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Variations in the abundance of occluded light hydrocarbons (C_1-C_5) and their relation to diagenetic changes, in the Salt Wash Member, Late Jurassic Morrison Formation, Slick Rock district, San Miguel County, Colorado

by

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Abstract

Abundances of light hydrocarbons (methane to pentane) adsorbed and occluded in sandstones within the Salt Wash Member, Late Jurassic Morrison Formation were determined and evaluated. Total concentrations of these hydrocarbons range from 10 to 1000 µl/g. Chlorite-bearing sandstones contain significantly more methane, ethane, and propane than sandstones containing kaolinite. The lower hydrocarbon abundances of kaolinite-bearing rocks are probably related to alteration of chlorite and dissolution of carbonate minerals. Among chlorite-containing samples, gray sandstones have twice the abundance of hydrocarbons as red sandstones. No systematic variations in hydrocarbon content were detected near uranium-vanadium deposits, or near faults, which were conduits for solutions from depth. The proportions of hydrocarbon gases 83 percent methane, 11 percent ethane, 4 percent propane and 2 percent other, are uniform among samples and indicate a homogeneous gas source. Ethane and propane suggest a thermogenic origin of the gas, which probably originated in the Pennsylvanian Hermosa Formation.

Interpretation of the results was limited by the lack of understanding on where and how hydrocarbons are retained in sandstones. Abundances of hydrocarbons in Salt Wash sandstones are apparently independent of the abundances of aluminum (clays) and carbonate minerals. To properly interpret results of this and similar studies, the mechanisms of occlusion, adsorption, and preservation must be better known.

INTRODUCTION

Sandstones in the Salt Wash Member, Late Jurassic Morrison Formation, southwestern Colorado have been altered extensively by diagenetic fluids (Breit, 1986). Interpretations of the altered and authigenic minerals suggest organic compounds were an important component of diagenetic processes. To test the involvement of hydrocarbons in these processes, we measured the abundances of light hydrocarbons (C_1-C_5) adsorbed and trapped in authigenic minerals (i.e. occluded). Although light hydrocarbons are relatively unreactive, they may reflect the passage of more complex compounds responsible for the alterations. In this study, we found variations in the abundance of hydrocarbons in the Salt Wash related to changes in the assemblage of authigenic minerals. The most significant variations can be related to the different diagenetic histories of the rocks studied.

Measurement of occluded hydrocarbons originally was developed for use in petroleum exploration (Horvitz, 1969). The abundance of gaseous hydrocarbons has been demonstrated to vary systematically near some petroleum and natural gas accumulations, although the cause of the anomalies is controversial (Price, 1986). Practitioners of the technique propose that light hydrocarbons migrate upward from petroleum reservoirs through overlying rocks (Price, 1986). These hydrocarbons become trapped in precipitating carbonates and adsorb on clay minerals. Treatment of rocks with acid releases the occluded as well as adsorbed hydrocarbons into a gas phase, which can be easily analyzed.

This investigation focused on the Slick Rock uranium-vanadium district, San Miguel County, Colorado (Fig. 1). The Salt Wash Member in the Slick Rock district and vicinity has been studied extensively because it hosts significant uranium-vanadium (U-V) deposits. In these deposits, uranium and vanadium minerals impregnate the host sandstones and form tabular layers that are peneconcordant with bedding. The deposits are spatially associated with coalified plant fragments and occur wholly within gray sandstone.

Despite extensive study, the origin of these U-V deposits is still uncertain (Thamm and others, 1981). Part of the uncertainty is because the host rocks were altered by processes post-dating ore formation. In all models proposed to explain the U-V deposits and some subsequent diagenetic changes, organic compounds most notably organic acids, play a major role. Shawe (1976) proposed that warm (120°C), reducing solutions, which originated in black shales of the Late Cretaceous Mancos Shale, were responsible for dissolution of authigenic and detrital iron oxides (bleaching) and transport of U and V to sites of accumulation. Spirakis and Hansley (1986) proposed that U-V deposits in the Salt Wash were initially similar to those containing epigenetic organic matter elsewhere in the Morrison Formation. They suggested that

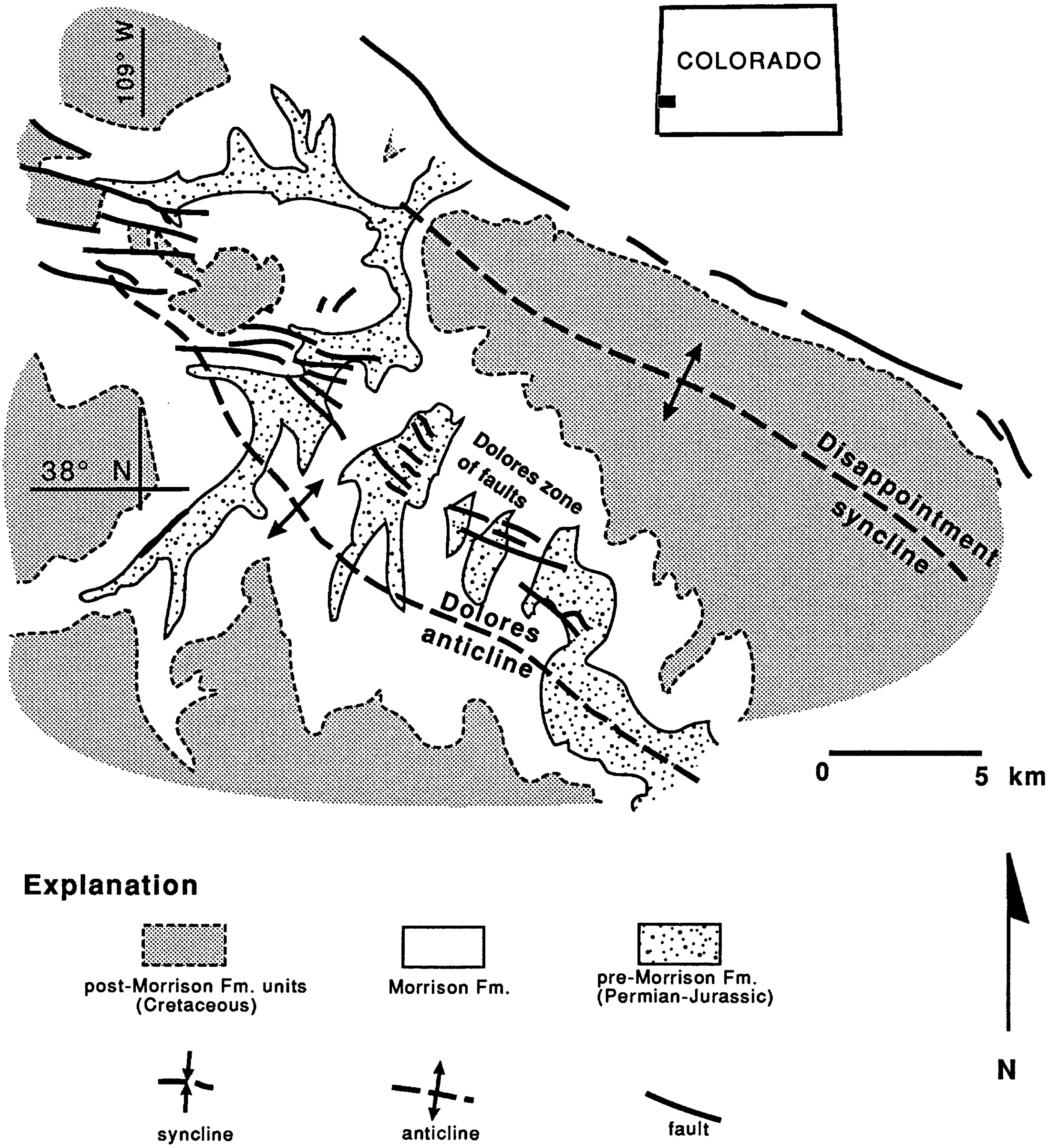

Figure 1: Generalized geologic map of the Slick Rock district, southwestern Colorado. Adapted from Shawe (1976)

subsequent thermal maturation and methanogenesis removed nearly all epigenetic organic matter. Breit and others (1987) determined that solutions, which originated in Pennsylvanian evaporites, moved upward along faults and laterally through the Morrison Formation. Minor amounts of asphaltite locally fill some fractures (Weir and Puffet, 1981), indicating petroleum may have been a component of these fluids. Considering these interpretations, hydrocarbons transported with solutions that altered Morrison sandstones may have been trapped in pore-filling carbonate cements or been adsorbed on clays.

As part of an oil field study in Wyoming, Fisher (1986) noted variations in the abundance of hydrocarbons occluded in soils and rocks collected over sandstone-hosted, roll-type uranium deposits. He interpreted high contents of hydrocarbons over the chemically reduced sides of the deposits to be related to the reduction and precipitation of uranium. Wyoming roll-type deposits are genetically different from Salt Wash deposits (Fischer, 1970), but similar hydrocarbon variations were apparent in a few samples collected across a Salt Wash-hosted deposit (Fisher, 1986). Detection of systematic variations in the abundance of gaseous hydrocarbons relative to U-V deposits could aid in locating these deposits as well as understanding their origin.

GEOLOGY

Geology of the Slick Rock uranium-vanadium district has been described by Shawe and co-workers (Shawe, 1968; Shawe and others, 1968; Shawe, 1970; Shawe, 1976). Outcrops along steep canyons expose a thick section of sedimentary rocks (Fig. 2) many of which are red beds deposited in continental environments. The district is located near the southern limits of the salt anticline province on the Colorado Plateau (Cater, 1970). Gentle folds within the district formed by the periodic, diapiric rise of evaporites in the Pennsylvanian Hermosa Formation (Cater, 1970; Atwood and Doelling, 1982). These evaporites are exposed along the axis of Gypsum Valley anticline due to collapse of overlying rocks after dissolution of some of the bedded salts.

Normal faulting within the Slick Rock district also is related to salt tectonics (Shawe, 1970). The Dolores zone of faults (Fig. 1) was periodically active during the Mesozoic with major movement during the Late Cretaceous and early Tertiary (Shawe, 1970). Vertical offset of the Morrison Formation along these faults increases from east (2 m) to west (30 m) across the district. Westward, the Dolores zone of faults trends into the Lisbon Valley fault, which has a maximum vertical displacement of 1200 m (Weir and Puffet, 1981).

