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IMPLICATIONS OF HYDROCARBONS IN CARBONACEOUS METAMORPHIC AND HYDROTHERMAL ORE-DEPOSIT ROCKS AS RELATED TO THE HYDROLYTIC DISPROPORTIONATION OF ORGANIC MATTER

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1.0 ABSTRACT

Petroleum-geochemical analyses performed on a large suite of crystalline and ore-deposit rocks, from worldwide settings, have demonstrated the presence of very low to moderately-low concentrations of solvent-extractable organic matter (OM) in these rocks. This observation in spite of the fact that some of these rocks were exposed to extremely high "burial" temperatures in the earth's crust. Detailed laboratory checks, and other considerations, demonstrate that our C_{12}+ extractable bitumen has no significant contribution from contamination. Biomarker and $\delta^{13}C$ analyses demonstrate that this extractable OM originated as sedimentary-derived hydrocarbons (HCS). However, the chemistry of the extractable bitumen in our rocks has been fundamentally transformed from that found in sediment bitumen and oils.

For example, asphaltenes and resins, as defined in the normal petroleum-geochemical sense, are completely missing. Also, the principal aromatic HCS present in oils and sediment bitumens (especially the methylated naphthalenes) are either in highly-reduced concentrations or are missing altogether. Instead, aromatic HCS normally present in sediment bitumens and oils in small concentrations are the dominant compounds, in conjunction with a number of unidentified compounds and oxygen-bearing compounds. Relatively high concentrations of alkylated benzenes (and other low-molecular-weight solvent-extractable OM?) were also present in our aromatic HCS. The "resin" fraction of our rocks is the dominant compound group by weight, and is composed of 6 to 8 dominant peaks which recur in all samples, despite the wide geologic provenance of our sample base. This, and other, observations suggest to us that a strong drive towards thermodynamic equilibrium exists in the "bitumen" of our rocks. The saturated HCS from our samples commonly exhibit a pronounced hump in both the n-paraffins and naphthenes, centered around the C_{19} to C_{26} carbon numbers. A minimum in the n-paraffin distribution around n-C_{12} to n-C_{14} is ubiquitous in our samples.

Many of our observations from the natural system dovetail with the expected consequences of a theoretical process (hydrolytic disproportionation of OM) proposed by Helgeson et al. (1993), wherein water and OM, including HCS with faculty exchange hydrogen or oxygen with one another under certain conditions. Moreover, the process appears to occur via well-known organic-chemical pathways. The conclusion that hydrolytic disproportionation affected the OM of our rocks, thus determining the chemical makeup of the extractable bitumen in our rocks, receives support from numerous previously-published organic-geochemical studies of ore-deposit and crystalline rocks by other investigators.

We believe that hydrolytic disproportionation of OM is a previously-unrecognized geologic agent of the first magnitude, involving reactions and equilibriums between mineral species, water, and OM, in our opinion, by ionic/carbonium ion redox reaction pathways. The process would play major roles in a

number of different geologic areas including, but not limited to, petroleum geology and geochemistry, heavy-metal ore deposition, and helping to set mineral-stability fields in rock metamorphism. Herein we provide evidence for, and examples of, the influence of hydrolytic disproportionation of OM as a controlling parameter in petroleum geology and geochemistry, and in heavy-metal ore deposition.

2.0 INTRODUCTION

2.01 HYDROLYTIC-DISPROPORTIONATION OF OM

Helgeson et al. (1993), from thermodynamic treatments, provided a theoretical background wherein rocks, water, and reservoired oil at the oil-water contacts in petroleum reservoirs are chemically-linked, and maintain a metastable equilibrium among themselves, via oxidized carbon species (such as CO_2) by exchanging hydrogen and/or oxygen with one another, as determined by the oxygen (or hydrogen) fugacity of the system. Shock (1988) and Helgeson and Shock (1988) had first proposed the concept of a metastable equilibrium between organic acids, reservoir rocks, oils, and reservoir brines. Helgeson et al. (1993, p. 3296) termed the process wherein this metastable equilibrium was achieved and maintained "hydrolytic disproportionation of OM", due to water disproportionating to charged ions which then react with OM, and defined the process as a reaction of a HC with water to form a lighter HC and an oxidized carbon species. Although the overall process is irreversible, hydrolytic disproportionation of OM was theorized to involve both reversible and irreversible reactions, depending on system conditions. The end products of this overall process were calculated to be CO_2 and CH_4; and in the drive towards this end point, there is a strong theoretical basis for the formation of significant concentrations of intermediate-step compounds: lower-molecular weight HCS and oxygen-bearing and other organic compounds.

Helgeson et al. (1993, p. 3307-3308) viewed hydrolytic disproportionation of OM as an oxidation-reduction (redox) reaction which could be electronically balanced by assigning nominal oxidation states to various carbon bonds. Carbon-hydrogen bonds were assigned a value of -1; carbon-carbon bonds, a value of 0; and carbon-oxygen, carbon-sulfur, or carbon-nitrogen bonds, a value of +1. Thus, the carbon in ethane (C_2H_6) would have an average oxidation state of -3, whereas the carbon in acetic acid (CH_3 COOH) would have an average oxidation state of 0. Therefore, ethane is significantly more reduced than acetic acid, and methane (CH_4) would be the most reduced HC possible, with a value of -4. During hydrolytic disproportionation reactions, within the OM, oxidation-reduction reactions must be balanced. If some carbon species are being oxidized (eventually to CO_2, but first to acids, esters, etc.), then other carbon species must be reduced, and they are reduced to methane or to other lower-molecular weight HCS. The overall reaction may be simplistically written (where OM is organic matter) as:

$$OM + H_2O \longrightarrow CH_4 + CO_2 \qquad (1).$$

Helgeson et al. (1993, p. 3322-3323) gave an example of a series of nine hydrolytic disproportionation reactions as the stepwise hydrolysis of decane to methane and CO_2, with the first two reactions being,

$$\underset{\text{(decane)}}{28\ C_9H_{20(l)}} + 2H_2O \longleftrightarrow \underset{\text{(nonane)}}{28\ C_8H_{18(l)}} + CO_{2\ (aq)} \qquad (2),$$

$$\underset{\text{(nonane)}}{25\ C_8H_{18(l)}} + 2H_2O \longrightarrow \underset{\text{(octane)}}{25\ C_7H_{16(l)}} + CO_{2\ (aq)} \qquad (3);$$

and the last reaction being

$$\underset{\text{(ethane)}}{4\ C_2H_{6(l)}} + 2H_2O \longrightarrow \underset{\text{(methane)}}{7CH_{4(l)}} + CO_{2\ (aq)} \qquad (4).$$

Helgeson et al. (1993) carried out their calculations for petroleum reservoirs along the Texas Gulf Coast (U.S.); however, they believed hydrolytic disproportionation of OM to be universally applicable at oil-water contacts in petroleum reservoirs in basins worldwide. Helgeson (1991, p. 716) had earlier noted that the reaction,

$$2CO_{2\ (aq)} + 2H_2O \leftrightarrow CH_3\ COOH_{(aq)} + 2O_{2\ (g)} \qquad (5),$$

"--- constitutes a bridge between oxidation/reduction mineral equilibria and metastable equilibria among oxidized carbon-bearing species in aqueous solutions and reduced hydrocarbons in petroleum". In other words, as Helgeson et al. (1993, p. 3325-3328) noted, hydrolytic disproportionation of OM would result in a mechanism by which the OM in a system could help to set mineral equilibria and drive mineral diagenesis reactions, as they noted, one possible result being the formation of secondary porosity.

Helgeson (1993, p. 3323) also observed that hydrolytic disproportionation between oil and water in a petroleum reservoir would be dependent on a pervasive intermixture of oil and water. They noted that in cases where this occurred (young dynamic basins with substantial fluid flow), the reaction could proceed. In cases where older static basins are involved, with much less fluid flow (more of a closed-fluid system), hydrolytic disproportionation of oil by pore waters would be impeded or halted altogether. Our work suggests that an open-fluid system is the primary requirement for hydrolytic disproportionation of OM to occur. The calculations carried out by Helgeson et al. (1993, p. 3301) also suggested "---that the partial pressure of methane would have to exceed geostatic pressure by several orders of magnitude to achieve metastable equilibrium between natural gas--- and oxidized carbon-bearing species in oil field waters...". This conclusion applied to C_6- HCS in general and possibly higher-carbon-numbered HCS, depending on the conditions. The inability of the light HCS to achieve metastable equilibrium in these systems both provides the drive for hydrolytic disproportionation reactions between HCS and water, and dictates that if the reactions occur, high concentrations of lower-carbon-numbered (C_6- to C_{10}-) HCS would result.

Helgeson et al. (1993, p. 3305) noted that increasing oxygen fugacity would favor the formation of dicarboxylic counterparts in systems with ongoing hydrolytic disproportionation of OM. Helgeson (1991, p. 707) in an earlier treatment of hydrolytic disproportionation of OM proposed "---metastable equilibrium among minerals, a CO_2-H_2O fluid, and hydrocarbon species..." during inorganic metamorphism at high temperatures and pressures. Helgeson (1991, p. 734-735) hypothesized that petroleum-like HCS could persist preserved in a metastable state with carboxylic acids dissolved in aqueous fluids, and high concentrations of CO_2, in low-grade carbonaceous metamorphic rocks to temperatures far in excess of those (150°-200°C) generally thought to result in the thermal destruction of C_4+ HCS (Tissot and Welte, 1984). All these predictions are corroborated by the data of this paper.

2.02 EVIDENCE FOR HYDROLYTIC DISPROPORTIONATION OF OM

The hypothesis of hydrolytic disproportionation of OM is supported by experiments carried out by Seewald (1994) in gold bags containing water, ethane, ethene, and the naturally-occurring mineral buffer: pyrite-pyrohotite-magnetite, which set the oxygen (hydrogen) fugacity of the system. When experimental conditions were modified by injecting ethane, ethene, or water into the system, or by changing the experimental temperature, the ethane/ethene ratio in the system would gradually change towards the equilibrium ratio expected from thermodynamic calculations, given the experimental conditions. The concentrations of CH_4, CO_2, H_2S, and H_2 would also change accordingly, demonstrating that carbon-carbon bonds were being broken. Seewald (1994) concluded that ethane, ethene, water, the mineral buffer, and the other dissolved species were all in reversible equilibrium, which was maintained by exchanging hydrogen and/or oxygen with one another.

The hypothesis of hydrolytic disproportionation of OM is also supported by earlier work of French (1964). He inadvertently produced measurable amounts of oxidized HCS (alcohols, organic-acids, ketones, etc.), and most probably HCS themselves, during elevated-temperature experiments examining siderite ($FeCO_3$) synthesis and stability. Palmer and Drummond (1986) and Bell et al. (1994) also inadvertently produced HCS from water and acetic acid, while experimentally examining aqueous acetic acid thermal stability. Lastly, Hoering (1968, 1984) deuterated both shale kerogen and HCS (n-docosane, n-C_{22}; and 1-octadecene) with deuterated water, also demonstrating that both kerogen and HCS exchange hydrogen with water. The degree of deuteration was markedly less in the n-docosane compared to the kerogen. However, that deuteration occurred at all is a key observation, because the experiment conclusively demonstrates that ionic water reacts with covalent HCS, at least in laboratory situations.

Giggenbach (1997) examined relative concentrations of CO_2 and CH_4 from three different geologic settings, and concluded that the gases were in chemical equilibrium with each other and their environments, and had reached these equilibria via redox reactions with their host rocks. His three geologic provinces were New Zealand geothermal wells; natural gas wells in the Taranakai Basin (New Zealand, geothermal gradient of 25°-30°C/km); and natural gas wells in the Gulf of Thailand (geothermal gradient 100°C/km).

Giggenbach (1997, p. 3780) also proposed that higher carbon-numbered HCS could be preserved to much higher temperatures, than called for by accepted petroleum-geochemical paradigm (Hunt, 1979), by redox reactions with the rocks and water in which the HCS exist. Where HC/rock ratios were high, Giggenbach (1997) hypothesized that the OM could generate its own redox environment (highly-reducing), which would favor preservation of organic compounds.

Giggenbach (1997) considered the chemical redox equilibria he measured could be controlled by one of three possible parameters: 1) metastable equilibrium (hydrolytic disproportionation) as proposed by Shock (1988), and Helgeson et al. (1993); 2) thermodynamic equilibrium; and 3) kinetic processes. Giggenbach (1997) dismissed the first control (metastable equilibrium) on the basis of, in our opinion, a series of flawed arguments; and attributed his observed equilibria to the latter two processes. We will not discuss in detail here Giggenbach's (1997) arguments for rejection of metastable equilibrium, save one, wherein he rejected the experiments of Seewald (1994) as a demonstration of metastable equilibrium. Giggenbach (1997, p. 3379) maintained that Seewald's (1994) experiments demonstrated an equilibrium only between ethane and ethene, and observed:

> "This finding however, is readily explained in terms of the comparatively low activation energies required to break C-H, as compared to C-C bonds. Attainment of internal, metastable equilibrium among organic molecules of a homologous series is highly unlikely as it requires the preferential breakage of highly stable C-C bonds. It is the associated high kinetic barriers which allow hydrocarbon entities to persist to high temperatures in the first place".

However, Giggenbach's (1997) opinion on this matter is quite simply erroneous. Seewald (1994) clearly stated multiple times, and provided the supporting analytical data, that by injecting either ethane or ethene into his experiments, the CO_2 and CH_4 concentrations were also changed as the system strove to reach new equilibrium. Clearly, C-C bonds were being broken in Seewald's (1994) experiments. Thus, we believe that the rock, water, and OM equilibria observed by Giggenbach (1997) can be attributed as possibly due to, and thus may be an example of, the results of hydrolytic disproportionation of OM in the natural system.

Hydrolytic disproportionation of OM has a strong theoretical foundation and has been demonstrated to occur in different laboratory experiments. In this paper, we provide evidence from the natural system that: 1) the predicted results of hydrolytic disproportionation between water and OM occur in a wide variety of geologic settings, and 2) both redox reactions and thus equilibriums between mineral species, water, and HCS appear to be commonplace in the natural system, probably via ionic/carbonium-ion reactions.

As an aside, this evidence emerged via serendipity from analyses of carbonaceousmetamorphic and ore-deposit rocks in an (unsuccessful) attempt to demonstrate a final thermal destruction of C_8+ HCS in Nature and to delineate the resulting high-rank HC compositions in the approach to this anticipated thermal destruction. Instead, we found HCS persisting to even higher ranks than those discussed in Price (1993). Moreover, our extractable OM had previously-unreported compositions, compositions which were predicted to occur as a result of hydrolytic disproportionation of OM (Helgeson et al., 1993).

3.0 SAMPLES AND METHODS

3.01 SAMPLES

Rock sample suites were obtained from different investigators (acknowledgments) from varied geologic environments involving both rock metamorphism and hydrothermal ore deposition (Table 1). Each of these sample suites are briefly described.

