			BICY-TW	
			Lithologic & WQ	Data./
	RICY	$-T\omega$		
		- 		
L	atito de	Long 1 to dee	Easting A	Vortering
1	<" 53' 35.694"N	81° 18° 33.812" W	398287.(576 987. 5

CORE ANALYSIS REPORT

FOR

SOUTH FLORIDA WATER MANAGEMENT

BICY-TW

COLLIER COUNTY, FLORIDA

These analyses, opinions or interpretations are based on observations and materials supplied by the client to whom; and for whose exclusive and confidential use; this report is made. The interpretations or opinions expressed represent the best judgment of Core Laboratories (all errors and omissions excepted); but Core Laboratories and its officers and employees, assume no responsibility and make no warranty or representations, as to the productivity, proper operations, or profitableness of any oil, gas or other mineral well or formation in connection with which such report is used or relied upon.



PETROLEUM SERVICES

February 26, 1998

SOUTH FLORIDA WATER MANAGEMENT 3301 Gun Club Road West Palm Beach, Florida 33416

> File No: 57181-17847 Subject: Drilled Sidewall Analysis BICY-TW Collier County, Florida

Gentlemen:

Sidewall Core Analysis was made on 5 drilled sidewall core samples received from client.

Gas expansion porosity and grain density were determined using Boyle's Law.

Gas detection was measured using a "Hot Wire Gas Detector" on gas in the sealed containers.

Air permeability was measured horizontally on drilled sidewalls.

Descriptions and fluorescence were visually determined micro-scopically.

The samples will be returned to client.

We trust these data will be useful in the evaluation of your property and thank you for the opportunity of serving you.

Very truly yours, CORE LABORATORIES, INC.

John Sebian Laboratory Supervisor

JS/ym

CORE LABORATORIES

Company : SOUTH FLORIDA WATER MANAGEMENT Well : BICY-TW

Location :

Co, State : COLLIER COUNTY, FLORIDA

Field : Formation : OCALA/SUWANNE/AVON PARK Coring Fluid : FRESH WATER MUD Elevation : 5' NGVD

File No.: 57181-17847 Date : 2-24-98 API No. : Analysts: SEBIAN

CORE ANALYSIS RESULTS

SAMPLE NUMBER	DEPTH ft	INCHES REC.	PERMEABILITY (HORIZONTAL) Kair md	POROSITY (HELIUM) %	GRAIN DENSITY gm/cc	GAS DETECTOR UNITS	DESCRIPTION	
DRILLED SIDEWALL ANALYSIS								
1 2 3 4 5	500.0 790.0 1350.0 1425.0 1500.0	0.2 0.7 1.2 0.5 1.8	19.8 112. 50.6 25.5	25.5 40.1 36.3 37.5	2.71 2.71 2.71 2.71	0. 0.	No Analysis, Lim, pp Lim, pp Lim, pp Lim, pp Lim, pp Lim, pp	

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DISTRIBUTION OF FINAL REPORT

3 COPIES ATTN: MICHAEL BENNETT 3301 GUN CLUB ROAD WEST PALM BEACH FL 33416

2 COPIES

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COLLIER CONSULTING ATTN: HUGHBERT COLLIER 741 WEST COLLEGE ST. STEPHENVILLE TX 76401



CORE LABORATORIES

South Florida Water Management 3301 Gun Club Road November 17, 1998

Subject : PDPK Measurements BICY-TW Collier County, Florida

West Palm Beach, Florida 33406

Dear Sir,

Enclosed you will find a copy of the requested Pressure-Decay-Profile Permeabilities (PDPK) measurements on the subject well's recovered drilled sidewall cores.

DISCUSSION OF ANALYSIS THEORY

The PDPK-300 device uses unsteady-state pulse decay methodology to determine permeability. The PDPK (permeability) device is designed to provide a detailed assessment of changes in permeability over very small intervals.

DISCUSSION OF ANALYSIS PROCEDURES

Four drilled sidewall cores were selected from the subject well by the client. Two profile permeability measurements were made on each faced end. Tabular data reported includes the measurement points (sample numbers), measurement cumulative point count, depth, PDPK air permeability and PDPK empirical liquid permeability.

We appreciated the opportunity to be of service to **South Florida Water Management**. Should you have any questions, please call.

Yours truly, Core Laboratories

John Sebian Laboratory Supervisor South Florida Water Mngmt. BICY-TW Well Location N/A Collier County, Florida

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> Field : N/A Ocala/Suwanne/Avon Park Fresh Wtr Mud 5' NGVD

57181-17847 November 17, 1998 API No. N/A Analyst : Eudaily

Sample Number	Point	Depth	Ka air permeability (md)	Kl liquid permeability (md)
2	1	790	36.5	32.3
2	2	790	15.2	13.1
2	3	790	16.4	14.1
2	4	790	26.9	23.6
3	5	1350	232	218
3	6	1350	221	207
3	7	1350	117	108
3	8	1350	113	105
4 4 4	9 10 11 12	1425 1425 1425 1425	70.9 59.8 53.6 78.3	65.2 54.6 48.9 72.1
5	13	1500	29.1	25.5
5	14	1500	30.2	26.6
5	15	1500	24.5	21.4
5	16	1500	24.3	21.3

ISOTOPIC MEASUREMENTS FROM THE FLORIDAN AQUIFER

Jordan F. Clark Dept. of Geological Sciences University of California Santa Barbara, CA 93106 clark@geol.ucsb.edu

FINAL REPORT

OBJECTIVES

In cooperation with the South Florida Water Management District, groundwater samples were collected from the Upper and Lower Floridan aquifers at 7 locations for dissolved noble gases, stable isotopes of water, chlorinitiy, and radiocarbon (¹⁴C), as part of the regional hydro-geochemical assessment project (Table 1 and 2). At each location, groundwater samples were collected from two or three depth intervals. Additionally, two shallow wells were sampled and analyzed for the same set of isotope tracers. Straits of Florida seawater samples were collected by NOAA and analyzed for stable isotopes (Table 3). The primary objectives for this study were to determine groundwater ages and circulation patterns using geochemical tracers. Ages were determined using three approaches. First, traditional ¹⁴C techniques were employed. Second, the geochemical data were used to identify glacial-aged water (15,000-25,000 yr old water) following the method developed by (Clark et al., 1997). Third, helium concentrations were used to establish a relative chronology.

INTRODUCTION

The Floridan aquifer system of southern Florida is composed chiefly of cavernous carbonate rocks with a vertical thickness of about 1000 m (Meyer, 1989). In the upper portions of the aquifer, freshwater derived from precipitation circulates. However, deeper in this system (below ~200 m), the groundwater becomes increasingly saline, eventually reaching salinities almost equal to those of the coastal ocean at depths below about 1000 m. Based on temperature measurements, Kohout (1965) determined that the high salinity groundwater was not stagnant, rather it was circulating through the Floridan aquifer system. Coastal seawater enters the aquifer at the bottom of the Straits of Florida at a depth of about 600 m and flows inland where it is heated. Subsequently, it migrates upwards and is forced to flow seawards by the freshwater flow system (e.g., Kohout, 1965; Meyer, 1989). Meyer (1989) hypothesized that the cyclic seawater circulation pattern was reduced during the glacial period (15,000 to 25,000 years ago) due to the 120 m lower seawater head (Fairbanks, 1989).

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Geochemical data can be used to determine groundwater ages and circulation patterns (e.g., Cook and Herczeg, 2000). The multi-tracer approach that uses radiocarbon, chlorinity (or salinity), stable isotopes, and dissolved noble gases has been most successful in complicated hydrological systems with flow times of thousands of years (e.g., Clark et al., 1997, 1998). This approach is often needed because, for each tracer, multiple factors can result in similar changes. For instance, interpretations ¹⁴C ages and stable isotopes in groundwater can often be ambiguous. This is because decreases in ¹⁴C concentrations can occur as a result of both water-rock interactions and radioactive decay and the composition of stable isotopes vary as a function of a number of factors including continentality, elevation, temperature, and long-term climate. With the multi-tracer approach, erroneous interpretations are minimized because of the complimentary nature of the isotopic systems.

Critical to the multi-tracer approach is the analysis of dissolved noble gases (He, Ne, Ar, Kr, Xe). Noble gas paleo-thermometry has become an accepted method for determining continental temperatures of past climates archived in groundwater systems (Stute et al., 1992, 1995; Clark et al., 1997, 1998; Stute and Schlosser, 2000). This method is based on the temperature dependence of the solubility of noble gases in For the two heaviest noble gases, Kr and Xe, the solubility equilibrium water. concentrations change by about 3% per degree centigrade and, thus, noble gas temperatures with uncertainties typically better than ±1° C can be determined. In most aquifers, as groundwater flows away from the water table, it warms due to geothermal heating. However because it can no longer exchange with the other fluid phases, concentrations of the heavier noble gases remain unchanged. Thus, paleoclimate records for the last 30,000 yrs have been determined by analyzing a series of noble gas samples from existing wells along flow paths (e.g., Stute et al., 1992, 1995; Clark et al., 1997). Included in the noble gas analysis is helium. Unlikely the heavier noble gases, helium concentrations change in groundwater due to the decay of uranium and thorium series nuclides within the aquifer and deeper in the crust (e.g. Bottomley et al., 1984; Torgersen and Ivey, 1985). The helium concentration increases with time in groundwater at rates that vary between aquifers. Thus, it can be used as an approximate chronometer.

METHODS

At nine locations throughout South Florida, water samples were collected from monitoring wells open to the surficial, Upper Floridan, and Lower Floridan aquifers following the standard sampling procedures of the South Florida Water Management District. All samples were collected using a suction pump after purging with approximately five well volumes.

Noble gas samples were collected in 15 ml copper tubes that were connected to the pump outlet with a short piece of tubing. At the outlet end of the copper tube, a clear plastic tube connected to a regulator valve was attached. The water pressure was raised within the copper tube by reducing the flow through the valve until no bubbles were detected. After thoroughly flushing at high pressure, the copper tubes were sealed at each end with steel pinch-off clamps. Noble gas concentrations were determined at the Lamont Doherty Earth Observatory of Columbia University on an MAP 215-50 noble gas mass spectrometer using the methods outlined by Stute et al. (1995). The system was calibrated using known quantities of air and equilibrated water standards. Absolute concentrations of the noble gases were determined with a precision of $\pm 1\%$ (Ar, and Xe) to $\pm 2\%$ (He, Ne, Kr).

