, 64
p., 1982
ISSN: 0275-0929 75 REFS.
Subfile: B
Country of Publ.: United States
Doc Type: SERIAL; MAP Bibliographic Level: MONOGRAPHIC Languages: English
Illus, 6 tables, geol. sketch map; 1:250,000; geol. maps

1164799 83-23626

Fluvial processes and geology in Washita River area, South-central Oklahoma

Harlin, J. M.
Univ. Okla., Norman, OK, USA
Oklahoma Geology Notes 42: 4, 168-178p., 1982
CODEN: OKGNBO ISSN: 0030-1736 21 REFS.
Subfile: B
Country of Publ.: United States
Doc Type: SERIAL Bibliographic Level: ANALYTIC
Languages: English
illus., sketch map

1150623 83-08948

Clinton Quadrangle, Oklahoma
Bloch, S.; Johnson, K. S.; Eutsler, R. L.; Myers, J. J. Okla. Geol. Surv., Norman, UK, USA
36p., 1982
137 REFS.
Subfile: B
Doc Type: REPORT; MAP Bibliographic Level: MONOGRAPHIC Languages: English

Report No.: PG://F-096(82)
Availability: Bendix Field Eng. Corp., Tech. Libr., Grand Junction, CD, United States
Note: National Uranium Resource Evaluation Program; includes microfiche, Illus., 4 tables; 1:500,000; econ. geol. maps

1145091 83-01079

Origin of the intermediate rocks of the Cold Springs intrusion breccia, Wichita Mountains, southwestern Oklahoma Vidnine, D. M.; Fernandez, L. A.; Grant, S. K. Univ. Missouri-Rolla, Dep. Geol. and Geophys., Rolla, MO, USA; Univ. New Orleans, Dep. Earth Sci., New Orleans, LA, USA

Abstracts of the 15th annual meeting of the Geological Society of America, South-Central Section

Anonymous
Geological Society of America, South-Central Section, 15th
annual meeting, San Antonio, TX, United States, April
13-14, 1981
Abstracts with Programs - Geological Society of America 13:

5, 264p., 1981 CODEN: GAAPBC ISSN: 0016-7592

Subfile: B
Country of Publ.: United States

Doc Type: SERIAL; CONFERENCE PUBLICATION Bibliographic Level: ANALYTIC

Languages: English

1119635 82-41830

Lawton Quadrangle, Oklahoma and Texas
Al-Shaleb, Z.; Thomas, R. G.; Stewart G. F.
Okla. State Univ., Dep. Geol., Stillwater, OK, USA
48p., 1982
Subfile: B*
Doc Type: REPORT; MAP Bibliographic Level: MONOGRAPHIC
Languages: English
Report No.: GJO-017(82)
Availabliity: Bendix Field Eng. Corp., Tech. Libr., Grand
Junction, CO, United States
Note: National Uranium Resource Evaluation Program,
111us., 5 tables, geol. maps; 1:500,000; geol. maps

1111051 82-29041

Geochemistry of the Cambrian Wichita Granite Group and revisions of its lithostratigraphy Myers, J. D.; Gilbert, N. C.; Loiselle, M. C. Univ. Wyo., Dep. Geol., Laramie, WY, USA; Okla. Geol. Surv., USA Oklahoma Geology Notes 41: 6, 172-195p., 1981

CODEN: DKGNBO ISSN: 0030-1736 36 REFS.
Subfile: B
Country of Publ.: United States
Doc Type: SERIAL Bibliographic Level: ANALYTIC
Languages: English
Illus., 9 tables



1107968 82-28713 Relationships between the new species Sorex scottensis and the fossil shrews Sorex cinereus Kerr Jammot, D. Mammalia 36: 3. 449-458p., 1972 CODEN: MAMLAN ISSN: 0025-1461 13 REFS. Subfile: 8 Country of Publ.: France Doc Type: SERIAL Bibliographic Level: ANALYTIC Languages: English Summary Languages: French illus., i table 1107876 82-31809 Uranium potential of the Cement District, southwestern Ok lahoma Allen, R. F Oklahoma State Univ., Stillwater, OK, USA 85p., 1980 Subfile: B Degree Level: Master's Country of Publ.: United States Doc Type: THESIS Bibliographic Level: MONOGRAPHIC Languages: English 1096580 82-20951 Assessment of geothermal potential in Oklahoma Prater, M. L.; Luza, K. V.; Harrison, W. E. Univ. Okla., Okla. Geol. Surv., Norman, OK, USA Geothermal Direct Heat Program; Glenwood Springs technical conference proceedings; Volume 1, Papers presented; State Coupled Geothermal Resource Assessment Program Ruscetta, C. A. (EDITOR); Foley, D. (EDITOR) Geothermal energy exploration and resource assessment technical conference, Glenwood Springs, CO, United States, May 4-6, 1981

Allen, R. F.
Oklahoma State Univ., Stillwater, OK, USA
85p., 1980
Subfile: B
Degree Level: Master's
Country of Publ.: United States
Doc Type: THESIS Bibliographic Level: MONOGRAPHIC
Languages: English

1063953 81-52128

011 in the fascinating Ouachitas
Morrison, L. S.
Lamina 011, Ardmore, OK, USA
011 and Gas Journal 79: 19, 170-179p., 1981
CODEN: 01GJAV ISSN: 0030-1388
Subfile: B
Country of Publ.: United States
Doc Type: SERIAL Bibliographic Level: ANALYTIC
Languages: English
Note: Full version appeared in Oct. 1980 issue of Shale
Shaker, Illus., sect., geol. sketch map

1063951 81-52115

Southwest finds may open up overlooked oil province McCaslin, J. C. Oil and Gas Journal 79: 17, 203-204p., 1981 CODEN: OIGJAV ISSN: 0030-1388 Subfile: B Country of Publ.: United States Doc Type: SERIAL Bibliographic Level: ANALYTIC Languages: English sketch map