3.011 Swiss Alps Liassic Black Shales

This is a rock suite of progressively-metamorphosed Liassic black shales, starting with unmetamorphosed shales from the Molasse Basin (Switzerland) and proceeding roughly south into the Swiss Alps, where these rocks reached maximal metamorphic temperatures of 550°C. Four such samples were analyzed (MF-647, MF-735, MF-898, and MF-903, Table 1). These four samples are the first samples analyzed from a larger suite in an ongoing study between L. Price and M. Frey. A complete description of the samples, including metamorphic grade, mineralogical changes, study area, etc. is in Frey (1970, 1978). MF-647 is from Guggenegg, northern Glarus Alps (corresponding to the Spitzmeilen area in Fig. 1 of Frey, 1978) and is anchizonal metamorphic grade (250-300°C). MF-735 is from Panixer Rotstock, southern Glarus Alps (corresponding to PP, or Panixerpass, in Fig. 1 of Frey, 1978) and is in the anchizone to epizone metamorphic transition (300-350°C). MF-898 and 903 are both from Val Gierm (Urseren Zone, Fig. 1 of Frey, 1978) and

Table 1.--Organic geochemical data for the samples analyzed in this study. GmRX are grams of rock Soxhlet-extracted for each sample. TOC is total organic carbon (in weight percent) for each sample. PPM are parts per million of extracted organics per dry weight of rock; mg/gOC are milligrams of extracted organics normalized to total organic carbon. For those last two categories: SATS are saturated HCS, AROS are aromatic HCS, RES are resins, ASP are asphaltenes, and TOTAL BIT is total bitumen extracted. SAT/ $\delta^{13}C$ is the $\delta^{13}C$ value for the saturated HCS. CO_3 is carbonate carbon (in weight percent). NA is not available.

			PPM					mg/gOC						
Sample	GmRX	TOC	SATS	AROS	NSO	ASP	TOTAL BIT.	SATS	AROS	RES	ASP	TOTAL BIT.	SAT $\delta^{13}C$	CO_3
BELT SERIES														
89C-10/502.8A	43.8	0.44	47.5	18.5	43.1	NA	109.1	10.8	4.20	9.79	NA	24.8	NA	1.41
89C-10/517.4	44.25	0.31	87.7	19.2	39.8	NA	146.7	28.3	6.19	12.8	NA	47.3	-28.03	1.22
JERRITT CANYON														
JGS-43	92.18	2.82	25.8	10.4	16.5	6.1	58.8	0.91	0.37	0.58	0.22	2.08	{27.14	NA
JGS-49	71.69	0.74	34.0	16.3	22.9	6.0	79.2	4.59	2.20	3.09	0.81	10.7		NA
LNGOSC-4	32.30	3.30	18.6	13.0	29.7	9.91	71.2	0.56	0.39	0.90	0.30	2.16	NA	NA
UPPER PLATE	44.23	4.20	33.5	7.46	22.8	47.7	111.5	0.80	0.18	0.54	1.14	2.66	NA	NA
HOMESTAKE MINE														
942-32	344.0	2.04	2.65	1.02	6.86	0	10.5	0.13	0.05	0.34	0	0.51	{	2.09
942-24	376.27	1.92	3.59	1.38	5.29	1.81	12.1	0.19	0.07	0.27	0.09	0.63	{-27.41	1.47
942-20	172.0	0.96	4.88	1.63	7.15	1.10	14.7	0.51	0.17	0.75	0.11	1.53	{	0.17
942-14	287.47	1.21	2.47	0.42	4.59	0.42	7.9	0.20	0.03	0.38	0.03	0.65	NA	3.18
942-19	308.16	3.48	2.82	0.88	4.51	2.53	10.7	0.08	0.02	0.13	0.07	0.31	NA	1.24
UNKNOWN PROVINENCE														
506C	176.78	0.74	39.4	9.73	17.9	6.39	73.4	5.32	1.31	2.42	0.86	9.92	-28.47	0.02
507C	226.02	0.78	61.1	14.6	20.0	3.36	99.1	7.83	1.87	2.56	0.43	12.7	NA	0.20
ANTHRACITES														
ANTHRACITE	290.33	80.14	5.51	8.61	9.92	5.54	29.5	0.007	0.011	0.012	0.007	0.037	-27.66	0.03
META-ANTHRACITE	354.22	28.42	4.00	2.51	10.6	1.92	19.1	0.014	0.009	0.037	0.002	0.067	-27.49	<0.02
SWISS ALPS														
MF-647	365.68	0.86	15.2	4.51	10.6	1.83	32.1	1.77	0.52	1.23	0.21	3.73	-27.77	5.46
MF-735	354.60	0.23	10.5	4.06	10.1	2.14	26.8	4.56	1.76	4.39	0.93	11.6	NA	0.10
MF-898	347.50	0.64	12.1	7.65	12.1	1.06	32.9	1.89	1.19	1.89	0.16	5.14	NA	<0.02
MF-903	302.80	1.68	6.74	3.37	7.46	1.29	18.9	0.40	0.20	0.44	0.08	1.12	-27.88	<0.02

are in the eipzone or lower low-grade greenschist facies (400°C). (All above comments on the "MF" rocks are based on written communication, Martin Frey, University of Basel, Zurich, January 2, 1995.)

3.012 Homestake Gold Mine-South Dakota

The Homestake, Gold Mine, Lead, southwestern South Dakota, U.S., excluding South Africa, is one of the larger gold mines of the world, having produced 39 million ounces of gold (DeWitt, 1996), and is still in operation. Five Precambrian 2 billion-year-old carbonaceous metamorphosed "black shales" from this mine were analyzed (Table 1). These samples (942-14,-19,-20,-24, and -32) are from three separate adjacent Formations (DeWitt, 1996). The 92m-thick Poorman Formation (the oldest rocks) are calcareous and variably-pyrrhotite rich. Due to isoclinal folding, the original thickness of the Poorman is unknown. The overlying iron-rich Homestake Formation, which can be pyrrhotite-rich or poor, varies in thickness from 3.1 to 15.2 m, and hosts the syngenetic stratiform gold ore, which is usually in pyrrhotite-rich rock, with or without arsenopyrite. In-situ veins, blobs, or irregular quartz masses developed in the Homestake Formation during a later regional metamorphic event. The Homestake Formation was deposited in a strongly-reducing environment and was originally thin to very-thin bedded and well laminated. The Ellison Formation overlies the Homestake and is a sequence of siltstones, with some shales, and graywackes over 152.4 m thick. The base of the Ellison contains both carbonate-rich, and variably pyrrhotite-rich beds.

Models for gold deposition at Homestake have varied with time. Early studies (Gustafson, 1933; Noble, 1950) suggested epigenetic vein deposition in iron-rich host rocks. Later isotopic investigations emphasized the layered ore, suggesting syngenetic mineralization (Rye and Rye, 1974; Rye et al., 1974a; Rye and Shelton, 1983). Recent structural studies (Caddey et al., 1991; Bachman and Campbell, 1990) emphasize a shear zone control over ore deposition. Both bedding-controlled and vein-controlled ore exist at Homestake, the latter clearly having been remobilized from the former (DeWitt, 1996). Gold deposits hosted in iron-rich bedded formations typically have both types of ore (Kerswill, 1993). Recent elemental and mineralogical considerations (DeWitt, 1996) support a syngenetic depositional model for the Homestake ore. However, whether this event was driven by hot-spring deposition or other hot water sources is unclear. The presence of bedded arsenopyrite in the ore suggest minimum deposition temperatures of 440°C. The Precambrian rocks of southwestern South Dakota were affected by a post- ore-deposition metamorphic event of between 360° to 580°C with 3.2 to 5.0 kilobars (kb) of fluid pressure (Kath and Redden, 1990). Homestake rocks were exposed to 480°C and 4.1 kb pressure during this metamorphism.

The two Poorman samples we analyzed (942-14 and 942-32) were typical for that unit, being fine-grained pyrrhotite-rich calcareous shales, although 942-14 is slightly more "silty". The Homestake sample (942-24) is pyrrhotite-poor, typical for that part of the Formation which did not have intense syngenetic ore deposition. The Ellison samples are a pyrrhotite-rich potassic "shale" (942-19) and a pyrrhotite-poor "siltstone"

(942-20). Major and minor element compositions of the Homestake samples rocks are in Table 2.

3.013 "Carlin" Type Gold Deposits - Jerritt Canyon, Nevada

Four carbonaceous metamorphosed "shales" from the Jerritt Canyon mining district, Elko County, Nevada (Range 41N, Township 116W) were provided for analysis by Joel Leventhal (U.S. Geological Survey, Denver, CO.). Samples JGS-43 and -49 (Table 1) are from the Devonian Roberts Mountain Formation and LNG-4 (LNGOSC-4) and UP-1 are from the Ordovician Snow Canyon Formation. Leventhal and Hofstra (1990) concluded that these rocks were metamorphosed from pumpellyite-actinolite to lowermost greenschist facies (250°-300°C) before gold mineralization. Three of the samples were taken from open-pit workings, whereas LNG-4 is an outcrop sample.

Geologic and geochemical studies (Rye et al., 1974b; Dickson et al., 1979; and Radtke et al., 1980) demonstrated that Carlin-type gold deposits were deposited from hydrothermal solutions between 175°-200°C. Radtke and Scheiner (1970) proposed that the carbon in the host rocks (Roberts Mountain Formation) at Carlin played a pivotal role in both the original deposition of the gold ore and in the recovery of the gold between weathered and unweathered rocks.

3.014 Precambrian Montana "Belt Series"

Two core samples (989C-10/502.8A, 89C-10/517.4, Table 1) from the Golden sunlight gold mine (Jefferson County, Montana, NE Sec. 30, T2N, R3W) were analyzed. These two samples are from the Precambrian (middle Proterozoic) LaHood Formation and ROCK-EVAL analyses of them yielded high T_{max} values (480°-500°C) and reduced hydrogen indices (5-20). Moreover, both samples contain clinochlore IIB chlorite indicating paleotemperatures above 200°C. Perry et al. (1995), from petroleum-geochemical analyses of these and other associated rocks, concluded that they were beyond the high-temperature end of the oil window.

3.015 506C/507C

Around 1979-1980, a suite of carbonaceous metamorphic rocks (all fresh outcrop samples) was obtained by L. Price for vitrinite reflectance (R_o) analyses. Since then, all correspondence relating to the provenance of these rocks was lost, thus the background of these samples is unavailable. Nonetheless, two samples were picked from this suite for analysis, both samples having the metamorphic fabric somewhere between slates and phylite schists.

3.016 Anthracite/Meta-Anthracite

Jane Eggleston (then of the U.S. Geological Survey, Reston, Virginia) supplied an anthracite and meta-anthracite for analysis. The anthracite is from the middle of the

Table 2. Major- and minor-element chemistry of rocks from the Ellison, Poorman, and Homestake Formations, Black Hills, South Dakota. Major elements in weight percent; minor elements, metals, and rare-earth elements in parts per million by weight. 942-19 is a carbon-rich phyllite with abundant pyrrhotite; 942-20 is a siliceous, biotite-rich phyllite; 942-14 is a dolomite-rich phyllite with moderate pyrrhotite; 942-32 is a carbon-rich, calcium-rich phyllite with minor pyrrhotite; and 942-24 is a siderite-quartz-chlorite iron-formation. Major elements analyzed by X-ray fluorescence; iron in sulfide minerals is listed as Fe; iron in non-sulfide minerals listed as FeO; minor elements by energy-dispersive X-ray fluorescence, unless otherwise indicated (ICP, which is inductively coupled plasma emission). Rare-earth elements by ICP mass spectrometry. Metals analyzed by ICP atomic emission spectroscopy (AES), except gold by combined atomic absorption and fire assay, silver by fire assay, mercury by cold vapor atomic absorption, and tellurium by hydride atomic absorption spectrometry; Uranium and thorium determined by delayed neutron activation. Analyses by U.S. Geological Survey and XRAL Laboratories, Toronto, Canada.

Rock unit	Ellison	Ellison	Poorman	Poorman
Sample number	942-19	942-20	942-14	942-32
Major elements				
SiO_2	49.56	78.00	48.74	57.40
TiO_2	0.47	0.34	0.31	0.43
Al_2O_3	10.87	7.38	7.64	11.45
Fe	9.05	< 0.04	5.13	3.18
FeO	2.55	4.80	2.46	0.57
MnO	0.19	0.18	0.57	0.12
MgO	3.98	2.76	5.56	4.57
CaO	2.60	0.53	8.02	4.76
Na_2O	0.52	< 0.15	< 0.15	0.31
K_2O	3.77	1.84	2.63	3.55
P_2O_5	0.11	0.09	0.08	0.09
H_2O+	1.70	1.85	0.90	1.30
CO_2	4.62	0.75	12.50	7.26
$C_{(org)}$	3.70	0.84	1.52	2.19
S	6.11	< 0.05	3.46	2.15
TOTAL	99.81	99.39	99.50	99.29
Minor elements				
Ba	448	280	235	368
Rb	130	63	73	134
Sr	54	22	112	49
Y	26	18	18	36
Zr	100	66	120	143
Nb	< 10	10	10	19
Sc (ICP)	16	8	9	12
Li (ICP)	35	29	16	48
Ga (ICP)	16	14	13	17
U	9.83	1.05	4.09	6.51
Th	11.49	7.34	4.62	< 3.5

Rock unit	Ellison	Ellison	Poorman	Poorman
Sample number	942-19	942-20	942-14	942-32
Metals				
Cu	131	< 10	74	84
V	244	57	101	180
Pb	22	13	33	11
Zn	147	45	156	211
Ni	75	16	32	35
Cr	109	54	93	126
Co	37	8	22	14
Mo	95	< 2	5	7
Au	0.011	< 0.002	0.008	0.004
Ag	0.49		0.59	0.89
Hg	< 0.02	< 0.02	< 0.02	0.13
Te	0.55	0.1		
Rare-earth elements				
La	31.90	20.00	21.60	42.00
Ce	53.75	34.00	35.60	75.00
Pr	6.31	3.30	4.10	8.60
Nd	24.55	13.00	16.00	32.00
Sm	5.29	2.50	3.08	5.90
Eu	1.26	0.40	0.86	1.30
Gd	5.52	3.00	3.12	5.30
Tb	0.76	0.40	0.46	0.70
Dy	4.84	2.60	2.98	4.40
Ho	0.83	0.50	0.56	0.80
Er	2.44	1.50	1.62	2.60
Tm	0.40	0.20	0.26	0.40
Yb	2.49	1.50	1.66	2.50

Southern Anthracite Field, near Llewellyn, Pennsylvania at the thickest part of the middle Pennsylvanian coal-bearing Llewellyn Formation of the Applachian Basin. The meta-anthracite is probably middle Pennsylvanian and is from the Masslite Quarry, Plainville, Massachusetts in the Narragansett Basin. The mean R_0 of the anthracite is 3.56% with a maximum value of 4.19%. The mean R_0 of the meta-anthracite is 4.92% with a maximum value of 5.61%. Both R_0 measurements were performed by M. Pawlewicz (U.S. Geological Survey, Denver, CO). The anthracite, although not a metamorphic rock, was analyzed for "calibration" against the meta-anthracite. The meta-anthracite was both highly foliated and folded and had a graphite-like silver sheen. Shaler et al. (1899) and Lyons (1977) discuss the geology of the Narragansett Basin; Quinn and Glass (1958), and Murray et al. (1979) discuss the metamorphic grades of the basin and Lyons and Chase (1979, 1981) discuss the rank of coals related to metamorphic grade in the basin.

3.02 METHODS

3.021 Sample Preparation/Solvent Extraction

All samples were whole rocks except for the Jerritt Canyon samples (JGS-43 and -49, LNG-4, and UP-1), which were supplied as powdered rock. Some rocks had sample numbers marked on them either by a felt-tip marker, or by a small area of white paint with an inked sample number, covered by a coat of clear varnish. Such markings were removed by scraping them with straight edge razors and a screwdriver whose edges were sharpened with a file. Microscopic examination revealed the penetration extent of these markings, and the rocks were scraped in the marked areas to depths beyond all visible signs of penetration. The exterior surfaces of all rocks were then thoroughly rinsed with dichloromethane to remove surficial organic contamination.

