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PRELIMINARY SCIENTIFIC RESULTS OF THE CREEDE CALDERA CONTINENTAL SCIENTIFIC DRILLING PROGRAM

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PRELIMINARY RESULTS ON THE ORGANIC GEOCHEMISTRY OF THE OLIGOCENE CREEDE FORMATION, COLORADO

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INTRODUCTION

The Creede mining district developed around an epithermal Ag-Pb-Zn-Cu-Au mineralization of volcanic rocks near the town of Creede in south central Colorado. Mineralization followed both the development of the Creede caldera (26.6 Ma) and the deposition of the lacustrine Creede Formation (26.5 Ma) by over a million years. The Oligocene Creede Formation includes lacustrine volcaniclastic and biogenic carbonate sediments, landslide breccias, fluvial/deltaic sediments, and travertine mounds. This study attempts to determine if the organic matter in the Creede Formation has been directly exposed to hydrothermal fluids. Evidence of direct contact may be expressed as chemical transformations of organic matter from high thermal stress and/or the presence of certain organosulfur compounds derived from reactions with sulfur in the hydrothermal fluids.

SAMPLES AND ANALYTICAL TECHNIQUES

The two core holes are called Hosselkus #6-1 (CCM-1) and Airport #10-1 (CCM-2). Sample splits were taken from parts of the core thought to contain some organic matter. Rock-Eval pyrolysis was done on 24 core samples and 10 outcrop samples to determine the quality and quantity of organic matter (see chapter by Leventhal). From this set, a subset of 7 core samples was powdered and extracted with chloroform for 60 hours in a Soxhlet apparatus (Table 1). A second extraction with toluene:methanol (50:50 v/v) for 72 hours was performed, and extracts were dried and weighed. The chloroform-extracted bitumen was separated by elution chromatography into saturated hydrocarbon, aromatic hydrocarbon, resin and asphaltene fractions. The elution columns were constructed from activated alumina and silica gel (Grade 923 and Grade 62).

Gas chromatography of the C_{9+} saturated hydrocarbon fractions was performed with a Hewlett Packard 5880A gas chromatograph (GC) equipped with a 50m x 0.32mm fused-silica capillary column (OV-5) and a flame ionization detector (FID). The GC temperature program was as follows: 50°C for two minutes, ramp from 50°C to 320°C at 4°C/minute, and hold at 320°C for 15 minutes. Selected aromatic hydrocarbon fractions were also run on a Perkin Elmer 8500 GC with a flame photometric detector (FPD) to detect organosulfur compounds. Biomarker distributions were determined by running hydrocarbon fractions on a computerized GC-MS system using a Hewlett Packard 5890 GC with a DB-1701 60 m x 0.32 mm column coupled with a VG7035 mass spectrometer. Dynamic mass resolution was 3000 (5% valley). Multiple ion detection was accomplished by switching the accelerating voltage at a constant magnetic field. The selected ions were m/z 191 (terpanes), m/z 217 (steranes), m/z 231 (triaromatic steroids) and m/z 253 (monoaromatic steroids). Full mass scan for the range m/z 50-450 was performed on selected aromatic hydrocarbon fractions. Peak identifications were based on elution time and mass spectra (Philp, 1985).

RESULTS

Bulk Geochemistry

The chloroform-extractable organic matter (EOM) concentrations in the samples are quite low (23-476 ppm) (Table 2) except for the "coal" (1R069, 9635 ppm) and the "algal" sample (1R006, 1137 ppm). After the chloroform extraction, from 2 to 10 times more organic matter was extracted using the toluene:methanol mixture. Only the "algal" sample yielded less organic matter in the second extraction. Elemental or labile organic sulfur released from the samples during the extraction procedure will react with added copper strips yielding a copper sulfide precipitate. The 1R006, 2R016 and 1R031 samples yielded large amounts of elemental sulfur while the other samples contain minor or trace amounts.
Hydrocarbons in the samples are generally aromatic (saturate/aromatic ratio less than 1) with the "coal" sample the most aromatic (S/A ratio = 0.31). The "coal" sample also has highest relative concentration of asphaltenes (39.1%) while the "algal" sample has the lowest (9.6%).