1084348 82-10227

Lake City, UT, United States

Report No.: DOE/ID/12079-39; ESL-59

247-248p., Subfile: B

Doc Type: REPORT Level: ANALYTIC Languages: English

Uranium potential of the Cement District, southwestern Oklahoma

Availability: Univ. Utah Res. Inst., Earth Sci. Lab., Salt

REPORT; CONFERENCE PUBLICATION Bibliographic

1057643 81-44289 Radioactive springs in the watershed of a proposed reservoir in Sequoyah County, Oklahoma; origin and environmental effect Bloch, S.; Craig, R. L. Okla. Geol. Surv., Norman, OK, USA; Okla. State Dep. Health, Geology (Boulder) 9: 5, 195-199p., CODEN: GLGYBA ISSN: 0091-7613 21 REFS. Subfile: B Country of Publ.: United States Doc Type: SERIAL Bibliographic Level: ANALYTIC Languages: English illus., tables, geol. sketch map 1043604 81-30331 Zur Kenntnis seltener Petralidae (Anthozoa, Rugosa) aus dem amerikanischen Obersilur Rare Petralidae (Anthozoa, Rugosa) from the Upper Silurian of the United States Weyer, D.

Rare Petralidae (Anthozoa, Rugosa) from the Upper Silurian of the United States
Weyer, D.
Z. Geol. Wiss. 8: 9, 1209-1216p., 1980
CODEN: ZGWSA7 ISSN: 0303-4534 26 REFS.
Subfile: B
Country of Publ.: German Democratic Republic
Doc Type: SERIAL Bibliographic Level: ANALYTIC
Languages: German Summary Languages: Russian

1037843 81-25805

Geologic importance of zooplankton fecal pellets in black shale associated with phosphate deposits Robbins, E. I.; Porter, K. G.

U. S. Geol. Surv., Reston, VA, USA; Univ. Ga., USA

Proceedings of the Eleventh annual meeting of the American Association of Stratigraphic Palynologists

Christopher, R. A. (EDITOR)
Eleventh annual meeting of the American Association of Stratigraphic Palynologists, Oct. 24-28, 1978
Palynology 4, 249-250p., 1980
ISSN: 0191-6122
Subfile: 8

Country of Publ.: United States
Doc Type: SERIAL; CONFERENCE PUBLICATION Bibliographic
Level: ANALYTIC
Languages: English

Ground water resources of the Rush Springs Sandstone of southwestern Oklahoma

Roles, J. S.

Hydrologic investigation maps
Publ: Okla. Water Resour. Board
unknownp., 1976
9 REFS.
Subfile: B
Country of Publ.: United States
Doc Type: MAP Bibliographic Level: MONOGRAPHIC
Languages: English
Note: In three sheets, colored hydrogeol map

1006793 80-43983

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Powell, B. N.; Gilbert, M. C.; Fischer, J. F.
Rice Univ., Dep. Geol., Houston, Tex., USA; Va. Polytech.
Inst. and State Univ., USA
Geol. Soc. Am., Bull. 91: 9, I 509-I 514, II 1875-II 1994 p., 1980
CODEN: BUGMAF ISSN: OO16-7606 85 REFS.
Subfile: B
Country of Publ.: United States
Doc Type: SERIAL Bibliographic Level: ANALYTIC
Languages: English
illus., tables, geol. sketch map; print, microfiche

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976488 80-15195 Correlation of the Carboniferous rocks of the Ouachita trough with those of the adjacent foreland Gordon, M., Jr.; Stone, C., G. U. S. Geol. Surv., Washington, D.C., USA; Arkansas Geol. Symposium on the geology of the Duachita Mountains, Volume I, Stratigraphy, sedimentology, petrography, tectonics, and paleontology Stone, C. G. (EDITOR) Symposium on the Geology of the Quachita Mountains: 7th Annual Meeting of the South-Central Section of GSA. Rock, Arkansas, United States, April 5-7, 1973 Publ: Arkansas Geol. Comm. 70-91p., 1977 76 REFS. Subfile: B Country of Publ.: United States Doc Type: BOOK; CONFERENCE PUBLICATION Bibliographic Level: ANALYTIC Languages: English Illus., geol. sketch maps, sects., plates, tables 969023 80-11814 Garber and Rush Springs aquifers, Oklahoma Bellis, W. H.; Haws, A. Eng. Enterp., USA National Water Well Associaton, Ground Water Technology Division. Technical education session Giduings, 1. (moderator)

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Subfile: B

Level: ANALYTIC Languages: English

United States, Oct. 10, 1979 Ground Water 17: 5, 496p.,

CODEN: GRWAAP ISSN: 0160-0974

Country of Publ.; United States

Basic data report on ground water levels in the Rush Springs Sandstone area of southwestern Oklahoma Uklahoma Water Resources Board, Okla., USA Okla. Water Resour. Board, Publ. 74, 7p., 1976 ISSN: 0472-0687 3 REFS. Subfile: B Country of Publ.: United States

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Doc Type: SERIAL; CONFERENCE PUBLICATION Bibliographic

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Doc Type: SERIAL Bibliographic Level: MONOGRAPHIC Languages: English Illus., tables, sketch maps

Geohydrology of the Arbuckle aquifer, south-central Oklahoma

Geohydrology of the Arbuckle aquifer, south-central Oklahoma Fairchild, R.(investigator); Davis, R. E.(investigator) U. S. Geol. Surv., Prof. Pap. 1100, 119p., 1978 CODEN: XGPPA9 Subfile: B Country of Publ.: United States Doc Type: SERIAL Bibliographic Level: ANALYTIC Languages: English Descriptors: +Oklahoma; *ground water; hydrogeology; surveys; Arbuckle Aquifer; Arbuckle Group; Simpson Group; hydrology; aquifers; United States; Arbuckle Mountains; Cambrian: Paleozoic; Ordovician; recharge; water quality; springs; seepage; carbonate rocks; levels