The Morrison Formation consists of fluvial and lacustrine units (Shawe and others, 1968) deposited in a seasonal, semi-arid

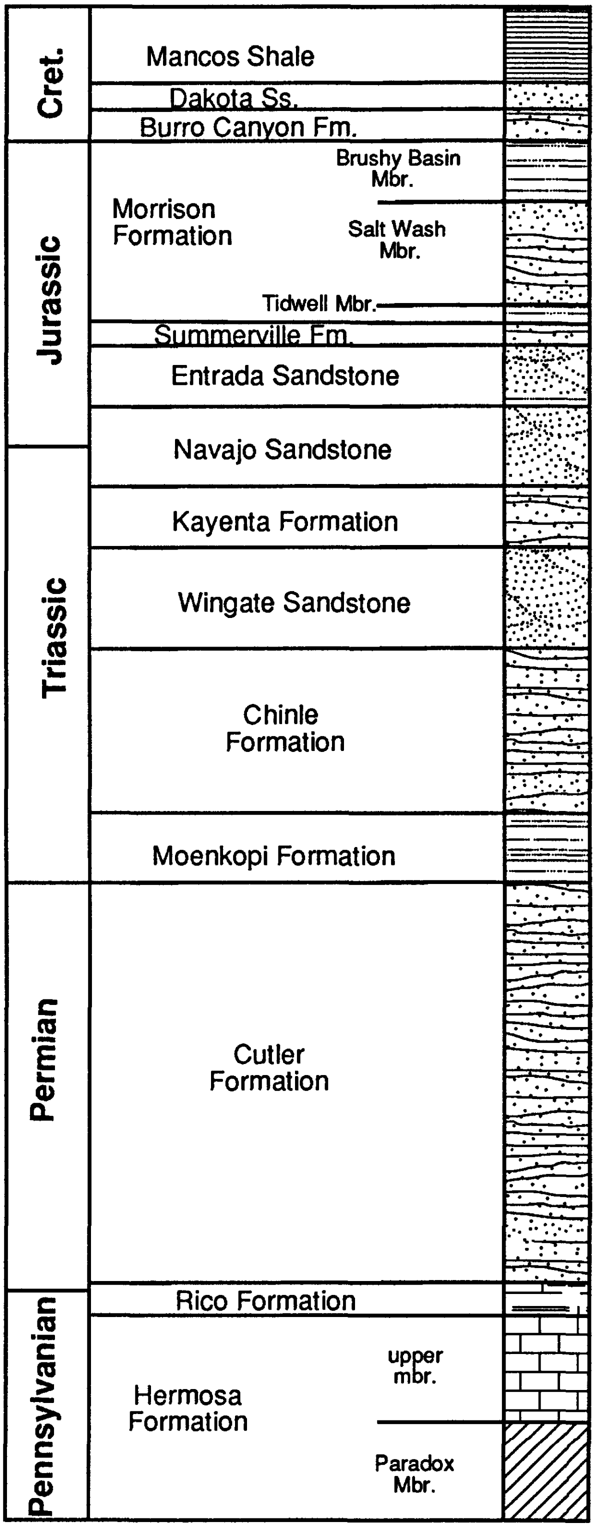

Figure 2: Generalized stratigraphic section of rocks within the Slick Rock district

climate (Tyler, 1981). From oldest to youngest, the Morrison in the study area is divided into the Tidwell, Salt Wash, and Brushy Basin Members. The Salt Wash is approximately 90 m thick and contains interbedded, fluvial sandstones and mudstones that were deposited in an aggrading alluvial system. Most samples examined in this study are from a laterally continuous sandstone which forms the upper 30 m of the Salt Wash. This sandstone is known as the ore sand because it hosts most of the U-V deposits.

Salt Wash sandstones are multicycle sedimentary rocks. They range from sublitharenites to quartz arenites (Tyler, 1981), are medium to fine-grained and are poorly to moderately sorted (Cadigan, 1967; Tyler, 1981). Constituent detrital grains include quartz, feldspars, chert, illite, and rock fragments (Cadigan, 1967; Shawe, 1968; and Tyler, 1981). Within the Slick Rock district, Salt Wash sandstones contain a complex and variable assemblage of authigenic minerals (Breit, 1986). This assemblage includes albite, barite, calcite, chlorite, chalcedony, dolomite, hematite, illite-smectite, kaolinite, pyrite, quartz overgrowths and smectite. Calcite is the most abundant authigenic phase. The assemblage of minerals in the Disappointment syncline (chlorite, Na-feldspar) differs from that on the Dolores anticline (kaolinite, dolomite) (Fig.3). The authigenic minerals formed during a complex diagenetic history which is summarized below.

Post-depositional changes to the Salt Wash sediments are divided into four broad episodes including 1) early diagenetic, 2) changes with increased burial, 3) alteration by solutions which entered through faults, and 4) weathering (Breit, 1986). Soon after deposition of the Salt Wash sediments, smectites, carbonates, and relatively pervasive ferric oxides precipitated from alkaline, generally oxidizing pore waters. As these early phases precipitated, reducing conditions were established near accumulations of detrital plant fragments. These reducing conditions favored accumulation of uranium and vanadium (Thamm and others, 1981). Concomitant with increased burial many of the early-formed minerals were recrystallized and redistributed. During deepest burial, 3-4 km (Late Cretaceous-Early Tertiary), warm (100°C), saline solutions entered the Morrison Formation through faults (Morrison and Parry, 1986). These solutions contained dissolved solids from evaporites in the Hermosa formation (Breit and others, 1987). Dolomite, calcite, barite, and minor amounts of asphaltite were precipitated, and iron oxides were dissolved locally by these solutions. In addition, these fluids formed copper deposits along the Lisbon Valley fault (Morrison and Parry, 1986) and enriched the copper contents of U-V deposits along the Dolores zone of faults (Shawe and others, 1959). As Late Tertiary erosion removed overlying rocks, meteoric water flowed preferentially through sandstones on the Dolores anticline. These solutions altered chlorite and plagioclase, and precipitated kaolinite (Fig. 3).

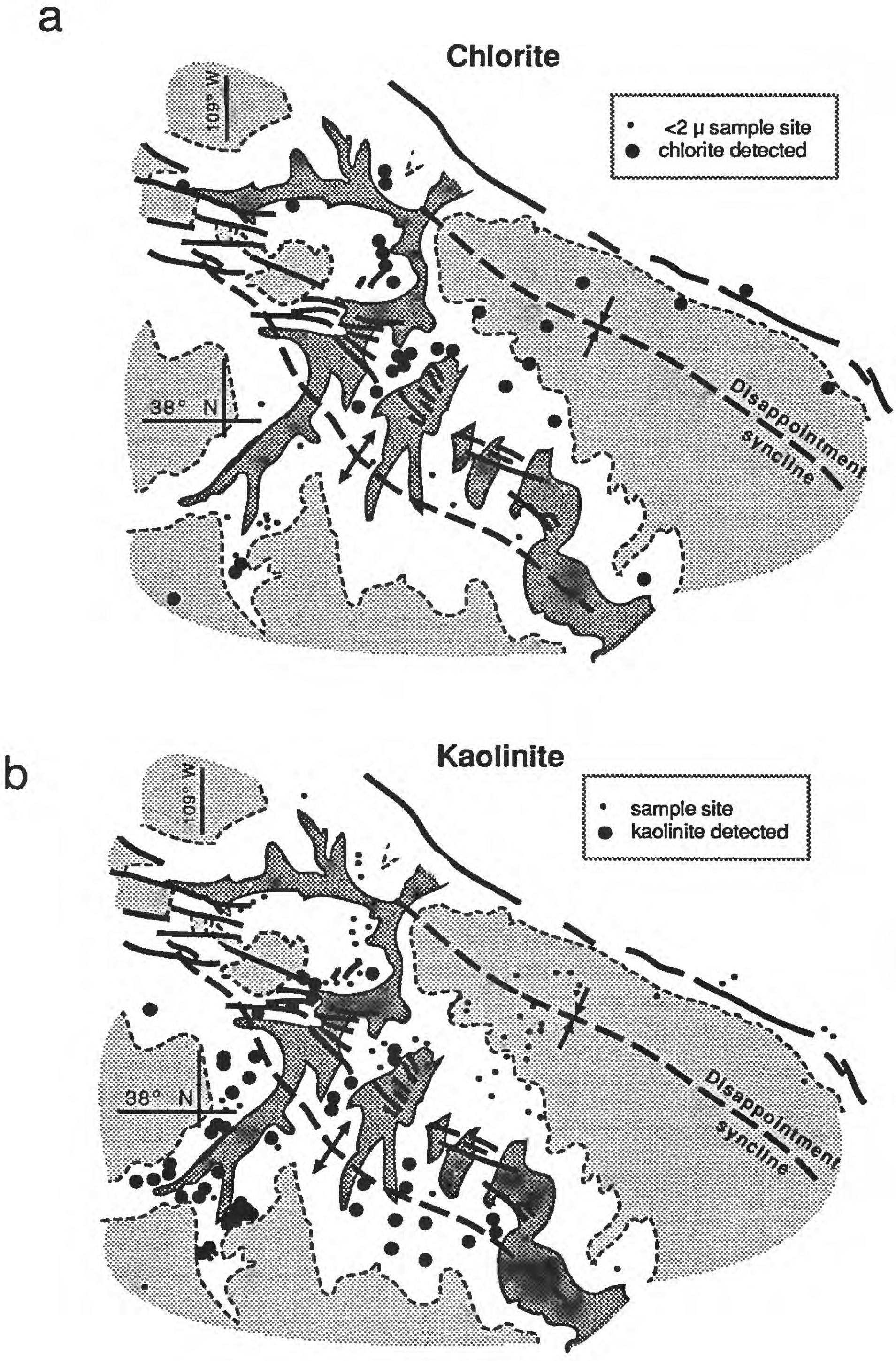

Figure 3: Distribution of a) chlorite, b) kaolinite, c) dolomite, and d) plagioclase in the upper sandstone of the Salt Wash Member, Morrison Formation within the Slick Rock district.