All rocks were smashed to 3 mesh (6.88 mm) or less with an iron sledgehammer in a 1.0 m (width) x 1.0 m (depth) x 0.5 m (height) steel "smashing box" (to contain flying chips). The resulting chips were then ground and sieved to pass 100 mesh (0.15 mm) or less, and Soxhlet-extracted with dichloromethane (CH_2CL_2) for 21 days in pretracted (3 days) cellulose thimbles. Copper strips in the roundbottom flask containing the solvent and extract removed elemental sulfur extracted from the rocks, which in some cases was significant. Instead of the typical 1 to 3 day extraction usually employed with petroleum-geochemical analyses, the 21-day extraction period was used because it was assumed that if HCS were present in these rocks, the HCS would be held more tightly in some of our samples compared to HCS in sedimentary rocks. Monitoring the faint resulting color of the solvent in the round-bottom flasks of this study's extractions, demonstrated that with most samples, a significant percentage of the extract was obtained *only after* 7-14 days of extraction.

3.022 Column Chromatography

After the 21-day extraction, the solvent extract was filtered and the solvent was passively evaporated in a 400 to 2000 ml beaker in a suction (fume) hood, thus retaining all C_9+ compounds. When about 25 ml of solvent remained in the beaker, the contents were quantitatively transferred to a 50 ml volumetric flask and a 5 ml aliquot was taken for a bitumen determination. The remaining 45 ml in the volumetric flask were passively evaporated to about 20 ml, and the contents quantitatively transferred to an 8-dram vial and passively evaporated to 1 ml. Ten ml of hexane were added to the 8-dram vial and the contents passively evaporated to 1 ml. This process was repeated twice to replace the CH_2Cl_2 with hexane and to precipitate dissolved asphaltenes. The precipitated asphaltenes were filtered from the solution, the deasphaltened-bitumen being caught in a three dram vial. The asphaltenes were mobilized from the filter by CH_2Cl_2 into a tared 2 dram vial, and weighed after solvent loss. The first two samples analyzed (89C-10/502.8A and 89C-10/57.4) were not deasphaltened, because of the assumption that no asphaltenes would remain in these high-rank samples. (The asphaltenes from these two samples were thus lost on the column in the next analytical step:silica gel-alumina column chromatography, discussed directly below). The deasphaltened bitumen in the 3 dram vial was passively evaporated to 0.5-1.0 ml for column chromatography.

Silica gel-alumina fraction-separation column chromatography was carried out with 5 ml serological pipettes 5.30 cm long. About 1.8 g of activated 923-grade silica gel was packed onto a glass-wool plug at the bottom of the column, followed by about 0.9 g of activated 62-grade silica gel, capped by 2.5 g of activated alumina. The columns were built in hexane. The 0.5-1.0 ml of asphaltene-free bitumen in hexane were quantitatively transferred to the column. Saturated HCS were eluted directly into a 10 ml volumetric flask with 10 ml of hexane, aromatic HCS were eluted with 30 ml of benzene into an 8 dram vial, and "resins" were eluted with 10 ml of 1:1 benzene-methanol. The eluted aromatic HC fractions were passively evaporated and then transferred into 10 ml volumetric flasks. Five ml were transferred from the 10 ml volumetric flasks into tared 2 dram vials for C_{15}+ saturated and aromatic HC weight determinations. The remaining 5 ml of solvent, with dissolved C_8+ saturated (or aromatic) HCS were never taken to dryness, being saved for C_8+ HC gas chromatography. The weight of the eluted resins was determined after solvent evaporation.

3.023 Gas Chromatography/Mass Spectrometry

Flame-ionization detection gas chromatography was performed on a DB -5, 50 m x 0.2 mm inside diameter, capillary column using helium as the carrier gas. Column conditions for the saturated HCS were: initial oven temperature 40°C for 10 minutes (min), followed by a 5°C/min. heating rate to 320°C, with a 9 min. final temperature (320°C) hold. Injector temperature was 340°C. Detector temperature was 350°C.

Aromatic HCS were run under the same conditions. Data processing was carried out with a Nelson Analytical System.

Samples were prepared for biomarker analysis by mass spectrometry by deasphaltening the bitumen aliquant in 0.5 ml of iso-octane. The iso-octane and deasphaltened bitumen were added to a disposable activated alumina (1 gram) column (Fisher Prep Sep P467R). Saturated and aromatic HCS were eluted with 5 ml of benzene leaving the resins on the column. The elutant was evaporated to dryness, 1 ml of iso-octane was added, and enough 5 angstrom molecular sieve was added to fill up the solution. The mixture stood in a tightly capped vial for 48 hours to completely remove the n-paraffins and the solution then was transferred to a tared vial by a transfer pipette, taken to dryness and weighed, such that another solution with an appropriate concentration (5-20 µg/µl) could be made up. 1.8 ul of this solution were injected onto a Hewlett Packard 5890 gas chromatograph with a 60 m x 0.31 mm I.D. column with a 0.15 micron coating of DB-1701 coupled to a VG-7035 double focusing magnetic sector mass spectrometer. Gas chromatograph conditions were: 10 psi helium head pressure; injection block temperature 300°C; initial column temperature 100°C, with a 2 min. hold; followed by a heating rate of 50°C/min. to 150°C, followed by a 3°C/min. heating rate to 300°C, with a 17 min. final temperature hold. Mass spectrometer conditions were: interface temperature 310°C, source temperature 225°C; source pressure 2 x 10-6 torr; source filament emission current 50 microamps;.source electron energy 70 eV; analyzer pressure 1×10^{-7} torr; electron multiplier voltage 2000 V; and amplifier gain 1×10^{8}. Selected ion monitoring was accomplished by accelerating voltage switching with a constant magnetic field controlled by a Kratos Mach 3 data system with which data processing was also carried out.

Whole-scan gas-chromatographic mass-spectrometric (GCMS) analysis was carried out on selected resin and aromatic-HC fractions. Aromatic-HC concentrations were 40 mg/g and resin concentrations were 15 mg/g. Mass-spectrometric and gas chromatographic conditions were the same as used with the biomarker analyses, except selected ion monitoring was not used.

Aromatic-HC peaks in gas chromatograms were identified by the use of aromatic HC standards (both single compounds in solution and multiple compounds in solution) and by published analyses (Radke et al.., 1982a, b, 1986; Radke and Welte, 1983; Alexander et al.., 1986; Rowland et al., 1986; Kvalheim, et al.., 1987; Püttman and Vilar, 1987; Wise et al.., 1988; Price and Clayton, 1990).

Because of both the small concentration of bitumen (Table 1) recovered from these rocks and the controversy within petroleum geochemistry surrounding the apparent stability of C_{15}+ HCS to high temperatures in nature (at least 250-350°C, Price, 1993), possible sample contamination was a paramount consideration of this study. This question was partially addressed by baking 280g of a 10-20 mesh beach sand at 400°C for 24 hours and using this sand as a blank through all analytical steps, including grinding to 100 mesh or less. The resulting 21-day extraction of this sand blank, and subsequent column chromatography followed by gas chromatography, yielded no measurable recovered "bitumen". We thus conclude that no contamination was introduced into the samples from the laboratory procedures over the C_{15}+ range.

A large unidentified peak was present in the aromatic fraction of all analyzed samples at about 48.5 minutes elution time. As discussed below in the "Resin and Asphaltene" section, this peak actually belongs in the resin fraction. The 30 ml of benzene we normally use to elute the aromatic HCS during column chromatography of oils and sediment bitumens apparently was too large of a volume to use with the bitumens of this study. This is because non-aromatic HCS were eluted with the aromatic HC fractions, whereas they should have been eluted with the resin fraction. Thus, we estimated aromatic HC weights free of this large peak at 48.5 minutes. This was done by subtracting the electronic response of the large 48.5 minute peak from that of the aromatic HC gas chromatogram as a whole for each sample (minus the counts due to baseline bleed) to obtain the corrected counts. The ratio of corrected counts/original counts was multiplied by the aromatic HC weight determined for that sample to arrive at an estimate of a 48.5 minute peak free weight (Table 1). By this calculation, the 48.5 minute peak originally made up between 15-59% of the aromatic HCS. The weight for each sample subtracted from the aromatic HCS was added to the resin fraction (Table 1).

4.0 RESULTS

4.01 QUANTITATIVE CONSIDERATIONS

The anthracite and meta-anthracite have among the lowest parts per million (ppm) and carbon-normalized values of extractable bitumen and HCS of the sample base (Table 1). Samples from deep wellbores (Price, 1993), which are at higher ranks than the anthracite, have HC and bitumen values orders of magnitude greater than those of the two anthracites. Moreover, the anthracite has a lower carbon-normalized saturated HC content than the higher-rank meta-anthracite. These observations suggest that a process other than C_{15}+ HC thermal destruction is controlling the bitumen and HC concentrations in these two coal samples. That parameter is here attributed to source rock HC expulsion by gas solution (Price et al., 1983; Price, 1989a,b).

The strong decrease in bitumen and HC concentrations, over ranks of R_o = 0.9-1.35%, which is almost always observed in sedimentary rocks with type III organic matter (OM), and is always observed in coals (Price, 1989b), has classically been attributed to C_{15}+ HC thermal destruction by petroleum geochemists (Hunt, 1979; Tissot and Welte, 1984). However, this explanation is contradicted by high bitumen and HC concentrations in much higher-rank rocks (R_o = 2.5-5.0%) with more hydrogen-rich OM (Price, 1993). Price (1989b) attributed these strong decreases in HC concentrations over R_o = 0.9-1.35% to the onset of efficient source rock expulsion by gas solution, arising from the onset of very large gas generation in type III OM (which includes most coals). With this expulsion mechanism, the higher the total organic carbon (TOC) content of the rock, the greater the expulsion efficiency. This is because greater amounts of gas are generated per unit rock weight than in rocks with lower TOC contents. Moreover, higher TOC content rocks have less mineral matrix to retain the generated HC gases. As such, correspondingly higher gas-phase concentrations are present in the rock porosity of high-TOC rocks. Thus C_{15}+ HCS are more effectively stripped from more organic-rich rocks. As such, coals which usually have TOC values of 70-95% always have very low extractable HC contents at $R_o \geq 1.2\%$. These considerations would explain why the anthracite (TOC = 80.14%) has a lower carbon-normalized saturated-HC content than the higher-rank meta anthracite (TOC = 28.42%). Thus, the very low bitumen and HC concentrations of these two coal samples are here attributed to intense expulsion by gaseous solution, and not to C_{15}+ HC thermal destruction.

The two ("89C-10") Precambrian belt series samples from the Golden Sunlight mine have the second and third lowest TOC contents of the sample set (0.31 and 0.44%), yet they have the highest carbon-normalized and ppm bitumen and HC concentrations of the sample set. In fact, the HC concentrations of these rocks are characteristic of background values found in low TOC rocks at high ranks (R_o - 5.0 = 7.0%) from deep wellbores; (Price, 1988; Price et al., 1981; and Price and Clayton , 1990). The elevated HC concentrations of the two 89C-10 samples (relative to the rest of the Table 1 sample set) suggest that these two samples have been exposed to less severe conditions than the other samples of Table 1. Qualitative considerations (discussed below) support this hypothesis. The two slates to phyllite schists (506C and 507C) of unknown provenance also have elevated HC concentrations relative to the other samples of Table 1.

Apart from the two anthracite samples, the five Homestake samples have the lowest ppm and carbon-normalized bitumen and HC concentrations of the sample set. However, features within the saturated HCS of these samples (discussed below) demonstrate that these low HC concentrations are not from C_{15}+ HC thermal cracking. The Jerritt Canyon samples have TOC contents similar to those of the Homestake samples and have been exposed to some of the same geologic processes as were the Homestake samples. Similar aspects of the Homestake and Jerritt Canyon saturated- and aromatic-HC gas chromatograms (discussed below) arise from the similarity of these processes. However, the Jerritt Canyon samples have higher HC concentrations than the Homestake samples. One Jerritt Canyon (outcrop) sample (LNG-4) has reduced HC concentrations relative to the other three Jerritt Canyon samples (JGS-43, -49, and UP-1). The saturated- HC gas chromatogram of the LNG-4 sample demonstrates that the sample has been significantly weathered (discussed below), thus, explaining the relatively lower HC concentrations.

The four Swiss Alps metamorphics have HC concentrations intermediate between the high and low extremes of Table 1. Note that even though there is a 150°C difference in the paleotemperatures of the Swiss Alps sample suite, HC concentrations do not decrease in the higher-temperature samples.

The samples of any suite of Table 1 have roughly equivalent ppm HC concentrations with the other samples of that suite. However, carbon-normalized HC concentrations within the samples of one suite vary widely, with the highest TOC rocks always having the lowest carbon-normalized HC concentrations. These observations suggest that open-fluid systems (through-going fluid movement) existed in all of these rocks, allowing the indigenous HCS to be somewhat evenly distributed among the rocks of that system. This is expected, because rock metamorphism requires an open-fluid system to redistribute ions to allow rock metamorphism to occur in the first place. Also, ore deposition requires pervasive fluid movement through rocks.

4.02 SATURATED HCS

4.021 Metamorphic Rocks

Saturated-HC gas chromatograms of five metamorphic rocks, and for comparison purposes, a mature crude oil, are presented in Figure 1. The oil is from the Scoria field, Williston Basin, North Dakota (41.7° API gravity, further details are in Table 1 of Price and LeFever, 1994). The characteristics of the saturated-HC gas chromatogram of this oil are those typical for both mature oils and mature sediment bitumens: 1) n-paraffin concentrations regularly decreasing with increasing carbon number (solid line); 2) significantly greater concentrations of n-paraffins than all adjacent peaks, including isoprenoid saturated HCS; 3) a smooth n-paraffin profile (as delineated by the line above the n-paraffins); and 4) a low or non-existent unresolved hump below the n-paraffins.

Saturated-HC gas chromatograms from the 506C (Fig. 1) and 507C (not shown) samples were almost identical except for smaller amounts of C_{22} to C_{24} n-paraffins in 507C. The 506C chromatogram (Fig. 1) is dominated by C_{14} to C_{20} n-paraffins, has a moderate naphthenic envelope, has low concentrations of C_{13}- and C_{21}+ n-paraffins, and has moderate isoprenoid peaks (i-C_{18}, pristane, and phytane) relative to adjacent n-paraffins. The first three characteristics are often observed in high-rank (R_o = 2.5-7.0%+) samples from deep well bores (see Figure 12 in Price, 1993) and are due to leaching effects from gas solution and loss of HCS to the drilling mud during drilling operations (Price and LeFever, 1992).