901095 78-31212

Ground-water records for eastern Oklahoma; Part 2, Water-quality records for wells, test-holes, and springs Havens, J. S.
U. S. Geol. Surv., Open-File Rep. 78-357, 130p., 1978 CODEN: XGROAG Subfile: B Country of Publ.: United States Doc Type: SERIAL; REPORT Bibliographic Level: MONOGRAPHIC Languages: English Availability: U. S. Geol. Surv., Open-File Serv. Sect., Br. Distrib., Denver, Colo., United States table



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Level: ANALYTIC
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A FINALOG' SEARCH

WATER RESOURCES ABSTRACTS DATABASE

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The attached report is the result of a search of the WATER RESOURCES ABSTRACTS (WRA) database using the DIA-LOG Information Retrieval Service.

WATER RESOURCES ABSTRACTS (WRA) is prepared from materials collected by over 50 water research centers and institutes in the United States. The file covers a wide range of water resource topics including water resource economics, ground and surface water hydrology, metropolitan water resources planning and management, and water-related aspects of nuclear radiation and safety. The collection is particularly strong in the literature on water planning (demand, economics, cost allocations), water cycle (precipitation, snow, groundwater, lakes, erosion, etc.), and water quality (pollution, waste treatment). WRA covers predominantly English-language materials and includes monographs, journal articles, reports, patents, and conference proceedings.

SAMPLE RECORD

The positions of the key fields are shown in the following sample record.

127158 W78-10051

TI

DE

Hydrological Application of LANDSAT Imagery Used in the Study of the 1973 Indus River Flood, Pakistan

AU Deutsch, M.; Ruggles, F. H. Jr

CS Geological Survey, Reston, VA. Geography Program; and Geological Survey, Reston, VA. Water Resources Div.

N SO Water Resources Bulletin, Vol 14, No 2, p 261-274, April 1978. 7 fig. 1 tab, 6 ref.,

Journal Announcement: SWRA1121

During August and September 1973, the Indus River Valley of Pakistan experienced one of the largest floods on record, resulting in damages to homes, businesses, public works, and crops amounting to millions of rupees. Tremendous areas of lowlands were inundated along the Indus River and major tributaries. Landsat data made it possible to easily measure the extent of flooding, totaling about 20,000 sq km within an area of about 400,000 sq km south from the Punjab to the Arabian Sea. The Indus River data were used to continue experimentation in the development of rapid, accurate, and inexpensive optical techniques of flood mapping by satellite begun in 1973 for the Mississippi River floods. The research work on the Indus River not only resulted in the development of more effective procedures for optical processing of flood data and synoptically depicting flooding, but also provided potentially valuable ancillary information concerning the hydrology of much of the Indus River basin. (Woodward-USGS)

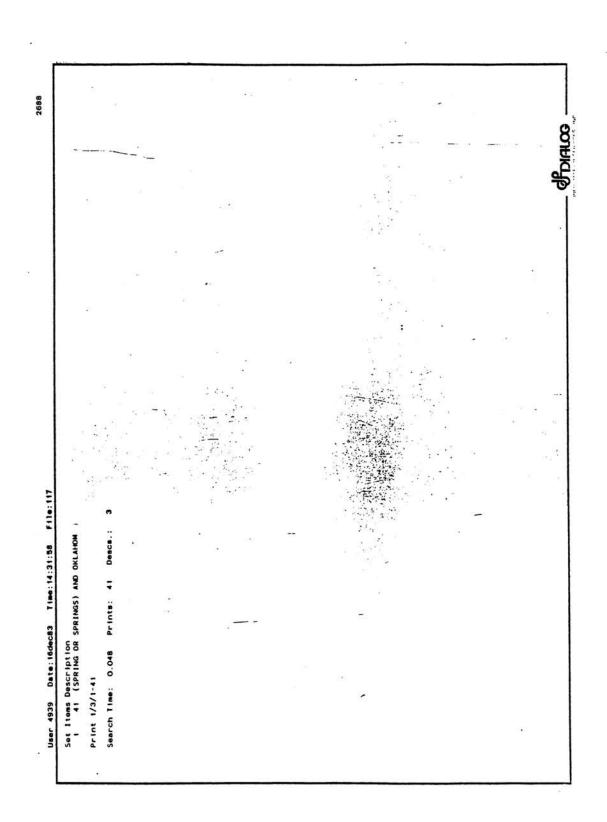
Descriptors: *Flood data ; *Remote sensing ; *Satellite(Artificial) ; *Photogrammetry ; *Indus River ; *Pakistan; Flood damage ; LANDSAT

Section Heading Codes: 78 (Resources Data--Data Acquisition); 4A (Water Quantity Management and Control--Control of Water on the Surface.

Key to Data Fields

AB	Abstract	JN	Journal Name
AN	SWRA Accession Number	PY	Publication Year
AU	Author	SH	Section Heading
CS	Corporate Source	SO	Source
DE	Descriptor	TI	Title
	Journal Announcement		

Data present in record depends on output format requested and type of record.



164494 W83-03347

The Biota of Oklahoma Springs: Natural Biological Monitoring of Groundwater Quality

Matthews, W. J.; Hoover, J. J.; Milstead, W. B. Oklahoma Univ., Kingston. Biological Station.

Available from the National Technical Information Service, Springfield, VA 22161 as PBB3-222455, Price codes: A04 in paper copy. A01 in microfiche. Water Resources Research Institute Completion Report, Oklahoma State Univ., Stillwater, May 1983. 64 p. 2 Fig. 4 Tab. 17 Ref. 1 Append. OWRT A-099-0KLA(1), 14-34-0001-1138.,

164319 V83-03109

Factors Controlling Blue-Green Algae Dominance in a Southwestern Reservoir

Toetz, D.