Gas Chromatography

The pristane/phytane ratios in the saturated hydrocarbon gas chromatograms (GC) are generally less than unity for all the samples except the "coal" sample (1.33) and sample 1R113 (Table 3). Phytane is especially dominant in samples 1R006, 2R016 and 1R031 while normal alkanes are lower in relative concentration. Normal alkanes dominate over isoprenoids in three samples (1R056, 2R013 and 1R113) with maxima at carbon numbers C_{15} and C_{29}. The n-alkane distributions show odd-carbon number predominance in the range of C_{24}-C_{30} in several of the samples and an even-carbon predominance in two samples (Table 3). Farnesane (i-C_{15}) is relatively lean in all the samples with the highest concentration in sample 1R113. Beta-carotane was not detected by GC in any of the samples but may be present in very small concentrations. However, hopanoid and steroid compounds are visible in the gas chromatograms of most of the samples.

Trace to moderate amounts of organosulfur compounds (OSC) were detected by GC (using the FPD) in the aromatic hydrocarbon fraction of the samples. In the two samples with the highest relative concentrations (1R113, 2R016) of OSC, peaks eluted at higher temperatures implying higher molecular weight. No homologous series of peaks was observed.

Molecular Geochemistry

All samples were analyzed for the distribution of biological markers (biomarkers) including steranes (m/z 217), hopanoids (m/z 191), monoaromatic steranes (m/z 253), and triaromatic steranes (m/z 231). Ratios are based on peak areas and are listed in Table 4. All of the samples may be characterized by high concentrations of C_{29} desmethyl steranes (51.6% to 84.4%) relative to C_{27} and C_{28} steranes (Table 4). The C_{28} triaromatic sterane is also more abundant than C_{26} or C_{27} triaromatic steranes. The sample with the highest C_{27} desmethyl sterane is

1R031 (30.1%), and the sample with the highest C_{28} is 1R006 (28.6%). However, methyl steranes (e.g. dinosterane) and C_{30} desmethyl sterane peaks are minor (1R113, 1R069) or missing altogether. All of the samples have low concentrations of diasteranes and pregnanes (C_{21} and C_{22} steranes) and moderate amounts of 5β steranes. All samples except one contain more steranes than hopanoids (hopane/hopane+sterane = 0.037 to 0.391). The one sample, 1R113, contains predominantly hopanoids (hopane/hopane+ sterane = 0.955).

The largest peak in the m/z 191 chromatogram of all the samples is 17α,21β C_{30} hopane except sample 1R113 which has a larger norhopane peak. All of the samples contain moderate amounts of gammacerane (13.9 to 47%) relative to C_{30} hopane but oleanane does not appear in any samples. Minor amounts of hopenes and 17β,21β hopanes are present in most of the samples. With one exception (2R013) the 18α trisnorneohopane (Ts) is minor or absent while the 17α trisnorhopane (Tm) is present in moderate amounts in all samples. The tricyclic terpanes and the tetracyclic terpanes are generally low in abundance, but all of the samples contain moderate to high amounts terpanes (m/z 191 fragment) with 20 carbons and less.

As noted above, sample 1R113 is unusual for several reasons: high pristane relative to phytane, high n-alkanes relative to acyclic isoprenoids, highest farnesane relative to other acyclic isoprenoids, high OSC, high hopanoids relative to steranes, high norhopane relative to hopane, high C_{28} triaromatic sterane relative to C_{26} and C_{27} triaromatic steranes. This sample also has the highest isomerization ratio of C_{29} S/S+R steranes and second highest triaromatic steranes relative to monoaromatic steranes. It is the deepest sample that was analyzed (1002 ft).

The aromatic hydrocarbon fraction of four samples (1R113, 1R069, 1R006, 2R016) was scanned for the mass range from 50 to 450 m/z for the identification of organosulfur compounds and aromatic hydrocarbons. The mass spectrum of every major peak (and many minor ones) was checked to determine the compound class, and in some cases, identify the specific compound. The relative abundances of selected compound classes (Table 5) were assessed based on the number and size of peaks in the representative mass chromatograms. Although the mass fragment ion is assumed to represent the listed compound class, other compound types may yield the same fragment ion.

