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PRELIMINARY SCIENTIFIC RESULTS OF THE CREEDE CALDERA CONTINENTAL SCIENTIFIC DRILLING PROGRAM

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ORGANIC GEOCHEMICAL STUDIES TO UNDERSTAND ORE GENESIS AT CREEDE

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INTRODUCTION

Geochemical and isotopic analyses of organic matter at Creede have been done to better understand natural processes and test the hypothesis (or to develop other working hypotheses) that the caldera sediments were the reservoir/source for the water that formed the Creede ore deposit (Bethke, 1988; Bethke and Rye, 1979). Some of the various forms (solid, liquid, gas) and occurrences (formation waters, sediment materials, veins, travertine and fluid inclusions) of organic carbon compounds that are found in the moat sediments and related rocks encountered in drilling have been analyzed in USGS laboratories by a variety of techniques. These studies consider organic matter as a tracer and/or control on redox conditions and mineral alteration/formation. As a result of this work, we will use organic geochemistry to aid in developing a better understanding of the chemistry of water-rock interaction, sulfur redox and lack of equilibrium of the system due to sluggish kinetics at low temperatures (Barton, 1967). Organic matter will also be used as a geothermometer to give estimates of temperatures (and limits on times) of heating using several different techniques.

SAMPLE COLLECTION

Representative samples of each lithology (even organic poor ones) were collected. We also collected samples of any organic rich layers, organic concentrates, organic stains, or samples containing visible organic matter. We even collected a deep sample with black specks (vitrinite?) that turned out to have < 0.02 percent organic C; the black was biotite. Special packaging of core samples for organic geochemistry included: samples were washed with clean (fresh) water to remove surface contaminants. (Samples of wash water and drilling additives also were collected for analysis, if organic contamination was suspected). Samples were wrapped tightly in aluminum foil to trap volatiles and formation waters and to exclude air and then put in a zip-lok plastic bag, again wrapping tightly to exclude air. A suite of specially selected organic-containing samples has been described (Leventhal, lab notes). Some of these samples were collected at the drilling site (October-November 1991) and the whole core washed and packaged in aluminum foil at that time (these samples have been split in my lab and half returned to core storage). Additional samples were taken at the core sampling "party" in May 1992.

PROCEDURES

All samples have been analyzed for total organic carbon and selected samples for forms of organic solvent-soluble compounds (Lillis, Chapter L, this Open-File Report). These samples have been extracted with organic-solvent mixtures and analyzed by gas chromatography for molecular distribution compounds (Lillis, Chapter L, this Open-File Report). In particular, the presence of sulfur-containing organic

compounds was ascertained. In some samples, the extract was separated into several fractions (aliphatic, aromatic, polar) by column chromatography prior to gas chromatography. Further characterization of the saturated hydrocarbon fraction for abundance and distribution of "biomarker" compounds (steranes and triterpanes) was determined by coupled gas chromatography and organic mass compounds (Lillis, Chapter L, this Open-File Report).

Insoluble organic matter was analyzed (after demineralization, if necessary) for thermal maturity and organic type by programmed pyrolysis (Rock-Eval) (Leventhal and others, 1986). Selected samples of insoluble organic matter also have been characterized by stepwise pyrolysis-gas chromatography (Leventhal, 1976). Elemental analysis was used to determine carbon, sulfur, and iron content of selected samples. Carbon isotope determinations have been made on total organic carbon for selected samples (Leventhal and Threlkeld, 1978).

RESULTS

Table 1 gives the results of Rock-Eval pyrolysis including carbon percent. Rock-Eval pyrolysis is the programmed ($25^{\circ}C$/min) heating of a sample from 250 to $600^{\circ}C$ in a helium atmosphere and detection of hydrocarbons evolved with a flame ionization detector and CO_2 from organic matter with a thermal conductivity detector. The results are expressed using several names: HI (hydrogen index) is the yield in mg/g of hydrocarbons normalized to total organic C. Tmax is the temperature (instrumental, not geologic) at which the pyrolysis products yield peaked. The oxygen index, OI, is the pyrolysis yield of CO_2 related to organic matter, that is the mg/g of CO_2 normalized to the percent organic carbon. S1 is the volatile (probably also organic solvent extractable) hydrocarbons in the sample that are released at $250^{\circ}C$ at the beginning of the heating cycle.

Twenty samples run by Rock-Eval show organic carbon contents from <0.1 to 2.1 percent (vitrinite-rich concentrates show 62 to 74 percent organic C). The Rock-Eval Tmax values indicate that most of this organic matter is immature with respect to petroleum generation, i.e. probably prolonged temperatures were below 80° C.

A few samples give Rock-Eval Tmax values in the petroleum generating (oil window) stage. One of us (Neely Bostick) has determined vitrinite reflectance on a suite of samples and finds R_o values of 0.3 to 0.35 (with no relationship to depth) also indicative of very little prolonged heating.

Because of this immaturity, a suite of samples was selected for organic-solvent extraction. Preliminary results indicate there was sufficient material for analysis by gas chromatography and for gas chromatography-mass spectrometry. Of special interest is the abundance of sulfur that was liberated by the organic-solvent extraction. Samples that released sulfur during solvent extraction still contained sulfur that was combined in organic molecules that was detected by the flame photometric sulfur-specific detector of the gas chromatograph.