Samples for stable isotopes of water (D/H and ¹⁸O /¹⁶O) were collected in 60 ml glass bottles. In addition to the groundwater samples, Straits of Florida seawater samples were collected during a NOAA oceanographic cruise offshore of Ft. Pierce. All stable isotope samples were analyzed at the University of California, Davis using standard mass spectrometry. The groundwater and Straits of Florida seawater were analyzed during the same run. The results are presented as per mil (‰) derivations from a water standard using the δ -notation:

$$\delta = \left(\frac{R}{R_{SMOW}} - 1\right) \times 1000$$

where *R* and *R*_{SMOW} are the isotope ratio of the sample and of the SMOW standard. The reproducibility for δ^{18} O and δ D were ± 0.05‰ and ±0.5‰, respectively.

Carbon isotope samples were collected in 250 ml glass bottles. At Lawrence Livermore National Laboratory, carbon was extracted from each sample by adding 1 ml of 100% phosphoric acid and vacuum stripping of the water. The CO₂ liberated was cryogenically trapped, separated from water vapor, and split for ¹³C and ¹⁴C analyses. ¹³C/¹²C ratios were determined on a mass spectrometry and ¹⁴C contents were determined by accelerator mass spectrometry after the CO₂ gas had been reduced to graphite. ¹³C analyses are reported in δ -notation relative to the PDB standard and ¹⁴C abundances are reported as percent modern carbon (pmc). Reproducibility for δ ¹³C and ¹⁴C are \pm 0.3‰ and \pm 1 pmc, respectively.

RESULTS

Groundwater collected from the surficial, Upper Floridan, and Lower Floridan aquifers were isotopically different (Table 4). On average, the Lower aquifer water has higher salinities, higher ¹⁴C concentrations, lower helium concentrations, lighter δ^{18} O values, and higher noble gas temperatures than the Upper aquifer. The surficial aquifer had the highest ¹⁴C concentration, lowest helium concentrations, and warmest noble gas temperatures.

Lower Floridan Aquifer

The stable isotope composition and noble gas temperature of the groundwater in the Lower Floridan aquifer is identical to seawater collected from depths greater than 550 m in the Straits of Florida (Table 3 + 4). This indicates that seawater enters the

Lower Floridan aquifer near the bottom of the straits as suggested by Kohout (1965). Because the isotope composition of the glacial ocean was significantly different ($\delta^{18}O$ was more than 1‰ heavier, Schrag et al. 1996; Mashisotta et al., 1999), the seawater must have entered the aquifer after the end of the last glacial period. Hence, the groundwater ages of the seawater circulating through the Lower Flordian aquifer must be less than about 10,000 years. This inference is supported by the relatively low 4helium concentrations and high ¹⁴C concentrations found in most samples. Absolute ¹⁴C ages are difficult to calculate because water rock interactions are difficult to quantify in carbonate aquifers (e.g., Clark et al., 1997). It is likely that the relatively low ¹⁴C content groundwater (e.g., BICY MZ4; MIU MZ1) is the result of water rock interactions, although a more detailed study is needed to verify this assertion. The salinity of the groundwater is slightly less than the salinity of bottom water from the Straits of Florida (35 ppt) indicating that these waters have mixed with a freshwater source. The proportion of freshwater ranges between 13% and 2%. There are two possible freshwater sources. First, it may be leaking down from the Upper Floridan aquifer. Second, it may be residual water left over from the glacial period when the freshwater circulation system may have penetrated to greater depths than today and into the Lower Floridan aquifer (Meyer, 1989).

Upper Floridan Aquifer

The Upper Floridan well samples were significantly more saline than the surficial wells suggesting that these samples are mixtures between circulating seawater and surface freshwater. Presumably, the seawater source is upwelling out of the Lower Floridan aquifer. The proportion of seawater ranges between 75% to 2%; most samples contain less than 16% seawater. The noble gas temperature of the samples averaged 19.2° C about 4° C cooler than the present day mean annual air temperature in South Florida (23.6° C) and about 8° C cooler than the surficial aquifer samples. These cooler noble gas temperatures suggest that the freshwater recharged during the cooler glacial period 15,000 to 25,000 years ago. The relatively high helium concentrations (>13 x 10⁻⁸ cc STP/gr) and low ¹⁴C concentrations support this inference. It is important to note that in the Flordian aquifer from southern Georgia, Clark et al. (1997) showed that glacial aged groundwater had helium concentrations greater than 10 x 10⁻⁸ cc STP/gr.

SUMMARY

The isotope and salinity data indicates that the groundwater in the Upper and Lower Floridan aquifers are distinct, although there is evidence for Lower aquifer water upwelling and mixing with Upper aquifer water. The data suggests that within this system relatively old freshwater circulate over relatively young seawater. The stable isotope data clearly identifies the seawater origin as Straits of Florida bottom water and indicates that the circulation time is less than 10,000 yr. Based primarily on the relatively cool noble gas temperatures and relatively high helium concentrations, the Upper aquifer groundwater must have recharged during the last glacial period. Hence, the travel time to these wells is between 15,000 and 25,000 year.

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Well	Date	Aquifer	Salinity	¹⁴ C	δ ¹³ C	δ18Ο	δD
		1	(ppt)	(pmc)	(‰)	(‰)	(‰)
BF-1	1/26/01	L. F.	34.06	5.4	-1.64	0.26	1.7
BF-1	10/24/00	L. F.	34.02	7.0	-1.69	0.26	1.3
BF-3	10/24/00	U. F.	n.d.	n.d.	n.d.	-1.11	-5.3
BICY MZ1	10/26/00	U. F.	n.d.	n.d.	n.d.	-1.60	-7.6
BICY MZ2	10/26/00	U. F.	n.d.	n.d.	n.d.	-1.51	-7.1
BICY MZ4	10/26/00	L. F.	35.35	0.3	-0.2	0.44	3.6
DMW3	5/23/01	Surficial	n.d.	72.1	-5.71	-2.42	-12.8
175 MZ2	10/25/00	U. F.	n.d.	1.0	-2.68	-1.16	-6.2
I75 MZ4	10/25/00	L. F.	34.80	19.5	-1.89	0.20	-0.1
LLC51	5/23/01	Surficial	n.d.	75.4	-8.61	-1.04	-4.0
MIU-MW2	12/13/00	U. F.	33.93	0.9	-2.08	0.28	0.1
MIU-MW1	12/13/00	L. F.	n.d.	n.d.	n.d.	-0.10	-1.5
PBF-3	10/23/01	U. F.	n.d.	1.0	-1.59	-1.31	-5.3
PBF-5	10/23/01	L. F.	31.91	4.9	-3.17	0.25	0.8
PWU-MZL	1/17/01	L. F.	30.22	16.4	-2.62	0.23	1.3
PWU-MZU	1/17/01	U. F.	n.d.	n.d.	n.d.	-1.42	-4.7
ZRL-DMW	15/2/00	L. F.	32.79	8.9	-2.39	0.20	-0.3
ZRL-UMW	15/2/00	U. F.	n.d.	n.d.	n.d.	-1.08	-5.7

Table 1: Isotope results

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n.d. = not determined; U. F. = Upper Floridan aquifer; L. F. = Lower Floridan aquifer

Table 2: Dissolved noble gas concentrations and noble gas temperature calculated assuming that the excess air fraction completely dissolves.

Well	Date	He	Ne	Ar	Kr	Xe	Tng	
		(cc stp/g)	(° C)					
BF-1	1/26/01	7.76E-08	1.65E-07	3.06E-04	7.16E-08	1.02E-08	9.3	
BF-1	10/24/00	6.97E-08	1.63E-07	3.11E-04	7.32E-08	1.05E-08	8.3	
BF-3	10/24/00	3.88E-07	2.21E-07	3.35E-04	7.24E-08	9.67E-08	19.8	
BICY MZ1	10/26/00	2.97E-07	2.20E-07	3.39E-04	7.31E-08	9.77E-09	19.2	
BICY MZ2	10/26/00	2.77E-07	2.54E-07	3.73E-04	7.76E-08	1.02E-08	18.0	
BICY MZ4	10/26/00	1.56E-07	1.82E-07	3.18E-04	7.36E-08	1.05E-08	8,7	<u> </u>
DMW3	5/23/01	5.02E-08	1.94E-07	2.79E-04	6.13E-08	8.04E-09	26.6	
175 MZ2	10/25/00	2.47E-07	2.13E-07	3.35E-04	7.32E-08	9.84E-09	19.0	
I75 MZ4	10/25/00	7.16E-08	1.81E-07	3.21E-04	7.54E-08	1.08E-08	7.7	
LLC51	5/23/01	4.78E-08	1.84E-07	2.72E-04	5.85E-08	7.57E-09	28.1	
MIU-MW2	12/13/00	1.37E-07	1.66E-07	3.12E-04	7.32E-08	1.06E-08	18.2	
MIU-MW1	12/13/00	1.68E-07	1.79E-07	3.16E-04	7.24E-08	1.03E-08	9.1	
PBF-3	10/23/01	2.66E-07	2.19E-07	3.47E-04	7.59E-08	1.01E-08	17.9	
PBF-5	10/23/01	1.19E-07	2.17E-07	3.34E-04	7.51E-08	1.04E-08	9.1	
PWU-MZL	1/17/01	8.28E-08	1.70E-07	3.08E-04	7.17E-08	1.02E-08	9.3	

18,6°C

PWU-MZU	1/17/01	2.45E-07	2.16E-07	3.37E-04	7.30E-08	9.82E-09	17.0
ZRL-DMW	15/2/00	1.37E-07	2.01E-07	3.30E-04	7.52E-08	1.07E-08	8.2
ZRL-UMW	15/2/00	2.45E-07	2.16E-07	3.37E-04	7.30E-08	9.82E-09	19.1

fut	Depth (m)	Temperature (° C)	Salinity (ppt)	δ ¹⁸ O (‰)	δD (‰)
- د م	20	25.93	36.14	+1.03	+7.0
62	50	25.94	36.14	+1.02	+6.3
1), 3(0	100	23.18	36.58	+1.09	+7.2
620	200	19.67	36.67	+1.07	+7.9
1085	350	14.70	35.92	+0.75	+4.3
1395	450	12.24	35.52	+0.54	+2.6
° ר _ו	^۲ ے 550	9.36	35.13	+0.35	+1.0
<u></u> (45	\$ 630	7.80	34.94	+0.28	+0.5

Table 3: Hydrographic and stable isotope data from the Straits of Florida at 27° 0.445N 79° 36.789W.