Organosulfur compounds are present in all four samples and are most abundant in 1R113. The largest peak on the total ion current chromatogram for this sample is an OSC - benzonapthothiophene. Samples 1R006 and 2R016 contain predominantly thiolanes and thianes and are deficient in sulfides and thiophenes (in contrast to 1R113 and 1R069). Only the isoprenoid thiolanes (m/z 101) and dithianes + alkylbenzenes (m/z 119) mass chromatograms show any pattern of homologous series of peaks.

Aromatic compounds that are terrestrial plant source indicators including cadelane, simonellite, norabietane bisnorsimonellite, retene, and tetrahydroretane are only abundant in sample 1R069. Aryl isoprenoids (alkylbenzene compounds)

are present in all four samples, and most abundant in 1R069. Most of the polyaromatic hydrocarbons (PAH) are in 1R113 and 1R069, including phenanthrenes, perylenes, triaromatic steroids, and chrysenes; the naphthalenes, however, are only abundant in 1R069.

Maturity parameters

Molecular composition of organic matter changes with thermal maturity due to a number of reactions that are temperature and time dependent. The Creede samples show a range of maturities based on biomarker maturity parameters, of which the most dynamic example is the aromatization of monoaromatic steranes to triaromatic steranes. This reaction is expressed as the ratio: triaromatic steranes/tri- + monoaromatic steranes or T/T+M (0.0 -> 1.0). The order of maturity based on T/T+M is listed on Table 6. Most other biomarker maturity parameters agree with relative maturity order based on T/T+M including: C_{29} sterane S/S+R, C_{21} tricyclic/hopane, C_{23} tricyclic/hopane, hopane/sterane, diasterane/sterane, pregnane/sterane, C_{27} diasterane S/S+R, and Ts/Tm. With the exception of sample 1R006 the following maturity parameters also agree with the T/T+M maturity order: C_{30} 17β,21β hopane/17α,21β hopane, C_{31} 17β,21β hopane/17α,21β hopane, hopene/hopane, C_{31} hopane S/S+R and the Tmax of the S_2 peak from Rock-Eval. Disagreement with the T/T+M order was observed in moretane/hopane and 5β sterane concentrations. In addition, the methyl phenanthrene index (MPI) shows 1R069 (0.37) slightly more mature than 1R113 (0.24) rather than the other way (MPI formula from Cassani and others, 1988).

Maturity normally increases with drilled depth because deeper sediments are usually both older and hotter. The Creede corehole samples generally show an increase in maturity with depth (Table 6) although the downhole maturity profile has a steep slope. The one exception (maturity inversion) is sample 1R056 at 151.5m (497 ft) which appears more mature than samples 1R069 (184.7 m = 606 ft) and 1R113 (305.4 m = 1002 ft). Because approximately 121.5 m (400 ft) of stratigraphic section is missing from CCM1 relative to CCM2, an adjusted depth is also listed in Table 6 in order to compare the two coreholes.

DISCUSSION AND CONCLUSIONS

Source of Organic Matter

Based on macroscopic microscope examination, as well as Rock-Eval data, the organic matter is largely Type III (terrestrial source). Molecular geochemistry supports this conclusion with strong odd carbon n-alkane predominance, relatively high C_{29} steranes concentrations, and with some samples containing specific biomarkers derived from higher plants (retene, cadenene, simonellite, norabietane, bisnorsimonellite, and tetrahydroretene). The biomarkers indicative of other source organisms include hopanoids (bacteria) and steroids (algae). High sterane concentration relative to hopane may be an indicator, in part, of significant algal input even though the C_{29} sterane is the dominant peak and may be derived from higher plants.

Depositional Environment

Organosulfur compounds (as well as diagenetic pyrite) require an inorganic source of sulfur. The most common source is hydrogen sulfide from bacterial sulfate reduction of dissolved sulfate. This lake probably contained moderate sulfate concentrations as volcanic rocks weathered and pyrite oxidized. Biomarker indicators of green and purple sulfur bacteria (which consume hydrogen sulfide) suggest a sulfate-sulfide aqueous environment. The presence of other biomarkers such as gammacerane and phytane are sometimes indicators of high salinity. However, beta carotane is not abundant in the samples (another indicator of high salinity). Another possible source may have been from the hydrothermal fluids containing dissolved sulfide. The predominance of highly aromatic OSC in some of the samples suggests that hydrothermal fluids may have contributed aqueous sulfide.