Oklahoma State Univ., Stillwater, Dept. of Zoology. Available from the National Technical Information Service. Springfield, VA 22161 as PB83-208892, Price codes: A03 in paper copy, AO1 in microfiche. Water Resources Research Institute Completion Report, Oklahoma State Univ., Stillwater, 39 p. 12 Fig. 1 Tab. 22 Ref. 1 Append. OWRT A-106-OKLA(1). 14-34-0001-1138..

162888 W83-01675

Water-Conserving Wheat Irrigation Schedules Based on Climatic Records

Greene, D. M.; Kirkham, M. B.

Baylor Univ., Waco, TX. Dept. of Geology.

Irrigation Science, Vol 1, No 4, p 241-246, 1980. 2 Fig. 15 Ref . .

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Davis, R. E.; Christenson, S. C.; Blumer, S. P.

Geological Survey, Oklahoma City, OK. Water Resources Div. Open-file Report 80-159, January 1981, 77 p. 1 Plate, 4 Tab.

3 Ref ..

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Distribution of Chironomids in the Littoral Zone of Lake Texoma, Oklahoma and Texas

Vaughn, C. C.

Oklahoma Univ., Norman. Dept. of Zoology.

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Effect of Artificial Destratification on Iron, Manganese, and Zinc in the Water, Sediments, and two Species of Benthic Macroinvertebrates in an Oklahoma Lake

Cover. E.; Wilhm, J.

Oklahoma State Univ., Stillwater. School of Biological Sciences.

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Robison, H. W.

Arkansas Univ., Fayetteville. Water Resources Research

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Oklahoma University, Norman; and Geological Survey, Norman,

Geology, Vol 9, No 5, p 195-199, May, 1981. 3 Fig. 4 Tab. 21

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130570 W79-00463
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Hall, R. W. Jr; Plumb, R. H.; Ihornton, K. W.; Eley, R. L.;
Lessem, A. S.
Army Engineer Waterways Experiment Station, Vicksburg, MS.
Environmental Effects Lab.
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Selected Water-Level Records for Western Oklahoma, 1975-1976
Goemaat, R. L.
Geological Survey, Oklahoma City, Okla. Water Resources Div.
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Havens, J. S.; Bergman, D. L.
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EFFECTS OF ARTIFICIAL DESTRATIFICATION ON POPULATIONS OF
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WILHM, J.
OKLAHOMA STATE UNIV., STILLWATER, SCHOOL OF BIOLOGICAL
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AVAILABLE FROM THE NATIONAL TECHNICAL INFORMATION SERVICE. SPRINGFIEL, VA. 22161. AS PB-250 125, \$5.00 IN PAPER COPY, \$2.25 IN MICROFICHE. OKLAHOMA WATER RESOURCES RESEARCH INSTITUTE, STILLWATER, COMPLETION REPORT, (1976). 92 P, 2 FIG, 50 TAB, 42 REF, APPEND. OWRT A-059-OKLA(1).

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WISCONSIN DEPT. OF NATURAL RESOURCES, MADISON.

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THEY'RE GETTING THE JUMP ON POLLUTION CONTROLS
GRAVES, R.; HARIMAN, C.
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CASLER, G. L.; LADUE, E. L.
NEW YORK STATE COLL. OF AGRICULTURE AND LIFE SCIENCES,
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079532 W75-01176
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HART. D. L. JR

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073036 W74-07992
PHYTOPLANKTON COMMUNITY STRUCTURE AND NUTRIENT RELATIONSHIPS
IN LAKE CARL BLACKWELL, OKLAHOMA

FAUST, A. R.

OKLAHOMA STATE UNIV., STILLWATER.

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THE LIMMOLOGY OF NITROGEN IN AN OKLAHOMA RESERVOIR: NITROGENASE ACTIVITY AND RELATED LIMMOLOGICAL FACTORS

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SCHOOF, RUSSELL R.; HARTMAN, MONROE A.; HUNT, CHARLES G. AGRICULTURAL RESEARCH SERVICE, CHICKASHA, OKLA. SOUTHERN PLAINS BRANCH.

INT ASS SCI HYDROL PUB NO 76, SYMP ON HYDROL ASPECTS OF UTIL OF WATER, BERN, SEPT 25-OCT 7, 1967, PP 89-97, 1968. 9 P, 6 FIG. 1 TAB. 1 REF..



APPENDIX B

CHEMICAL PROCEDURES

ALKALINITY

INTERFERENCE:

None

REAGENTS:

Distilled-deionized water
0.1 N HCl - Should be obtained commercially (N/10 standard)

APPARATUS:

Conductivity Meter Conductivity cell Magnetic stirrer with stir bar 50 ml Buret 200 ml Beaker

SAMPLING:

Sample should be stored in plastic Sample should be stored at $^{4}{}^{\circ}{}^{}$

PRECISION AND ACCURACY:

If proper laoratory procedures are followed than precisison should be within 1% If > 1 meq/1 or 5% IF < 1 meq/1

PROCEDURE

- ** Let conductivity meter warm up for> 15 minutes or longer.
- Transfer 100 ml of sample (or diluted to 100 ml) in a beaker. Add stir bar and place on magnetic stirrer. Allow sample to equilibrate to room temperature.
- 2) Rinse the buret with 0.1 N HCl three times, then fill and place over beaker. The tip of the buret should be 3-5 mm above the surface of the sample.
- 3) Place the conductivity cell in the sample and mount it so that the cell is **not** touching the stir bar.
- 4) Check conductivity of the sample. If it is greater than 20 micromhos, dilute with distilled-deionized water until conductivity is below 20 micromhos.
- 5) Record initial conductivity. Then add 0.1-0.3 ml of HCl. Record volume and conductivity, read the buret to 0.02 ml. Repeat four times.