2

Table 2 lists the results of vitrinite reflectance, total sulfur, organic carbon, and degree of pyritization (DOP) (see paper by Leventhal, Chapter K, this Open-File Report). Table 2 also gives the drill depth (feet), the corrected stratigraphic depth for drill hole-core CCM-1 (add 450 ft relative to CCM-2) and the estimated maximum depth of burial (adding 1,800 ft).

Table 3 contains isotope results. Carbon isotope values are given for two selected end member organic types: vitrinite and amorphous (algal?) organic matter. Sulfur isotope values are given for three sulfur-rich samples. The sulfur isotope value was measured on the sulfur extracted from the sample by refluxing (approx 50 to 70°C) in chloroform and then in methanol-chloroform mixture. This sort of extraction-reflux is normally done to remove soluble organic matter, but was modified here to recover the sulfur (on a copper metal foil strip) for isotope measurements. Sulfur isotopes were determined on three of these samples. Pyrolysis-gas chromatography of the solid insoluble organic matter to determine origin and thermal history has been performed on selected samples.

DISCUSSION

Organic matter maturity and type
Both vitrinite reflectance and Rock-Eval Tmax are used for maturity determination (also organic mass spec for biomarkers (see paper by Paul Lillis Chapter L, this Open-File Report). Vitrinite reflectance values are all around R_o 0.3 (0.28 to .32) except for one value at 0.45, that is based on fewer and irregular individual measurements (fig 1). The R_o values show no linear trend with depth (fig 2). The 0.3 value is indicative of lignite rank (soft-hard brown coal) maturity, which probably represents long-term basinal heating to less than 50°C (the one higher value represents 50°C). The high R_o sample is based on only six recognizable organic particles that show values of from 0.3 to 0.65 (fig 2). This is the deepest of the samples analyzed for vitrinite reflectance, and the high value may indicate some anomalous heating. (See paper by Paul Lillis (Chapter L, this Open-File Report on organic mass spectrometry biomarker maturity information.)

Rock-Eval Tmax values range from immature with respect to petroleum generation (400°C) to values (435°C) in the range of petroleum (oil window) generation (Tissot and Welte, 1984). They show an increase with depth in the core (fig 3). One of the most interesting results is that the Rock-Eval Tmax values are much higher than expected for normal geothermal gradients (10-20°C per km) as shown on figure 4. Figure 5 shows a plot of all the Tmax data. Note that only samples with low amounts of organic carbon (TOC) have anomalous Tmax values (anomalously high values >490°C and low values <390°C) that have not been used on figures 3 and 4. However, the exact temperature for oil generation is not known: at the lower maturity levels, it is a time-temperature dependent relationship and is probably in the range of 125 to 150°C for geologically short times (i.e. less than the age of the host rocks or only thousands or 10,000s of

years). The discrepancy between the vitrinite reflectance (except 1 high value) and Tmax results may be due to the fact that the vitrinite particles are much larger and have a smaller surface area to volume ratio than the amorphous dispersed organic matter that is being measured in the Tmax determination. Thus a geologically short event involving warm/hot solutions would be expected to have a greater effect on the bulk amorphous organic matter than on the larger vitrinite particles. In addition, the reaction kinetics of vitrinite organic matter are different than those of dispersed organic matter.

The plot of HI vs OI is similar to a plot of atomic H/C vs O/C and can be used to infer organic matter source. The three lines on figure 6 show the positions of normal algal-lacustrine (I), marine (II), and terrestrial (III) organic matter. A combination of organic matter types will plot in intermediate positions. Only thermally immature or oxidized organic matter gives OI values greater than 150. The presence of small amounts of carbonate minerals can also lead to elevated OI values. On first inspection, most of the organic matter seems to plot around type III terrestrial organic matter. Treatment of samples CCM-2-R034, CCM-2-R050, and CCM-2-R103 with HCl changes their results: the OI decreases and HI increases, probably by acid hydrolysis of oxygen-containing functional groups (causes decrease of OI and increase of HI) and perhaps by removal of small amounts of carbonate minerals (causes decrease of OI). Thus the origin of these three samples may be lacustrine-aquatic (results after HCl leach) rather than terrestrial (before leach). The presence of visible vitrinite in many samples is evidence of some terrestrial organic matter. However, the most abundant organic matter in most samples is physically structureless or amorphous, which could be of terrestrial or aquatic origin.

Table 3 gives the isotope results. The carbon isotope value (-22) is rather normal for vitrinite, which generally is in the range of -24 permil. However, the value of around -23 permil is heavier (less negative) than expected for the "algal" organic matter. It is likely that this isotopically heavy organic matter results from low or limiting amounts of available CO_2 in the lake water and resulting lack of fractionation (McKenzie, 1985) and low productivity. It is also possible that there was an anomalously heavy CO_2 source from thermal waters that fed the lake and resulted in the isotopically heavy aquatic organic matter.