As discussed in Price (1993), in laboratory experiments, at the onset of C_{15}+ HC thermal cracking, the size of the higher-molecular weight isoprenoid peaks i-C_{18}, pristane (i-C_{19}), and phytane (i-C_{20}) decrease relative to adjacent n-paraffins, because the isoprenoid HCS are thermally-unstable relative to the n-paraffins. Also, the size of the naphthenic envelope dramatically decreases because naphthene rings are also thermally-unstable relative to n-paraffins. As will become evident, moderate to large i-C_{18}, pristane, and phytane peaks relative to adjacent n-paraffins, and moderate to large naphthenic envelopes, were present in all samples of this study. These are pivotal

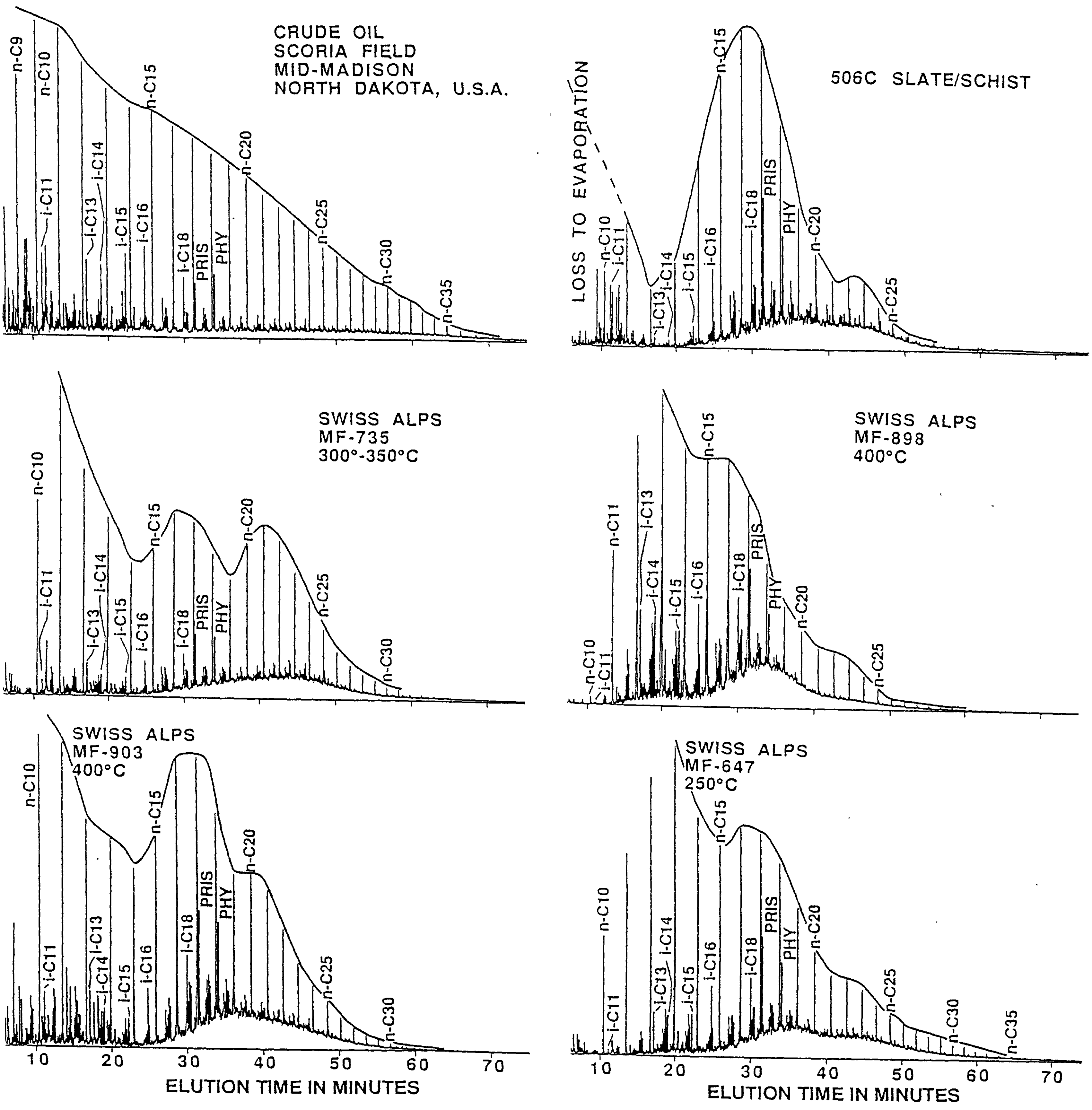


Figure 1. Saturated-HC gas chromatograms for one crude oil and five metamorphic rocks. Metamorphic temperatures are shown for the 4 Swiss Alps samples. N-paraffins are labeled by n-C and their respective carbon number. Isoprenoid HCS are shown by i-C and their respective carbon number. Solid lines above each chromatogram are explained in the text.

observations, dictating that none of these samples have even approached the onset of true C_{15}+ HC thermal destruction, a startling observation.

Saturated-HC gas chromatograms of the four Swiss Alps samples (Fig. 1) also have moderate to large i-C_{18} to i-C_{20} peaks and large naphthenic envelopes. Moreover, these Swiss Alps chromatograms have other similarities to chromatograms from shales in sedimentary basins. There are no characteristics in these chromatograms to suggest that the samples are metamorphic rather than sedimentary rocks. Furthermore, some characteristics in these chromatograms would normally be considered immature, such as multimodal n-paraffin distributions in three samples (MF-647, -735, and -903), and the very irregular n-paraffin profiles of all four samples. Bimodal n-paraffin distributions are occasionally observed in sedimentary rocks, but trimodal n-paraffin distributions in mature sedimentary rocks, such as present in MF-735, are uncommon. Moreover, 3 of 4 samples from a mature rock suite having bimodal n-paraffin distributions is highly unusual.

Solvent extraction and gas chromatography have been performed on over 80 additional carbonaceous high-rank crystalline rocks in research subsequent to this study. The saturated HCS of these newer samples invariably have a minimum in the n-paraffins somewhere between n-C_{12} to n-C_{15}, most often at n-C_{14}. Equivalent minima are portrayed by solid lines above the n-paraffins in the chromatograms of the 5 metamorphic rocks of Figure 1. We attribute the n-C_{12} to n-C_{15} n-paraffin minima of Figure 1 (and Figure 2) to a preferential chemical reaction of these compounds, via hydrolytic disproportionation, relative to adjacent carbon numbers. Note that there was a loss of C_{10}- to C_{12}- compounds in the Figure 1 saturated HCS of the five metamorphic rocks due to an analytical step suggested for our laboratory by a USGS Safety Officer. That analytical step has since been discontinued.

4.022 Ore-Deposit Rocks and Anthracites

Saturated-HC gas chromatograms from the other sample suites of this study are shown in Figure 2. The five Homestake saturated-HC chromatograms were all very similar, but none were exactly the same. Two representative examples of the five Homestake saturated-HC gas chromatograms are given in Figures 2 and 3 (942-14 and 942-19, respectively). All five chromatograms had a pronounced "hump" from n-C_{16} to n-C_{34} which was maximized around n-C_{21} to n-C_{23}. A minimum in peak heights was always present at n-C_{14}, with the amount of n-C_{13}- material variable. Also, peak distributions among the C_{13}- compounds was different among the five Homestake samples.

The shape of the Homestake saturated-HC chromatograms (Figs. 2 and 3) immediately suggests contamination from a petroleum distillate. However, five points refute this interpretation. First, no Homestake aromatic HC gas chromatograms had such pronounced humps (Fig. 3), which would be the case if an oil distillate were

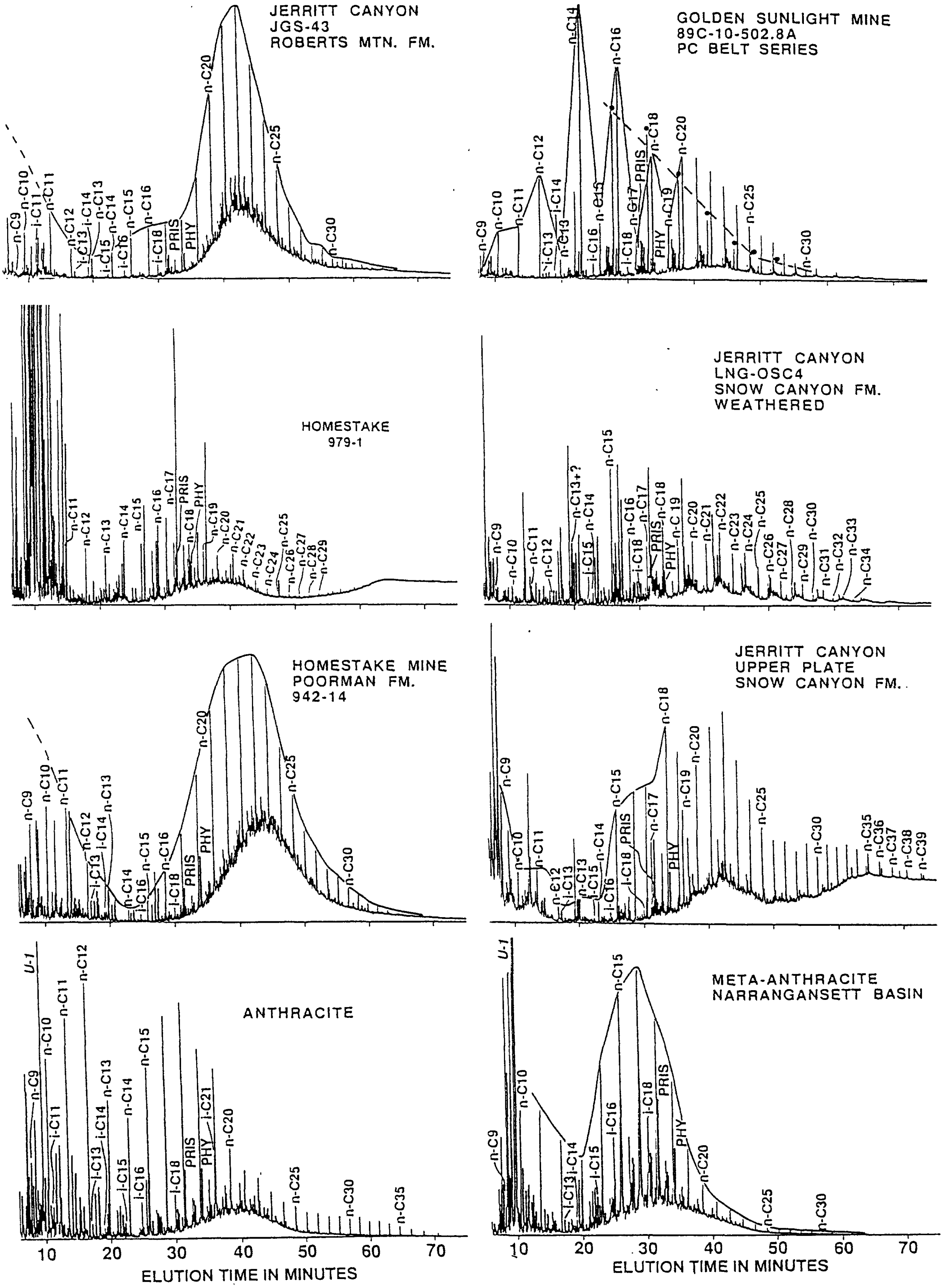


Figure 2. Saturated-HC gas chromatograms from 6 carbonaceous rocks from hydrothermal ore deposits and two coals. Labeling as in Figure 1 caption. The peak labeled U-1 in the two coals is a contaminant from the solvent used for extraction. Solid and dashed lines explained in the text.

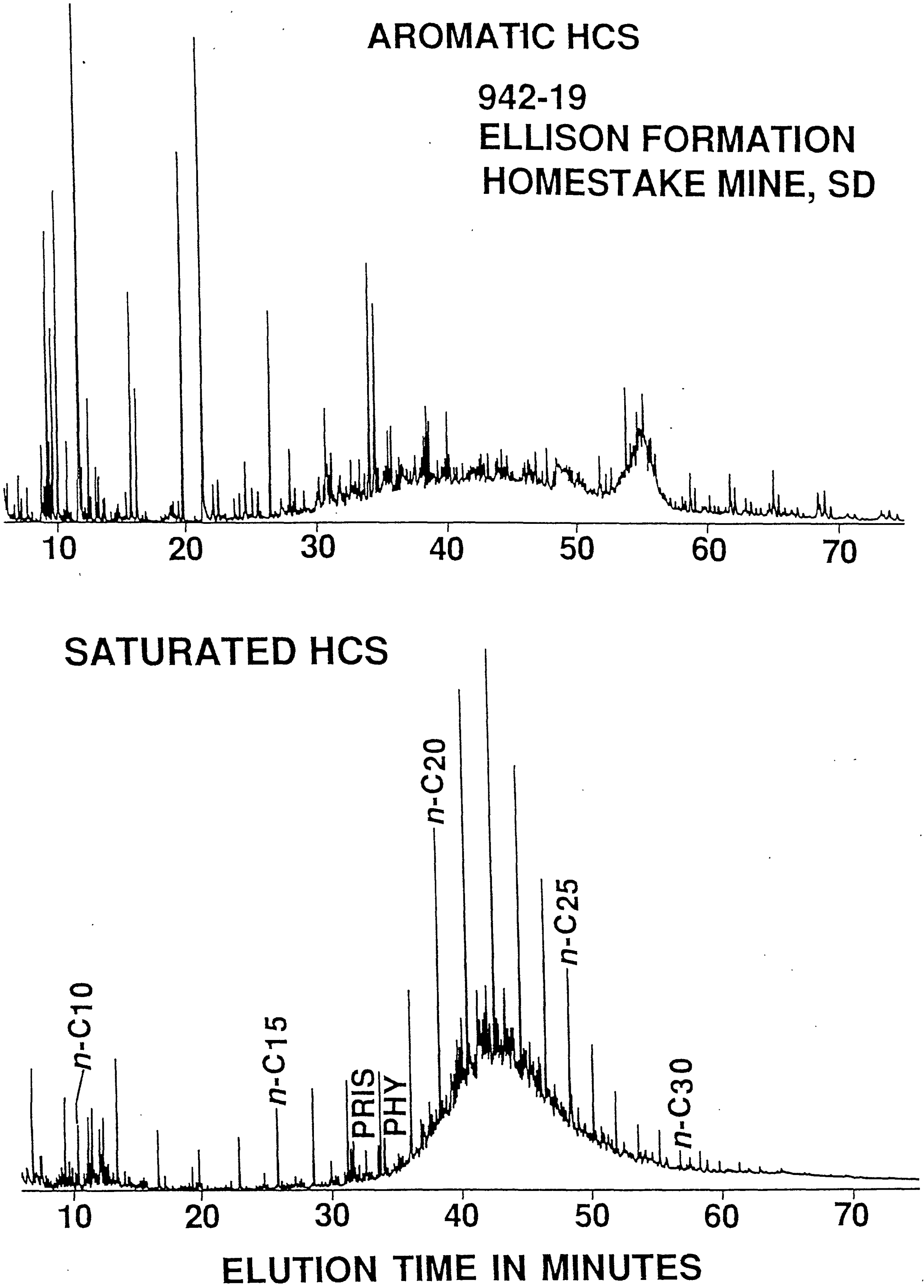


Figure 3. Saturated- and aromatic-HC gas chromatograms of bitumen from a carbonaceous rock from the Homestake gold mine.

contaminating these samples. *This consideration alone negates the possibility of distillate contamination.* Second, as discussed below, the compound distribution in the aromatic HCS is most unusual and not possibly from a petroleum distillate. Third, although the five chromatograms were similar, they were not exact matches, which would be the case with distillate contamination. Fourth, saturated-HC chromatograms of some samples from other rock suites have a similar distribution, or a tendency to this distribution, suggesting that these humps originate from a process control. Fifth, if the Homestake rocks were contaminated by an oil distillate, elevated HC concentrations would result. However, the Homestake samples have the lowest HC ppm concentrations of the entire sample set (Table 1), and especially low aromatic HC concentrations.

Existing experimental data (Price, 1981) demonstrate that HC aqueous solubilities decrease with increasing molecular weight, especially among the saturated HCS. Thus, we could hypothesize that the humps in the Homestake saturated HCS Figure 3 near here. could have resulted from the hot waters which moved through these rocks (ore-deposition and the later metamorphic event). The front end of these humps would thus be from these waters having decreasingly less solution capacity with increasing HC molecular weight beyond n-C_{16}. The back end of the humps is from the usual decrease in HC amount with increasing molecular weight, typical of all rock bitumens. However, the presence of the lower molecular weight (n-C_{13}-) saturated HCS in the Homestake gas chromatograms of Figures 2 and 3 (and also the presence of relatively abundant lower-molecular aromatic HCS in Homestake bitumens, discussed below) refutes the possibility of either aqueous or gaseous solution having caused these "humps". C_{15}+ HC thermal cracking cannot be responsible for these humps, because the highest molecular-weight, most-thermally-unstable HCS remain in relative abundance in these samples.