- 6) Add 3-5 ml of HCl. Record volume and conductivity. Add 0.5-1.0 ml of HCl. REcord volume and conductivity. Repeat additions of 0.5-1.0 ml four times.
- 7) Determine volume added at each conductivity reading and record.
- 8) Enter data into HCO₃ program. Conductivity on y-axis and volume added on x axis. The results generated are in mg/l HCO₃. Use the first and last three data points only.

CHLORIDE

Method 325.3 (Titrimetric, Mercuric Nitrate)

STORET NO. 00940

- Scope and Application
 - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
 - 1.2 The method is suitable for all concentration ranges of chloride content; however, in order to avoid large titration volume, a sample aliquot containing not more than 10 to 20 mg Cl per 50 ml is used.
 - 1.3 Automated titration may be used.
- 2. Summary of Method
 - 2.1 An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.
- Comments
 - 3.1 Anions and cations at concentrations normally found in surface waters do not interfere.
 - 3.2 Sulfite interference can be eliminated by oxidizing the 50 ml of sample solution with 0.5 to 1 ml of H₂O₂.
- 4. Apparatus
 - 4.1 Standard laboratory titrimetric equipment including a 1 ml or 5 ml microburet with 0.01 ml graduations.
- . Reagents
 - 5.1 Standard sodium chloride, 0.025 N: Dissolve 1.4613 ±0.0002 g (dried at 600°C for 1 hour) in chloride-free water in a 1 liter volumetric flask and dilute to the mark.
 - 5.2 Nitric acid, HNO₃ solution (3 + 997)
 - 5.3 Sodium hydroxide solution, NaOH, (10 g/1)
 - 5.4 Hydrogen peroxide (30%), H₂O₂
 - 5.5 Hydroquinone solution (10 g/liter): Dissolve 1 g of purified hydroquinone in water in a 100 ml volumetric and dilute to the mark.
 - 5.6 Mercuric nitrate titrant (0.141 N): Dissolve 25 g Hg(NO₃)₂•H₂O in 900 ml of distilled water acidified with 5.0 ml conc. HNO₃ in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.141 N and check. Store in a dark bottle. A 1.00 ml aliquot is equivalent to 5.00 mg of chloride.
 - 5.7 Mercuric nitrate titrant (0.025 N): Dissolve 4.2830 g Hg(NO₃)₂•H₂O in 50 ml of distilled water acidified with 0.5 ml conc. HNO₃ (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard

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- sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.025 N and check. Store in a dark bottle.
- 5.8 Mercuric nitrate titrant (0.0141 N): Dissolve 2.4200 g Hg(NO₃)₃·H₂O in 25 ml of distilled water acidified with 0.25 ml of conc. HNO₃ (sp. gr. 1.42) in a 1 liter volumetric flask and dilute to the mark with distilled water. Filter if necessary. Standardize against standard sodium chloride solution (5.1) using procedure 6. Adjust to exactly 0.0141 N and check. Store in a dark bottle. A 1 ml aliquot is equivalent to 500 ug of chloride.
- 5.9 Mixed indicator reagent: Dissolve 0.5 g crystalline diphenylcarbazone and 0.05 g bromophenol blue powder in 75 ml 95% ethanol in a 100 ml volumetric flask and dilute to the mark with 95% ethanol. Store in brown bottle and discard after 6 months.
- 5.10 Alphazurine indicator solution: Dissolve 0.005 g of alphazurine blue-green dye in 95% ethanol or isopropanol in a 100 ml volumetric and dilute to the mark with 95% ethanol or isopropanol.

Procedure

- 6.1 Place 50 ml of sample in a vessel for titration. If the concentration is greater than 20 mg/1 chloride, use 0.141 N mercuric nitrate titrant (5.6) in step 6.6 or dilute. If the concentration is less than 2.5 mg/1 of chloride, use 0.0141 N mercuric nitrate titrant (5.8) in step 6.6, a 1 ml or 5 ml microburet, and determine an indicator blank on 50 ml chloride-free water using procedure 6.6. If the concentration is less than 0.1 mg/1 of chloride concentrate an appropriate volume to 50 ml.
- 6.2 Add 5 to 10 drops of mixed indicator reagent (5.9), shake or swirl solution.
- 6.3 If a blue-violet or red color appears add HNO₃ solution (5.2) dropwise until the color changes to yellow.
- 6.4 If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (5.3) dropwise until the color changes to blue-violet; then add HNO₃ solution (5.2) dropwise until the color changes to yellow.
- 6.5 Add 1 ml excess HNO₃ solution (5.2).
- 6.6 Titrate with 0.025 N mercuric nitrate titrant (5.7) until a blue-violet color persists throughout the solution. See 6.1 for choice of titrant normality. Alphazurine indicator solution (5.10) may be added with the indicator to sharpen the end point. This will change color shades. Practice runs should be made.
- 6.7 Additional steps to eliminate particular interferences:
 - 6.7.1 If chromate is present at < 100 mg/1 and iron is not present, add some alphazurine indicator solution (5.10) and acidify to pH 3 (indicating paper). End point will then be an olive-purple color.</p>
 - 6.7.2 If chromate is present at > 100 mg/1 and iron is not present, add 2 ml of fresh hydroquinone solution (5.5).
 - 6.7.3 If ferric ion is present use volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion. Add 2 ml fresh hydroquinone solution (5.5).
 - 6.7.4 If sulfite ion is present, add 0.5 ml of H₂O₂ solution (5.4) to 50 ml sample and mix for 1 minute.