Table 4: Geochemical characteristics of groundwater from the Lower and Upper Floridan aquifers.

	Surficial	Upper Floridan ^a	Lower Floridan
Salinity (ppt)		1.6 to 8.4 ^b	30.2 to 35.4
$^{14}C (pmc)$	72 to 75	1.0 to 0.4- 1.0c	0.3 to 20
Helium (10^{-8} cc STP/gr)	4.8 to 5.0	13.7 to 38.8	7.0 to 16.8
δ ¹⁸ O (‰)	-1.0 to -2.4	-1.1 to -1.6	+0.2 to +0.4
Noble gas Temperature (° C)	26.6 to 28.1	17.0 to 19.8	8.7 to 9.3

^aMIU-MW2 excluded from the summary. This well appears to contain a large component of seawater derived from the lower aquifer.

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^bSouth Florida Water Management District data. ^cOnly two of the eight samples were analyzed.

Inorganic and Isotope Geochemical Data

Introduction

Geochemical data (including measurements of dissolved constituents, field parameters, stable isotopes, and unstable carbon isotope) compliment physical geology and hydrogeology investigations. The SFWMD plans to use the geochemical data collected at this site in a regional investigation to better understand the groundwater circulation patterns of the Floridan Aquifer System (Kohout 1965, 1967; Meyer 1989).

The geochemical composition of groundwater reflects both the source(s) of water and process(es) that modify the chemical and isotopic compositions; each source and process leaves a distinctive geochemical mark or "fingerprint" on the water.

Table below summarizes some of the fingerprints for sources and processes commonly associated with the Floridan Aquifer System. Ocean water produces high dissolved constituent concentration (total dissolved solids or TDS) in groundwater; more specifically, when ocean water recharges groundwater, the groundwater becomes more highly concentrated than fresh groundwater with sodium and chloride to becoming the dominant ions. In addition, other constituents will change to reflect ocean water; calcium concentration declines relative to magnesium, and the stable isotope compositions of oxygen, hydrogen and carbon (\bullet ¹⁸0, \bullet D and \bullet ¹³C) increases in similarity to the ocean water standards (Standard Mean Ocean Water or SMOW for \bullet ¹⁸0 and \bullet D; Pee Dee Formation Belemnite or PDB for \bullet ¹³C). Low calcium concentrations of ocean water reflect the effect of shell-forming organisms in the ocean on the overall water composition.

Precipitation or meteoric water contains very little dissolved constituency and the oxygen and hydrogen stable isotope compositions fall along a documented line of measurements called the Global Meteoric Water Line (GMWL). Once within the groundwater system, dissolution of the carbonate aquifer framework commonly occurs and the ratio of Ca increases with respect to Mg, and the carbon stable isotope composition (• ¹³C) becomes more similar to the composition of the aquifer material.

and processes.		
Source	Dissolved Constituents	Stable Isotopes
Ocean Water	High TDS (33,000 mg/L)	Oxygen and Hydrogen
	Na-Cl Type water	Isotopes = SMOW
	More Mg than Ca	$(\bullet^{18}0 \text{ and } \bullet D = 0.00\%)$
	_	Carbon Isotope = PDB
		$(\bullet^{13}C = 0.00\%)$
Precipitation	Low TDS	Samples plot along the
-		$GMWL (\bullet D = 8 \bullet^{-18}0 + 10)$
Dissolution of Carbonates	Usually more Ca than Mg	• ${}^{13}C_{gw} = {}^{13}C_{carbonate}$
Diffusion of Salts	Solutes increase	• ³⁷ Cl becomes more
	differentially	negative along diffusion
		path

Table . Summary of geochemical characteristics of the possible water and solute sources and processes.

Dissolved Constituent and Field Parameters at the BICY Site

Tables ?, ? and ? contain the dissolved constituent and field parameter measurements from water obtained at the BICY site in 1997. From the IAS through the UF, temperature increases steadily with increasing sample depth, although the rate of change is only about half the typical geothermal gradient (Freeze and Cherry, 1979). In the LFA, the geothermal gradient reverses. Kohout (1965) and Meyer (1989) associate reverse temperature gradient anomalies with direct inflow from the ocean.

Among the IAS, UFA and MCU samples, pH is relatively unchanged, remaining between 7.4 and 7.5, slightly less than would be produced by dissolution of carbonate aquifer material in a confined aquifer (Garrels and Christ 1964). LFA samples both show a drop in pH to 7.13 and 7.28, suggesting differences in water origin or lithology.

The Piper Plot suggests the role of ocean as a source of dissolved constituents. On Figure G1, the samples plot on the right portion of the diamond. If ocean water were plotted on this figure, it would occur just where all the samples plot.

Stiff Diagrams (Figures G2 and G3) also indicate ocean water as the source of solutes, with Na and Cl as the dominant ions, followed by Mg and SO₄, and Ca and carbonate species showing the lowest concentrations. However, the smaller mille-equivalent values on figure G2 suggest dilution with fresh water. Samples BICY PT-5 and BICY PT-4 indicate relatively pure ocean water. The Stiff Diagrams for all the other samples appear to result mixing of ocean water and fresh water.

Although the Stiff Diagrams and Piper Plot suggest mixing of ocean and fresh water, ion ratios indicate uneven mixing of the ions. Figure (G4 in graph file) shows the plot of the ratios Cl/Na versus Ca/Mg. Four of the samples plot along a trend of increasing Cl/Na with increasing Ca/Mg. Sample BICY PT-2 plots well below the line, probably because it is from the IAS rather than the Floridan aquifer system. Of the remaining samples, all from the Floridan aquifer system, the Cl/Na value of BICY PT-3 is lower than if it resulted simply from mixing. The isotope evaluation below indicates the Ca/Na value may be consistent with the effects of diffusion.

Calcite dissolution as an influence of dissolved constituent chemistry is supported by saturation indexes calculated for calcite, the primary mineral in limestone (Table ? below). The table indicates that all the samples are at saturation with respect to calcite or above.

Table ?. Calcite saturation indices obtained from WATEQF.SampleAquiferSaturation Index for CalciteBICY PT-2IAS-0.073BICY MZ-2UFA-0.033BICY PT-3UFA0.047

BICY MZ-3	UFA	0.318
BICY PT-5	LFA	-0.047
BICY PT-4	LFA	0.076

Dissolved constituency suggests a gradual dilution from the IAS into the LFA and little variation in relation to calcite in the aquifer. The overall impression is that there is no isolation of flow zones, that constituents from each flow zone mix gradually as the water moves through the aquifer.

Stable Isotopic Composition at the BICY Site

Table ? contains the measured isotope compositions of groundwater from the BICY site. The measurements that most directly reflect on the origin of the water and constituents, as well as the nature of the flow system are \bullet ¹⁸O, \bullet D, \bullet ³⁷Cl, \bullet ¹³C, and the corrected ¹⁴C age.

Water samples collected during the packer tests and from completed monitor intervals were sent to the University of Waterloo Environmental Isotope Laboratory (EIL) for stable isotope determination. • ¹⁸O values were determined by CO₂ equilibration using standard procedures outlined by Epstein and Mayeda (1953), and Drimmie and Heemskerk (1993). Hydrogen isotope compositions were determined using the methods of Coleman et al (1982) and Drimmie et al. (1991). The results are presented as per mil (‰) deviations from a standard using the • (delta) notation:

• $x = \bullet_{x-\text{std}} = ([R_x/R_{\text{Standard}}] - 1) \times 1000$ (Equation 5)

Where R_x is the isotope ratio of the sample (e.g. ²H/¹H, ¹⁸O/¹⁶O) and $R_{Standard}$ is the isotope ratio of the standard. By convention, the standard used with the stable isotope compositions of oxygen and hydrogen is Standard Mean Ocean Water (SMOW). The precision for • ¹⁸O is +/- 0.05‰, and for • D is +/- 0.05‰.

Chloride, in samples received by EIL for • 37 Cl, is converted to methyl chloride by reaction with methyl iodide, purification through a gas chromatograph. The chlorine isotope ratio (35 Cl/ 37 Cl) is measured by mass spectrometry(Long et al. 1993; Kaufmann 1984). Isotope ratios are then compared to the chlorine standard: Standard Mean Ocean Chloride (SMOW). Results are presented as per mil (‰) deviations with respect to the standard using the • (delta) notation (see Equation 5 above).

Water samples received by EIL for • ¹³C determinations were acidified under vacuum with phosphoric acid. The released CO₂ which is produced from dissolved inorganic carbon (DIC) in the sample is then purified using cold distillation and the isotope ratio (¹²C/¹³C) measured by mass spectrometry (Drimmie et al., 1990). Isotope ratios of the samples are then compared to the carbon standard: CO₂ liberated from the belemnites of the Cretaceous Pee Dee Formation of South Carolina. Results are presented as per mil (‰) deviations with respect to the standard using the • (delta) notation (see Equation 5 above).

Figure ? shows a plot of hydrogen stable isotope composition as a function of oxygen stable isotope. The plot has two points of reference, ocean water (SMOW) and the Global Meteoric Water Line (GMWL). Harmon Craig (1961) published the results of worldwide observations of oxygen and hydrogen stable isotope composition in rainwater. Data plot in on a line with warmer climates near ocean water composition (• ${}^{18}O = • D = 0.00\%$) and colder climates to the lower left portion of the figure.

In Figure ?, the three shallow BICY groundwater samples plot to the right of the GMWL indicating evaporation prior to infiltration. The three deepest samples plot near ocean water. Despite the presence of fresh water in BICY MZ-3, it plots close to ocean water. The distribution implies that rainfall is the dominant water source in the three shallower samples.

Groundwater may acquire constituent ratios similar to ocean water and maintain isotopic meteoric identity by dissolution of marine aquifer material with saline fluid inclusions and molecular diffusion from the ocean.

The • 37 Cl, with a precision of 0.1‰, shows significant variation among the BICY samples. Two of the samples vary significantly from SMOC, BICY PT-3 and BICY MZ-3 with values of -0.26 and +0.21. The leading hypothesis to explain this variation is diffusion.

Diffusion involves the gradual mixing of solutes along the flow path via random molecular movements known as Brownian Motion. The relation between movement and concentration is given by Fick's Law (Equation 6).

 $\begin{array}{rcl}
dm & \bullet c \\
\hline
 & ---- & = & -D ---- \\
dt & \bullet x
\end{array}$ (Equation 6)

Where d is the derivative change, m mass, t time, c concentration, and x distance along the diffusion path. D is the diffusion coefficient. The analytic solution of the second derivative of Fick's Law along one dimension is provided in Equation 7 (Crank 1956) and is especially useful in groundwater.