Thermal Exposure

For a given thermal history, the kinetic parameters of each biomarker reaction determine the extent of the reaction. For example, Mackenzie and McKenzie (1983) observed that in cool-old basins (slow heating rate), the S/S+R isomerization reaction of C_{29} steranes has reached a greater extent than the aromatization of monoaromatic steranes. In hot young basins (high heating rate), the reverse is true. The Creede sample data plot along the hot-young basin trend (Fig. 1). The high heating rate may also explain the presence of thermally labile biomarkers such as 17β,21β hopanes (all but one sample), 5β steranes (all but one sample) and hopenes (all but two samples) in more mature samples as measured by T/T+M. Furthermore, the dramatic maturity change with depth (slope of the down-hole maturity profile) indicates a high geothermal gradient at some time in the geologic past: 1R006 at 21.9 m (72 ft) has a T/T+M value of 0.038 while 1R031 at 87.8 m (288 ft) has a T/T+M value 0.692, and 1R056 at 151.5 m (497 ft) has a T/T+M of 0.98.

Two samples (1R069, 1R113) have anomalously high ratios of phenanthrene to methyl phenanthrenes (0.84 and 1.88, respectively). Similar values have been observed in petroleum generated near hydrothermal vents on the ocean floor (Kvenvolden and Simoneit, 1990) as well as in kerogen that has been heated in a laboratory at temperatures between 310 and 410 °C (Ishiwatari and Fukushima, 1979). The abundance of phenanthrene and other non-alkylated PAH suggests that some of the Creede Formation was exposed to very high temperatures.

Based on biomarker maturity parameters as well as the abundance of polyaromatic hydrocarbons and highly aromatic OSC, some of the Creede Formation has experienced significant heat exposure in a relatively short geologic time period. This thermal history was due to the brief epithermal mineralization event which occurred soon after deposition of the Creede Formation. The inverted downhole maturity profile suggests that the primary transport mechanism of heat may have been hydrothermal fluids migrating along local fracture systems (convective heat) rather than high conductive heat flow.

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FIGURE CAPTIONS

Figure 1. Aromatization of monoaromatic steroids to triaromatic steroids vs. isomerization of C_{29} desmethyl steranes. Creede Formation samples in CCM1 are circles, Pannonian Basin samples are crosses, and North Sea samples are triangles. The Pannonian Basin is a Tertiary basin with a high geothermal gradient and the North Sea is a Mesozoic basin with a low geothermal gradient (MacKenzie and McKenzie, 1983).

Table 1. List of Creede Formation core samples for detailed organic geochemical analysis. 1R samples are from Hosselkus #6-1, 2R samples are from Airport #10-1.

Sample	Depth (ft)	Lab Code	Description
1R006	72.0	92050-001	"algal"
1R031	288.1	92050-003	
1R056	497.8	92136-004	
1R069	606.0	92035-009	"coal-vitrinite"
1R113	1002.1	92035-005	
2R013	251.5	92035-003	
2R016	263.6	92050-002	

Table 2. Bulk geochemistry*

Sample	EOM	EOM_2	S/A	SAT	ARO	NSO	ASP
1R006	1137	684	0.84	21.9	26.1	42.4	9.6
1R031	296	773	0.61	19.1	31.1	35.9	13.9
1R056	23	327	0.65	18.4	28.4	35.5	17.7
1R069	9635	16615	0.31	9.5	30.7	20.8	39.1
1R113	32	231	1.04	20.6	19.7	38.7	21.0
2R013	31	319	1.08	19.7	18.2	41.0	21.1
2R016	476	942	0.58	8.3	14.2	52.7	24.9

*EOM = ppm wt extractable organic matter/wt rock - first extraction in chloroform; EOM_2 = ppm wt extractable organic matter/wt rock - second extraction in toluene:methanol 50:50 v/v; S/A = ratio of saturated to aromatic hydrocarbons; SAT = normalized percent saturated hydrocarbons; ARO = normalized percent aromatic hydrocarbons; NSO = normalized percent NSO compounds
ASP = normalized percent asphaltene compounds.