7. Calculation

mg chloride/1 =
$$\frac{(A - B)N \times 35,450}{\text{ml of sample}}$$

where:

A = ml titrant for sample

B = ml titrant for blank

N = normality mercuric nitrate titrant

mg NaCl/1 = mg chloride/1 x 1.65

8. Precision and Accuracy

8.1 Forty two analysts in eighteen laboratories analyzed synthetic water samples containing exact increments of chloride, with the following results:

Increment as	Precision as	Accuracy as		
Chloride mg/liter	Standard Deviation mg/liter	Bias,	Bias, mg/liter	
17	1.54	+2.16	+0.4	
18	1.32	+3.50	+0.6	
91	2.92	+0.11	+0.1	
97	3.16	-0.51	-0.5	
382	11.70	-0.61	-2.3	
398	11.80	-1.19	-4.7	

(FWPCA Method Study 1, Mineral and Physical Analyses)

- 8.2 In a single laboratory (EMSL), using surface water samples at an average concentration of 34 mg Cl/1, the standard deviation was ±1.0.
- 8.3 A synthetic unknown sample containing 241 mg/1 chloride, 108 mg/1 Ca, 82 mg/1 Mg, 3.1 mg/1 K, 19.9 mg/1 Na, 1.1 mg/1 nitrate N, 0.25 mg/1 nitrite N, 259 mg/1 sulfate and 42.5 mg/1 total alkalinity (contributed by NaHCO₃) in distilled water was analyzed in 10 laboratories by the mercurimetric method, with a relative standard deviation of 3.3% and a relative error of 2.9%.

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SULFATE

Method 375.4 (Turbidimetric)

STORET NO. Total 00945

- 1. Scope and Application
 - 1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes.
 - 1.2 The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO₄/1.
 - 1.3 The minimum detectable limit is approximately 1 mg/1 sulfate.
- 2. Summary of Method
 - 2.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer or spectrophotometer and compared to a curve prepared from standard sulfate solutions.
 - 2.2 Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted.
 - 2.3 Silica in concentrations over 500 mg/1 will interfere.
- 3. Comments
 - 3.1 Proprietary reagents, such as Hach Sulfaver or equivalent, are acceptable.
 - 3.2 Preserve by refrigeration at 4°C.
- Apparatus
 - 4.1 Magnetic stirrer, variable speed so that it can be held constant just below splashing. Use identical shape and size magnetic stirring bars.
 - 4.2 Photometer: one of the following which are given in order of preference.
 - 4.2.1 Nephelometer
 - 4.2.2 Spectrophotometer for use at 420 nm with light path of 4 to 5 cm.
 - 4.2.3 Filter photometer with a violet filter having a maximum near 420 nm and a light path of 4 to 5 cm.
 - 4.3 Stopwatch, if the magnetic stirrer is not equipped with an accurate timer.
 - 4.4 Measuring spoon, capacity 0.2 to 0.3 ml.
- Reagents
 - 5.1 Conditioning reagent: Place 30 ml conc. HCl, 300 ml distilled water, 100 ml 95% ethanol or isopropanol and 75 g NaCl in solution in a container. Add 50 ml glycerol and mix.
 - 5.2 Barium chloride, BaCl₂, crystals, 20 to 30 mesh.
 - 5.3 Sodium carbonate solution (approximately 0.05N): Dry 3 to 5 g primary standard Na₂CO₃ at 250°C for 4 hours and cool in a desiccator. Weigh 2.5 ±0.2 g (to the nearest mg), transfer to a 1 liter volumetric flask and fill to the mark with distilled water.

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- 5.4 Standard sulfate solution (1.00 ml = 100 ug SO₄): Prepare by either 5.4.1 or 5.4.2.
 - 5.4.1 Standard sulfate solution from H2SO4
 - 5.4.1.1 Standard sulfuric acid, 0.1N: dilute 3.0 ml conc. H₂SO₄ to 1 liter with distilled water. Standardize versus 40.00 ml of 0.05 N Na₂CO₃ solution (5.3) with about 60 ml distilled water by titrating potentiometrically to pH about 5. Lift electrodes and rinse into beaker. Boil gently for 3-5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na₂CO₃ weighed into 1 liter

B = ml Na2CO3 solution

C = ml acid used to inflection point

- 5.4.1.2 Standard acid, 0.02 N: Dilute appropriate amount of standard acid, 0.1 N (5.4.1.1) to 1 liter (200.00 ml if 0.1000 N). Check by standardization versus 15 ml of 0.05 N Na₂CO₃ solution (5.3).
- 5.4.1.3 Place 10.41 ml standard sulfuric acid, 0.02 N (5.4.1.2) in a 100 ml volumetric and dilute to the mark.
- 5.4.2 Standard sulfate solution from Na₂SO₄: Dissolve 147.9 mg anhydrous Na₂SO₄ in distilled water in a 1 liter volumetric flask and dilute to the mark with distilled water.
- 6. Procedure
 - 6.1 Formation of barium sulfate turbidity
 - 6.1.1 Place 100 ml sample, or a suitable portion diluted to 100 ml, into a 250 Erlenmeyer flask.
 - 6.1.2 Add exactly 5.0 ml conditioning reagent (5.1).
 - 6.1.3 Mix in the stirring apparatus.
 - 6.1.4 While the solution is being stirred, add a measuring spoonful of BaCl₂ crystals (5.2) and begin timing immediately.
 - 6.1.5 Stir exactly 1.0 minutes at constant speed.
 - 6.2 Measurement of barium sulfate turbidity
 - 6.2.1 Immediately after the stirring period has ended, pour solution into absorbance cell.
 - 6.2.2 Measure turbidity at 30 second intervals for 4 minutes.
 - 6.2.3 Record the maximum reading obtained in the 4 minute period.
 - 6.3 Preparation of calibration curve.
 - 6.3.1 Prepare calibration curve using standard sulfate solution (5.4).
 - 6.3.2 Space standards at 5 mg/1 increments in the 0-40 mg/1 sulfate range.