 $C = C_o (erfc x/2 \bullet Dt)$ (Equation 7)

Where C is concentration at a point along the flow path (x), and C_o is the initial concentration of the reservoir. The term (erfc) is the complement of the error function. The isotope fractionation occurring to chlorine during diffusion is given in Equation 8 (Kaufmann et al. 1988).

$$S = (C/C_0)_{37}/(C/C_0)_{35} = (erfc x/2 \bullet D_{37}t)/(erfc x/2 \bullet kD_{37}t)$$
 (Equation 8)

Chloride does not move by diffusion alone, advection is usually a factor. Advection does not change the concentration along the diffusion path nor does it produce any

fractionation of the isotopes, so Equation 8 can be modified by adding a factor P that accounts for the accelerated change in distance with respect to concentration (Kaufmann et al. 1988), as presented in Equation 9.

$$S = (C/C_0)_{37}/(C/C_0)_{35} = (\operatorname{erfc} x/2 \bullet D_{37}t) + P/(\operatorname{erfc} x/2 \bullet kD_{37}t) + P \quad (Equation 9)$$

P is calculated as the difference between the observed change in concentration with depth, and that concentration predicted by Equation 7. The differential diffusion, variable k in Equation 9, is approximated as 1.008, as suggested by Desaulniers et al. (1986).

The model predicts that after traveling 400 feet via diffusion and advection, the fractionation is about -4%, similar to -4% that was observed. The model also indicates that this value is obtained if diffusion took place over 30,000 years (see ¹⁴C dating section below).

Carbon stable isotope measurements contribute to understanding the groundwater flow system at the BICY site in two ways, as an indicator of ocean water and in age correction calculations with ¹⁴C. The value for ocean water for carbon isotopes is around 0.00% -2.2‰, close to the groundwater values BICY. The next section discusses age calculation of ¹⁴C age with • ¹³C.

¹⁴C Isotopic Composition at the BICY Site

The Rafter Radiocarbon Laboratory (Institute of Geological and Nuclear Sciences, New Zealand) determined the radiocarbon age by accelerator mass spectrometry (AMS), reporting results as delta ¹⁴C, and in percent modern carbon (pmC). The ¹⁴C activities are absolute percent of modern carbon, relative to the U.S. National Bureau of Standards (NBS) oxalic acid standard corrected for decay since 1950. The activity of "modern carbon" is 95% of the ¹⁴C in the 1950 NBS oxalic acid, close to the activity of 1890 wood grown in a fossil-fuel free environment (Clark and Fritz 1997).

Delta ${}^{14}C = A_s / A_{abs} - 1 x 1000$ (Equation 10)

Where A_s is the activity of the sample and A_{abs} is the activity of the standard. The modern activity of ¹⁴C is set at 13.56 decays-per-minute per gram of carbon. The "zero year" for this activity is 1950 CE (pre thermonuclear testing) with an activity of 100 pmC. The conventional radiocarbon age (¹⁴C Age) is determined in the following manner:

$$T = -8033 \ln (A_{sn}/A_{on}) \qquad (Equation 11)$$

Where A_{sn} is the normalized sample activity and A_{on} is the normalized oxalic acid activity (count rate). T is the calculated time elapse represented by the difference in activities between the standard and the sample.

Unfortunately, T is not the actual date of recharge because ¹⁴C may be preferentially added or removed as the water moves through the geologic environment. Soil activities can concentrate ¹⁴C, and dissolution of carbonate aquifer material with "dead carbon" can dilute the ¹⁴C activity. In order to calculate the date of recharge, Equation (12) must be modified as follows:

 $t = -8267 \ln (A_t / A_o)$ (Equation 12)

Where t is the time since recharge, A_t the current ¹⁴C activity and A_o the initial ¹⁴C activity. Determining time since recharge requires knowledge of the current ¹⁴C activity (A_t), which is measured, and the initial activity (A_o), which must be estimated.

Pearson and Hanshaw (1970) developed an equation for correcting the initial age estimate (as obtained from Equation 7) that considers both soil processes and carbonate dissolution. This correction method uses approximations of the • ¹³C values of the soil and aquifer material, along with knowledge of activities of each to evaluate initial activity of the groundwater at time of recharge. Equation 13 presents the Pearson and Hanshaw correction equation.

$$A_{o} = [(A_{g} - A_{c})(\bullet_{T} - \bullet_{c})/(\bullet_{g} - \bullet_{c})] + A_{c}$$
 (Equation 13)

(A) represents ¹⁴C activity, (•) represents • ¹³C stable isotope ratio, (g) stands for soil gas, (c) stands for solid carbonate, (T) stands for total dissolved inorganic carbon. Table ? gives the corrected

Table ?. Correc	ted ¹⁴ C ages
	CY Samples.
	Pearson-
	Hanshaw
	¹⁴ C age in
Sample	Years BP
BICY PT2	24,028
BICY MZ2	25,227
BICY PT3	29,045
BICY MZ3	30,485
BICY PT5	11,843
BICY PT4	14,495

¹⁴C age of the groundwater, if not corrected with Equation 13, is between 13,181 and 44,670 years B.P. If the ages are corrected using Pearson and Hanshaw (1970), which applies to carbonate aquifers that are closed to the atmosphere, the age ranges are between 11,843 and 30,485 years B.P.

Application of Inorganic and Isotope Geochemistry to Flow at the BICY Site The inorganic and isotope geochemistry data apply to the hydrogeologic characteristics of the BICY Site, to the extent that they indicate interconnection between flow zones, and the role of diffusion at this site.

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Drilling suggests four major flow zones, indicated as IAS, UFA, MCU and UFA. The zones are lacking in uniqueness suggesting interchange of water and mixing. The zones possess dissolved constituent distributions similar to ocean water, and both meteoric and ocean water sources. The hypothesis that the zones grade is supported by the Piper Plots Stiff Diagrams that indicate ocean water is the source of most the solutes. Equilibrium modeling suggests that calcite dissolution is also a solute-contributing process. Other characteristics and interpretations are as follows:

- The IAS sample (BICY PT-2) has a TDS value that similar to the samples in the UFA (BICY MZ-2 and BICY PT-3), and both IAS and UFA have hydrogen and oxygen stable isotope compositions more similar to meteoric water than the deeper samples.
- The MCU sample (BICY MZ-3) seems to be a transition sample, with only about 78% the TDS of the LFA, and oxygen and hydrogen stable isotope composition similar to ocean water. The deeper two samples (BICY PT-5 and BICY PT-4) both have chemical and isotopic qualities similar to ocean water.
- The chlorine stable isotope composition between samples BICY MZ-3 and BICY PT-3 vary by about 4.5‰. Modeling supports the hypothesis that this difference is due to diffusion and implies interconnection between the UFA and MCU. If the hydrologic connection extends to the LFA, than the fresh/salt waters contact is about 30,000 years old and ocean water has been actively pushing into the LFA toward the MCU during the last 11,000-14,000 year.

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Kaufmann, R.S. 1984. Chlorine in Ground Water: Stable Isotope Distribution. Dissertation, University of Arizona, 137 pp.