Table 3. Saturated hydrocarbon gas chromatography data*

Sample	Pr/Ph	Pr/17	Ph/18	A/N	%Fa	%Ph	CPI
1R006 "algal"	0.15	un	un	1.54	0.0	79.9	0.54
1R031	0.42	un	un	3.13	0.0	59.3	2.44
1R056	0.99	1.38	1.42	0.38	6.8	18.8	1.87
1R069 "coal"	1.33	5.14	9.58	3.05	5.2	26.7	un
1R113	4.45	1.39	0.32	0.19	8.5	6.6	2.13
2R013	0.47	1.76	14.86	0.39	0.0	62.8	4.39co
2R016	0.09	un	un	3.71	0.0	90.8	0.73

* Pr = pristane; Ph = phytane; 17 and 18 are normal hydrocarbons with 17 and 18 carbons, respectively; A/N = ratio of acyclic isoprenoids to normal alkanes; Fa = farnesane; %Fa and %Ph are normalized percent of total acyclic isoprenoids; un = undefined due to lack of n-alkanes; co = coelution problems.
All values based on peak area except Carbon Preference Index (CPI) based on peak height in carbon range of C_{24}-C_{30}.

Table 4. Biomarker ratio data*

Sample	1R006	1R031	1R056	1R069	1R113	2R013	2R016
Ts/Ts+Tm	0.000	0.000	0.114	0.238	0.000	0.617	0.000
norhopane/norhopane+hop	0.125	0.153	0.425	0.244	0.547	0.276	0.247
C_{29}Ts/C_{29}Ts + norhopane	0.393	0.392	0.079	0.481	0.000	0.348	0.000
norhopane+C_{29}Ts/nor+C_{29}Ts+hop	0.191	0.228	0.446	0.384	0.547	0.369	0.247
normoretane/normoretane+moretane	0.632	0.579	0.446	0.521	0.473	0.586	0.238
hopene I/hopene I+hop	0.017	0.042	0.000	0.047	0.000	0.111	0.000
normoretane/normoretane+hop	0.165	0.178	0.304	0.250	0.412	0.321	0.188
hopene II/hopene II+hop	0.029	0.045	0.000	0.016	0.000	0.381	0.120
moretane/moretane+hop	0.103	0.136	0.352	0.235	0.438	0.251	0.426
C_{31} hopane/C_{31} hopane +hop	0.048	0.148	0.435	0.271	0.482	0.231	0.000
C_{31} hopane S/S+R	0.601	0.503	0.548	0.468	0.599	0.824Z	0.000
gammacerane/gammacerane+hop	0.470	0.139	0.261	0.218	0.276	0.292	0.328
$C_{30}\beta\beta$ hopane/$\beta\beta$+hop	0.043	0.054	0.000	0.242	0.021	0.266	0.275
$C_{31}\beta\beta$ hopane/$\beta\beta$+hop	0.000	0.000	0.000	0.000	0.000	0.143	0.124
$C_{32}\beta\beta$ hopane/$\beta\beta$+hop	0.000	0.000	0.000	0.000	0.000	0.046	0.000
C_{30}+C_{31}+C_{32} $\beta\beta$/$\beta\beta$+hopane	0.043	0.054	0.000	0.242	0.021	0.366	0.343
C_{32} hopane/C_{32} hopane+hop	0.027	0.056	0.229	0.149	0.266	0.142	0.169
C_{32} hopane S/S+R	0.000	0.345	0.528	0.577	0.608	1.000Z	1.000Z
C_{33} hopane/C_{33}+hop	0.013	0.031	0.129	0.127	0.149	0.099	0.000
C_{33} hopane S/S+R	0.000	0.000	0.385	0.436	0.531	0.347	0.000
hop/C_{27}-35 hopanes	0.829	0.766	0.648	0.591	0.555	0.410	0.443
C_{20} Tricyclic /C_{20} + hop	0.021	0.000	0.027	0.059	0.000	0.021	0.117
C_{21} Tricyclic /C_{23} + hop	0.009	0.032	0.068	0.131	0.000	0.033	0.045
C_{23} Tricyclic /C_{23} + hop	0.013	0.000	0.087	0.097	0.032	0.063	0.000
C_{24} Tricyclic /C_{24} + hop	0.000	0.015	0.061	0.072	0.021	0.054	0.104
C_{24}Tetracyclic /Tetra + hop	0.000	0.000	0.036	0.052	0.051	0.024	0.000
C_{27}-35 hopanes/all steranes+hopanes	0.111	0.229	0.178	0.037	0.955	0.039	0.391
C_{27} $\alpha\alpha\alpha$ R/C_{27}+C_{28}+C_{29} steranes	0.121	0.301	0.203	0.270	0.087	0.083	0.072
C_{28} $\alpha\alpha\alpha$ R/C_{27}+C_{28}+C_{29} steranes	0.286	0.182	0.175	0.178	0.116	0.156	0.084
C_{29} $\alpha\alpha\alpha$ R/C_{27}+C_{28}+C_{29} steranes	0.592	0.516	0.622	0.553	0.797	0.761	0.844
C_{21} pregnane/ all steranes	0.000	0.011	0.014	0.033	0.000	0.000	0.000
C22 pregnane/ all steranes	0.000	0.003	0.006	0.011	0.041	0.000	0.000
C_{21}/C_{22} pregnanes	0.000	3.436	2.579	2.916	0.000	0.000	0.000
C_{27} R dia-/dia- + C_{27} $\alpha\alpha\alpha$ R sterane	0.000	0.030	0.035	0.031	0.000	0.000	0.000
C_{27} $\beta\alpha\alpha$/$\beta\alpha\alpha$ + $\alpha\alpha\alpha$ R sterane	0.227	0.467	0.365	0.437	0.000	0.347	0.411
C_{28} $\beta\alpha\alpha$/$\beta\alpha\alpha$ + $\alpha\alpha\alpha$ R sterane	0.211	0.275	0.264	0.356	0.000	0.296	0.310
C29 $\alpha\alpha\alpha$S/$\alpha\alpha\alpha$S + $\alpha\alpha\alpha$ R sterane	0.066	0.082	0.199	0.090	0.275	0.041	0.000
C_{29} $\beta\alpha\alpha$/$\beta\alpha\alpha$+ $\alpha\alpha\alpha$ R sterane	0.195	0.299X	0.317X	0.434X	0.212X	0.261	0.285
T/T+M (all peaks)	0.053	0.411	0.906	0.553	0.835	0.145	0.864