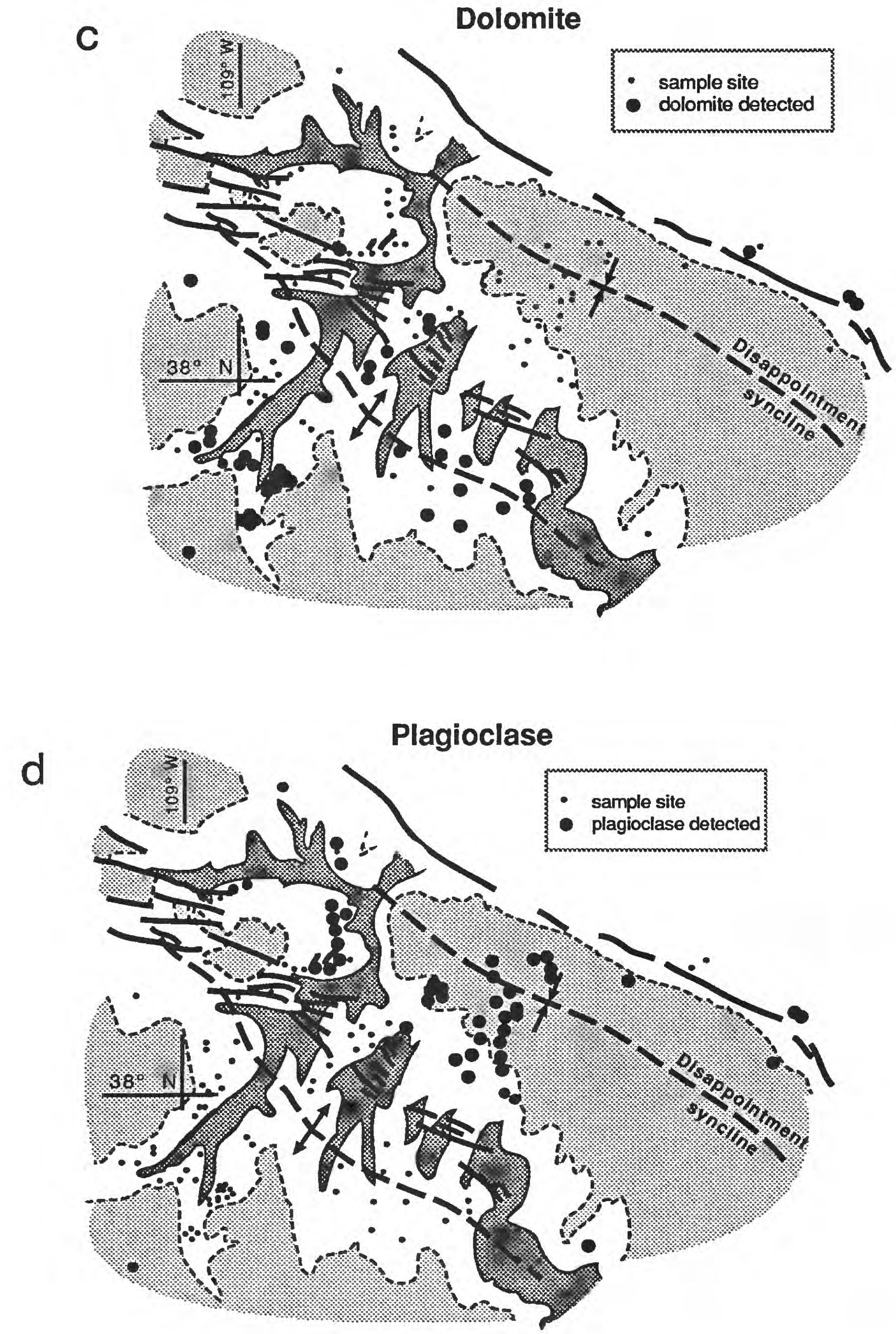

Figure 3: (cont.)

A product of Morrison diagenesis is the contrast between gray/green and red rocks. The gray/green color is generally attributed to reducing solutions which contained organic compounds. Proposed sources of the organic-bearing solutions include the Mancos Shale (Shawe, 1976), Morrison depositional waters (Breit, 1986), and brines from underlying evaporites (Breit and others, 1987). Preserved organic matter within the Morrison Formation in the Slick Rock district is limited to scattered accumulations of coalified plant fragments. No petroleum or natural gas accumulations have been detected in the Morrison near the study area. However, the Mississippian Leadville Limestone and the Hermosa Formation are important oil producers along the western edge of the district.

METHODS

This study was conducted in two phases. The first phase determined whether a) Salt Wash sandstones contain detectable and variable amounts of occluded and adsorbed hydrocarbons, and b) differences in hydrocarbon contents among samples containing different assemblages of authigenic minerals. The results of this evaluation indicate samples from the Disappointment syncline (contain chlorite) consistently had higher hydrocarbon contents. Therefore, the second phase focused on samples from the syncline. The detailed study was designed to examine variations in the abundance of hydrocarbons related to a) rock color, b) proximity to U-V deposits, and c) distance from faults.

Samples were selected to optimize areal coverage within the Slick Rock district and to test variations relative to the U-V deposits. Locations are plotted on Figures 4 and 5. Samples from a drill core located in a relatively undeformed area 17 miles west of the Slick Rock district (EP1875; S28,T32S,R24E) were selected for comparison. Samples from this core contain the same assemblage of authigenic minerals as samples from Disappointment syncline.

Outcrop and core samples were disaggregated in a ceramic mortar and pestle. Core samples were generally more competent and were first broken into 1/2" pieces using a hammer and plate. The greater hardness of core samples is due mainly to better preservation of carbonate cements. During disaggregation, care was taken not to break many of the detrital grains. Light grinding was intended to concentrate the carbonate minerals and clays in a fine size fraction which was concentrated by sieving to -170 mesh (0.090 mm). Horvitz (1969) reviews the advantages of analyzing the fine size fraction. Replicate splits were separated prior to grinding.

Splits of the -170 mesh fraction used in the second phase of the study were analyzed to determine the abundance of total and

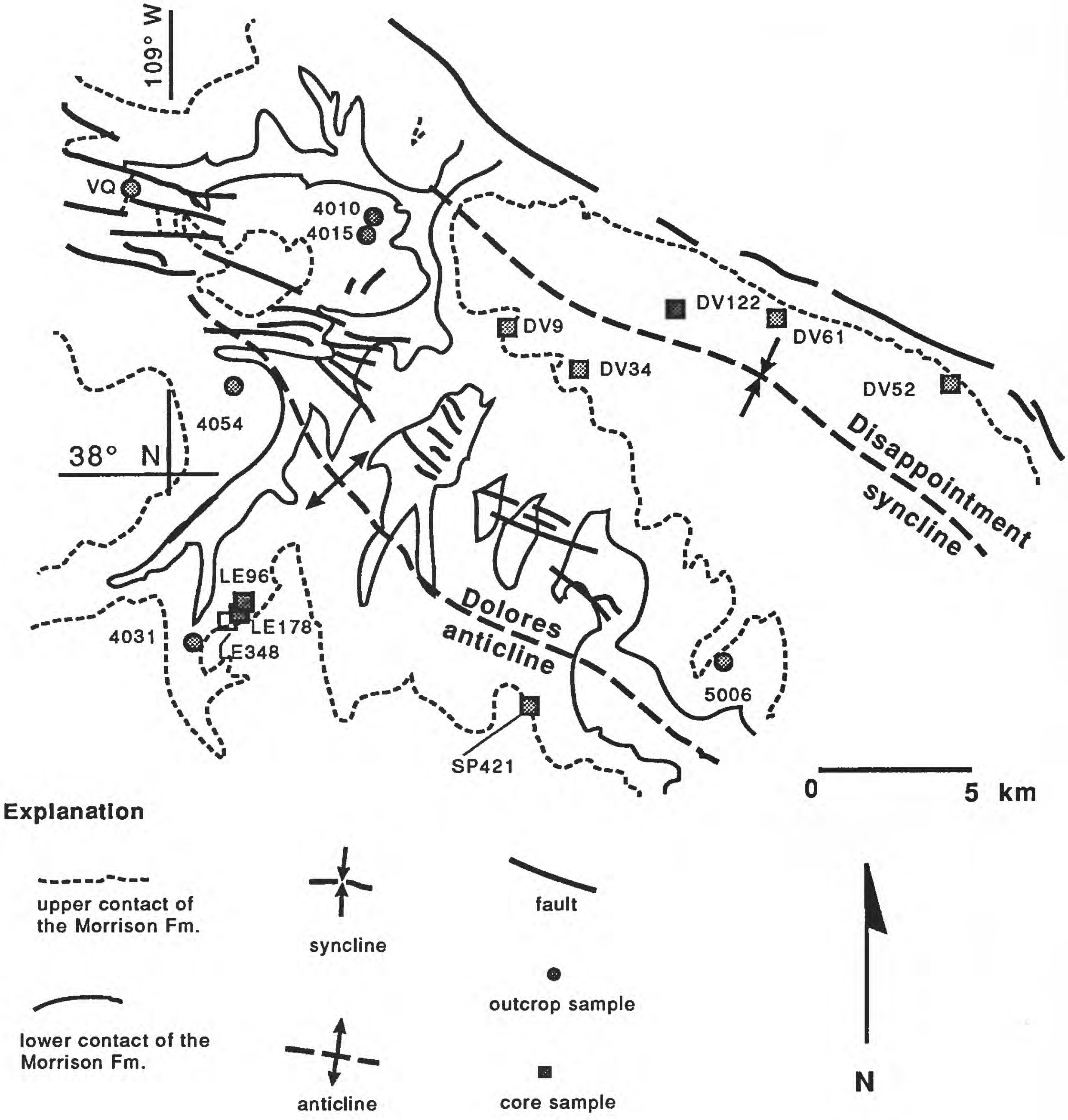

Figure 4: Location of samples used in the first phase of the study -- evaluation of the technique