- 6.3.3 Above 50 mg/1 the accuracy decreases and the suspensions lose stability.
- 6.3.4 Check reliability of calibration curve by running a standard with every 3 or 4 samples.
- 6.4 Correction for sample color and turbidity.
 - 6.4.1 Run a sample blank using the procedure 6.1 and 6.2 without the addition of barium chloride (6.1.4).
- 7. Calculations
 - 7.1 Read mg SO4 from calibration curve

$$mg SO_4/1 = mg SO_4 \times 1,000$$

- 8. Precision and Accuracy
 - 8.1 Thirty-four analysts in 16 laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate with the following results:

Increment as	Precision as	Accuracy as		
Sulfate mg/liter	Standard Deviation mg/liter	Bias,	Bias mg/liter	
8.6	2.30	-3.72	-0.3	
9.2	1.78	-8.26	-0.8	
110	7.86	-3.01	-3.3	
122	7.50	-3.37	-4.1	
188	9.58	+0.04	+0.1	
199	11.8	-1.70	-3.4	

(FWPCA Method Study 1, Mineral and Physical Analyses).

8.2 A synthetic unknown sample containing 259 mg/1 sulfate, 108 mg/1 Ca, 82 mg/1 Mg, 3.1 mg/1 K, 19.9 mg/1 Na, 241 mg/1 chloride, 0.250 mg/1 nitrite N, 1.1 mg/1 nitrate N, and 42.5 mg/1 total alkalinity (contributed by NaHCO₃) was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

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APPENDIX C

X-RAY FLUORESCENT ANALYSIS

718 Sherman Street (rear) Denver, Colorado 80203 Phone (303) 837-1396 Merlyn L. Salmon, Manager

ZXXX QUALITATIVE

XXXX SEMI-QUANTITATIVE

QUANTITATIVE

ANALYTICAL REPORT

TO:

Oklahoma State Univ

A. Hounslow

Job Nu	mber_	31780		
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Date		40.00		

SAMPLE: BKCR1

Copper	.1800	Lanthanum
Silver	Cobalt	Cerium
Gold46	Nickel	Praseodymium
Zinc46	Cesium	Neodymium
Cadmium	Rubidium	Samarium
Mercury	Barium 95	Europium
Gallium	Strontium 140	Gadolinium
Indium	Titanium	Terbium
Thallium	Zirconium 150	Dysprosium
Germanium	Hafnium	. Holmium
Tin	Thorium	Erbium
Lead200	Vanadium	Thulium
Arsenic	Columbium	Ytterbium
Antimony	Tantalum	Lutetium
Bismuth	Chromium	Yttrium
Selenium	Molybdenum	
Tellurium	Tungsten	
Bromine	Uranium	
Iodine	Manganese 110	

The values above are estimated elemental concentrations in:

______ per cent _____xxxx_ parts per million ______ grams per lite.

No check was made for elements with atomic numbers less than 22.

By Mark & Solmon

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718 Sherman Street (rear) Denver, Colorado 80203 Phone (303) 837-1396 Merlyn L. Salmon, Manager

XXXX QUALITATIVE

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ANALYTICAL REPORT

TO:

Oklahoma State Univ

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5000000	6	Nov	1984	_r ages
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DABR or UABR (indistinct marking) SAMPLE:

Copper	33	Iron	9400	Lanthanum
Silver		Cobalt		Cerium
Gold		Nickel	150	Praseodymium
Zinc	36	Cesium		Neodymium
Cadmium		Rubidium	160	Samarium
Mercury		Barium	900	Europium
Gallium		Strontium	170	Gadolinium
Indium		Titanium		Terbium
Thallium		Zirconium		Dysprosium
Germanium		Hafnium		Holmium
Tin		Thorium		Erbium
Lead		Vanadium		Thulium
Arsenic		Columbium		Ytterbium.
Antimony		Tantalum		Lutetium
Bismuth		Chromium		Yttrium50
Selenium		Molybdenum_		
Tellurium		Tungsten		
Bromine		Uranium		
Iodine		Manganese	160	

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	per cent	XXXX	parts per million	grams	per liter

No check was made for elements with atomic numbers less than 22.

By Wengs Italian

Lead

Arsenic_ Antimony_

Bismuth_

Selenium_

Tellurium___ Bromine____ Iodine____

718 Sherman Street (rear) Denver, Colorado 80203 Phone (303) 837-1396 Merlyn L. Salmon, Manager

_XXXX_QUALITATIVE XXXX SEMI-QUANTITATIVE QUANTITATIVE

31780 ANALYTICAL REPORT 10 TO: Oklahoma State Univ 6 Nov 1984 DJCR3 SAMPLE: 3400 Lanthanum_ Silver_ Cobalt Cerium. 40 Gold_ Nickel_ Praseodymium__ 36 Zinc Neodymium.___ Cesium_ Cadmium_ Rubidium_ Samarium____ 560 Barium Europium___ Mercury___ 1800 Gallium_ Strontium Gadolinium___ Indium_ Titanium. Terbium_ 460 Thallium_ Zirconium_ Dysprosium.__ Hafnium_ Holmium____ Germanium_ Tin_ Thorium. Erbium_

Vanadium_

Tantalum_

Columbium_

Chromium_

Molybdenum_

Tungsten	the second secon
Uranium	
Manganese	
The values above are estimated elen	
per cent <u>xxxx</u> parts per	r million grams per liter

By Muly Lehum

Thulium_

Ytterbium_

Lutetium_

Yttrium_

No check was made for elements with atomic numbers less than 22.