Table 4 (Continued)

Sample	1R006	1R031	1R056	1R069	1R113	2R013	2R016
T/T+M (MacKenzie, 1983)	0.038	0.692	0.983	0.844	0.956	0.061	0.564
C_{28} S/S+R triaromatic steranes	0.473	0.508	0.581	0.505	0.582	0.501	0.000
C_{20}+C_{21} tri-/all triaromatic steranes	0.042	0.029	0.019	0.150	0.129	0.097	0.000
C_{28} S+R tri-/C_{26}+C_{27}+C_{28} S+R tri-	0.450	0.647	0.669	0.539	0.706	0.673	1.000

* Most ratios are in the form X/(X+Y); Z = coelution problems; hop = 17α,21β C_{30} hopane; Tm = 17α(H) 22,29,30-trisnorhopane; Ts = 18α(H) - 22,29,30-trisnorneohopane; all steranes = C_{21}+C_{22} +C_{27}+C_{28}+C_{29} steranes; βαα = 5β(H),14α(H),17α(H); ααα = 5α(H), 14α(H), 17α(H); dia- = diasterane; X = coelution of βαα with αββ 20R sterane; T/T+M = triaromatic steranes/triaromatic steranes + monoaromatic steranes; tri- = triaromatic sterane.

Table 5. Relative abundances of aromatic and organosulfur compounds in the Creede Formation based on representative (m/z) mass chromatograms* See text for explanation.