Sulfur isotope values are measured on what is usually called "free" or elemental sulfur. This sulfur was extracted (mobilized or solubilized) with organic solvents (chloroform first, then toluene and methanol) during the Soxhlet-reflux of the sample. This sulfur could result from elemental sulfur, oxidation of iron monosulfides, volatile organic sulfur compounds or thermal lability of organic sulfur compounds, present in the sample. Elemental sulfur has not been observed during microscopic analysis of the samples (Bostick, Bethke, oral commun., 1993). The organic sulfur compounds likely to contribute are not the mercaptans or pyrroles with sulfur in a 5- or 6-member ring, but sulfur functional groups such as thiols (Orr, 1990). The wide range for the S isotope values is similar to that found in the sulfides by Plumlee and Rye (1994) and Rye (oral comm., 1993 and this volume) and can be explained either by bacterial or inorganic

4

sulfide processes.

Pyrolysis-gas chromatography of selected samples shows results that are typical of aquatic (marine-lacustrine) organic matter. Samples CCM-1-R006, CCM-2-R016 and CCM-2-R034 show a series of regularly spaced peaks similar to those for Green River shale lacustrine organic matter. Such a series of regularly spaced peaks is indicative of lacustrine organic matter. Another type of pyrogram was produced from CCM-2-R102 in which a large number of peaks are clustered in the middle of the pyrogram. This result is unusual and unexpected. However, it is very similar to the results (Leventhal, 1976) from a sample related to the Kupferschieffer mineralized strata in central Europe. This can be interpreted as resulting from alteration of organic matter by thermal, ore-forming fluids.

CONCLUSIONS

The relative immaturity of the organic matter of the samples indicates no high-temperature events (>100ºC) for long periods of time (>1 my). This is supported by Rock-Eval, vitrinite reflectance and biomarker data (see Lillis, Chapter L, this Open-File Report). Based on the shallow burial of these samples, this is expected. However, if a mineralizing system was present, is there any evidence of it?

Several factors indicate an unusual history for these samples: anomalous (high) sulfur to organic carbon ratios and cross plots (Leventhal, this volume); the wide range and anomalously high values for degree of pyritization determinations (Leventhal, this volume); wide range in Rock-Eval Tmax values that indicate an anomalously high thermal gradient and the unusual abundance of sulfur in the organic extracts (solvent labile sulfur that was collected on the copper strip) indicating a sulfur-rich system. These results are suggestive of the type of fluids related to mineralization. Furthermore, one sample has a pyrogram indicative of hydrothermally altered organic matter.

Two important questions remain to be considered for further study: (1) the possibility of unusual reactions caused by a S-rich system and (2) higher temperature heating for a relatively short (1000's of years) time period than usually encountered in basin burial.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1. Examples of histograms from vitrinite reflectance (R_0)measurements. Top is typical of most samples with good histogram. Bottom is results from core sample CCM-1 R113 showing wide range in small number of measurements (see text).

Figure 2. Plot of vitrinite reflectance results vs. corrected depths. Note there is no trend with depth except that sample CCM-1-113, the deepest, is off-set toward higher maturity. Filled symbols represent CCM-2.

Figure 3. Rock-Eval Tmax results vs. corrected depth. Note a trend of higher Tmax with increasing depth. Filled symbols represent CCM-2.

Figure 4. Rock-Eval Tmax results vs. corrected depth plotted with results from samples in other petroleum producing basins. Note that Creede results show anomalously high range of values for the range and relative depth of burial. James is Miocene basin, California, with moderately high geothermal gradient. Hod is Pliocene basin, Hungary, with moderately high geothermal gradient.

Figure 5. Rock-Eval Tmax results vs. percent organic carbon (TOC). Note several very high or low Tmax values that are very low in TOC and are not reliable and were not plotted on Figs. 3 and 4.