We believe that these humps were caused by extensive hydrolytic disproportionation of the original bitumen in these rocks, with the reaction extending over n-C_{10} to perhaps n-C_{20}, but being centered over the n-C_{12} to n-C_{14} carbon-number range. This reaction is dependent on multiple pore-volumes of waters flowing through rocks in open-fluid systems. The greater the flow of fluids, the greater the reaction extent. Rocks associated with hydrothermal ore deposition usually have many pore volumes of water move through them. Please note again that there has been a loss of C_{10}- to C_{12}- saturated HCS in the Figure 2 gas chromatograms from an inappropriate analytical step we performed.

In subsequent solvent extractions of over 20 additional Homestake samples, we have taken care to preserve the lower-molecular-weight compounds in the extracts. In all the subsequent extractions, the amount of C_{11}- saturated HCS absolutely drawf the C_{13}+ saturated HCS. A representative example is shown in Figure 2 with the 979-1 chromatogram, wherein the molecular-weight distribution is most unusual. In fact, we have never previously observed, in our research, or seen a published example of, such a distribution. However, the hypothesis of hydrolytic disproportionation (Helgeson et al., 1993) predicts that very high concentrations of lower-molecular-weight HCS will be formed during intense cases of hydrolytic disproportionation, such as would be the case in heavy-metal deposition.

Two saturated-HC gas chromatograms from Jerritt Canyon samples (JGS-43, -49, only JGS-43 shown in Fig. 2) were very similar to one another and had a moderately-similar appearance to the saturated-HC chromatograms of the Homestake samples (Figs. 2 and 3), including a maximum in the hump around n-C_{22}. The Jerritt Canyon JGS-43 saturated HCS, like the Homestake saturated HCS, also appear to be contaminated by a petroleum distillate. Nonetheless, as discussed below, the Jerritt Canyon aromatic-HC gas chromatograms: 1) do not exhibit these pronounced humps, and 2) like the Homestake aromatic HCS have very unusual compositions, completely unlike those found in crude oils and distillates thereof. Moreover, Leventhal and Hofstra (1990) went to great lengths to avoid any contamination in these samples, including not taking samples near "ANFO" (diesel and ammonium-nitrate) blast holes. Thus, because of both these reasons and those listed above, the hump in the saturated HCS of the JGS-43 and -49 samples (only JGS-43 shown in Fig. 2) cannot be attributed to contamination. Instead, we ascribe these humps, and those in the Homestake saturated HCS, to extensive hydrolytic disproportionation of OM which we hypothesize to have occurred during ore deposition.

Two other chromatograms from Jerritt Canyon samples are shown in Figure 2. One (outcrop) sample (LNG-OSC4) has greatly reduced n-paraffin concentrations and very unusual peak patterns. From our experience, such compositions result from significant rock weathering, which lead to a loss of rock bitumen in general, but especially n-paraffins. Deep weathering occurred throughout the Carlin gold trend (Radtke and Scheiner, 1970). The last Jerritt Canyon chromatogram (Upper Plate; Fig. 2) has the beginnings of a "hump" centered around n-C_{22}; and even without the hump overn-C_{19} to n-C_{26}, the n-paraffin profile is very irregular. The n-C_{26} to n-C_{34} n-paraffins have a noticeable odd preference. Such immature characteristics surviving to such a high rank is unexpected. However, concurrently, the ratios of the i-C_{18} to i-C_{20} isoprenoid HCS to their adjacent n-paraffins are very low. This is a "mature" characteristic usually attributed to HC thermal destruction.

Regarding the two anthracites of Fig. 2, as discussed above, because coals generate so much gas and have such high TOC values, HC expulsion by gaseous solution strips almost all generated HCS from them. Because, the bitumen from both the anthracite and meta-anthracite would be strongly affected by gaseous solution, characteristics of their saturated-HC gas chromatograms (Fig. 2) should reflect this. Furthermore, because both samples are high-rank coals, their indigenous HCS should have similar qualitative characteristics which they do. Both saturated-HC chromatograms: 1) are depleted in C_{20}+ n-paraffins, the meta-anthracite especially so; 2) relative to n-paraffin peak heights have large naphthenic envelopes; and 3) have an n-paraffin maximum from n-C_{14} to n-C_{19}. All these characteristics are due to heavy leaching of bitumen by gaseous solution.

The saturated HC gas chromatograms of the two Montana Precambrian Belt Series ("89C-10") samples were very similar to one another and thus only one sample (89C-10-502.8A) is shown in Figure 2. Both chromatograms had very unusual characteristics, unrelated to rank, but due instead to the original depositional facies of these rocks. For example (Fig. 2), a strong even-carbon preference exists over n-C_9 to n-C_{20} (delineated by the solid line). This immature characteristic has been retained in spite of the high-rank of these samples. However, the C_{20}+ n-paraffins of these two samples have a normal distribution. The i-C_{11} to i-C_{21} isoprenoid HCS are in very low concentrations, a characteristic which is most likely facies dependent and not a result of thermal cracking. A perhaps homologous series of compounds, decreasing in peak height with increase in molecular weight, was present in these two samples, designated in Figure 2 by the dashed line and the dots above the peaks. No effort was made to identify these compounds.

The saturated-HC qualitative characteristics of the two Belt Series samples support the conclusion made above on quantitative considerations that these are the lowest rank, or least "stressed", samples that we examined. However, by other petroleum-geochemical measurements (Perry et al., 1996), these samples are "beyond post-mature", having gone through the HC-generation stage. The unusual qualitative saturated-HC characteristics in these samples, characteristics that normally would be considered "immature", are thus unexpected. These characteristics dictate two conclusions: First, the HC-generation process did not obliterate the strong facies control in these samples. Second, no significant HC thermal cracking has occurred in these samples, cracking which certainly would have moderated these "immature" qualitative characteristics.

4.03 AROMATIC HCS

4.031 Gas Chromatography

4.0311 Normal Peak Distribution

Figure 4 is an aromatic HC gas chromatogram from a moderately mature oil from the Lower Mississippian to Upper Devonian Bakken Formation, Williston Basin, North Dakota (North Dakota Geological Survey #12617, see Price and LeFever (1994), their Table 2, for details). The numbers identifying the peaks in Figure 4 are in Table 3 of this paper. The aromatic-HC peak distribution of this sample is universally characteristic of mature oils and sediment extracts worldwide, namely: 1) Alkylated benzenes (especially methyl-, dimethyl-, trimethyl-, and tetramethyl-benzenes) are in high concentrations (peaks 1 to 35). 2) The methyl- (peaks 73 and 77), dimethyl- (peaks 98-106), and trimethyl-naphthalenes (peaks 123-129) are the dominant compound groups. 3) Phenanthrene (peak 179) and the methyl- (peaks 196-200) and dimethyl-

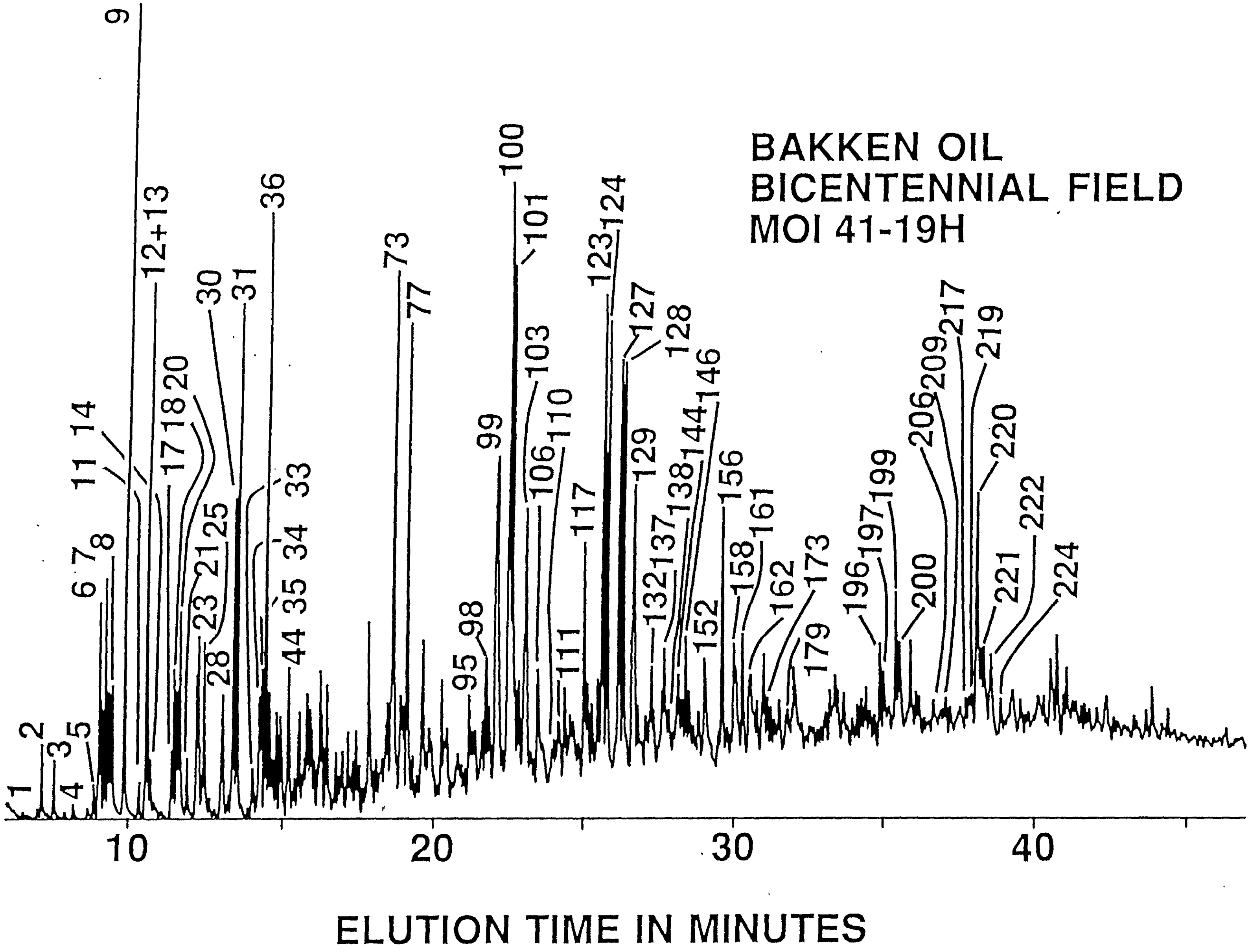


Figure 4. Aromatic-HC gas chromatogram of a typical oil (North Dakota Geological Survey Number -12617; Meridian Oil Incorporated (MOI) 41-19H) or sediment bitumen. Peak identifications of the numbers on the chromatogram are in Table 3.

Table 3. List of aromatic HCs identified in Figures 4-6. MW is molecular weight.

Peak Number	Compound
1.	Ethylbenzene
2.	Para- and metaxylenes
3.	Orthoxylene
4.	Isopropylbenzene
5.	N-propylbenzene
6.	Para- and meta-ethyltoluene
7.	Unknown (MW-120)
8.	Orthoethyltoluene
9.	1,2,4- ; + 1,3,4-trimethylbenzenes
10.	Isobutylbenzene
11.	Sec-butylbenzene
12.	1,2,3-trimethylbenzene
13.	Unknown (MW-120, Trimethylbenzene?)
14.	Unknown (MW-120, Trimethylbenzene?)
18.	Metadiethylbenzene
20.	Paradiethylbenzene +Tert-butylbenzene
21.	Orthodiethylbenzene
24.	1,3-dimethyl, 4-ethylbenzene
25.	Unknown Alkyl Benzene (MW-134)
26.	Unknown Alkyl Benzene (MV-148)
27.	Unknown Alkyl Benzene (MV-148)
28.	Unknown Alkyl Benzene (MV-148)
30.	1,2,4,5-tetramethylbenzene
31.	1,2,3,5-tetramethylbenzene
32.	Unknown Alkyl Benzene (MV-148)
33.	Unknown Alkyl Benzene (MV-148)
34.	Unknown Alkyl Benzene (MV-148)
35.	Unknown Alkyl Benzene (MV-148)
36.	1,2,3,4-tetramethylbenzene
44.	Naphthalene
73.	2-methylnaphthalene
77.	1-methylnaphthalene
95.	Biphenyl
98.	1-ethylnaphthalene
99.	2,6-;+2,7-dimethylnaphthalenes
100.	1,3-;+1,7-dimethylnaphthalenes
101.	1,6-dimethylnaphthalene
103.	2,3-;+1,4-dimethylnaphthalenes
106.	1,5-;+1,2-dimethylnaphthalenes
109.	Acenaphthene
110.	Unknown (MW-168)methylbiphenyl?
111.	Unknown (MW-168)methylbiphenyl?
117.	Unknown (MW-170)ethylmethylnaphthalene?
123.	1,3,7-trimethylnaphthalene
124.	1,3,6-trimethylnaphthalene
127.	1,3,5-;+1,4,6-trimethylnaphthalenes
128.	2,3,6-trimethylnaphthalene
129.	1,2,7-;+1,6,7-;+1,2,6-trimethylnaphthalenes
132.	Unknowns (MW-170+182; trimethylnaphthalene + dimethylbiphenyl?)
137.	Tetramethylnaphthalene + ?
142.	Tetramethylnaphthalene
144.	Tetramethylnaphthalene
146.	Tetramethylnaphthalene
147.	Tetramethylnaphthalene
152.	Tetramethylnaphthalene
156.	Tetramethylnaphthalene
158.	Tetramethylnaphthalene
161.	Tetramethylnaphthalene
162.	Methylfluorene
163.	Methylfluorene
164.	Methylfluorene?
168.	2-methylfluorene
169.	1-methylfluorene
173.	Dibenzothiophene
179.	Phenanthrene
191.	4-methyldibenzothiophene
195.	2-;+3-methyldibenzothiophenes
196.	3-methylphenanthrene
197.	2-methylphenanthrene
199.	4-;+9-methylphenanthrenes
200.	1-methylphenanthrene
204.	Ethyl?(or dimethyl)dibenzothiophene
206.	Dimethyldibenzothiophene
207.	Dimethyldibenzothiophene
208.	Dimethyldibenzothiophene
209.	Dimethyldibenzothiophene
215.	Dimethyldibenzothiophene
216.	Dimethyldibenzothiophene
216A.	Dimethyldibenzothiophene + ?
218.	3,5-;+2,6-dimethylphenanthrene
219.	2,2-dimethylphenanthrene
220.	1,3-;+3,9-;+2,10-;+3,10-dimethylphenanthrene
221.	1,6-;+2,9-;+2,5-dimethylphenanthrenes
222.	1,7-;+4,9-;+4,10-dimethylphenanthrenes
224.	1,9-;+4,9-;4,10-dimethylphenanthrenes
225.	Pyrene
227.	Trimethyldibenzothiophene
231.	Chrysene + Triphenylene

(peaks 218 to 224) phenanthrenes are also prevalent. In fact, in many cases the phenanthrenes are in higher concentrations than in Figure 4, but are always less abundant than the methylated naphthalenes. 4) Aromatic humps are usually minimal in mature samples. However, that of the 12617 chromatogram (Fig. 4, from about 25 minutes onward) is atypically large because of the naphthenic-aromatic nature of the organic matter (OM) which sourced this oil. The Figure 4 chromatogram, and all other aromatic-HC chromatograms of this study, were cut off at 47 minutes (just after where chrysene and triphenylene elute). This was because few large peaks elute after this point, and this higher-molecular weight region of the aromatic HCS is not well-understood. Thus, the better- known lower-molecular-weight region of the aromatic HC chromatograms was correspondingly expanded laterally to better illustrate details.