Sample	1R113	1R069	1R006	2R016
Organosulfur compounds				
2,5 dialkyl thiolane (m/z 87)	-	m	-	-
2,5 dialkyl thiophene (m/z 97)	m	-	m	+
isoprenoid thiolanes (m/z 101)	+	++	++	++
highly branched thiolane (m/z 115)	-	++	m	++
dithiane + alkylbenzene (m/z 119)	+	+	++	+
alkylthiophene (m/z 111)	-	-	-	++
highly branched isoprenoid thiophene (m/z 125)	m	-	m	++
isoprenoid thiolene (m/z 145 157)	+	+	-	+
2,4 dialkyl benz-(β) thiophene (m/z 147)	+	m	m	-
isoprenoid benzothiophene (m/z 175)	m	+	-	-
isoprenoid bithiophenes + trimethyl phenanthrenes (m/z 220)	m	++	m	m
isoprenoid bithiophene (m/z 221)	m	+	-	-
thiolane hopanoid + dimethyl-phenanthrene (m/z 191)	m	+	-	-
C_{18} tricyclic sulfone (m/z 233)	++	+	-	-
benzonapthothiophene (m/z 234)	++	-	-	-
bicyclic terp. sulfide (m/z 183)	+	++	+	-
C_{15} bicyclic terp. sulfide (m/z 240) Note1	++	m	-	-
C_{16} bicyclic terp. sulfide (m/z 254)	+	+	-	-
tricyclic terpenoid sulfide (m/z 251)	++	m	-	-
dibenzothiophene (m/z 184)	+	+	-	-
methyl dibenzothiophene (m/z 198)	m	-	m	-

Table 5. (Continued)

Sample	1R113	1R069	1R006	2R016
Aromatic hydrocarbons - polycyclic				
perylene (m/z 252)	++	++	-	-
methyl perylene (m/z 268)	+	-	-	-
diels HC (m/z 217)	m	+	-	-
chrysene (m/z 218) Note 2	++	++	-	-
triaromatic steranes (m/z 231)	++	++	-	-
chrysene (m/z 228)	++	++	-	-
methyl chrysene (m/z 242)	+	-	-	-
naphthalenes (m/z 142 155, 156, 170, 184)	m	++	-	-
phenanthrene (m/z 178)	++	++	m	-
m phenanthrene (m/z 192)	+	+	m	-
dimethyl phenanthrene + chrysene (m/z 206)	+	-	-	-
biphenyl (m/z 154)	+	+	+	+
2,2 diethyl biphenyl (m/z 181)	+	-	-	-
pyrene + fluoranthene (m/z 202)	+	-	+	+
Aromatic hydrocarbons - Source dependent				
cadelene (m/z 183)	m	+	m	-
Simonellite (m/z 252)	-	+	-	-
norabietene	-	+	-	m
bisnorsimonellite	-	+	-	m
tetrahydroretene	-	+	-	-
retene (m/z 219, 234)	-	+	-	m
Aromatic hydrocarbons - aryl isoprenoids				
alkyl benzene (m/z 92)	m	+	-	m
di- tri- alkylbenzene (m/z 119)	+	++	+	m
trialkyl benzene (m/z 133)	m	+	m	-
dimethyl benzene (m/z 91 106)	-	-	-	+

*m/z = mass/charge; - = not detected; m = minor; + = moderate; ++ = abundant. Note 1- mostly 1-benzothieno 4,5 benzothiophene in 1R113; Note 2 - also benzobinaphtho 2,3-difuran and compound A (Philp, 1985, p.225) have m/z 218.

Table 6. Order of maturity from lowest to highest based on steroid aromatization ratio (T/T+M)* See text for explanation.

Sample	R_o	T/T+M	T_{max}	Drilled Depth (ft)	Adjusted Depth (ft)
1R006		0.038	411	72.0	472.0
2R013		0.061	401	251.5	251.5
2R016	0.30	0.564	416	263.6	263.6
1R031		0.692	409	288.1	688.1
1R069	0.29	0.844	421	606.0	1006.0
1R113	0.46	0.956	433	1002.1	1402.1
1R056		0.983	381	497.8	897.8

* R_o = vitrinite reflectance in oil (see Leventhal and others, this volume); T/T+M = triaromatic steranes/triaromatic steranes + monoaromatic steranes (see Table 4); T_{max} = maximum temperature of S_2 peak from Rock-Eval; Adjusted depth = 121.9m (400) added to CCM-1 samples.