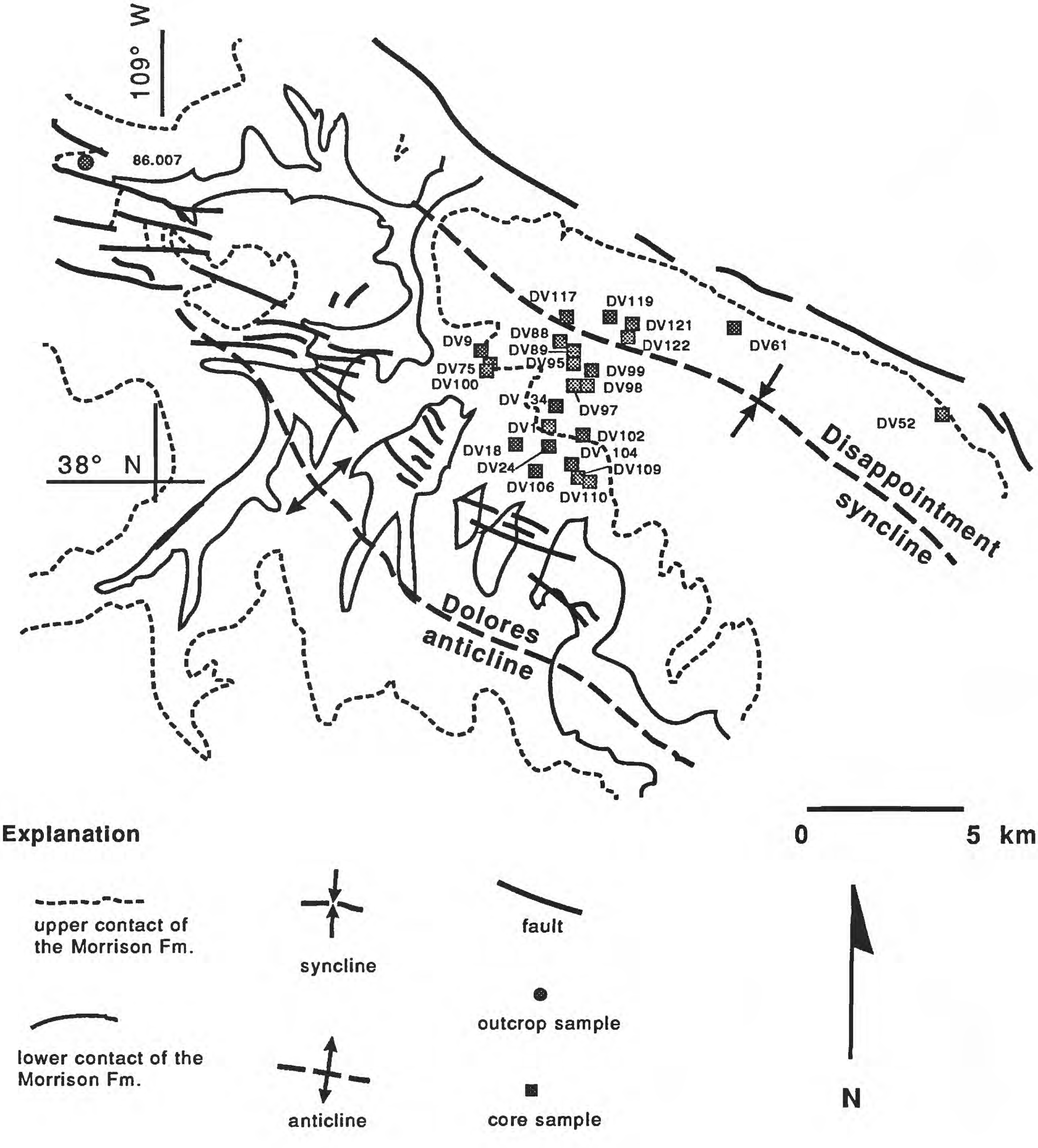

Figure 5: Location of samples used in the detailed study of Salt Wash Member sandstones from Disappointment syncline.

organic carbon using a Leco® induction furnace according to the method of Stanton and others (1983). Previous analyses (Breit, unpublished data) determined that only samples with visible coalified plant fragments contained detectable organic carbon (C_{org}) (> 0.05 wt. percent). Samples that contain visible organic matter and their organic carbon contents are DV1 566, 0.05 wt.percent; DV9 806, 5.2 wt.percent; DV 18 276, 0.2 wt.percent and DV-122 1263, 0.2 wt.percent. Organic carbon abundances were determined by analyzing samples after treatment with HCl (Stanton and others (1983). This pre-treatment releases occluded hydrocarbon gases, therefore they are not included in the amount of organic carbon measured.

A random, one gram, -170 mesh sample was placed in a glass test tube capped with a rubber septum. The tube was evacuated to remove atmospheric gases, mixed with 50 percent phosphoric acid, and heated to approximately 70°C until effervescence ceased. Evolved gas, composed mainly of CO_2 from dissolution of carbonate minerals, was collected in a syringe and gas remaining in the test tube was displaced with water. Total gas volume was recorded. One milliliter of evolved gas was injected into a gas chromatograph equipped with an activated alumina column, and a flame ionization detector. Helium was the carrier gas. In small gas samples, a known volume of purified nitrogen was added to ease sample handling. The abundance of gases was determined by peak area integration. Retention time and concentrations of hydrocarbon gases were calibrated by analyzing mixed-gas standards. A typical chromatogram is presented on Figure 6. Variations in the amount of CO_2 evolved per gram of sample resulted in different detection limits. For 10 ml of total evolved gas the detection limit of the hydrocarbon gases is approximately 0.02 µl/g.

Statistical analysis of the data was performed using StatviewII®. The data more closely approximate normal distributions after logarithmic transformation; therefore, all calculations and statistical tests were conducted on log transformed data. In performing the statistical analysis, hydrocarbon gas concentrations below the detection limit were replaced by 0.01 µl/g in all calculations

RESULTS

First Phase - evaluation of the technique

Abundances of occluded hydrocarbons vary in samples from the Slick Rock district and define two different populations (Table 1). A Student's t-test comparison of the means of samples from the anticline and syncline indicate that methane, ethane, propane, and isobutane are significantly more abundant in samples from the

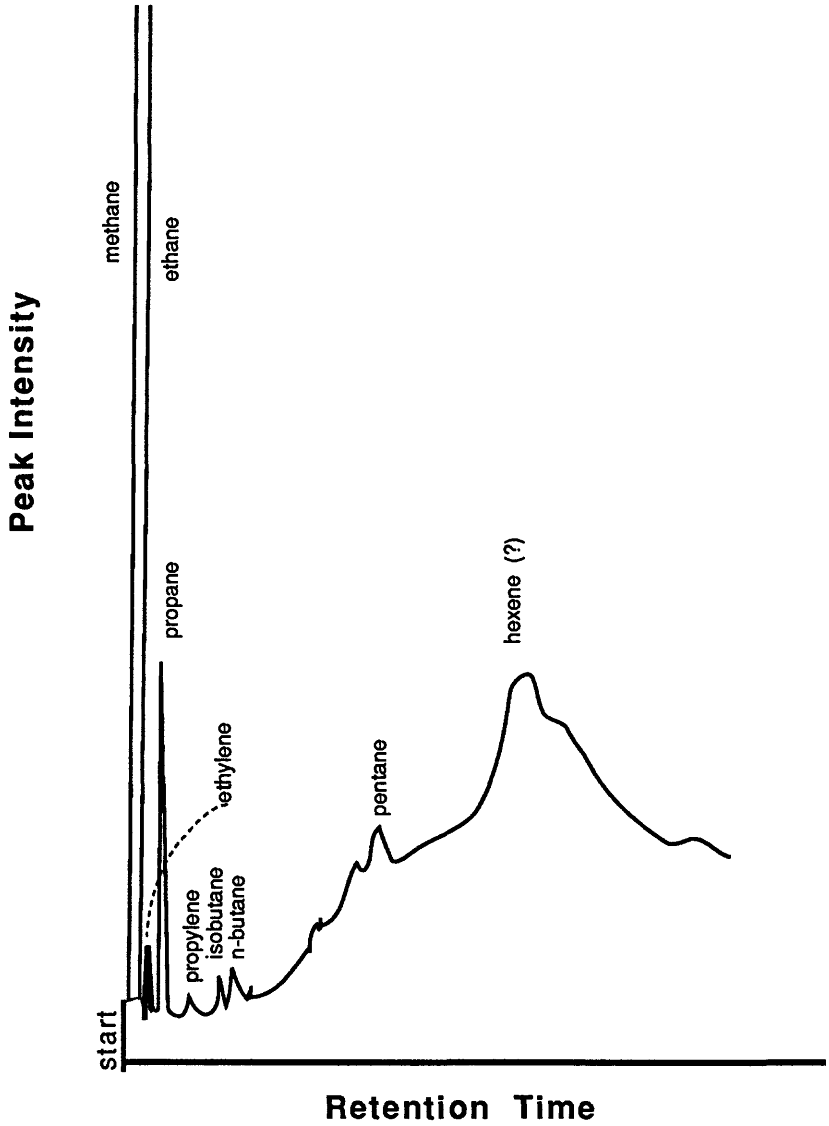

Figure 6: Typical chromatogram of gas extracted from a sandstone sample of the Salt Wash Member, Morrison Formation

Table 1: Results of analyses of samples used in the preliminary study. Sample locations are plotted on Fig. 4. Samples designated by LE, SP, DV are from drill core. Number following the core number is the depth interval in feet. --- - below limit of detection. Type indicates location of sample: 1 - outcrop from Dolores anticline, 2 - core from the Dolores anticline, 3 - outcrop from the Disappointment syncline, 4 - core from the Disappointment syncline, 5 - samples of uranium-vanadium ore.

SAMPLE NUMBER	TYPE	VOLUME OF GAS	METHANE µl/g	ETHANE µl/g	ETHYLENE µl/g	PROPANE µl/g	PROPYLENE µl/g	ISOBUTANE µl/g	BUTANE µl/g	PENTANE µl/g
4031	1	33	66	8.8	2.6	2.7	1.3	---	0.4	2.0
4054	1	7.0	6.9	9.9	0.5	0.4	0.8	---	0.4	1.9
LE96 15.6	2	2.0	3.3	0.7	0.8	1.3	0.1	6.1	0.2	0.2
LE178 146	2	22.5	43	5.8	2.9	2.6	1.4	---	0.6	0.7
LE348 127	2	13.5	7.7	1.6	1.9	0.8	0.8	---	0.5	0.7
SP421 528	2	33.5	19	2.8	1.8	1.2	0.5	---	0.3	---
SP421 554	2	22.5	20	2.7	1.9	0.8	0.5	---	---	---
SP421 600.5	2	28.5	45	4.1	1.4	1.7	---	---	---	---
4010	3	55.5	230	34	---	11	---	3.9	4.5	---
4015	3	55	76	11	2.5	4.1	---	---	---	---
VQ	3	3.5	250	30	1.3	6.6	0.6	0.8	1.7	0.4
DV9 520	4	8.0	220	25	1.7	7.8	0.4	1.8	2.3	1.2
DV9 754	4	16	41	5.7	3.5	2.7	2.3	---	1.3	0.7
DV9 791	4	118.5	1000	130	2.7	35	6.0	---	7.6	1.8
DV9 812	4	18	660	90	3.1	390	0.9	160	58	3.9
DV9 817	4	21.5	600	98	2.7	38	0.7	8.5	9.7	4.5
DV9 827	4	19	440	70	2.2	28	0.5	7.1	7.4	2.6
DV34 680	4	4.0	150	14	2.9	3.2	1.0	0.5	1.0	0.4
DV52 1278	4	182	280	37	12	35	6.2	100	---	---
DV52 870	4	15.5	110	17	4.4	5.6	2.6	0.6	1.4	---
DV52 1164	4	11	190	25	11	8.6	4.7	0.8	2.4	0.6
DV61 1327	4	20.5	110	10	1.2	2.2	---	---	---	---
DV122 1250	4	10.5	320	46	4.6	14	2.5	3.2	4.0	2.5
5006	5	44	1400	210	3.2	80	18	20	6.6	2.9
DV9 800	5	6.0	370	84	2.3	26	1.4	2.2	9.5	3.8

syncline (Table 2). The few samples collected from outcrop have hydrocarbon contents similar to core samples from the same area. Differences between anticline and syncline samples were detected despite the similar amounts of carbonate minerals (as indicated by similar volumes of evolved gas) in both sample sets.