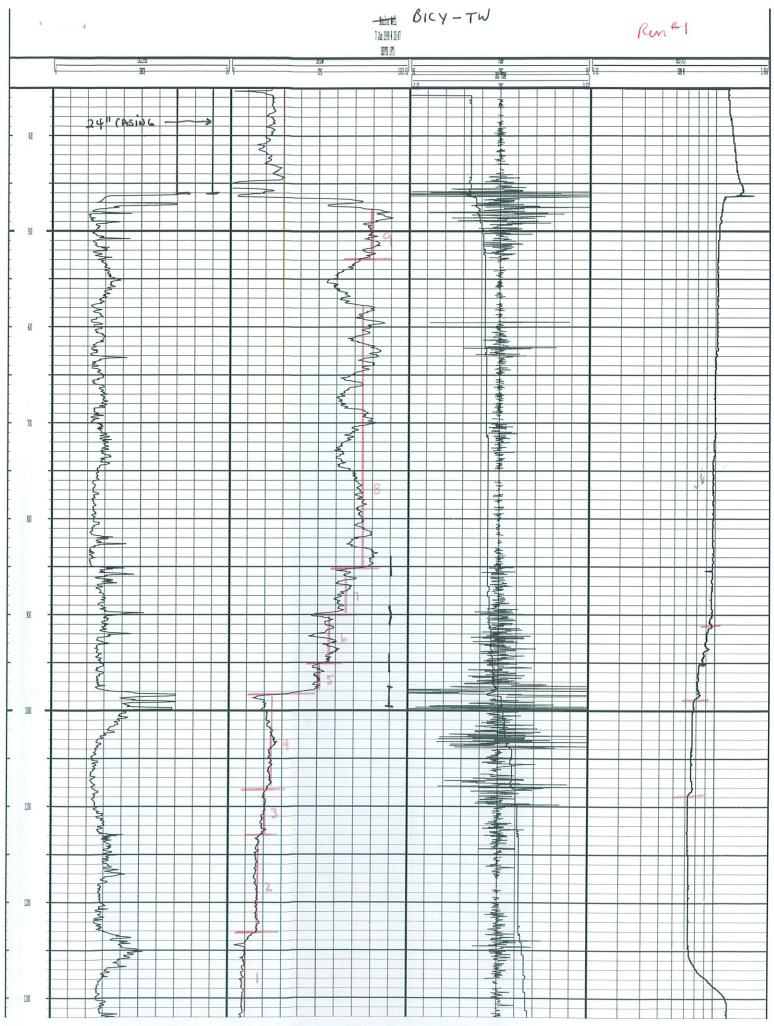
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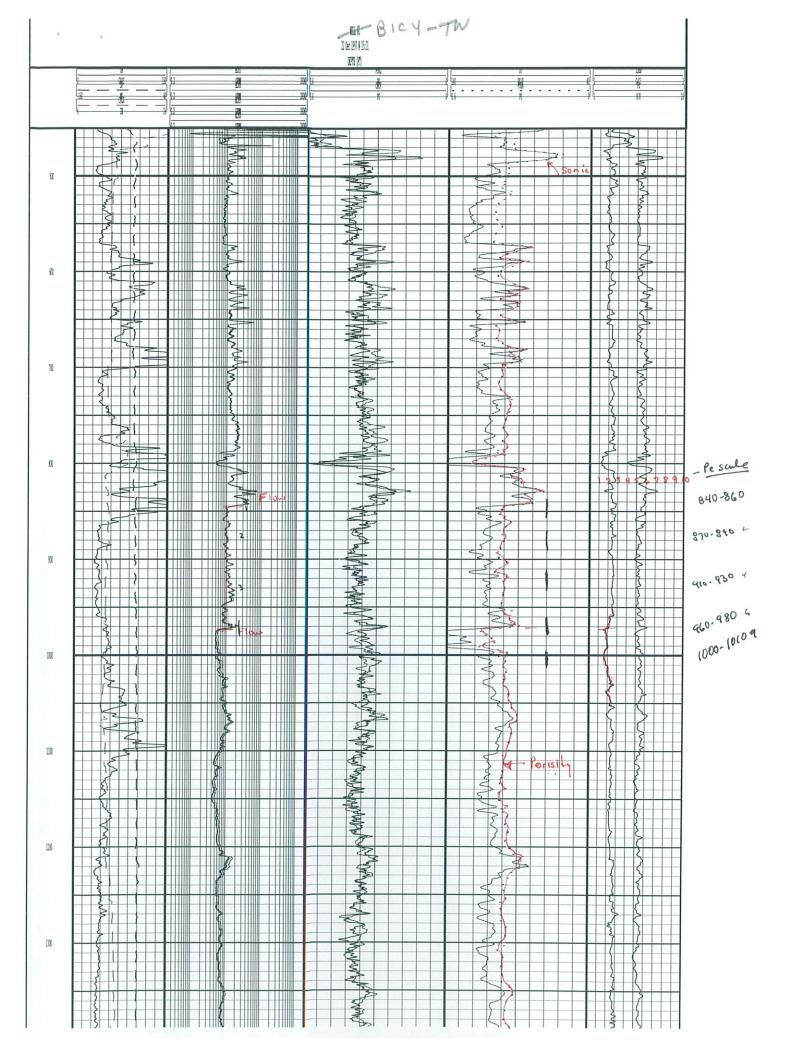
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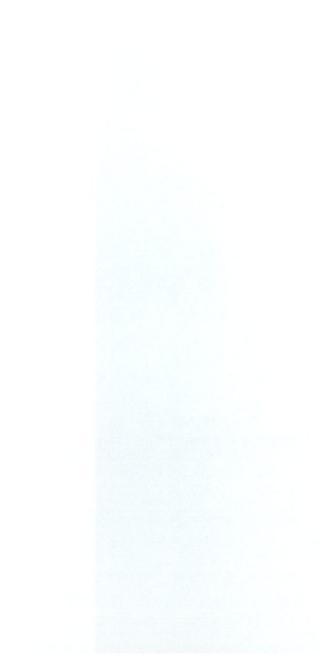
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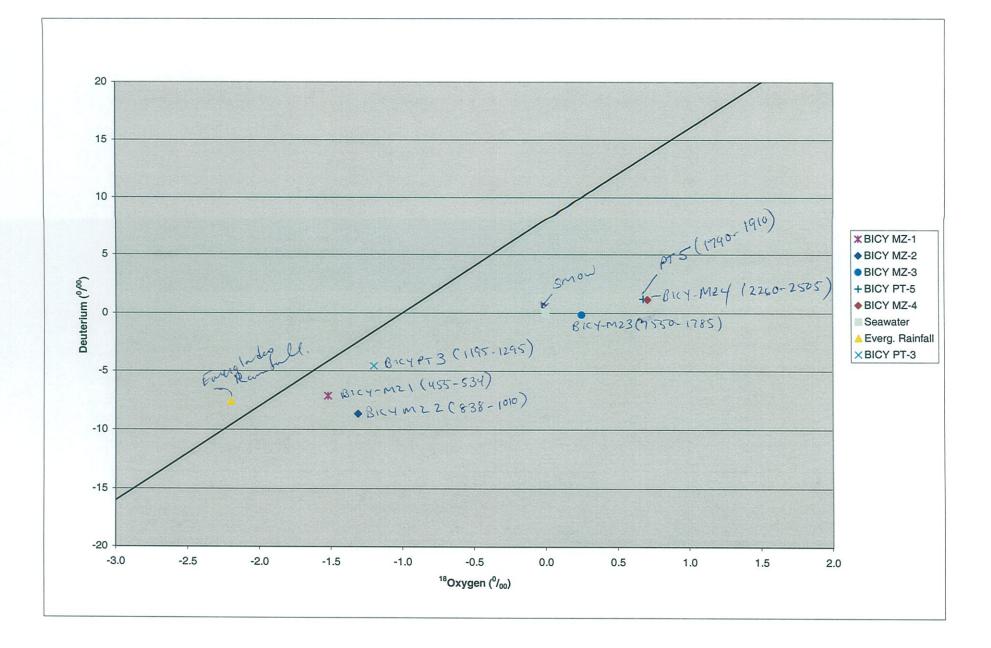


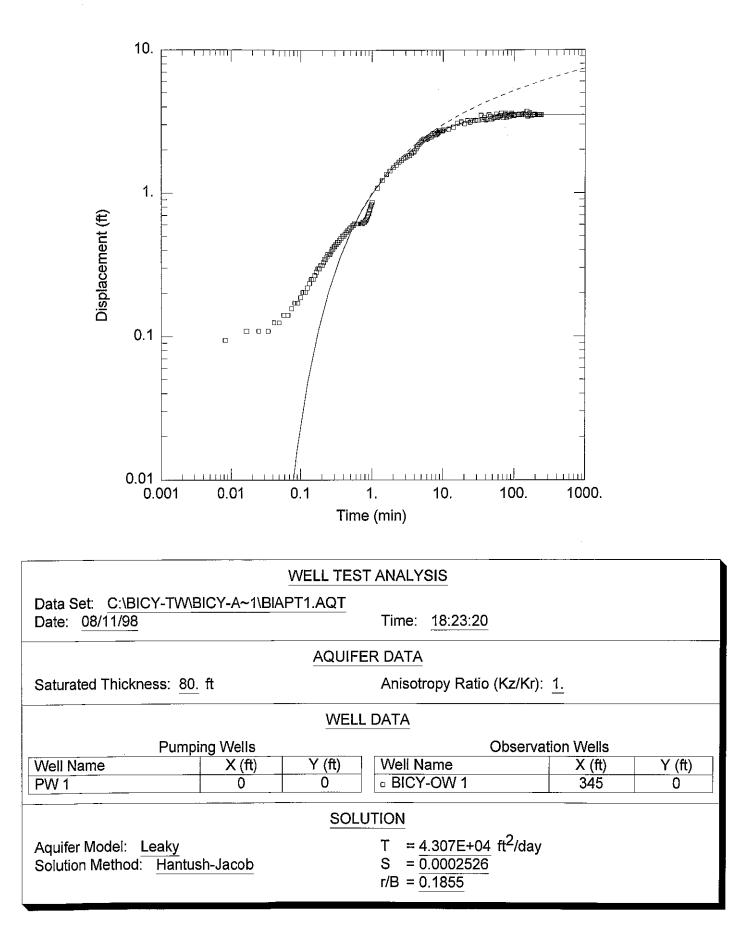
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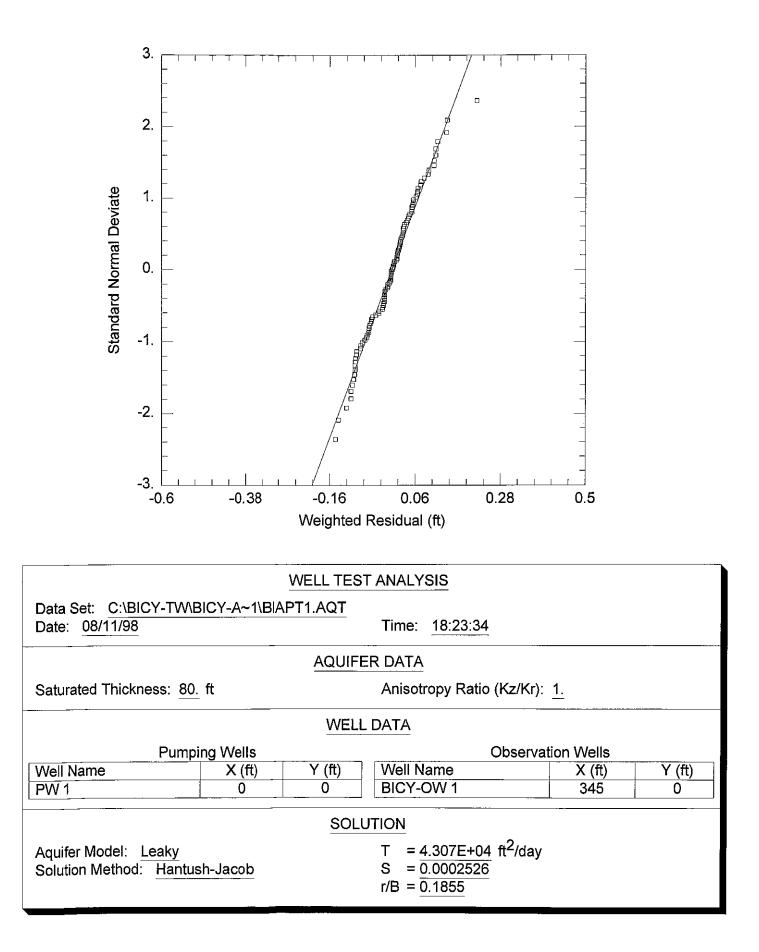