Figure 6. Hydrogen index (HI) vs. oxygen index (01) plot of Rock-Eval results. Curves marked 1, 11, and III represent main organic matter types and converging evolution pathways with thermal maturity. Numbers are samples, filled symbols CCM-2, diagonal line through symbol is HCI pre leach (see text).
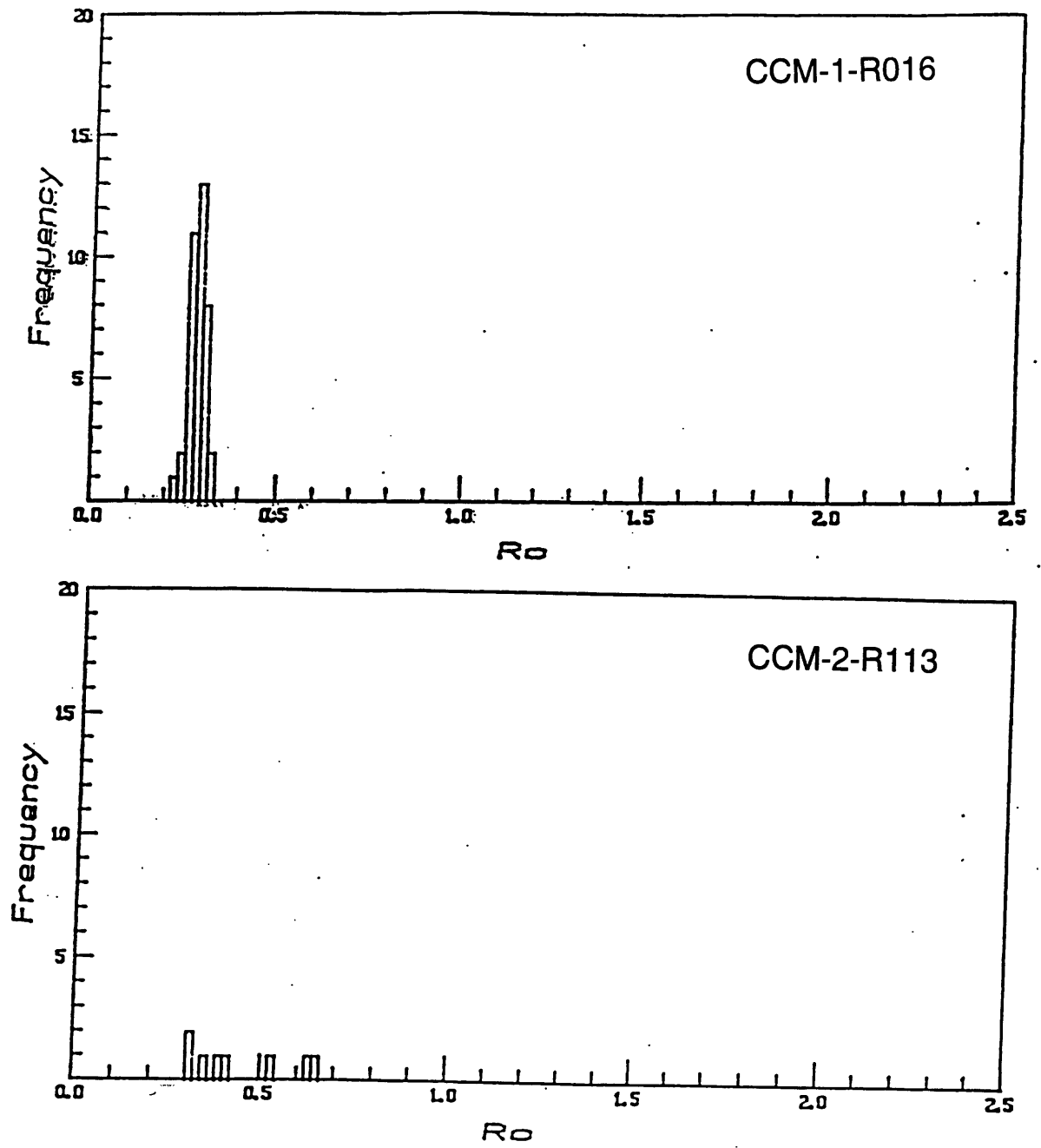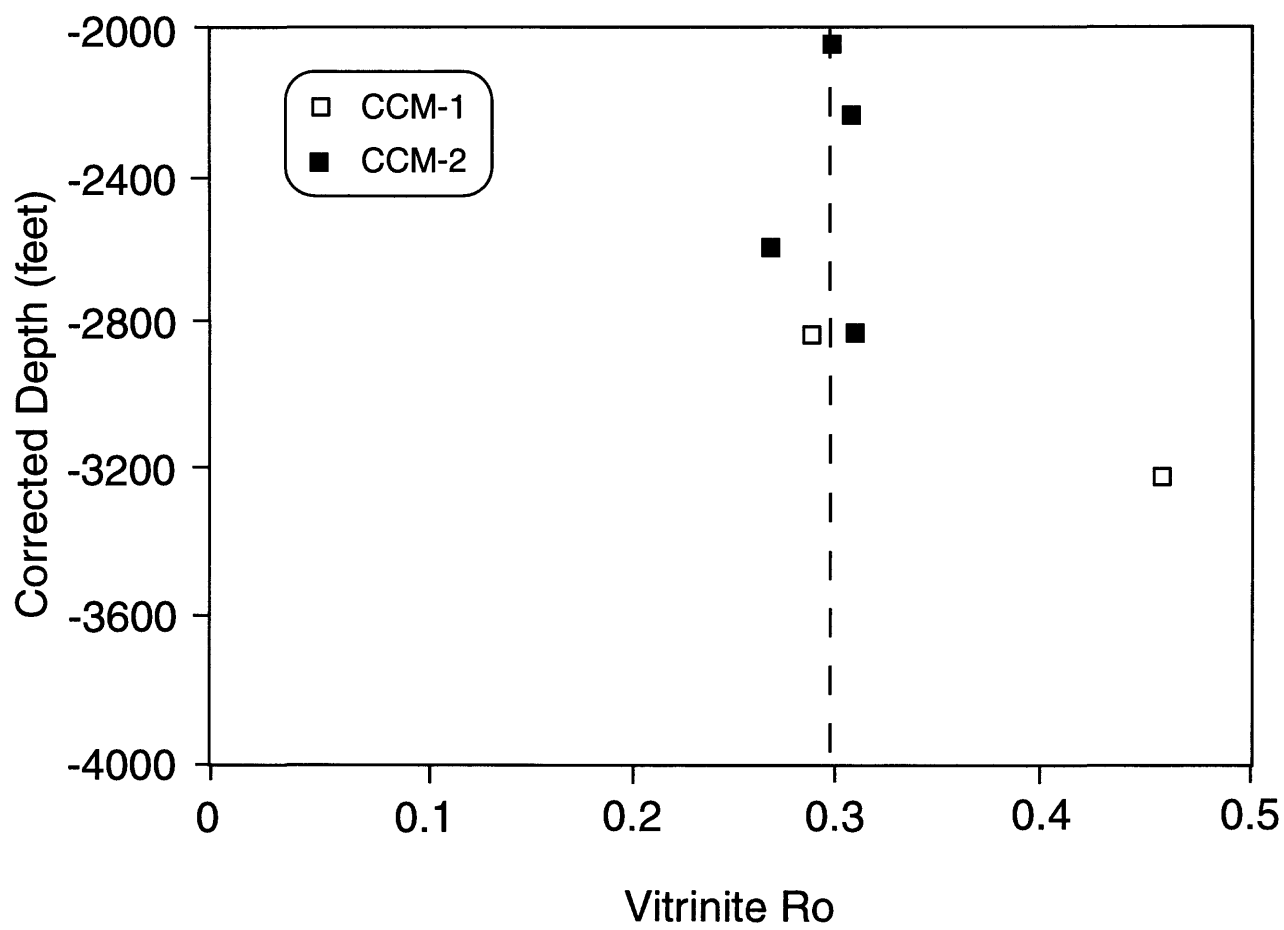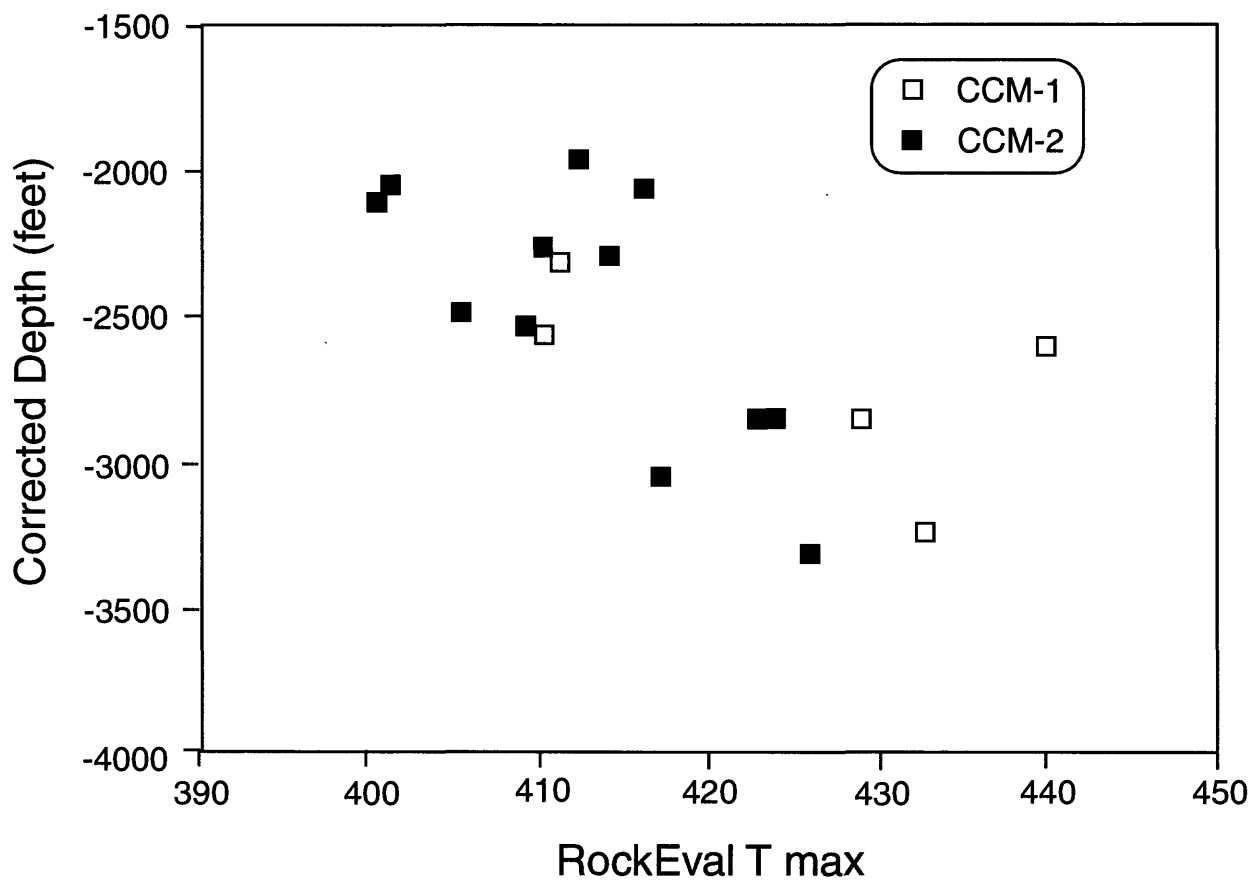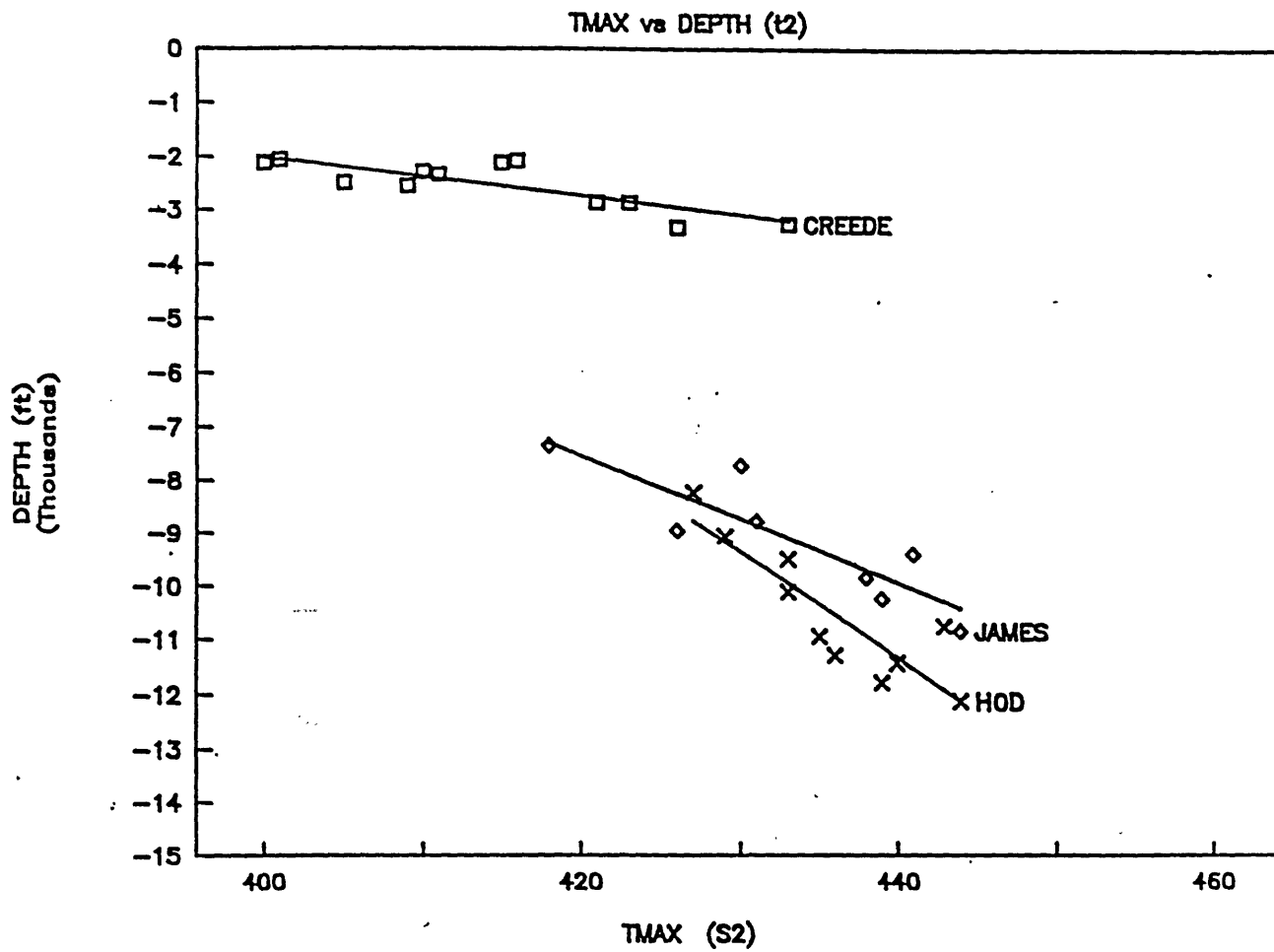
Figure 1