The higher hydrocarbon contents in syncline samples may reflect preferential supply of hydrocarbons to the syncline or more efficient occlusion or adsorption processes (chlorite may be a better hydrocarbon adsorber than kaolinite). Alternatively, the lower contents in anticline samples could reflect gas loss related to processes responsible for the the different assemblage of authigenic minerals in anticline and syncline samples (Fig. 3). As shown below, the difference is probably related to alteration. Although the total abundance of gases is different, the relative amounts of component gases in both anticline and syncline samples are similar. Gases occluded in samples from the syncline average 82 percent methane, 11 percent ethane, 4 percent propane, and 3 percent other; anticline samples contain 76 percent methane, 15 percent ethane, 5 percent propane, and 4 percent other.

Second Phase - Detailed study

Results of the detailed study conducted on samples from the Disappointment syncline are presented in Table 3. Analysis of variance (ANOVA) of the replicate analyses indicate that total carbon, gas volume, methane, ethane, and propane have a greater variance among samples than between analytical replicates (Table 4). These variables are considered measurably different among samples and were used in other statistical tests. Propylene and n-butane also were detected with good precision. However, the large number of values below detection restricted interpretation of propylene and n-butane abundances and these compounds were not considered further. Much of the variance in replicates was detected in sample DV24 347. Analyses of this replicate detected significant differences in the gas volume as well as the amounts of hydrocarbons. The cause of this deviation is uncertain, but may reflect sample heterogeneity. Such large deviations limit the interpretation of small differences in the data.

Hydrocarbon contents of samples from the core drilled outside the Slick Rock district (EP1875) are more similar to samples from the Disappointment syncline than samples from the Dolores anticline. Like samples from the syncline, chlorite is the most abundant authigenic clay in samples from EP1875. Although not conclusive, these results suggest the lower contents of hydrocarbons in samples from the Dolores anticline are related more to the differences in authigenic clay minerals than to structure.

Table 2: Results of the Student's t-test comparison of Salt Wash sandstones from the Dolores anticline and Disappointment syncline. Means and deviations are geometric * - differences considered significant (95% level).

VARIABLE	DOLORES ANTICLINE mean (deviation)	DISAPPOINTMENT SYNCLINE mean (deviation)
gas volume	13 (2.6)	19 (3.1)
methane*	18 (2.9)	260 (2.5)
ethane*	3.4 (2.4)	36 (2.7)
ethylene	1.5 (1.8)	2.2 (4.6)
propane*	1.2 (1.9)	14 (3.9)
propylene	.36 (5.3)	.73 (9.8)
isobutane*	0.02 (9.7)	1.0 (22)
n-butane	.15 (5.5)	1.5 (13)
pentane	0.16 (11)	0.35 (12)

TABLE 3: Results of hydrocarbon analyses of samples from Disappointment syncline. Locations are plotted on Fig. 5. Samples are identified by core number (DVx, EP) and the depth in feet. Type of sample classsified by color and location; 1 - red sandstone, 2 - gray sandstone, 3 - U-V ore, x.0 not within 1000 feet of known U-V deposit, x.3 - U-V deposit detected in an adjacent core; x.5 - U -V deposit detected in the same core but host sandstone is separated by an interveneing mudstone, x.7 within the same sandstone as U-V deposit, and x.9 within 1 m of U-V deposit. * - replicate samples. --- - below detection limit.

Sample Number	TYPE	Total Carbon wt.%	vol. gas ml	METHANE µl/g	ETHANE µl/g	ETHYLENE µl/g	PROPANE µl/g	PROPYLENE µl/g	I-BUTANE µl/g	N-BUTANE µl/g	PENTANE µl/g
DV1 557	2.9	0.44	3.0	520	50	1.3	11	0.3	1.1	2.4	1.4
*DV1 566	3.0	0.90	18	240	37	1.2	15	---	3.4	3.3	4.6
*DV1 566	3.0	0.86	17	240	37	0.6	15	---	---	---	---
DV1 690	1.5	0.74	15	140	23	1.9	8.3	---	1.6	---	2.0
DV1 783	1.5	3.4	77	140	17	1.2	7.5	---	1.5	---	23
DV9 754	1.5	0.66	11	21	2.5	1.1	1.0	0.1	---	---	1.5
DV9 791	2.7	0.56	8.0	380	53	3.9	23	---	5.1	5.0	0.5
DV9 806	3.0	5.8	6.0	150	24	1.9	7.4	1.6	0.7	2.0	1.0
DV9 827	2.7	0.72	14.5	320	51	1.7	24	0.4	6.1	5.1	10
DV9 843	2.5	0.3	4.0	64	6.3	1.5	1.9	0.4	0.3	0.4	1.4
DV18 276	2.0	2.9	34	82	12	1.0	6.1	---	1.2	---	5.6
DV18 347	1.0	3.0	72	45	4.2	1.0	1.2	---	---	---	4.3
DV18 366	1.0	1.0	21	230	43	0.4	19	---	---	---	---
DV18 426	1.0	0.40	6.5	60	8.0	2.8	3.1	1.0	0.5	0.6	2.0
*DV18 455	1.0	1.8	44	190	23	1.4	9.6	---	0.7	---	1.8
*DV18 455	1.0	1.9	46	210	25	0.8	10	---	---	---	1.7
DV18 485	1.0	1.4	37	210	28	2.4	14	---	2.8	2.1	---
*DV24 347	1.5	1.2	29	820	93	1.6	38	---	9.5	9.0	5.4
*DV24 347	1.5	1.3	14	290	33	0.4	15	---	3.5	3.2	1.3
DV24 372	2.5	1.0	19.5	132	22	1.6	11	---	3.8	3.0	10
DV24 357	2.5	0.07	1.0	26	2.1	1.4	0.9	---	0.5	---	0.9
DV24 439	2.5	2.2	56	360	49	3.6	20	---	0.8	---	---
DV34 762	1.7	0.17	2.0	13	1.8	1.0	0.9	0.5	0.3	0.2	1.5
DV34 824	2.7	0.20	3.5	78	11	0.8	4.3	0.2	0.8	0.9	0.2
*DV34 836	2.7	0.83	17	130	19	1.7	8.9	---	---	---	9.2
*DV34 836	2.7	0.82	15	110	17	0.9	6.8	---	---	---	2.9
DV52 889	2.5	1.2	22	110	15	5.8	5.5	---	---	---	3.3
DV52 921	1.0	0.60	10	550	83	2.1	32	---	8.5	7.0	4.8
DV52 1152	2.5	0.67	14	100	12	3.0	4.6	---	0.5	1.0	1.3
DV61A 1229	2.5	2.2	51	200	26	0.5	9.4	---	---	---	---
DV61A 1257	2.7	1.6	32	200	32	3.2	11	---	1.7	1.8	2.7
*DV61A 1302	2.7	1.2	38	200	29	2.9	12	---	3.3	2.4	7.7
*DV61A 1302	2.7	1.2	27	140	20	1.8	6.4	---	---	---	---
DV75 813	2.3	0.56	8.0	62	9.5	0.5	3.8	---	---	---	---
DV75 842	2.3	0.47	9.0	290	47	1.2	21	0.6	4.3	5.0	3.7

Table 3: (cont.)

Sample Number	TYPE	Total . Carbon wt.%	vol. gas ml	METHANE µl/g	ETHANE µl/g	ETHYLENE µl/g	PROPANE µl/g	PROPYL µl/g	I-BUTANE µl/g	N-BUTANE µl/g	PENTANE µl/g
DV-75 883	2.3	1.1	25	340	40	1.8	27	---	5.8	6.0	---
DV88 1004	2.5	0.61	11	180	30	7.3	13	4.4	2.5	3.0	4.2
DV89 999	1.5	1.1	20	79	11	1.3	4.9	---	1.7	0.9	---
DV89 1090	2.9	0.73	17	300	46	3.2	18	1.4	3.1	3.8	3.7
DV95 1005	2.7	0.56	8.0	180	30	1.5	11	---	1.6	2.1	0.2
DV97 840	2.9	0.54	10	130	18	1.1	6.6	0.4	1.1	1.4	3.2
DV97 871	2.5	0.47	9.5	66	9.1	3.3	3.8	0.2	---	---	---
DV97 889	2.5	2.3	53	410	63	1	22	---	---	---	---
DV98 827	2.5	3.7	92	740	67	3.1	29	---	6.3	6.0	27
DV98 845	2.7	0.16	1.0	5.6	0.4	0.2	0.2	---	---	---	---
DV98 882	2.7	4.8	107	390	46	1.9	17	---	---	---	25
DV98 893	2.7	2.6	57	360	44	3.0	20	---	3.9	3.5	8.3
DV99 1098	2.3	2.6	58	190	34	---	11	---	---	---	---
DV100 379	1.5	2.0	45	29	2.5	0.3	0.5	---	---	---	---
DV100 391	1.5	0.79	17	49	5.3	0.9	2.7	---	0.6	---	3.1
DV100 429	2.7	0.41	7.5	83	11	0.7	5.7	---	1.2	1.2	1.9
DV100 442	2.9	0.76	14	400	67	2.1	33	---	6.1	6.3	6.7
DV102 904	1.0	2.3	50	180	18	5.8	6.8	---	---	---	---
*DV104 376	2.3	0.54	9.0	260	42	2.3	19	0.4	4.6	3.9	6.1
*DV104 376	2.3	0.53	8.0	150	21	1.4	8.6	0.5	2.2	2.0	3.6
DV104 382	2.3	0.91	26	350	56	2.6	25	---	5.0	4.6	4.4
DV106 354	1.0	1.4	35	270	36	0.7	16	---	6.1	3.0	---
DV106 354	1.0	1.4	33	240	33	0.3	14	---	2.1	2.4	---
DV106 364	2.0	0.55	8.5	110	17	2.2	8.5	1.6	2.3	0.4	6.6
DV109 465	2.0	1.6	37	120	18	1.0	7.1	---	---	---	4.5
DV110 511	2.0	0.59	11	170	28	1.0	13	---	2.6	2.5	3.3
DV117 1005	1.3	0.60	11	43	4.6	2.2	1.8	---	0.6	---	6.6
DV119 1064	1.3	0.30	4.0	16	2.1	1.2	1.0	0.5	---	0.1	---
DV119 1095	1.3	0.47	7.0	65	9.9	0.9	3.5	---	---	---	---
DV119 1120	2.3	0.80	11.5	180	27	0.8	9.6	---	1.9	2.1	1.3
DV119 1150	1.3	0.30	6.0	130	18	0.4	5.9	---	0.7	1.1	---
DV121 1074	1.5	0.24	3.5	74	7.7	0.7	2.8	0.3	0.6	0.5	1.5
DV121 1160	1.7	0.92	27	48	4.3	1.1	1.4	---	---	---	---
DV122 1147	1.3	0.62	9.0	680	76	1.1	16.0	---	1.7	2.9	---
DV122 1232	2.3	0.76	15	180	27	2.2	9.8	0.7	1.4	2.0	2.0
DV122 1263	2.3	3.4	67	590	70	2.3	19	---	---	---	---
DV122 1250	2.3	0.57	5.5	160	23	2.6	9.2	0.3	2.0	1.9	4.5
EP1875 595	2.0	0.87	22	57	6.1	2.7	2.2	---	---	---	3.4
EP1875 604	2.0	0.20	73	53	4.1	1.0	1.4	---	---	---	---
*EP1875 624	1.0	2.2	54	130	17	0.9	6.4	---	---	---	---
*EP1875 624	1.0	2.2	49	110	15	1.3	6.0	---	---	---	---
EP1875 655	2.0	1.8	40	81	10	1.6	5.4	---	---	---	3.0

Table 4: Results of the analysis of variance of replicate samples and comparison of groups. Groups were divided based on their color (red and gray) and proximity to U-V deposits (see table 3). * - variables with greater variance among samples than among replicates at the 90% significance level; # - variables with greater variance between groups than within groups at the 98% significance level.