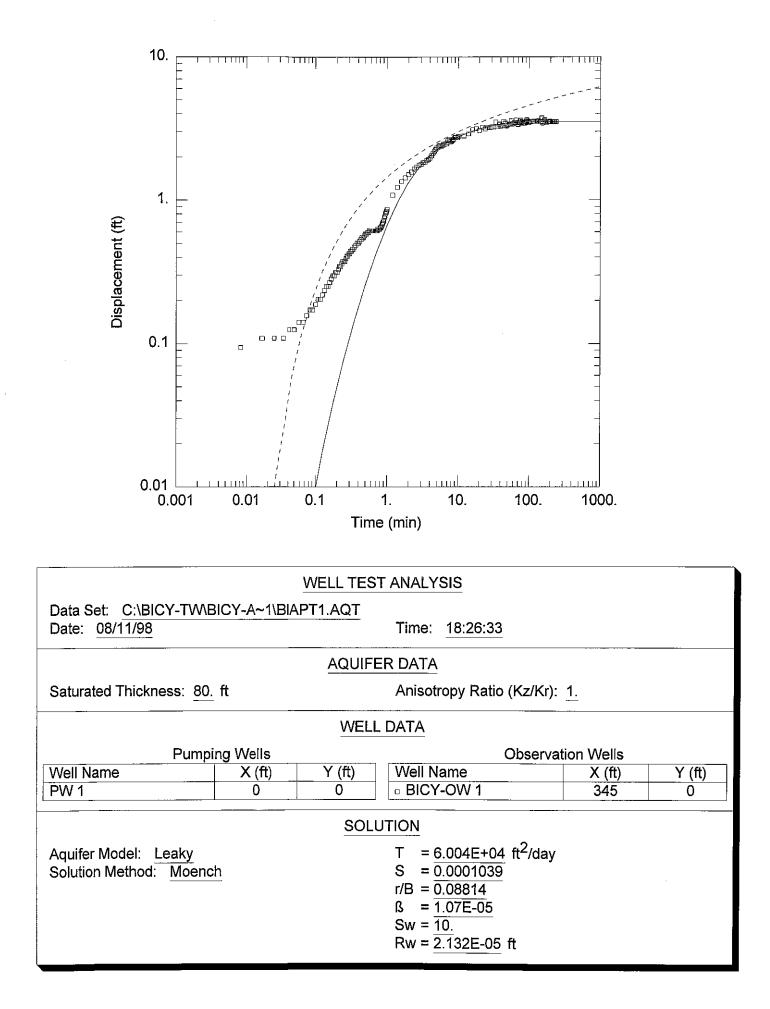
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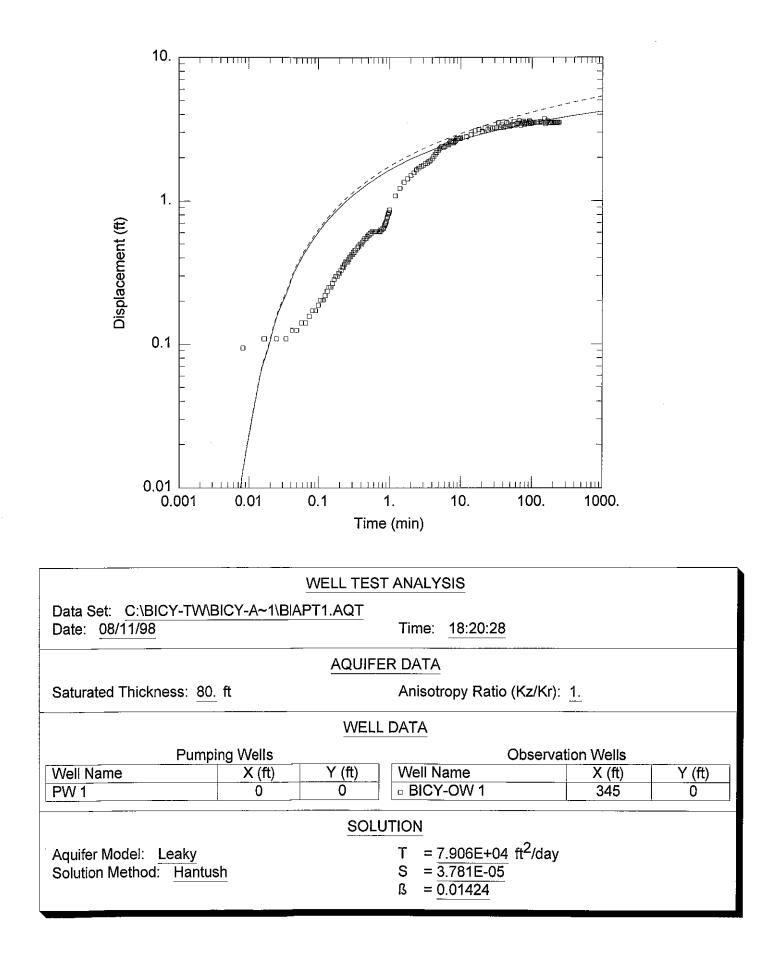