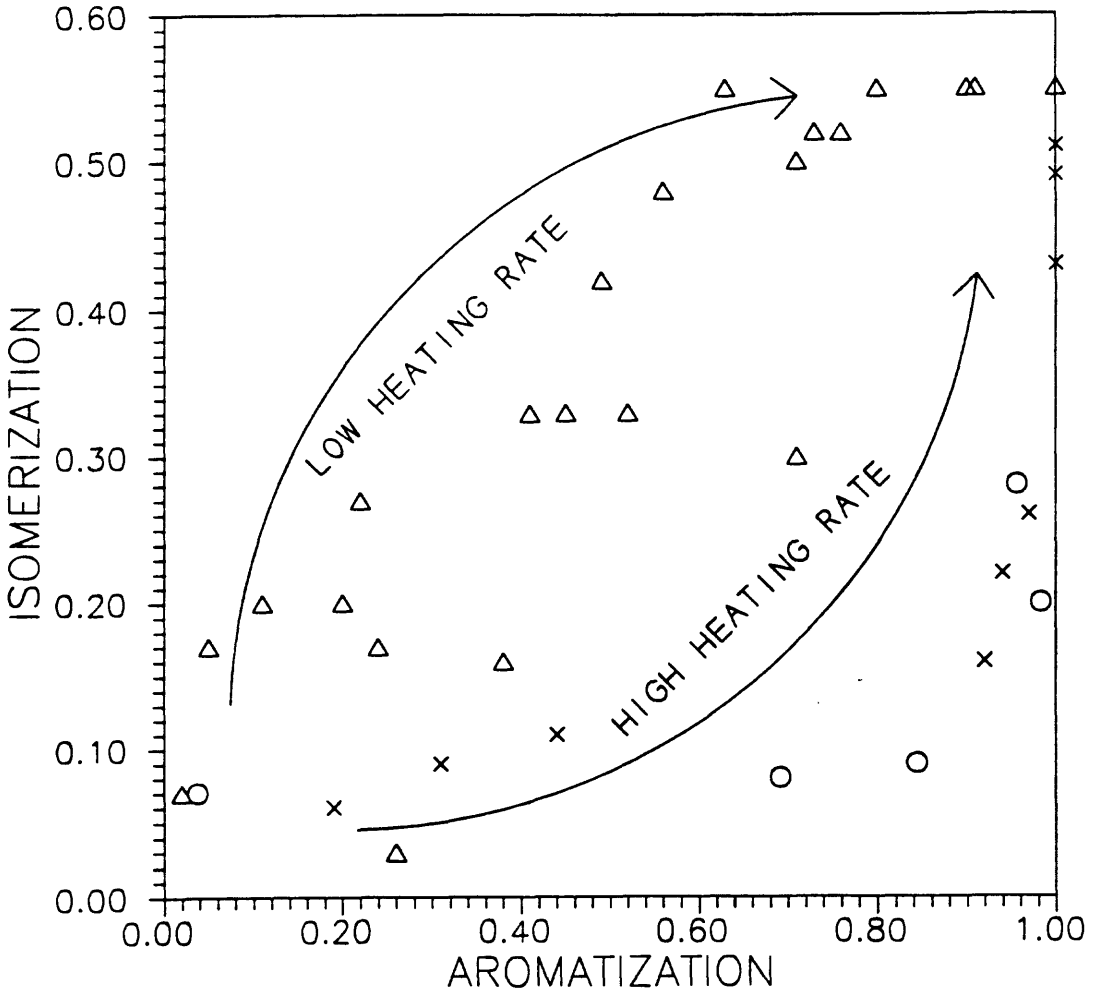

Figure 1. Aromatization of monoaromatic steroids to triaromatic steroids vs. isomerization of C_{29} desmethyl steranes. Creede Formation samples in CCM1 are circles, Pannonian Basin samples are crosses, and North Sea samples are triangles. The Pannonian Basin is a Tertiary basin with a high geothermal gradient and the North Sea is a Mesozoic basin with a low geothermal gradient (MacKenzie and McKenzie, 1983).