VARIABLE	REPLICATES F-test value	BETWEEN GROUPS F-test value
Carbon	389*	0.866
Gas volume	17*	1.21
Methane	4.12*	2.68#
Ethane	3.03*	2.90#
Ethylene	1.77	---
Propane	3.025*	2.79#
Propylene	1160*	---
Isobutane	2.355	---
n-Butane	3.604*	---
Pentane	0.89	---

Total carbon abundance and gas volume have a linear relation (Fig. 7) with a slope that is consistent with almost all of the carbon occurring in carbonate minerals. Samples deviating from the line, with higher than predicted carbon values, contain organic carbon in the form of visible coalified plant fragments. The sample containing the highest concentration of organic carbon is a sample of high grade U-V ore (DV-9 806). Despite the abundance of visible plant fragments, the concentration of light hydrocarbons in this and other carbonaceous samples (DV1 566, DV18 265, DV122 1265) are not appreciably higher than others lacking organic matter (Table 3). Consistent with results of the pilot study, there appears to be no relation between the abundance of carbonate (gas volume) and the amount of methane (Fig. 8) or other gases in the syncline samples.

Methane has strong linear relations with ethane and propane (Fig. 9). The strong correspondence of these gases reflects their constant relative abundance, which on average is approximately 83 percent methane, 11 percent ethane, 4 percent propane and 2 percent other. The high proportion of ethane and propane suggest the trapped hydrocarbons did not originate exclusively from biogenic processes (Tissot and Welte, 1984) but instead include a component of thermogenic gas.

Within samples from Disappointment syncline, gray sandstones contain greater concentrations of methane, ethane, and propane than red sandstones (Table 5). Differences between these groups were further examined by dividing the samples based on color and location relative to the U-V deposits. These groups are defined in Table 3. Variations related to the proximity of U-V deposits were anticipated because of the prominence of organic compounds in the formation of the deposits. In particular, coalified plant fragments in the deposits may have contributed to the abundance of methane in adjacent sandstones.

The abundance of methane, ethane, and propane in the defined groups were compared by analysis of variance (Table 4). Methane, ethane, and propane have a significant variance between groups. A comparison of the means of different groups indicates red sandstones near the U-V deposits (Types 1.3 and 1.5) have low concentrations of hydrocarbons relative to samples of gray sandstone collected near the deposits. However, the abundance of hydrocarbons in red sandstone away from the U-V deposits (Type 1.0) is similar to the content of gray sandstones near the ores. The proportion of gases in the individual groups is nearly constant, and identical to the total average. The average relative abundance of methane in the individual groups ranged only from 83 to 85 vol. percent of the total hydrocarbon gases. No increases near the U-V deposits and their associated wood accumulations were noted. Vertical variations in cores through U-V deposits were also looked for but no consistent patterns were detected.

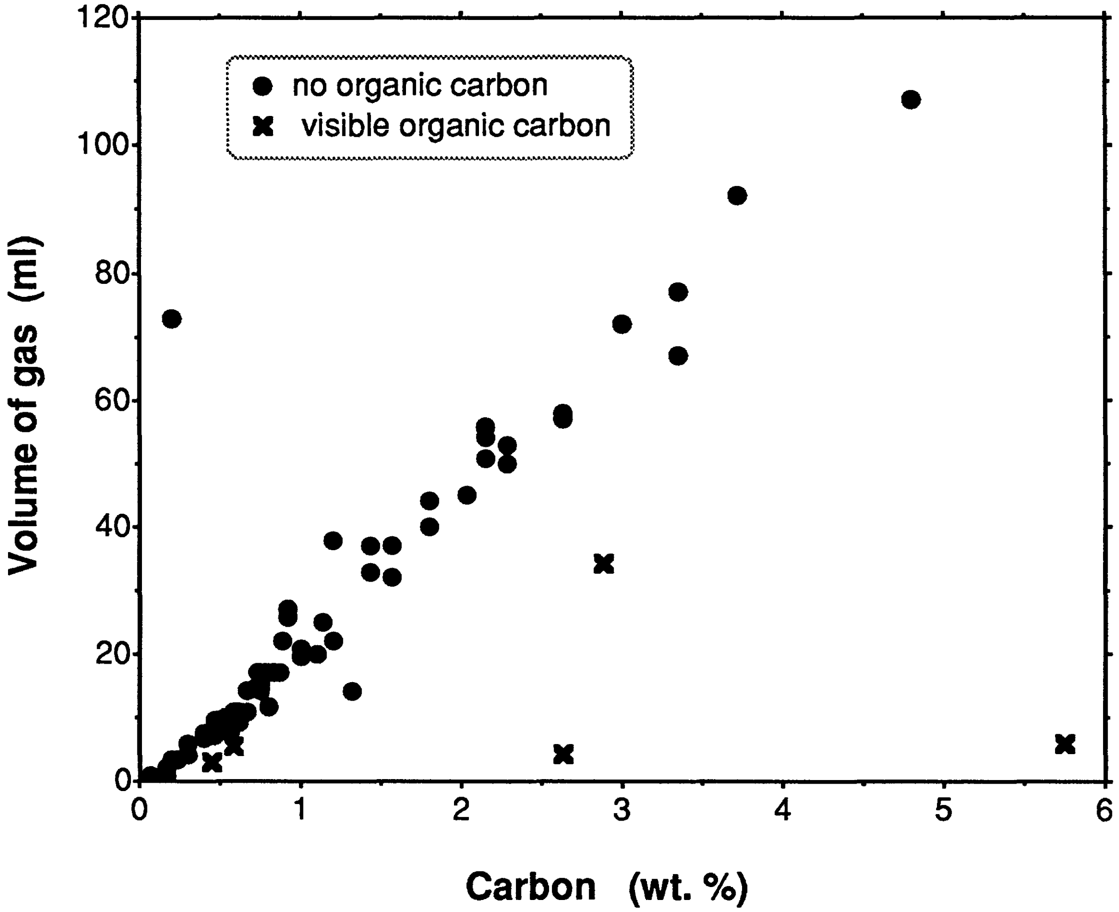

Figure 7: Abundance of total carbon vs. the amount of gas evolved during acid treatemnt of sandstones from Disappointment syncline.

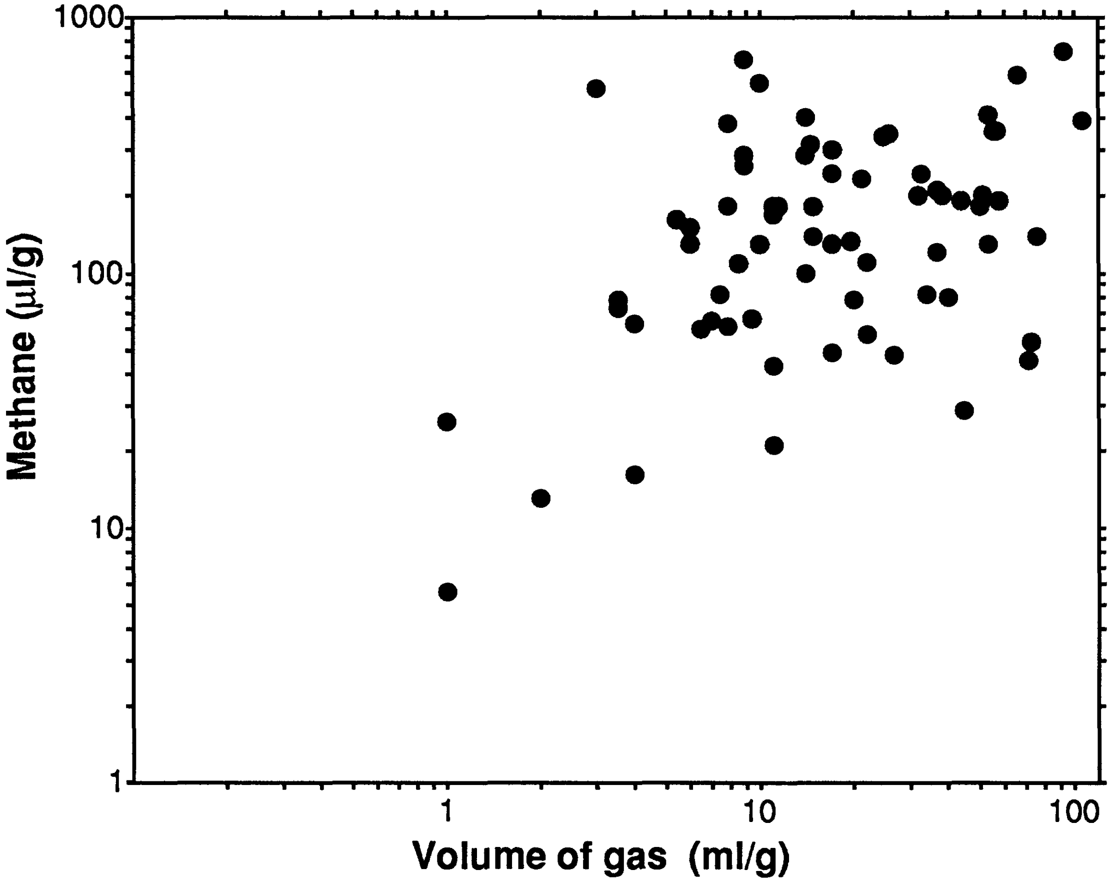

Figure 8: Total volume of gas evolved during acid treatment vs. the volume of methane evolved per gram of sample. All samples from Disappointment syncline.