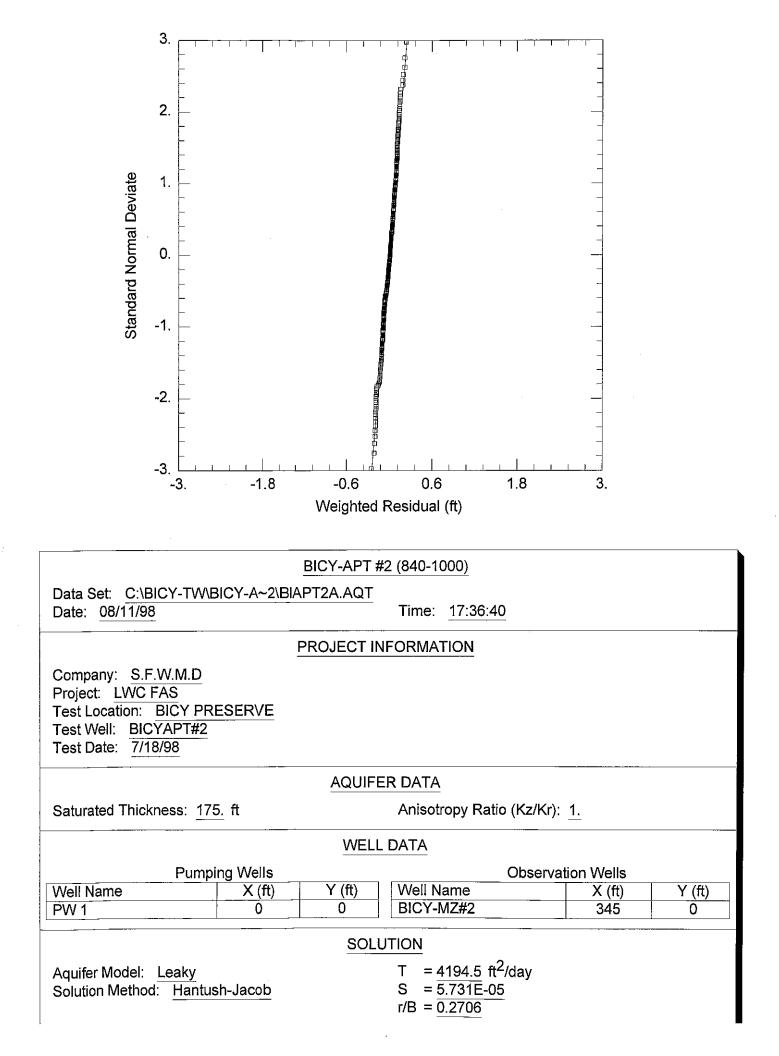


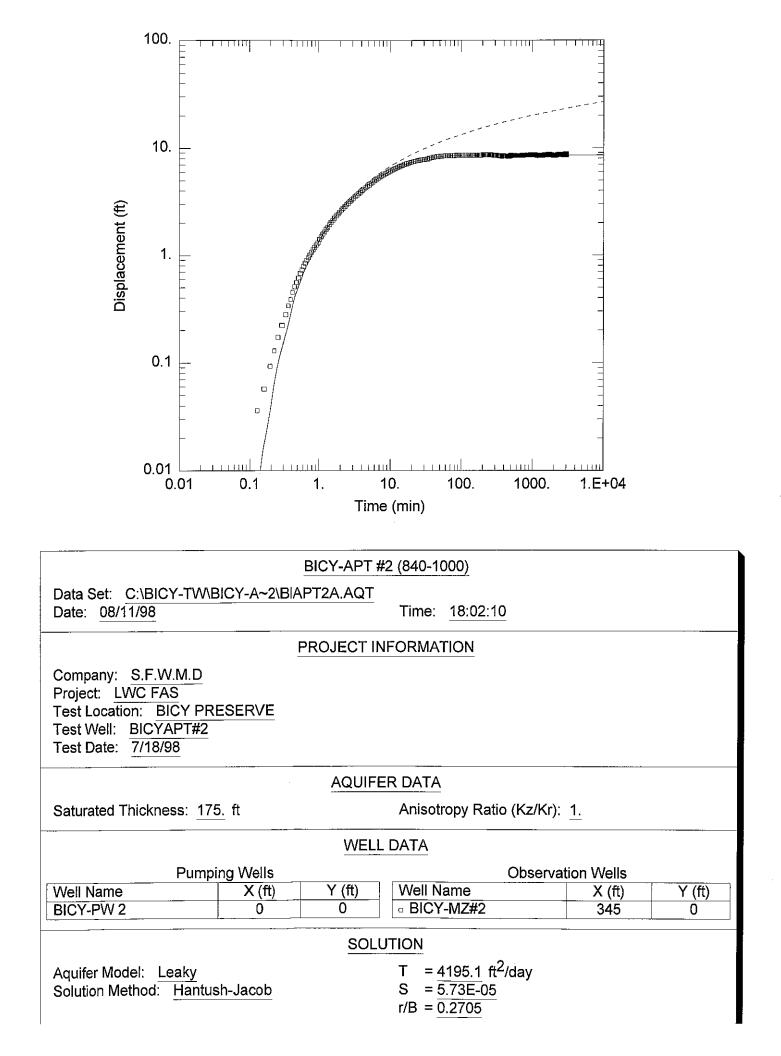


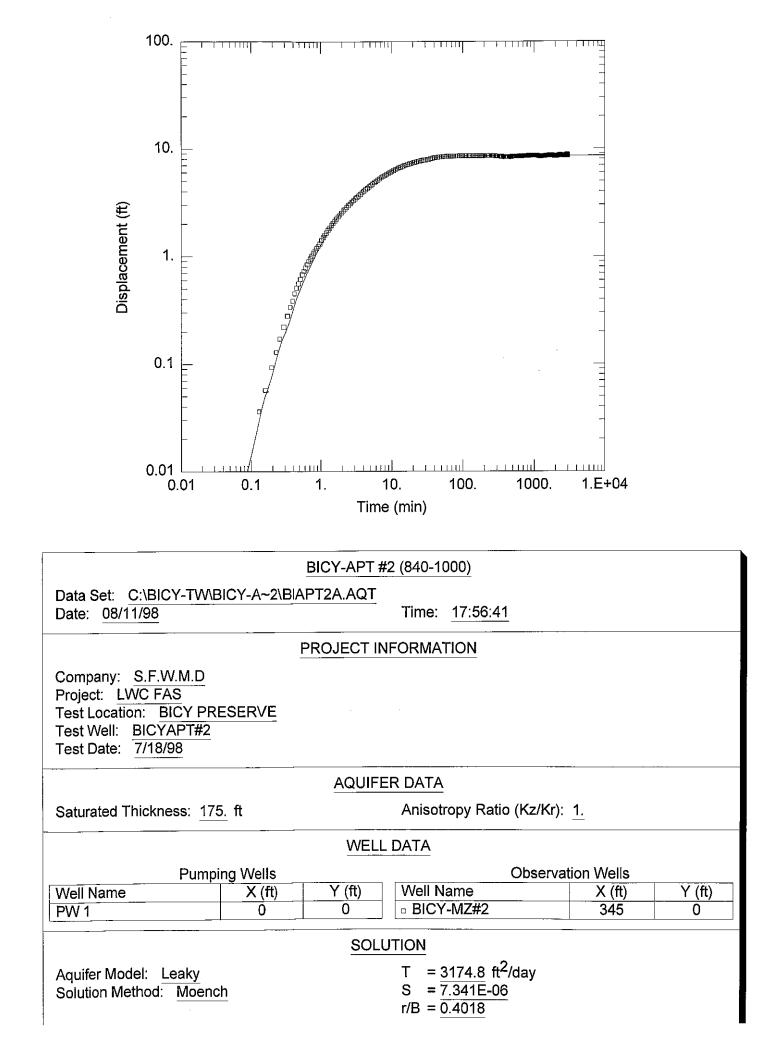








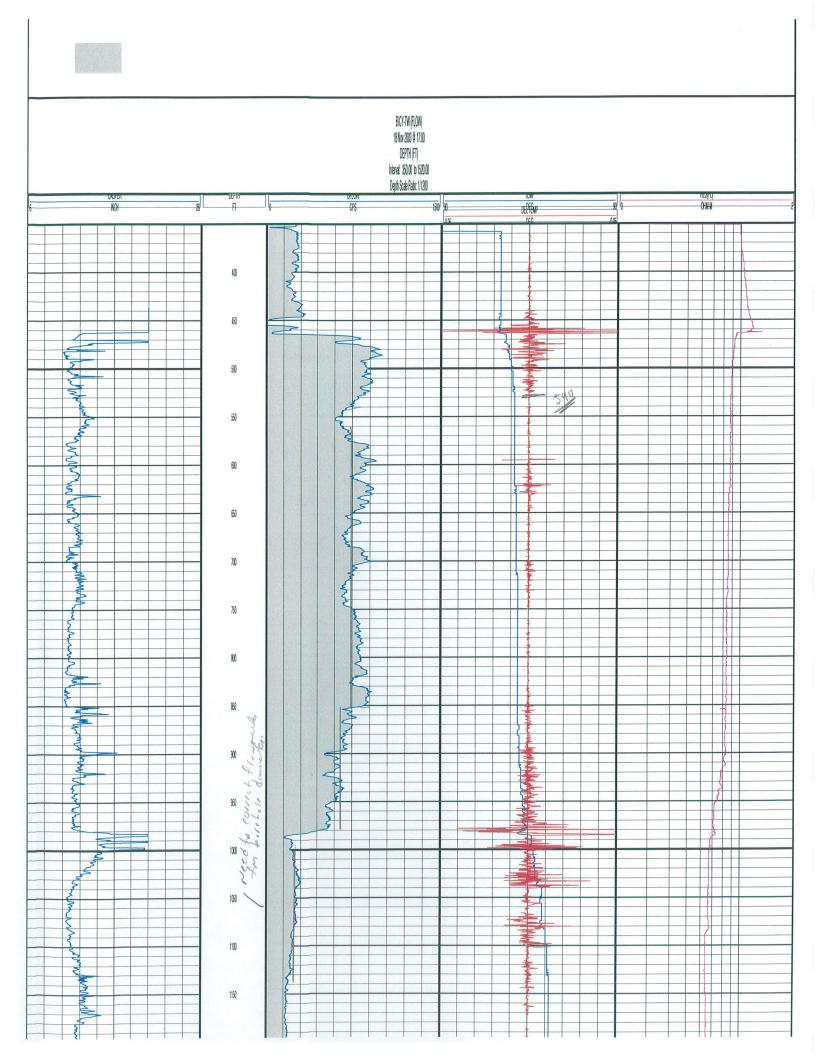




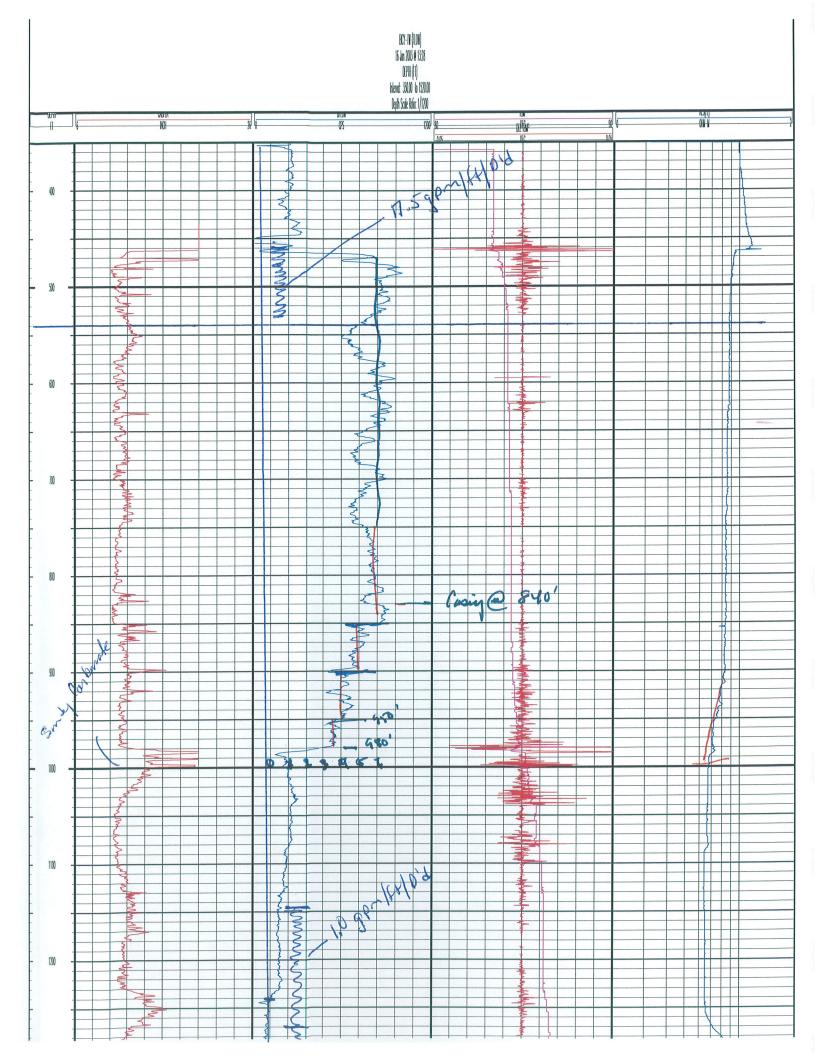
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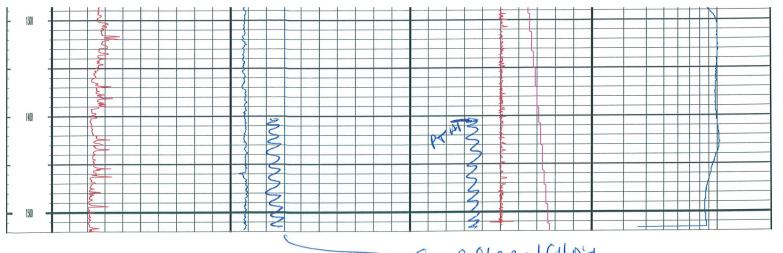
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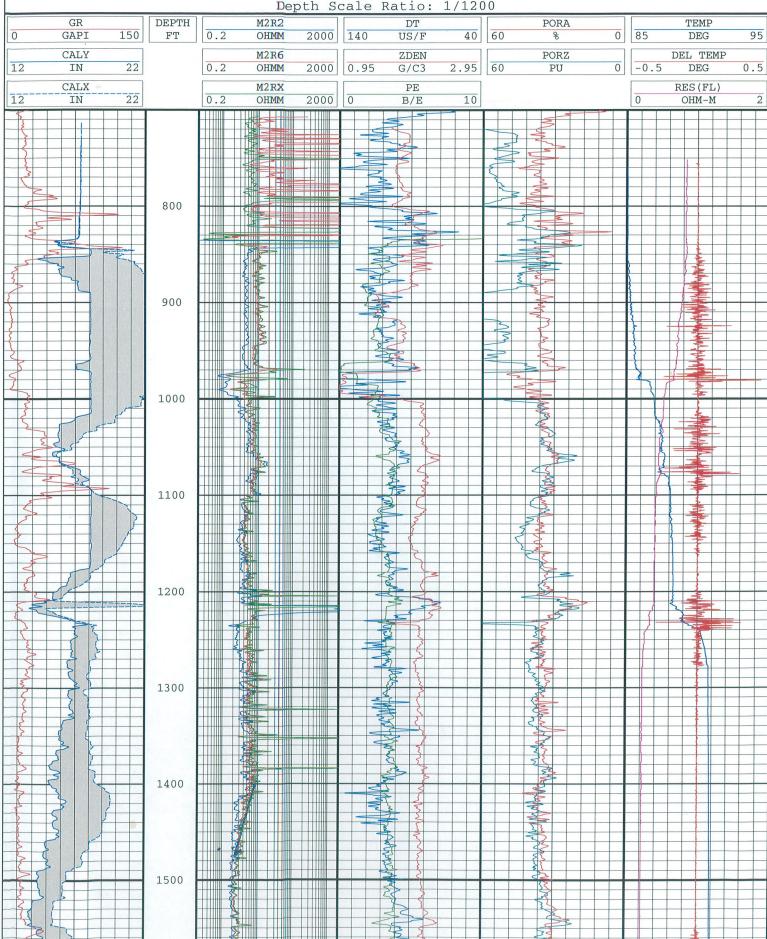
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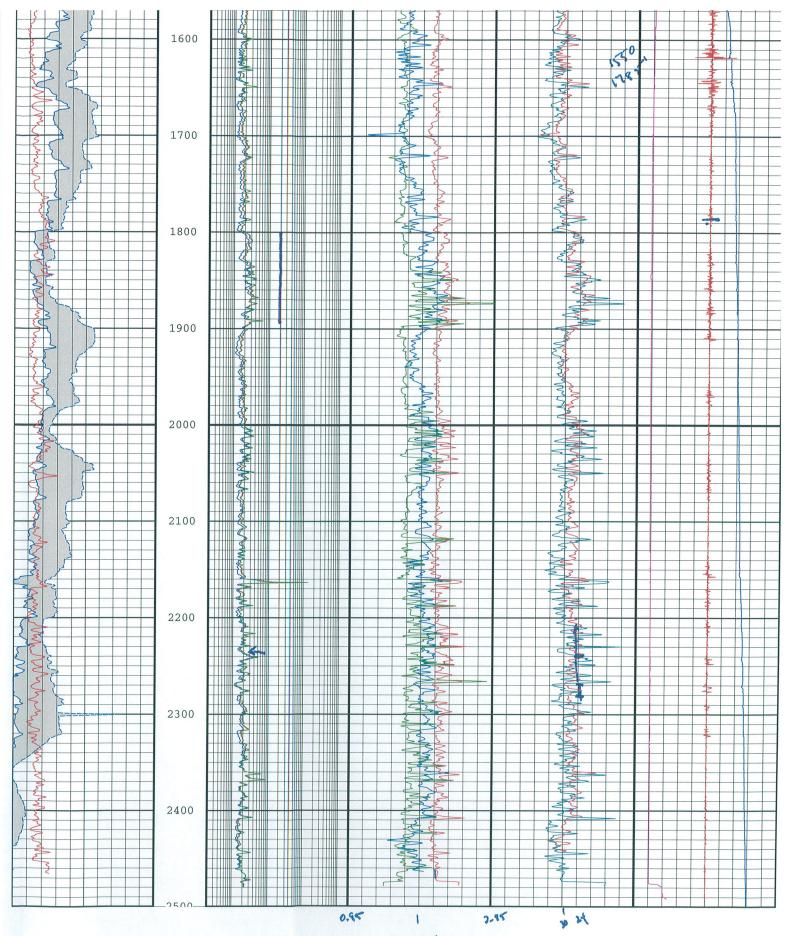
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CORRELATION OF BICY-TW CUTTINGS AND BICY-PW CORES