Denver, Colorado 80203 Phone (303) 837-1396 Merlyn L. Salmon, Manager

XXXX QUALITATIVE XXXX SEMI-QUANTITATIVE __QUANTITATIVE

ANALYTICAL REPORT

TO:

Oklahoma State Univ

Job Number	mber31/80			
Page4		of 1	10 Pages	
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SAMPLE:

DMR1

Copper	37	Iron 560	Lanthanum
Silver		Cobalt	Cerium
Gold		Nickel	Praseodymium
Zinc	36	Cesium	Neodymium
Cadmium		Rubidium	
Mercury		Barium 90	Europium
Gallium		Strontium 92	Gadolinium
Indium		Titanium	Terbium
Thallium		Zirconium	Dysprosium
Germanium		Hafnium	Holmium
Tin		Thorium	Erbium
Lead	200	Vanadium	Thulium
Arsenic		Columbium	Ytterbium
Antimony		Tantalum	Lutetium
Bismuth	-	Chromium	Yttrium 100
Selenium		Molybdenum	
Tellurium		Tungsten	
Bromine		Uranium	
Iodine		Manganese	

The	values above	are estimated elemental con	centrations in:
	per cent	xxxx parts per million	grams per liter

No check was made for elements with atomic numbers less than 22.

By Meul L'Salm

718 Sherman Street (rear) Denver, Colorado 80203 Phone (303) 837-1396 Merlyn L. Salmon, Manager

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D:	0.0	a State Ur	ANALYTICAI	REPORT	Job Number 31760 Page 5 10 Page 6 Nov 1984
MPLE:	DMR 2				
Co	pper	33	Iron	1800	Lanthanum
Sil	ver		Cobalt	40	Cerium
Go	old	36	Nickel		Praseodymium
Zi	nc	30	Cesium		Neodymium
Ca	dmium		Rubidium	950	Samarium
Me	ercury		Barium		Europium
Ga	llium		Strontium	1600	Gadolinium
In	dium		Titanium	180	Terbium
Th	nallium		Zirconium	510	Dysprosium
Ge	ermanium		Hafnium		Holmium
Ti	n	5/	Thorium	220	Erbium
Le	ad		Vanadium		Thulium
Ar	rsenic		Columbium	35	Ytterbium
A	ntimony		Tantalum		Lutetium
Bi	smuth		Chromium		Yttrium55
Se	lenium		Molybdenum_		
Te	ellurium		Tungsten		
Br	romine		Uranium	95	
Io	dine		Manganese		

The values above	are estimated elemental con	icentrations in:
per cent	xxxx_ parts per million	grams per liter

No check was made for elements with atomic numbers less than 22.

By Mengn Redmon

718 Sherman Street (rear)

Denver, Colorado 80203 X RAY Phone (303) 837-1396 SPEC TROGRAPHIC Merlyn L. Salmon, Manager Analytical Laboratory XXXX QUALITATIVE SEMI-QUANTITATIVE QUANTITATIVE ANALYTICAL REPORT 10 TO: 6 Nov 1984 Oklahoma State Univ DTFR1 SAMPLE: 1100 Copper_ Iron Lanthanum___ Silver__ Cobalt Cerium___. ____ Gold_ Praseodymium___ Nickel. 120 Neodymium ____ Cesium_ Cadmium_ Rubidium Samarium__ 180 Mercury_ Europium_ Barium. 550 Gallium_ Gadolinium_ Strontium. Indium_ Titanium_ Terbium_ 170 Thallium_ Zirconium_ Dysprosium_ Germanium Hafnium_ Holmium_ Tin___ Thorium_ Erbium___ Lead_ Vanadium_ Thulium _____ Arsenic_ Columbium_ Ytterbium__ Antimony_ Tantalum. Lutetium_ Bismuth. Chromium. Molybdenum_ Selenium_ Tellurium_ Tungsten. Bromine_ Uranium_ lodine_ Manganese_ The values above are estimated elemental concentrations in: per cent _____ parts per million _____ grams per liter

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By Muly LSImon

No check was made for elements with atomic numbers less than 22.

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Merlyn L. Salmon, Manager

_____QUALITATIVE
_____SEMI-QUANTITATIVE
_____QUANTITATIVE

ANALYTICAL REPORT

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TO:

Oklahoma State Univ

SAMPLE: DTFR2

Copper	110	Iron	6200	Lanthanum
Silver		Cobalt		Cerium
Gold		Nickel	40	Praseodymium
Zinc	33	Cesium		Neodymium
Cadmium		Rubidium	140	Samarium
Mercury		Barium	340	Europium
Gallium		Strontium	880	Gadolinium
Indium		Titanium		Terbium
Thallium		Zirconium	130	Dysprosium
Germanium		Hafnium		Holmium
Tin		Thorium		Erbium
Lead	390	Vanadium		Thulium
Arsenic		Columbium	66	Ytterbium
Antimony		Tantalum		Lutetium
Bismuth		Chromium		Yttrium 50
Selenium		Molybdenum_		
Tellurium		Tungsten		
Bromine		Uranium		4
Iodine		Manganese	140	

The values above	are estimated elemental cor	icentrations in:
per cent	XXXX parts per million	grams per liter

No check was made for elements with atomic numbers less than 22.

By Well Lalmin

VITA

Cindy Lynn Smith

Candidate for the Degree of

Master of Science

Thesis: NATURAL GROUND WATER SYSTEMS AND ASSOCIATED FRESHWATER CARBONATE DEPOSITS IN SOUTHERN OKLAHOMA

Major Field: Geology

Biographical:

Personal Data: Born in Houston, Texas, October 17, 1955, the daughter of Mr. and Mrs. Bob Lee Smith.

Education: Graduated from Norwalk High School, Norwalk Conneticut, in August, 1973; recieved Bachelor of Arts degree in geology from Boston University, Boston, Massechusetts, January, 1980; completed requirements for the Master of Science degree with a major in geology. at Oklahoma State University in December, 1984.

Professional Experience: Data Management Specialist, Association of Oklahoma Governments, 1980-1981; Geologist, US Army Corp of Engineers, Omaha District, 1981-1983; research assistant, Oklahoma State University, 1983-1985.