Price (1993) discussed compositional trends observed in aromatic HCS from high-temperature aqueous-pyrolysis experiments. Naphthenic-aromatic humps were minimized from destruction of relatively thermally-unstable naphthene rings. Alkyl-side chains longer than methyl groups became unstable, and also the higher the number of methyl groups on the compound, the more unstable the compound. Moreover, in the high-temperature experiments, a highly simplified suite of aromatic HCS persisted to higher temperatures than any of the saturated HCS. In the highest-temperature experiments, parent compounds (e.g., fluorene, naphthalene, phenanthrene, etc.) were the only remaining aromatic HCS, as all methyl side chains were lost. These trends were not observed in any of the aromatic HCS of this study.

4.0312 Metamorphic Rocks

The aromatic HC distributions of this study (Figs. 3, 5 and 6) are the most unusual we have ever observed. Such distributions have never before been reported from rocks in petroleum basins. Aromatic-HC gas chromatograms from three of the Swiss Alps samples (MF-735, -647, and -898) are presented in Figure 5. The MF-735 chromatogram has characteristics typical of all aromatic-HC gas chromatograms of this study, to wit: 1) The alkylated benzenes (peaks 1-36, Table 3) are generally the dominant, or among the dominant peaks. 2) There is a small to moderate unresolved hump. 3) These are simple chromatograms, with only a few, to a moderate number, of dominant peaks. 4) Unidentified peaks (labeled by "U" and a number), not found in abundance (and perhaps not found at all) in either oils or sediment extracts, appear in all but one (the anthracite) of the samples of this study. Besides the alkylated benzenes, other identified peaks present in significant amounts in MF-735 were naphthalene (44, Table 3), the methyl- naphthalenes (73, 77, Table 3), biphenyl (95), phenanthrene (179), and to a lesser extent, the methyl- (196, 197, 199, 200) and dimethyl-phenanthrenes (219, 220, 221, 224). Biphenyl was the largest peak of the MF-735 aromatic-HC chromatogram, as in most of the other aromatic-HC chromatograms of this study.

Conspicuous by their absence in the MF-735 chromatogram (Fig. 5) are the di- and trimethyl-naphthalenes, the two most important compound classes, by volume, in oils and sediment extracts. These two compound classes were either in very small relative concentrations, or missing altogether, in all the samples of this study. The

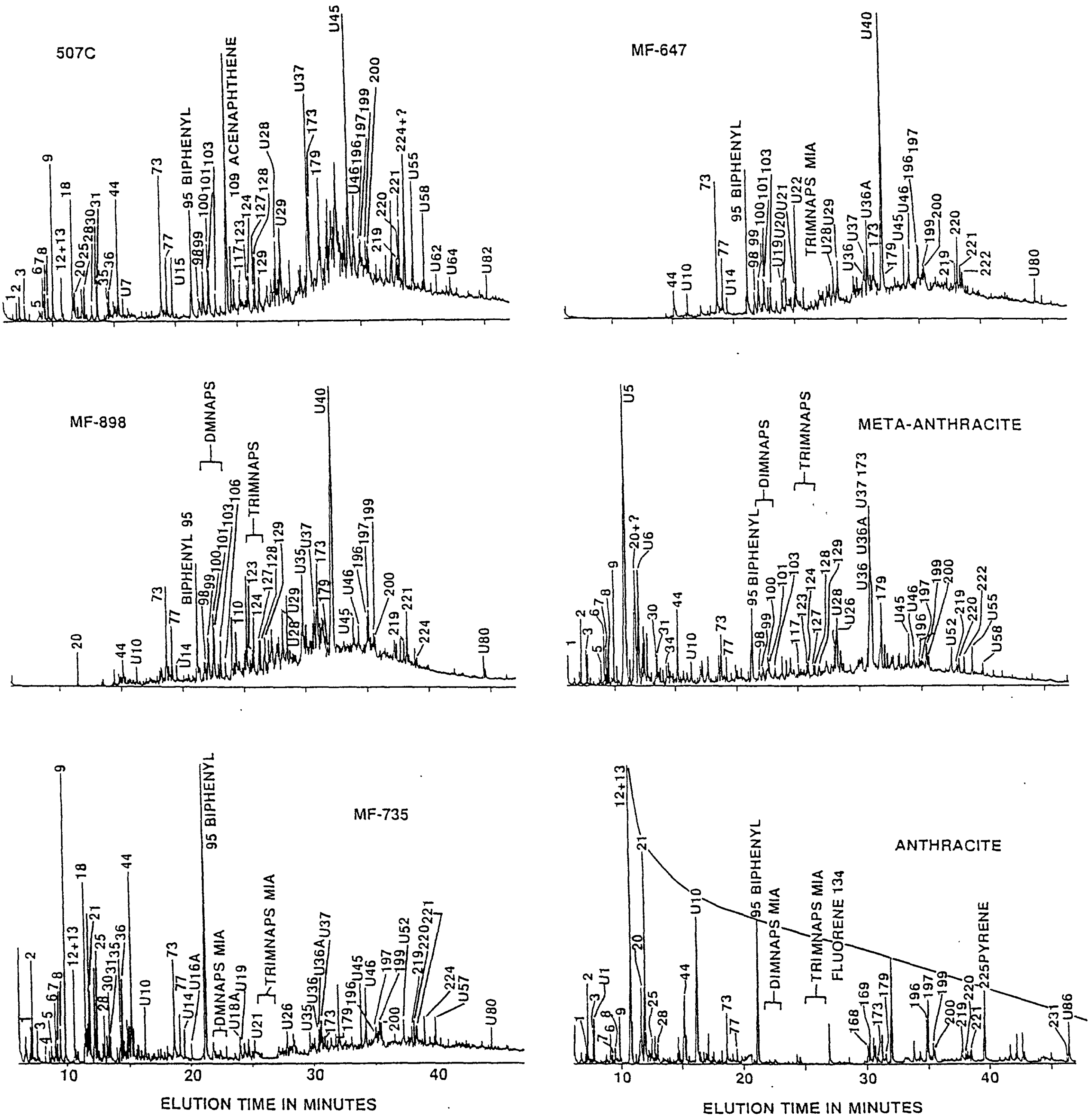


Figure 5. Aromatic-HC gas chromatograms of 4 carbonaceous metamorphic rocks and 2 anthracites. Compounds corresponding to the numbers on the peaks of Figure 5 are in Table 3. Unknown compounds (some of which repeat in all samples) are designated by an "U" and a number. DIMNAPS are dimethyl-naphthalenes, TRIMNAPS are trimethyl-naphthalenes. MIA signifies missing.

reduced amounts of the methyl- and dimethyl-phenanthrenes in the MF-735 chromatogram (Fig. 5), (and in all other samples of this study) is also a surprising observation.

The aromatic HCS of the other two Swiss Alps samples (MF-647,-898, Fig. 5), inadvertently were taken to dryness during analytical workup. Thus the lower molecular-weight HCS (mainly alkylated benzenes) were lost. However, apart from this loss, the MF-647 and -898 chromatograms are similar to one another, and different from the MF-735 chromatogram. To wit: 1) The dominant peak in MF-647 and -898 is an unknown peak (U40), as opposed to the usually-dominant biphenyl (MF-735). This difference was not caused by the loss of the lighter aromatic HCS in MF-647 and -898. 2) The dimethyl- (and trimethyl -, in MF-898) naphthalenes and methyl- and dimethyl-phenanthrenes are more prevalent in the MF-647 and -898 chromatograms than in the MF-735 chromatogram. However, these compounds are still in much lower concentrations than always observed in oils and sediment extracts. 3) Most of the major unknown peaks are present in the same proportions in MF-647 and -898; and although these peaks may be present in MF-735, the proportions are different.

The dimethyl-naphthalenes are in higher concentrations in MF-898 than in MF-647 (Fig. 5). The trimethyl-naphthalenes, although present in MF-898, are absent in MF-647. Thus, the absence, or lower-than-normal concentrations, of the methylated naphthalenes cannot be from thermal stability, because MF-898 had a metamorphic temperature about 150°C higher than that of MF-647. In fact, because the MF-647 and -898 aromatic HC chromatograms are very similar (both having the same unusual appearance) in spite of a 150°C temperature difference, we may conclude that HC thermal stability is playing a minor, if any, role in affecting the aromatic HC compositions in these rocks.

Not only are the dimethyl-naphthalenes present in MF-898, but the peak distribution of these compounds is also like that found in most oils (and distillates thereof) as well as in mature sediment extracts (compare the MF-898 dimethyl-naphthalene distribution (Fig. 5) to that of the 12617 oil sample in Figure 4). In oils and sediment extracts, the distribution of the di- and tri-methylnaphthalenes and the methyl- and dimethyl-phenanthrenes varies within limited bounds, with infrequent exceptions (Price and LeFever, 1994). However, in the samples from this study, the peak distributions of these four compound groups, when these peaks were even present, had wide variations and were atypical of the peak distributions of these compounds in oils and in sediment extracts (compare the dimethyl-naphthalene distribution in MF-647 to that of the oil in Figure 3).

These unusual aromatic HC distributions carry two important implications: First, the HCS extracted from the rocks of this study cannot possibly be due to contamination from petroleum, or petroleum-derived products, both of which have completely different aromatic-HC distributions. Second, for the same reason, the HCS in our rocks cannot be from a late-stage, low-temperature fluid movement into these rocks, wherein such fluids were carrying HCS derived from sedimentary rocks. Thus, our unusual aromatic-HC distributions dictate that the bitumen of our rocks must be indigenous.

Three controls can be envisioned as possibly affecting the aromatic HCS of the Swiss Alps samples: 1) HC-thermal stability; 2) aqueous solution; and 3) gaseous solution. Evidence that thermal stability has had no control over the compositions of the Swiss Alps aromatic HCS was discussed above. In addition, thermal stability does not explain the MF-735 aromatic-HC chromatogram, because if the dimethyl- and trimethyl-naphthalenes were thermally destroyed, then the dimethyl-phenanthrenes could not possibly be persisting in this sample, being less thermally-stable than the methylated naphthalenes. Also, past work demonstrates that the methylated naphthalenes are relatively thermally-stable compounds (Price, 1993). Furthermore, the higher-temperature MF-898 sample has an oil-like distribution of dimethyl-naphthalenes, while the lower temperature MF-647 sample does not. The lower-temperature MF-735 sample (compared to MF-898) does not even retain any dimethyl-naphthalenes. Lastly, from Figure 1, the Swiss Alps saturated HCS have not been detectably affected by thermal decomposition, and the saturated HCS are less thermally-stable than the aromatic HCS (Price, 1993).

Multiple "pore" volumes of hot waters moved through all the rocks of this study. Thus, we may expect to see evidence of aqueous (or even gaseous) solution of the rock bitumens via the composition of the HCS left behind (after solution occurred) in the aromatic (and saturated) HCS in our rocks. Two major controls are applicable to either solution mechanism. First is the solubility of the solutes to be dissolved in water or gas. Second is the mole fraction each specific compound makes up of the total original mixture which is subjected to aqueous or gaseous solution. We would have no way of knowing the original composition of the bitumen in our rocks, before a possible leaching event from aqueous solution would have occurred, so the possible effects from the second control are a complete unknown. Likewise, the first control is also an unknown because the parameters which affect aqueous and gaseous solubilities (pressure, temperature, gas content, salinity of the water, and what other dissolved organic species would have been present) are all unknown or can only be guessed at. In fact, we have not even identified all the major peaks in our extracts. In spite of these limitations, the composition of the bitumen remaining in our rocks provides significant insight into the possible effects that aqueous or gaseous solution could have had.

For example, the methylated benzenes have among the highest HC solubilities (Price, 1976), yet these are the most abundant compounds in the MF-735 aromatic HCS. If aqueous solution had strongly affected this rock, for the rock to have the relatively high concentrations of alkylated benzenes that it does have, the original alkylated-benzene concentrations would have to have been far higher than we have ever observed (except possibly in some gas-condensates), relative to the higher-molecular-weight compounds in the aromatic-HC fraction. There is no immediate explanation of how such relatively high methylated-benzene concentrations could have ever originated. Likewise, given the normal ranges of relative concentrations observed for the different compound classes within aromatic HCS, it is impossible to explain how the methylated naphthalenes could be completely, to almost completely, leached from the bitumen by aqueous solution, while simultaneously leaving behind the higher-molecular weight methylated phenanthrenes and the lower-molecular weight methylated benzenes. For this to occur, the methylated naphthalenes would have had to have originally been present in only very small concentrations in the aromatic HCS. This also would be an impossible situation to explain, especially considering, as discussed above, the methylated naphthalenes are normally the dominant compound group in naturally-occurring aromatic HCS. Other compositional considerations also disallow the possibility that aqueous solution can explain the final aromatic HC compositions in our rocks. However, these considerations will not be discussed here.

Gaseous solution explains certain aspects of the MF-735 chromatogram but not others. For example, with a normal starting aromatic-HC composition, gaseous solution would result in the observed abundance naphthalene >methyl-naphthalenes >di- and tri-methylnapthalenes (missing) and phenanthrene > methyl-phenanthrenes in the MF-735 chromatogram (Fig. 5). On the other hand, with a normal starting aromatic-HC composition, and with significant gaseous solution, the methyphenanthrenes should be more abundant than the dimethylphenanthrenes, and they are not in MF-735 (Fig. 5). Also, the alkylated benzenes would preferentially be removed by gaseous solution, yet these compounds are the most abundant compound class in the MF-735 aromatic HCS (Fig. 5). To explain these two compositional observations as due to gaseous solution, we would have to assume a highly-abnormal original composition of the aromatic HCS, which again would be impossible to explain. Thus, we conclude that gaseous solution cannot be playing a major role either, in determining the composition of these aromatic HCS. No commonly-recognized process can account for the aromatic-HC compositions in these rocks (Figs. 5 and 6).

The gas chromatograms of the aromatic HCS from the two slates (506C and 507C, only 507C shown in Fig. 5) were similar to each other, but different from those from the Swiss Alps aromatic HCS (3 "MF" samples, Fig. 5). In the 506C and 507C samples, acenaphthene and the unknown compound (U-45) were the dominant peaks. The alkylated benzenes are, unlike the case with other samples of this study, secondary peaks. Also, unlike the case with most other samples of this study, the di- (99-101, 103) and tri- (123, 124, 127-129) methylnaphthalenes were at least visible and their peak distributions were somewhat "sedimentary-like" (compare 507C to the 12617 oil, Fig. 4). However, overall, the aromatic-HC chromatograms of these two samples were also very unusual and unlike aromatic HCS from oils and bitumens of sedimentary rocks.

4.0313 Anthracites

The aromatic-HC gas chromatograms of the two anthracite samples (Fig. 5) provide insight into possible processes affecting the other samples of this study. As discussed in section 3.016, the anthracite is from a deep-sedimentary basin setting (now uplifted and eroded), and as such, is more akin to the samples discussed in Price (1993), than to the rocks of this study. The anthracite was subjected to deep-basin burial with the accompanying intense expulsion of indigenous fluids during both its burial history and basinal structuring at maximal burial. During this burial, fluid flow was outward from the sample with no incoming (hotter) fluids. Any subsequent fluid flow through the rock had to occur late in this rock's geologic history as uplift and erosion maximized. Moreover, these fluids would have been cool meteoric waters. However, unlike other situations where significant meteoric water movement results in heavy biodegradation of coals (Rice, 1993, Northern San Juan Basin, U.S.A.), the Figure 5 anthracite exhibits no evidence of biodegradation and/or weathering, such as the LNG-4 sample (Fig. 2). The principal geochemical events of interest affecting this coal were intense HC generation and very efficient expulsion, by gaseous solution, of all HCS generated from the anthracites.