Figure 2

Figure 3

Figure 4
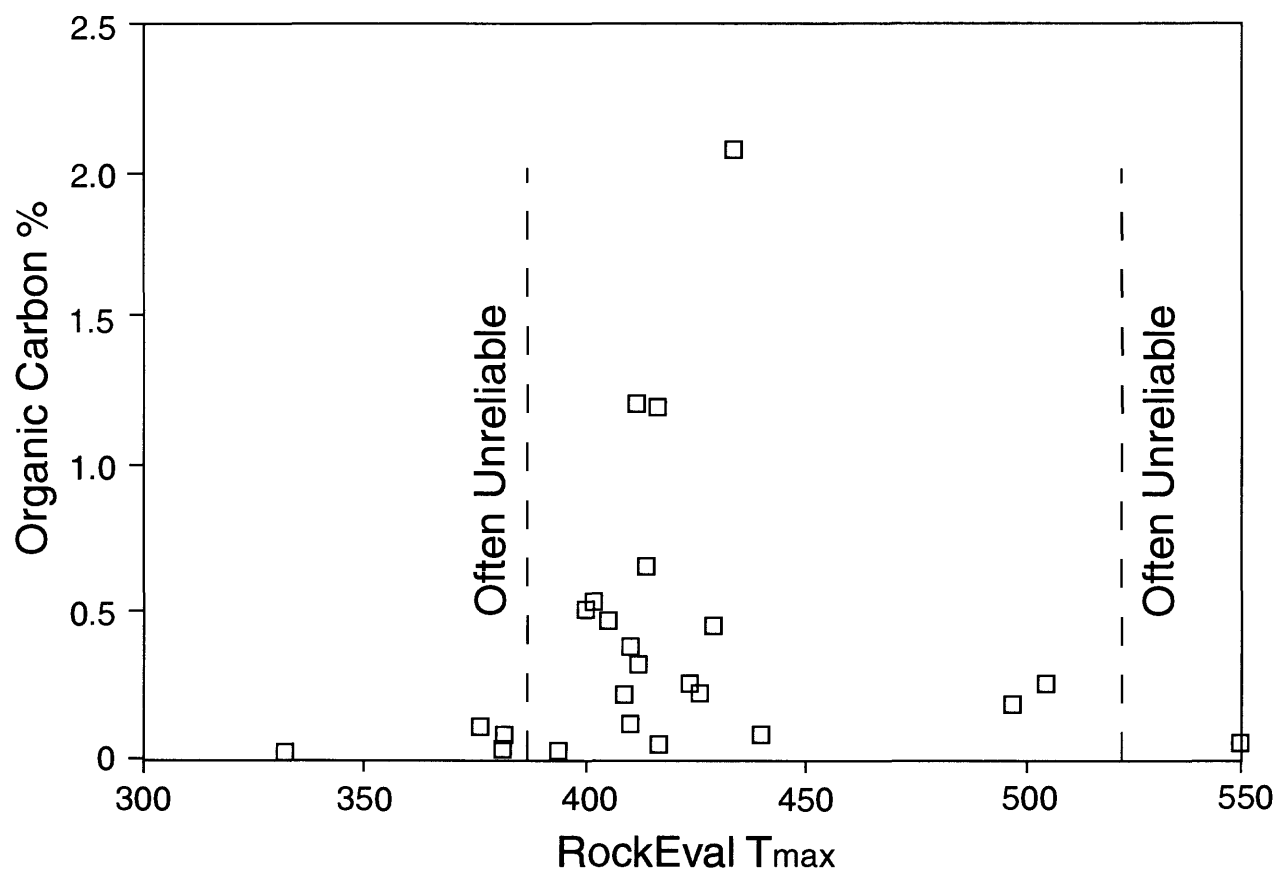
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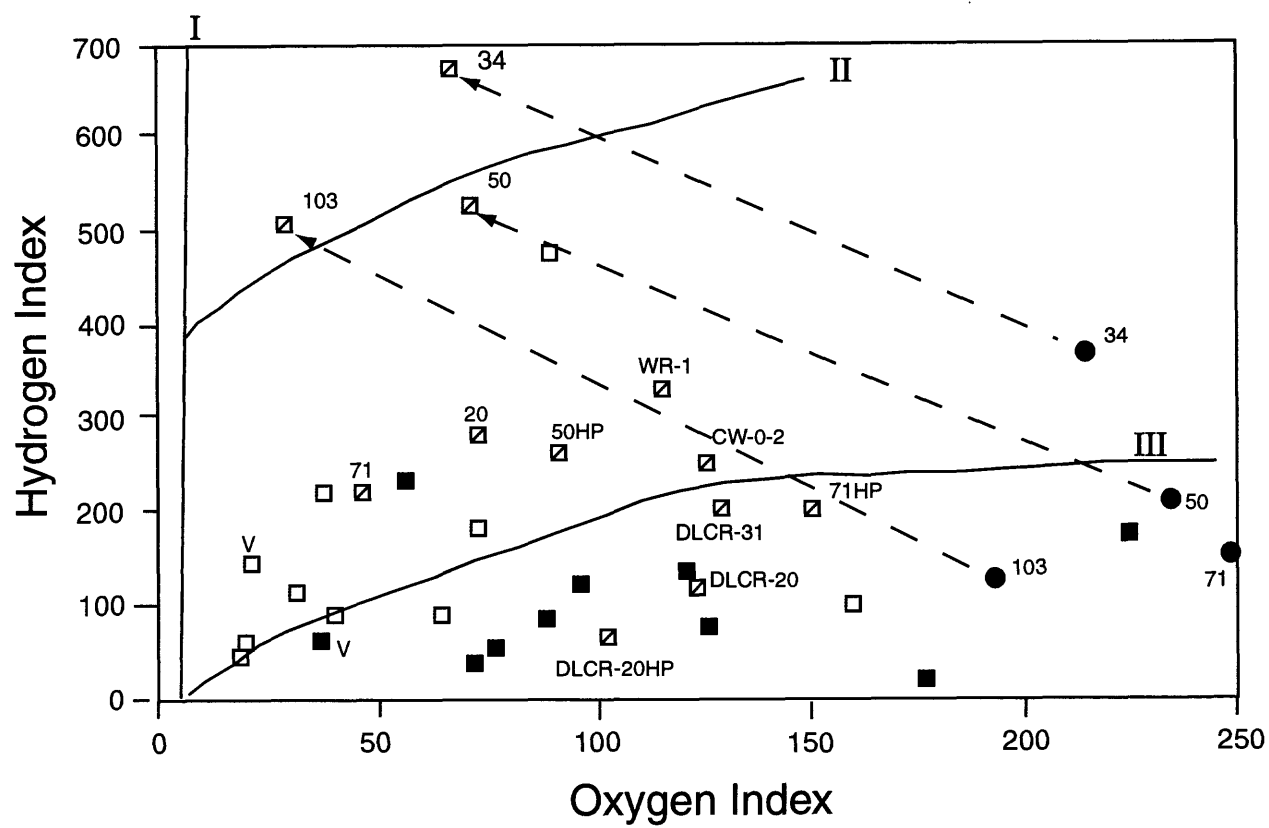
Figure 6