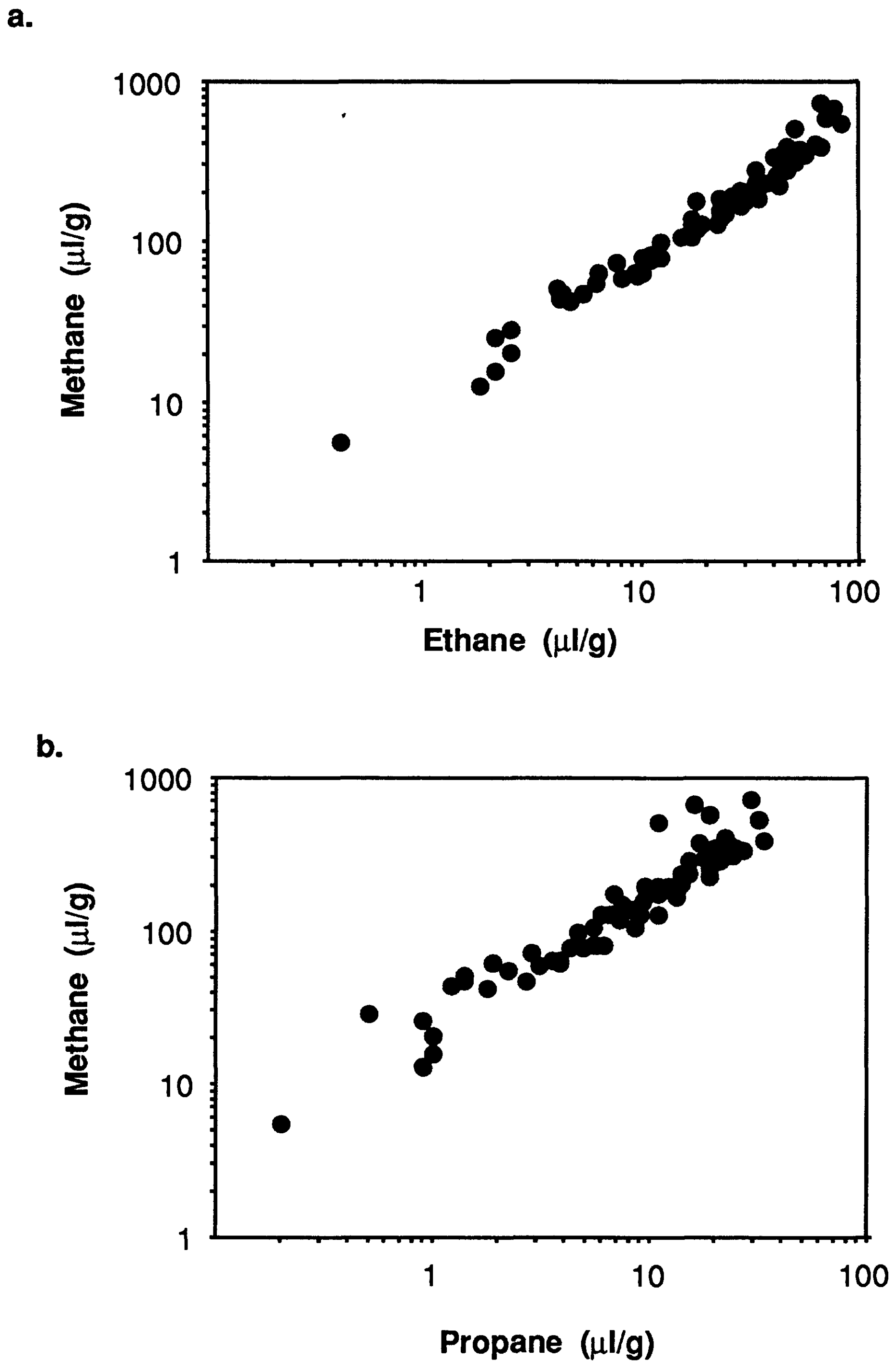

Figure 9: Abundance of a) ethane and b) propane vs. the abundance of methane in sandstones from the Salt Wash Member in Disappointment syncline.

Table 5: Geometric means and deviations of defined sample populations collected in the Disappointment syncline. 1 - red sandstone, 2 - gray sandstone, 3 - U-V ore, x.0 not within 1000' of a known U-V deposit, x.3 - U-V deposit detected in an adjacent core; x.5 - U-V deposit detected in the same core but host sandstone is separated from the sampled sandstone by an intervening mudstone, x.7 within the same sandstone interval as the U-V deposit, and x.9 within 1 m of a U-V deposit.

ROCK TYPE	NUMBER OF SAMPLES		CARBON wt.%	Vol. gas ml	METHANE µl/g	ETHANE µl/g	PROPANE µl/g
		ALL SAMPLES					
ALL	70	MEAN	0.3	16	130	17	6.7
		DEVIATION	2.4	2.9	2.7	3.0	3.0
		DIVIDED BY ROCK COLOR					
red sandstone	24	MEAN	0.86	16	93	11	4.4
		DEVIATION	2.3	2.7	2.9	3.0	3.1
gray sandstone	46	MEAN	0.89	15	150	21	8.4
		DEVIATION	2.5	3.0	2.5	2.8	2.8
		DIVIDED BY COLOR AND PROXIMITY TO U-V DEPOSITS					
1.0	9	MEAN	1.3	29	160	21	8.3
		DEVIATION	1.9	2.2	2.1	2.4	2.7
1.3	5	MEAN	0.40	7.0	83	11	3.6
		DEVIATION	1.4	1.5	4.1	3.9	2.9
1.5 and 1.7	10	MEAN	0.82	15	60	7.0	2.7
		DEVIATION	2.4	3.0	2.6	2.7	3.0
2	7	MEAN	0.80	21	77	9.7	4.4
		DEVIATION	2.4	2.5	1.8	2.2	2.3
2.3	10	MEAN	0.92	17	220	33	13
		DEVIATION	2.0	2.3	1.8	1.7	1.8
2.5	11	MEAN	1.1	17	150	18	7.2
		DEVIATION	3.0	3.8	2.6	2.9	2.9
2.7	11	MEAN	0.78	14	140	19	8.2
		DEVIATION	3.0	3.8	3.4	4.1	3.8
2.9 and 3	6	MEAN	0.93	9.5	260	37	13
		DEVIATION	2.5	2.0	1.7	1.6	1.8

Systematic variations within the study area, particularly relative to the Dolores zone of faults were evaluated graphically. A plot of the abundance of methane relative to distance from the faults (Fig. 10) is typical of the patterns observed. No trend away from the faults is apparent.

DISCUSSION

Samples from Disappointment syncline contain greater concentrations of occluded and adsorbed hydrocarbons than those from the Dolores anticline. The lower contents on the anticline are most likely the result of hydrocarbon loss due to alteration. This alteration was the result of meteoric water that flowed preferentially through Salt Wash sandstones on the Dolores anticline (Breit, 1986). Kaolinite is the main product of this alteration and formed from altering chlorite and feldspars. This alteration was not simply the result of near-surface weathering because all outcrop samples from Disappointment syncline contain chlorite. Chlorite in syncline sandstones rims detrital grains and in turn is commonly coated by pore-filling calcite cement. Meteoric water that flowed through sandstones on the anticline may have moved along detrital grain-cement contacts preferentially and dissolved chlorite. Consistent with this analysis, carbonate pore-filling cements were dissolved along some contacts with detrital grains (Breit, 1986). Hydrocarbons released by this alteration originally may have been adsorbed to chlorite or trapped in small inclusions along detrital grain-cement contacts.

Part of the difference in hydrocarbon contents between the Dolores anticline and Disappointment syncline samples may be related to the difference in carbonate mineralogy. Dolomite and calcite are abundant cements in Salt Wash sandstones on the anticline; calcite was the only carbonate cement detected in samples from the syncline. Calcite may occlude and retain gaseous hydrocarbons better than dolomite. However, this hypothesis cannot account for the 10 times greater abundance of hydrocarbons in syncline compared to anticline samples, because nearly equal amounts of dolomite and calcite occur in anticline samples (Breit, 1986). Alternatively, carbonates in the anticline samples may have precipitated from a fluid lower in hydrocarbons. Although not conclusive, the carbon and oxygen isotope compositions of carbonates from the anticline and syncline are very similar suggesting they precipitated from similar solutions (Breit, 1986).

Within samples from Disappointment syncline, gray sandstones contain greater amounts of hydrocarbons than red sandstones. This difference may reflect several different controls on hydrocarbon abundance. Hydrocarbons may have been consumed by oxidation during incomplete reductive dissolution of ferric oxides in the red sandstones. Likewise hydrocarbons were preserved in the