Even though the anthracite has had a geologic history different than the other samples of this study, the anthracite aromatic HC gas chromatogram (Fig. 5) appears more equivalent to those of the samples of this study (Figs. 5 and 6), than to those from mature sedimentary rocks or oils (Fig. 4). However, scrutiny reveals that this is not the case and that the characteristics of the anthracite aromatic HCS (Fig. 5) are due to gaseous solution: 1) The alkylated benzenes, unlike in other samples of this study, are not major peaks. 2) Peaks of the parent compound (i.e., naphthalene, biphenyl, fluorene, phenanthrene, pyrene, etc.) are always larger than all methylated variants thereof. 3) As the degree of methylation increases in a compound group, the peak height decreases. Gaseous solution yields all these compositional characteristics. Because these compositional characteristics are not present in the aromatic HCS of the other samples of this study, we conclude that gaseous solution has not played a significant role in those other samples.

Quantitative considerations (above) suggested that even though the meta-anthracite was exposed to higher temperatures than the anthracite, gaseous solution was more intense in the anthracite because of its higher TOC content (80.14 versus 28.42%) and therefore, lower mineral content to impede expulsion. The aromatic-HC gas chromatograms of these two samples support this conclusion (Fig. 5). The meta-anthracite has slightly higher concentrations of alkylated benzenes, and still retains detectable di- and tri-methylnaphthalenes. Also the meta-anthracite chromatogram is more complex with more peaks than that of the anthracite. All these characteristics would result from less intense stripping by gaseous solution in the meta-anthracite.

The meta-anthracite has a large complex of peaks at 31 minutes, not present in the anthracite. Attempted identification of these peaks was unsuccessful. The two coal chromatograms (Fig. 5) also have three other dominant unknown peaks in the alkyl benzene region (U1, U5, U6), peaks which were not significant in the other aromatic HC chromatograms of this study.

4.0314 Ore-Deposit Rocks

The dominant peaks of the aromatic-HC gas chromatograms of the three Homestake samples of Figure 6 (942-19, 942-32, and 942-20), were biphenyl and various unusual or unidentified compounds (Fig. 6). In all Homestake samples: 1) Alkylated

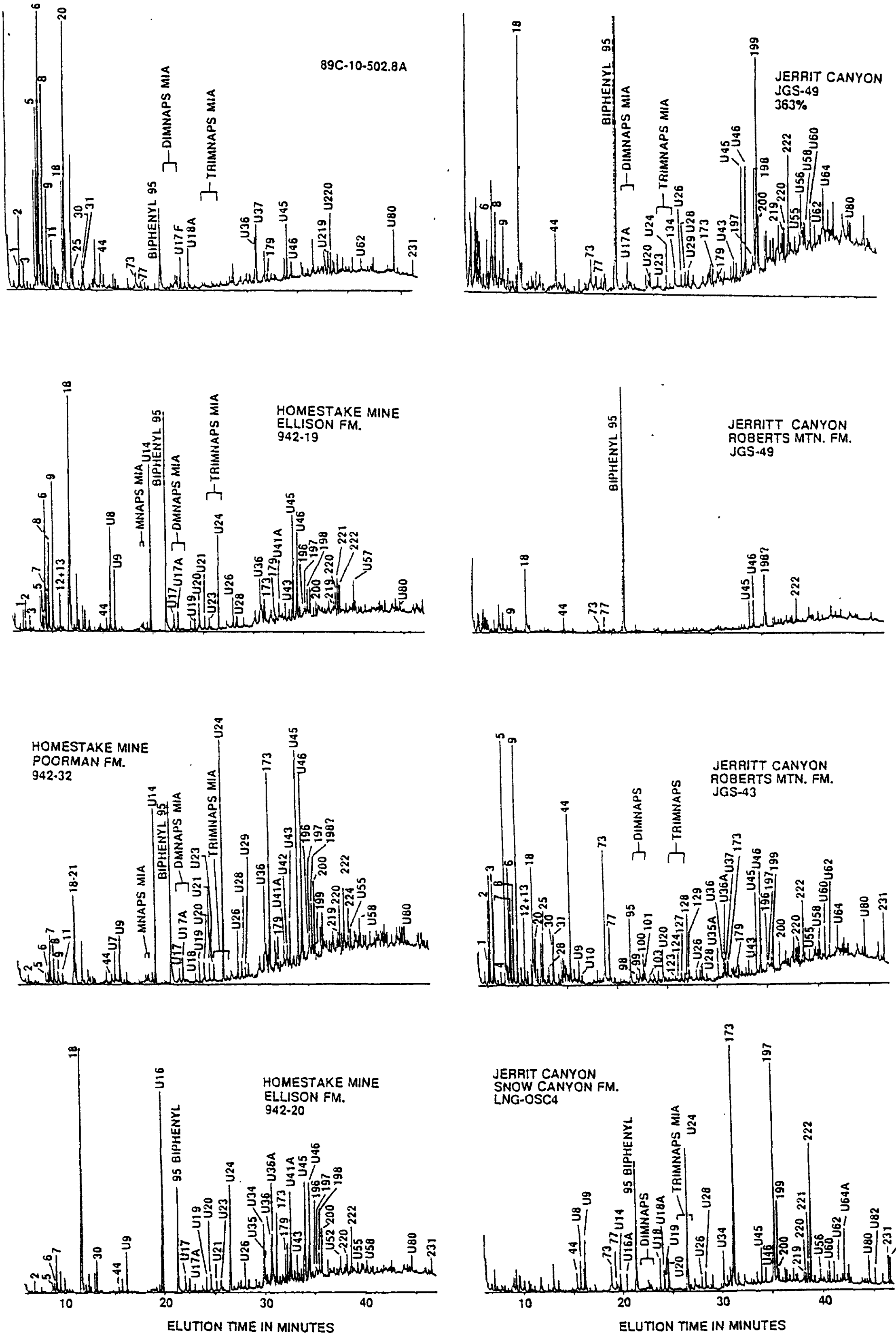


Figure 6. Aromatic-HC gas chromatograms from the carbonaceous ore-deposit rocks of this study. Labeling as in the Figure 5 caption.

benzenes had variable relative concentrations from moderate to large. 2) Naphthalene and all methylated variants thereof, were either missing or were small peaks. 3) Phenanthrene was always a small peak. 4) The methyl- and dimethyl-phenanthrenes were moderate-sized peaks; however, their peak distributions were completely different than the distributions found in oils and sediment extracts. Although the Homestake saturated-HC gas chromatograms were very similar to one another (Fig. 2), this was not true of the aromatic-HC gas chromatograms (Fig. 6). Moreover these differences cut across "stratigraphy". Thus, the 942-14 (not shown, Poorman Formation) and 942-20 (Fig. 6, Ellison Formation) chromatograms were somewhat similar to one another, but different from the 942-32 (Fig. 6, Poorman Formation) and 942-24 (not shown, Homestake Formation) chromatograms, which were quite similar. The 942-19 (Fig. 6, Ellison Formation) chromatogram was different from the other 4 Homestake chromatograms. Because the aromatic-HC chromatograms are not all the same, the similar nature of the saturated HCS in these samples cannot be ascribed to contamination.

Although the Jerritt Canyon samples are also from an ore depositional setting, the aromatic-HC gas chromatograms from these samples are unlike those from the Homestake samples. Moreover, only 2 of the 4 Jerritt Canyon samples are similar to one another. The saturated HC gas chromatograms of the Jerritt Canyon samples, JGS-43 and -49 were very similar to one another, and also were similar to the Homestake saturated HCS (Fig. 2). However, the aromatic HCS from the JGS-43 and -49 samples are different from one another. In contrast, the JGS-49 aromatic-HC chromatogram has one dominant peak (biphenyl, 95), and several smaller peaks (Fig. 6). This chromatogram is also vertically expanded 363% (Fig. 6) to show details of the smaller peaks: Unsubstituted parent aromatic HCS are in very low concentrations or are missing altogether. Most of the peaks are unknown compounds and the alkylated benzenes are in low concentrations. In contrast, the JGS-43 aromatic-HC gas chromatogram (Fig. 6), has high concentrations of alkylated benzenes (peaks 1 to 36, Table 3) and naphthalene (44), detectable di- (99-101, 103) and tri- (123, 124, 127-129, Table 3) methylnaphthalenes, and is strikingly different than the JGS-49 aromatic HC chromatogram. The presence of high relative concentrations of lower-molecular-weight aromatic HCS and low relative concentrations of lower-molecular weight saturated HCS in the same sample dictates that the JGS-43 saturated HCS (Fig. 2) are not the result of contamination from a petroleum distillate.

The Upper Plate and LNGOSC-4 (only LNGOSC-4 shown in Fig. 6) aromatic-HC gas chromatograms were similar to each other but different from both the JGS-43 and -49 chromatograms (Fig. 6). The LNGOSC-4 outcrop sample is weathered. However, this weathering has not significantly affected the aromatic HCS of this sample, because of the similarity of the LNGOSC-4 aromatic HCS to the unweathered Upper Plate aromatic HCS (not shown).

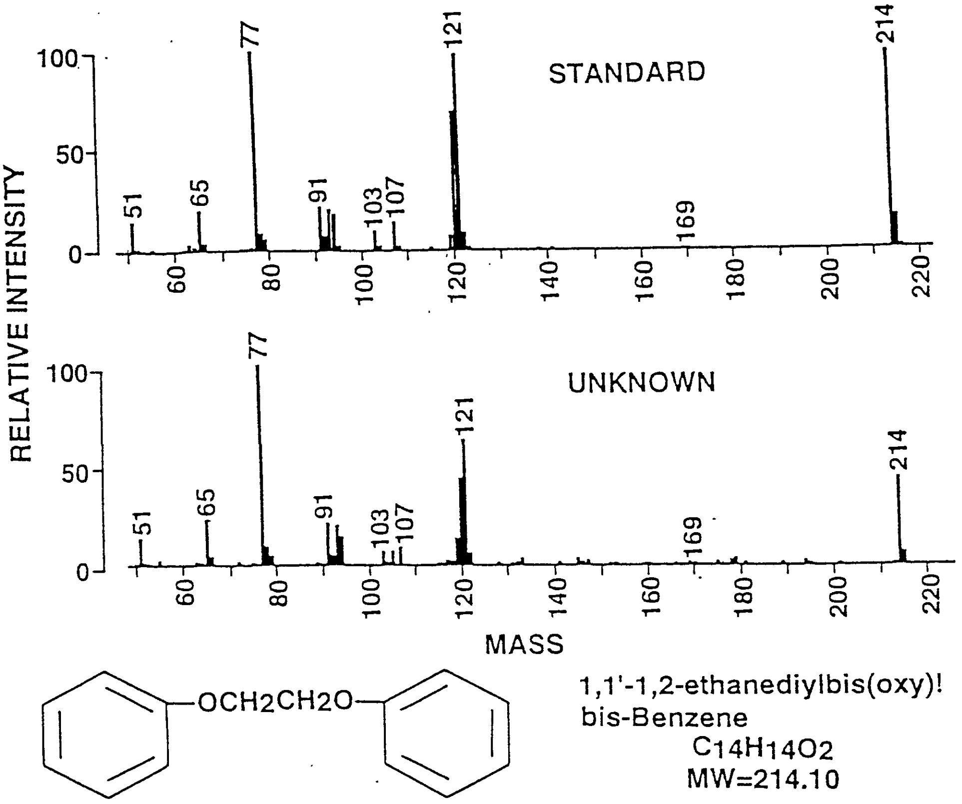
The saturated HCS (Fig. 2) from the two Precambrian Belt Series samples (only one shown in Fig. 2) were very similar to one another with unusual facies characteristics. This observation allowed the hypothesis that the bitumen of these rocks had been less affected by the process under discussion than the other rocks of this study. Thus, we may expect the aromatic HC chromatograms from these two samples to have a more normal, sediment-like appearance. They do not (Fig. 6). The aromatic HC chromatograms from the two Belt-series samples were similar to one another. The alkylated benzenes (peaks 1-36, Table 3) were dominant peaks, naphthalene (44), and the methyl- (73, 77), dimethyl-, and trimethyl- naphthalenes were in small concentrations (or missing altogether) as were phenanthrene, and the methyl- and dimethyl-phenanthrenes. Apart from the alkylated benzenes, biphenyl again is a dominant peak, and a number of unknown peaks are also present. The aromatic HCS from these two samples are not at all sediment-like. Moreover, they have many of the same unknown peaks and unusual characteristics of the other aromatic HCS of this study. The strong modification of the aromatic HCS, versus the unmodified nature of the saturated HCS in these two samples, suggests that the aromatic HCS react preferentially to the saturated HCS during hydrolytic disproportionation of OM.

4.032 Mass Spectrometry

All of the aromatic HC fractions of this study had numerous unknown peaks in their gas chromatograms. These peaks could not be identified by the usual qualitative gas-chromatographic approaches we employ (discussed above in "Methods" section). Thus, full-scan gas-chromatographic mass-spectrometric (GCMS) analysis was run on 3 samples (506C, 89C-10/517.4, 942-32; all Table 1) selected on the basis of the three samples having large examples of the unknown peaks common to all the samples of this study. Ionic spectra of unknown peaks were compared with the ionic spectra of reference compounds in the Kratos mass-spectrometric library. Two examples of spectral matches between such reference (standard) compounds, and unknown peaks, are shown in Figure 7. In both cases, there are slight differences between the unknown and standard ionic spectra, because our unknown peaks are coeluting with other smaller peaks. This coelution changes the ionic spectra of the unknown peak slightly compared to that of the standard.

Whole-ion fragmentograms of two of the three samples so analyzed are presented in Figure 8 with numbers above different peaks. The numbers refer to peak identifications in Table 4. Note that the response of a given peak is different between the flame-ionization detector used for gas chromatographic analysis and the mass spectrometer. Also different columns and different column conditions were used for gas chromatography of the aromatic HC fractions (Figs. 3-6) compared to the GCMS whole-scan analysis (Fig. 8). Thus, the peak distributions of the aromatic-HC gas chromatograms (Figs. 3-6) and the aromatic-HC whole-scan fragmentograms (Fig. 8) are significantly different and are difficult to directly compare. Therefore, we have not attempted to assign the identifications from Figure 8 and Table 4 to the unknown peaks ("U") in Figures 5 and 6.