Table 1

Sample Number	Depth (feet)	% Organic Carbon	Tmax	HI	OI	S1
CCM-1-R006	72	1.21	411	220	36	0.02
CCM-1-R031	288	0.22	409	113	0.31	0.01
CCM-1-R043	430	0.25	424	184	72	<0.01
CCM-1-R056	497					
CCM-1-R063	606	0.46	429	60	19	<0.01
CCM-1-R069	606v	74.8	421	145	20	2.43
CCM-1-R090	808	0.05	417	100	160	<0.01
CCM-1-R099	990	0.25	504	476	88	0.08
CCM-1-R113	1002	2.08	433	45	18	0.02
CCM-2-R016	265	1.2	416	232	55	
CCM-2-R020	305	0.52	400	90	88	
CCM-2-R013	246	0.54	401	124	96	
CCM-2-R037	463	0.38	410	55	76	
CCM-2-R062	683	0.47	405	91	63	
CCM-2-R102	1005v	62.1	423	66	36	
CCM-2-R126	1285	0.09	382	22	177	
CCM-2-R142	1436	0.19	497	136	1221	
CCM-2-R150	1515	0.23	426	91	39	
CCM-2-R157	1585	0.02	(333)	(200)	(1050)	<0.01
CCM-2-R199	1968	0.06	(549)	(1066)	(816)	0.03
CCM-2-R203	2005b	<0.02	(394)	0	0	<0.01

Parentheses indicate data is not reliable

15

Table 2

Sample Number	Depth (feet)	Corrected Depth*	Depth of Burial	Ro	DOP	Total Sulfur %	Organic Carbon %	T max
CCM-1-R006	72	522	2322		0.75	2.37	1.21	411
CCM-1-R031	288	738	2538		0.73	1.62	0.22	409
CCM-1-R043	430	880	2680		0.65	0.69	0.25	424
CCM-1-R056	497	947	2747		0.15	0.30	0.03	381
CCM-1-R069	606	1056	2856	0.29	0.36	0.68	0.46	429
CCM-1-R090	808	1250	3050		0.65	0.41	0.05	417
CCM-1-R099	990	1440	3240				0.25	504
CCM-1-R113	1002	1452	3252	0.46	0.48	0.30	2.08	433
CCM-2-R004	163		1963				0.32	412
CCM-2-R013	246		2046		0.61	1.48	0.54	401
CCM-2-R016	265		2065	0.3	0.70	1.59	1.2	416
CCM-2-R020	305		2105		0.71	1.21	0.52	400
CCM-2-R037	463		2263	0.31	0.50	0.84	0.38	410
CCM-2-R037	463		2263				0.11	376
CCM-2-R050	497		2297				0.66	414
CCM-2-R062	683		2483		0.74	1.89	0.47	405
CCM-2-R071	765		2565				0.12	410
CCM-2-R076	815		2613				0.08	440
CCM-2-R076	815		2615	0.27	0.58	0.82	0.08	440
CCM-2-R102	1055		2855	0.31			62.1	423
CCM-2-R126	1085		3085		0.52	0.52	0.09	382
CCM-2-R142	1436		3236		0.72	1.65	0.19	487
CCM-2-R150	1515		3315		0.60	0.63	0.23	426
CCM-2-R157	1585		3385		0.56	0.47	0.02	333
CCM-2-R199	1968		3768				0.06	549
CCM-2-R203	2005		3805		0.23	0.20	0.02	394

*Depth of CCM-1 samples corrected to account for 450 foot estimated stratigraphic displacement between holes.

Table 3

Sample Number	$\delta^{34}S$‰	Total S %	$\delta^{13}C$‰	Organic C %	Comment
CCM-1-R006	16.7	2.37			Organic soluble sulfur
CCM-1-R031	15.6	1.62			Organic soluble sulfur
CCM-2-R016	1.4	1.59			Organic soluble sulfur
CCM-1-R069			-21.96	74.8	Vitrinite
CCM-1-R006			-23.02	1.21	"Algal"