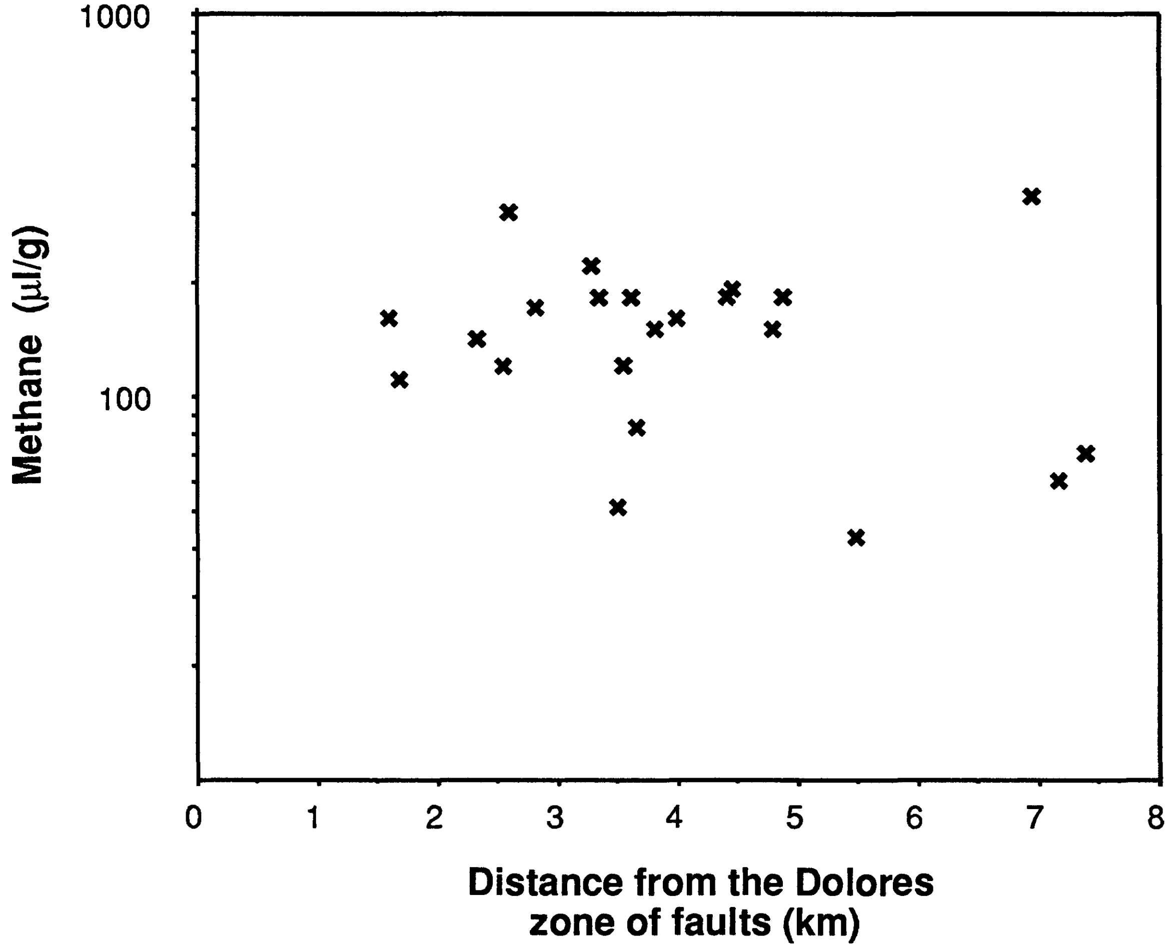

Figure 10: Distance of drill core from the Dolores zone of faults vs. the average abundance of methane in samples from that core.

reduced (gray) sandstones because these rocks lack oxidants. In general, red sandstones have higher detrital clay contents than gray sandstones. The clays decrease permeability and may have limited flow of hydrocarbon-bearing fluids through the red sandstones. Conclusive determination of whether the higher contents of hydrocarbons in gray rocks are related to supply or preservation will require further research.

The difference between gray and red sandstones is not apparent when populations are subdivided based on proximity to U-V deposits. The abundance of hydrocarbons in red sandstones away from known deposits is not appreciably different from gray sandstones adjacent to the U-V deposits (Table 5). In addition, no variations in the abundance of methane, ethane, and propane relative to the location of the deposits were noted. Absence of systematic variations may reflect a) light hydrocarbons were not important in the formation of the U-V deposits; b) occlusion of hydrocarbons was a variable process, hence the data are incapable of showing small systematic differences; or c) subsequent diagenetic changes homogenized spatial differences.

At the start of the study, systematic variations in the abundance of hydrocarbons relative to the Dolores zone of faults were anticipated. Breit and others (1987) interpreted preferential bleaching of sandstones on the structurally higher Dolores anticline and the occurrence of asphaltite along faults to be the result of fluids associated with oil and gas accumulations. However, no indication of hydrocarbons entering the Morrison from faults is reflected in the abundance of hydrocarbons. The lower concentrations of hydrocarbons detected on the Dolores anticline seem inconsistent with the preferential bleaching of sandstones on this structural high. In addition, Figure 10 does not suggest a systematic decrease in hydrocarbon concentration away from the Dolores zone of faults. The lack of systematic variation reflects either the complexity of the flow system, variability in the trapping and preservation mechanisms, or that the abundance of trapped hydrocarbons is unrelated to reducing solutions that moved along the faults.

The composition of trapped hydrocarbons and their probable source are the only parameters that favor the movement of hydrocarbons along faults. The high contents of ethane and propane trapped in Salt Wash sandstones suggest an at least partially thermogenic origin for the hydrocarbons. Data from gas producing wells in Pennsylvanian and Mississippian reservoir rocks within and near the study area contain a range of gas compositions which include the proportions measured in this study (Moore and Sigler, 1987). Because thick, impermeable beds of salt overly the Mississippian reservoirs, the Pennsylvanian Hermosa Formation is the probable source of gas. The simplest way of introducing these gases into Salt Wash sandstones is through the Dolores zone of faults. Therefore, the lack of systematic variation in the abundance of occluded hydrocarbons in Salt Wash sandstones away from the faults is most likely due to complexities in trapping and preservation. Coal beds in the Cretaceous Dakota Sandstone are also a possible source of light hydrocarbons. However, geologic analysis and vitrinite reflectance indicate this unit was not heated sufficiently to generate the observed hydrocarbons.

This discussion has been limited by the lack of knowledge on the residence of occluded and adsorbed hydrocarbons and the relative importance of carbonate minerals and clays. The lack of a systematic relation between the abundance of hydrocarbons and the abundance of calcite, may in part reflect multiple generations of calcite. Oxygen isotope data detected multiple generations of calcite in the Salt Wash sandstones (Breit, 1986), which are not distinguishable using standard petrographic techniques. Therefore, detailed evaluation of gaseous hydrocarbon contents in rocks may require extensive petrographic and isotopic study to identify carbonate minerals cogenetic with hydrocarbon-containing solutions.

The importance of clays as a site of trapped hydrocarbons was evaluated by plotting the whole-rock aluminum abundance in 33 samples (Breit, unpublished data) against the abundance of methane (Fig. 11). Although aluminum in these rocks is contained in clays and feldspars, most variation in aluminum abundance is due to the amount of clay minerals (Breit, unpublished data). Again there is no significant positive correlation; instead, the trend of the data suggests a negative relation. Unfortunately, the measure of aluminum not only indicates authigenic clays likely to trap hydrocarbons but also detrital clays. Detrital clays have relatively little surface area exposed to pore fluids and therefore are unlikely to adsorb significant amounts of hydrocarbons. Future studies that evaluate adsorbed hydrocarbons should quantify the abundance, mineralogy, and origin of clay minerals.

IMPLICATIONS FOR GEOCHEMICAL EXPLORATION STUDIES

Despite the limitations, the abundances of occluded hydrocarbons do vary in patterns consistent with diagenetic alteration in the Slick Rock district. Therefore, users of occluded hydrocarbons in soils for geochemical exploration of petroleum should recognize the importance of mineralogical differences in underlying lithologies. Sparse soils developed from the Salt Wash in the Slick Rock district may tend to retain many of the minerals found in underlying rocks. If differences between samples on the anticline and the syncline are preserved in overlying soils, substantially different background values would be needed for recognizing anomalies in the two areas.

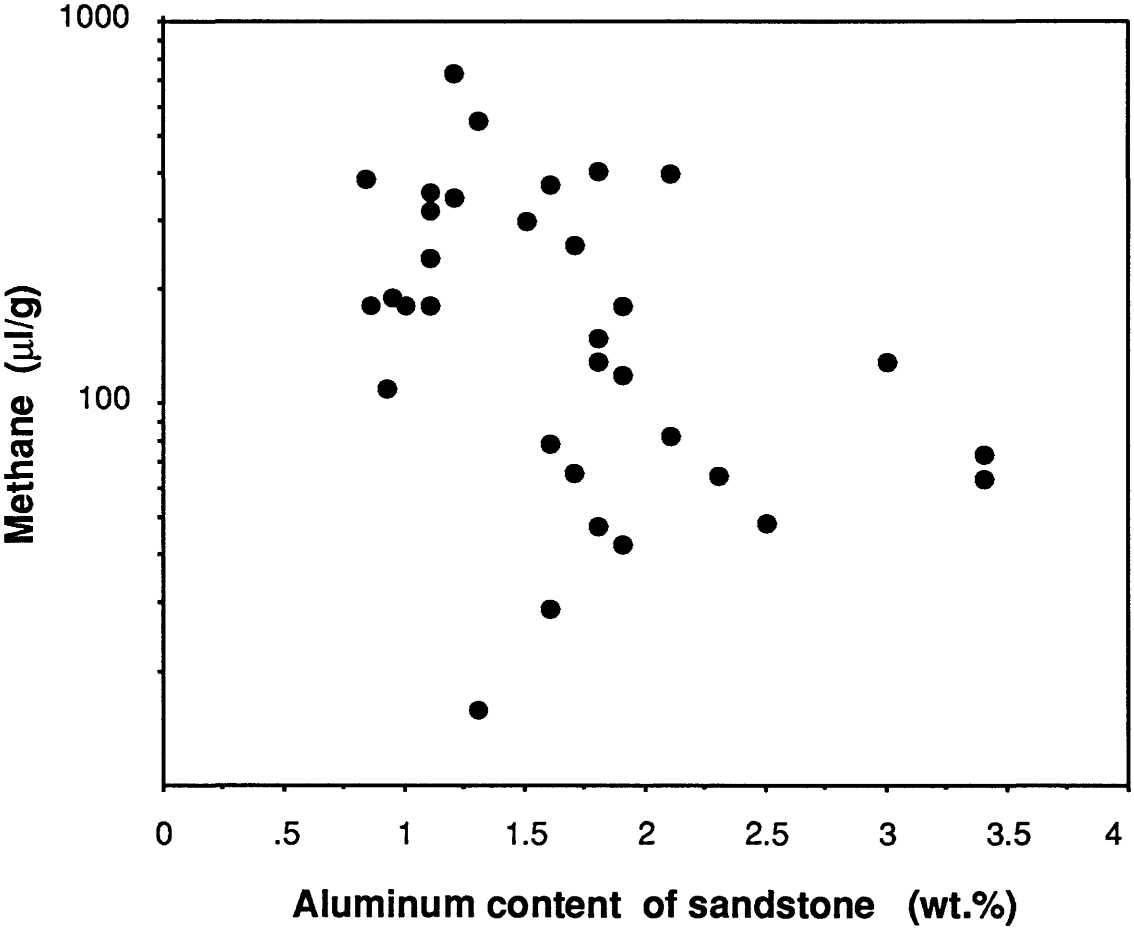

Figure 11: Abundance of aluminum in some sandstones from the Disappointment syncline vs. their methane content.

CONCLUSIONS

Significant differences in the abundance of light hydrocarbons were detected in sandstones of the Salt Wash Member, Morrison Formation, Slick Rock district. These differences are related to changes in the assemblage of authigenic minerals. Higher contents were detected in gray sandstones than red sandstones, and samples altered by recent meteoric water have methane, ethane and propane contents a factor of 10 lower than unaltered sandstones. No consistent differences were detected relative to the the location of the U-V deposits or to faults, which were conduits for solutions from depth. The observed differences can be explained by variable preservation, supply, and occlusion/adsorption. Better understanding of parameters affecting these processes is necessary before any relation between trapped hydrocarbons and diagenesis can be fully evaluated.

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