Seven transgressive markers are present in the SFWMD BICY-TW cuttings; five can be correlated with the SFWMD BICY-PW cores. The BICY-PW and the BICY-TW can be correlated on the basis of lithofacies type, fauna content, and facies. One of the best transgressive lithofacies markers is a transgressive lithofacies overlying a regressive mound complex in both wells. The transgressions are identified mainly on the basis of the deeper water fauna, fauna diversity, and foram assemblages. The following correlations of the transgressive markers were made:

BICY-TW		BICY-PW
1. 820-825'		No core
2. 840-845'		850-854.2'
3. 870-875'		Core gap
4. 895-900'		899.2-900.5'
- 900-905'	regressive sequence	900.5-901'
5. 915-920'		921.5-922.2'
6. 940-945'		941.1-941.1'
7. 975-980'		970-976.4'

The upper transgressive lithofacies at 825 to 830' in the BICY-TW consists of an echinoid-foram-pellet packstone to foram wackestone. It does not correlate with the BICY-PW core because no core exists for this interval.

The transgressive facies at 840-845' in BICY-TW consists of a sandy echinoid-skeletal-pellet packstone, which correlates with the foram intraclasticmolluscan wackestone at 850-854.2' in the BICY-PW. An assemblage of red algae, echinoids, and deeper water forams indicates a transgression in the BICY-TW. This unit also has a high gamma ray reading.

The transgressive lithofacies at 870-875' in the BICY-TW consists of skeletal-bryozoa-foram-pellet packstone. It correlations with a core gap at 862.4-879' in the BICY-PW.

A transgressive lithofacies at 895-900' in the BICY-TW consists of a foram-pellet packstone to skeletal-algal-foram-pellet packstone. It correlates with a transgressive pellet-foram packstone at 899.2-900.5' in the BICY-PW.

The previously described transgression overlies a major regressive sequence present in both wells. This regressive lithofacies in the BICY-TW consists of an algal-bryozoan boundstone, while in the BICY-PW the lithofacies consists of a coral boundstone. Both lithofacies indicate shallow mound complexes throughout the area of the two wells.

A slight transgression occurred at 915-920' in the BICY-TW. It consists of an echinoid-coated grain-foram-pellet packstone to echinoid-foram-pellet packstone. This lithofacies correlates to a pelecypod wackestone to pellet-foram packstone in the BICY-PW at 921.5-922.2'.

A transgressive lithofacies at 940-945' in the BICY-TW consists of a slightly sandy peloid-pellet-foram packstone. It correlates with a pelecypod coquina-grainstone at 941.1-941.4' in the BICY-PW well. The BIC-TW lithofacies at 940-945' contains an abundant and diverse foram assemblage consisting of deeper water forams.

The transgressive lithofacies at 975-980' in the BICY-TW consists of an echinoid-coated algal-peloid-foram-pellet packstone. It correlates to a very sandy pellet-intraclast packstone to very sandy intraclastic-pelecypod coquina at 980-981.6' in the BICY-PW well. The lithofacies in the BICY-TW also contains a diverse and abundant assemblage of forams.

The transgressive lithofacies at 1010-1015' starts the top of the next overlying transgression. This lithofacies in the BICY-TW consists of coated grain-peloid-foram pellet packstone-sandy foram wackestone. This lithofacies represents the beginning of a transgression and is characterized by echinoids and the beginning of a foram fauna change. The lithofacies in the BICY-TW does not correlate to the BICY-PW because it is below the BICY-PW core interval.

Generally, the BICY-TW is more shoreward of the BICY-PW. The BICY-TW contains much more sand throughout, more dolomite, and a more <u>shoreward</u> sequence of lithofacies. Coated grains and peloids are a more common allochem. Also there are much fewer molluscan fragments and coquinas observed in the BICY-TW than in the BICY-PW. The BICY-TW foram assemblage is a more shallow assemblage, except in the transgressive lithofacies.

October 10, 2001

Ron Shaw Hughbert Collier

		Measurement	- Horizontal- Permeability	Porosity		
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		855.4				
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859.0 - 862.4	FORAM MOLLUSCAN PACKSTONE	859.3		10.5		
		860.1				
		861.3				
		862.5		·	1	
		Mean			l .	
l		· · · · · · · · · · · · · · · · · · ·	·	·	1	
879.0 - 882.2	FORAM PELECYPOD PACKSTONE	879.9	164.00	32.0	4	
077.0 - 0.0		880.3			4	
<u> </u>		880.3 Mean			1	
			1/00.00	VI. 140	1	
				074	1	
899.0 - 899.2	GASTROPOD-PELECYPOD COQUINA	899.1	712.00	27.4	1	
<u>⊦</u>	<u> </u>	L	ليجتب	L	1	
899.2 - 900.5	PELLET-FORAM PACKSTONE	900.1	492.00	34.4	1	
					1	
900.5 - 901.0	CORAL BOUNDSTONE	901.1	11069.00	38.4	1	
			·		1	
	/				1	
919.0 - 920.5	GASTROPOD-PELECYPOD WACKSTONE-PACKSTONE	919.3	76.70	36.4	1	
-		919.8			1	
		Mean			1	
<u> </u>			+		1	
920.5 - 921.5	C APTO OPON CO ATED OD AINC OD AINCTÓNIE	920.8	1660.00	37.2	i	
920.3 - 921.5	GASTROPOD-COATED GRAINS GRAINSTONE	820.0	1000.00	37.2	i i i i i i i i i i i i i i i i i i i	
			1500.00		i	
921.5 - 922.2	PELECYPOD WACKESTONE-PELLET FORAM-PACKSTONE	921.5	4569.00	32.6	i i i i i i i i i i i i i i i i i i i	
		L	<u>نے ب</u>	<u> </u>	i i i i i i i i i i i i i i i i i i i	
922.2 - 923.0	CHALKY INTRACLASTIC WACKSTONE-PACKSTONE	922.2	1.18	22.1	<i>i</i>	
			·	·	i	
940 - 941.1	CHALKY COATED GRAINS INTRACLASTIC PACKSTONE	940.5	0.81	21.8	i i i i i i i i i i i i i i i i i i i	
			·	·	i i i i i i i i i i i i i i i i i i i	
970-976.4	CHALKY FORAM PELOID PELLET PACK-GRAINSTONE	970.6	81.40	31.5	i i i i i i i i i i i i i i i i i i i	
	TO	971.7	170.00		i i i i i i i i i i i i i i i i i i i	
	SANDY INTRACLASTIC FORAM PELLET PACKSTONE	972.1	3238.00			
	SANDT INTRACKONST CHAINT ELECT CHOINE STOL	972.1			, · · ·	
			581.00			
		975.7	1.45	24.1	,	
		Mean	814.37	31.46		
		·				
980 - 981.6	VERY SANDY PELLET-INTRACLAST PACKSTONE	980.9	17.80	26.6	,	
			·			
981.6 - 983.8	VERY SANDY SLIGHTLY INTRACLASTIC PELECYPOD COQUINA	981.6	4033.00			÷
		982.1	1724.00			
	· · · · · · · · · · · · · · · · · · ·	983.1	7562.00			
		Mean	3334.20			
			0007.20			
		0941		26.0		
984 - 985.3	SANDY, SLIGHTLY INTRACLASTIC PELECYPOD COQUINA	984.1	5720.00	26.0		
	174/14.14 · .	984.5	3695.00	31.3		
		Mean	4707.50	28.65		
		<u> </u>				
985.3 - 987.4	SANDY, CHALKY FORAM PELLET PACKST, ONE	985.6	91.80	23.9		
		986.5	9.19	24.3		
		Mean	50.50	24.10		
		·		<u> </u>		
987.4 - 988.2	CHALKY, SANDY INTRACLASTIC MUDSTONE-WACKESTONE	987.2	1.37	29.8		
	Cartan proto a material and a	987.7	2.02	29.0		
		967.7 Mean				
		- Wiçanı	1.70	28.75		
	A MARTINE A MARTINE A MARTINE A MARTINE	Gun u	48.60	30.0		
990 - 991.6	INTERBEDDED CHALKY SANDY COQUINA w/ SANDY, CHALKY SANDSTONE					
990 - 991.6	INTERBEDDED CHALKY SANDY COQUINA w SANDY, CHALKY SANDSTONE	991.2 Mean	11.20 29.90	18.0 24.00		

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