Perusal of the Table 4 compounds reveals that some of these compounds are not HCS at all, but instead, oxygenated moieties of aromatic and saturated HCS, and some chlorinated moieties. The existence of these compounds is predicted by the theory



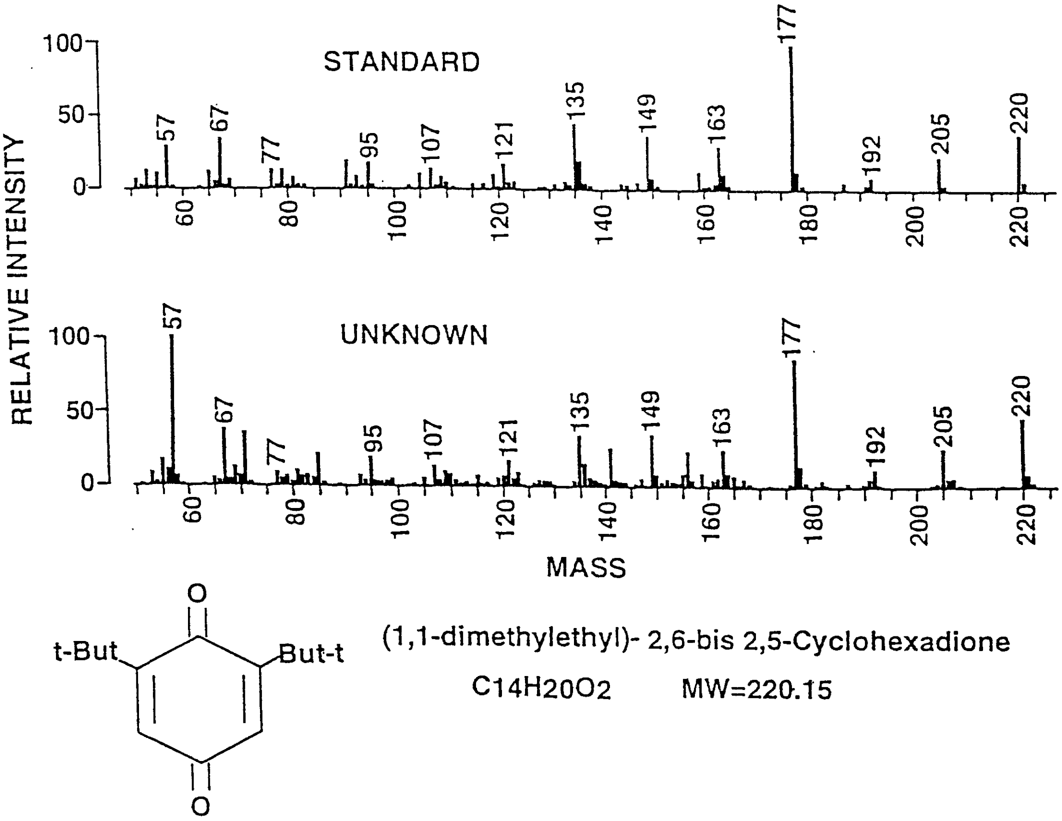


Figure 7. Two examples of ionic spectra of unknown peaks identified in our aromatic-HC fractions.

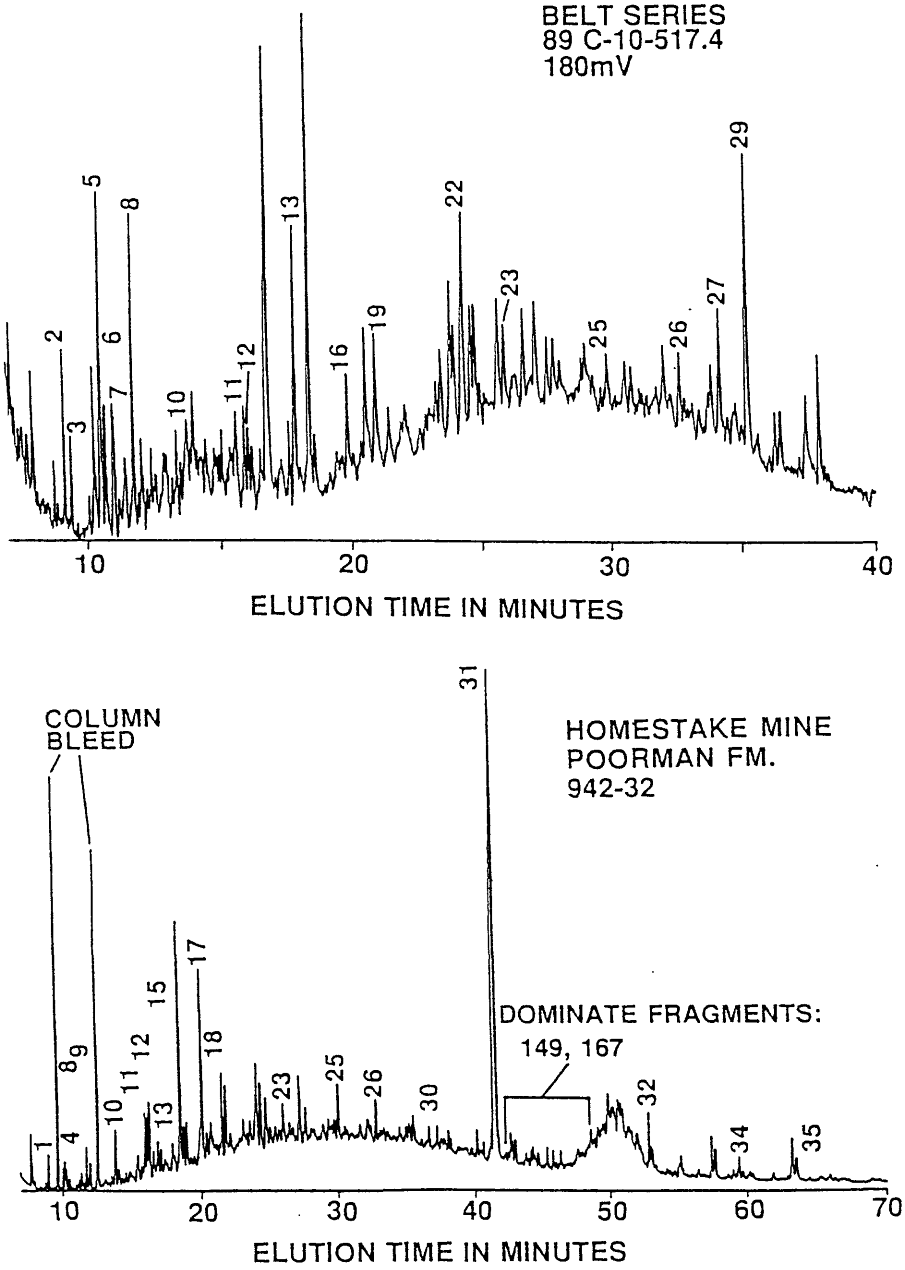


Figure 8. Whole-ion fragmentograms of two of the aromatic-HC fractions of this study on which whole-scan mass spectrometry was performed. Peak identifications corresponding to the numbers in Fig. 8 are in Table 4.

Table 4.--Compounds identified by whole scan mass spectrometry of the aromatic HC fractions from samples of this study. Peak numbers refer to Figure 8. MW is molecular weight. Two series of n-alkonic acids and/or alcohols were tentatively identified but are not included in this table, pending further analyses. Compounds were identified by comparison with the Kratos Mach 3 Library Search Program, with the actual library being the Wiley Registry of Mass Spectral Data (5th Edition, John Wiley and Sons, Inc., New York). Compound names are from the Kratos Mach 3 Library.

Peak	MW	Compound
1	160.125200	Benzene, cyclohexyl
2	142.078250	Naphthalene, 1-methyl
3	142.078250	Naphthalene, 2-methyl
4	154.078250	1,1' Biphenyl
5	162.023628	Naphthalene, 1-chloro
6	156.093900	Naphthalene, 1,4-dimethyl-
7	156.093900	Naphthalene, 1,3-dimethyl-
8	170.167065	2-Undecanone---(coeluting with): 2,5-Cyclohexadiene-1,4-dione, 2,6-bis (1,1-dimethylethyl)-
9	168.093900	1,1'-Biphenyl, 4-methyl-
10	170.109550	Naphthalene, 1,6,7-trimethyl-
11	222.089210	1,2-Benzenedicarboxylic acid, diethyl ester
12	254.260965	2-Heptadecanone
13	210.140850	1,1'-Biphenyl, 2,2'-diethyl-
15	182.167065	11-Dodecen-2-one
16	212.083730	Benzoic acid, phenylmethyl ester
17	268.276615	2-Pentadecanone, 6,10,14-trimethyl
18	208.052430	9,10-Phenanthrenedione (9.10-Phenanthrenequinone)
19	214.099380	Benzene, 1,1'-1,2 ethanediylbis (oxy)! bis-
22	290.260965	5.β.,8.β.H,9.β.H,10.α. -Labd-14-ene, 8-13-expoxy -
23	278.151810	1,2-Benzenedicarboxylic acid dibutyl ester
27	284.214015	1-Phenanthrenecasboxaldehyde, 1,2,3,4,4a,9,10,10a,-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, 1R-(1.α. 4.β.,10a.α.)!-
29	314.224580	1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester, 1R-(1.α.,4a.β.,10a.α.)!-
30	357.844418	3,4,5,3',4',5'-Hexachlorobiphenyl; (or :)
	357.844418	1,1'-Biphenyl, 2,2',4,4'-hexachloro-
31	278.151810	1,2-Benzenedicarboxylic acid, bis (2 methylpropyl) ester
32	534.537580	9-Hexadecenoic acid, eicosyl ester, (Z)-
34	506.506280	9-Hexadecenoic acid, octadecyl ester, (Z)-
35	508.52193	Hexadecanoic acid, octadecyl ester

hydrolytic disproportionation of OM (Helgeson et al., 1993), and thus supports our contention that hydrolytic disproportionation of OM is responsible for the origin of these compounds. *The presence of these compounds in our samples is one of the pivotal observations of this study.*

4.04 RESINS AND ASPHALTENES

The resins and asphaltenes from this study were much lighter in color (yellow to yellow brown) than resins and asphaltenes from oils and/or sediment bitumens. Note that in many of the Table 1 samples, the resins, and especially the "corrected resins", are in concentrations equal to or greater than the saturated HCS, and in all samples, the resins are in significantly greater concentrations than the aromatic HCS. Moreover, in all but one sample (Jerritt Canyon UP-1), the resins are in greater concentrations than the asphaltenes, sometimes by a factor of 5-10 or more (Table 1). In mature oils and/or mature to ultra-mature sediment bitumens, the saturated and aromatic HCS are commonly in significantly greater concentrations than the resins, which are usually about equal to the asphaltenes (Price, 1982). Thus, the resins from the samples of this study are in unusually high relative concentrations compared to typical high-rank sediment samples.

In comparison to the saturated and aromatic HCS, the resin fraction of sediment bitumens and oils is not well understood. Gas chromatograms of resins from bitumens of higher molecular weight compounds, with numerous unidentified peaks on the hump (Fig. 9, Bakken Shale 8663'-8667'). The size and number of the peaks on the hump depend on the respective sample. However, gas chromatograms of the resins from our samples are characterized by 2 to 8 dominant peaks, *peaks which recur in all samples (Fig. 9)*. In the majority of our samples, peak 22 is the largest peak, with peaks 14, 20, 23-26, 28 and/or 29 also being large peaks, but smaller than peak 22 (Fig. 9). As stated, in our samples, the resins invariably were the largest fraction from column chromatography, by weight (Table 1). Thus, a significant part of the extractable bitumen in our rocks is represented by 4 or 5 recurring compounds. This, in spite of the fact, that these samples originated from widely-separated geographic localities, and had widely-diverse geologic histories. These observations (the recurrence of the same compounds and their very high relative concentrations) suggest to us that these organic compounds have been strongly driven towards a thermodynamic equilibrium by the reaction responsible for the compounds, which we believe to be hydrolytic disproportionation of OM.

In Figure 10, the vertical scale of eight of the resin gas chromatograms has been greatly expanded, from a range of 408 to 1000 millivolts to around 100 millivolts, so that the peaks in the "grass" portion of the chromatogram, between the 2 to 8 large peaks ("trees"), would become evident, if they were present. In Figure 10, the resin chromatograms of 4 of the 7 samples have numerous peaks in the grass portion of the chromatograms (MF-544, 942-19, LNGOSC-4, and 507C). In contrast, 3 of the other vertically-expanded chromatograms (MF-898, -903; and JGS-43) have few peaks at the

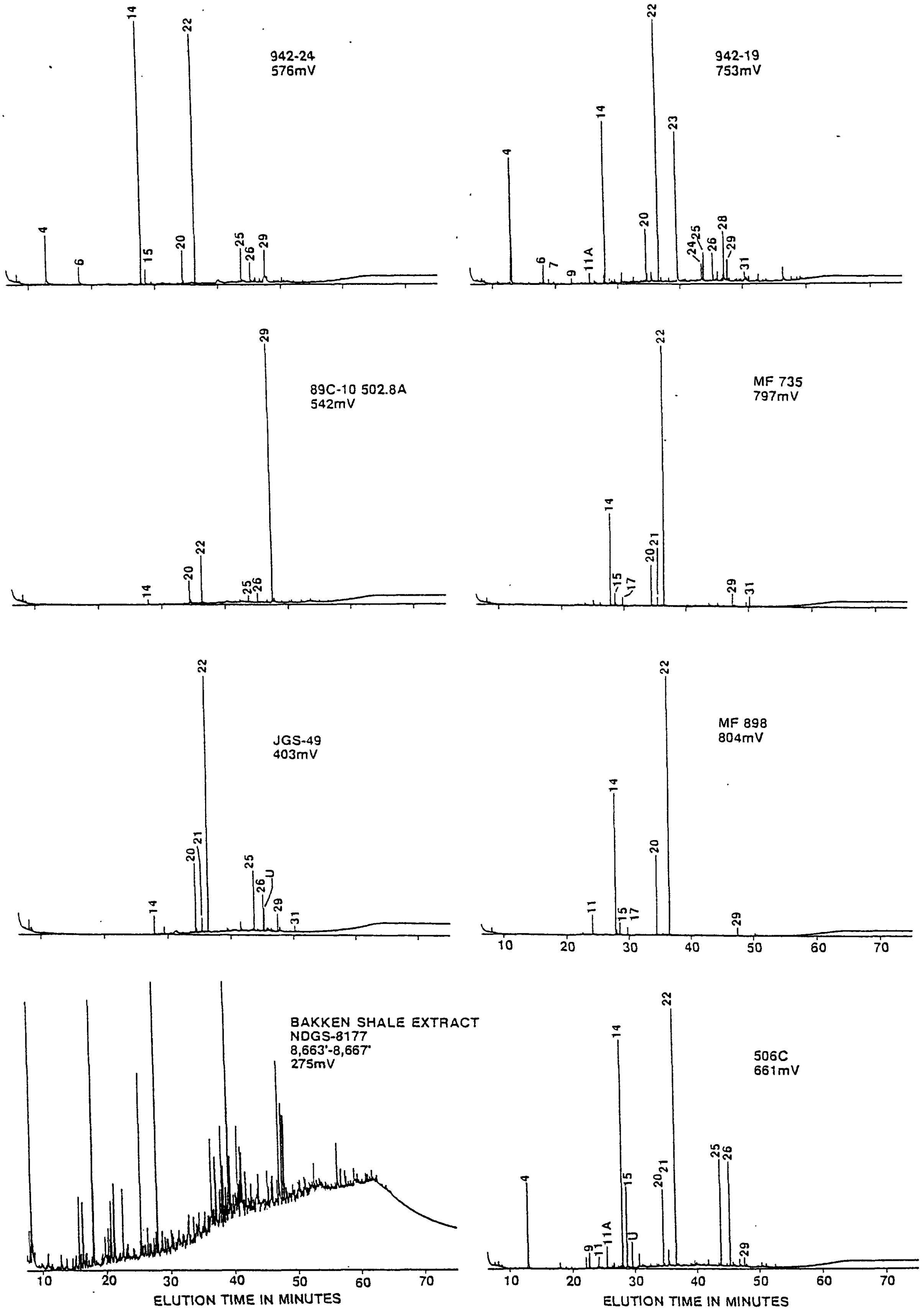


Figure 9. Gas chromatograms of the resins from 7 of the samples of this study plus a representative gas chromatogram of a resin fraction from a sediment extract (lower Mississippian-upper Devonian Bakken shale, NDGS-8177; details of this sample in Price et al., 1984). The numbers above the peaks identify (unknown) peaks recurring in all resin chromatograms. Full scale signal peak intensities are shown in millivolts (mV).

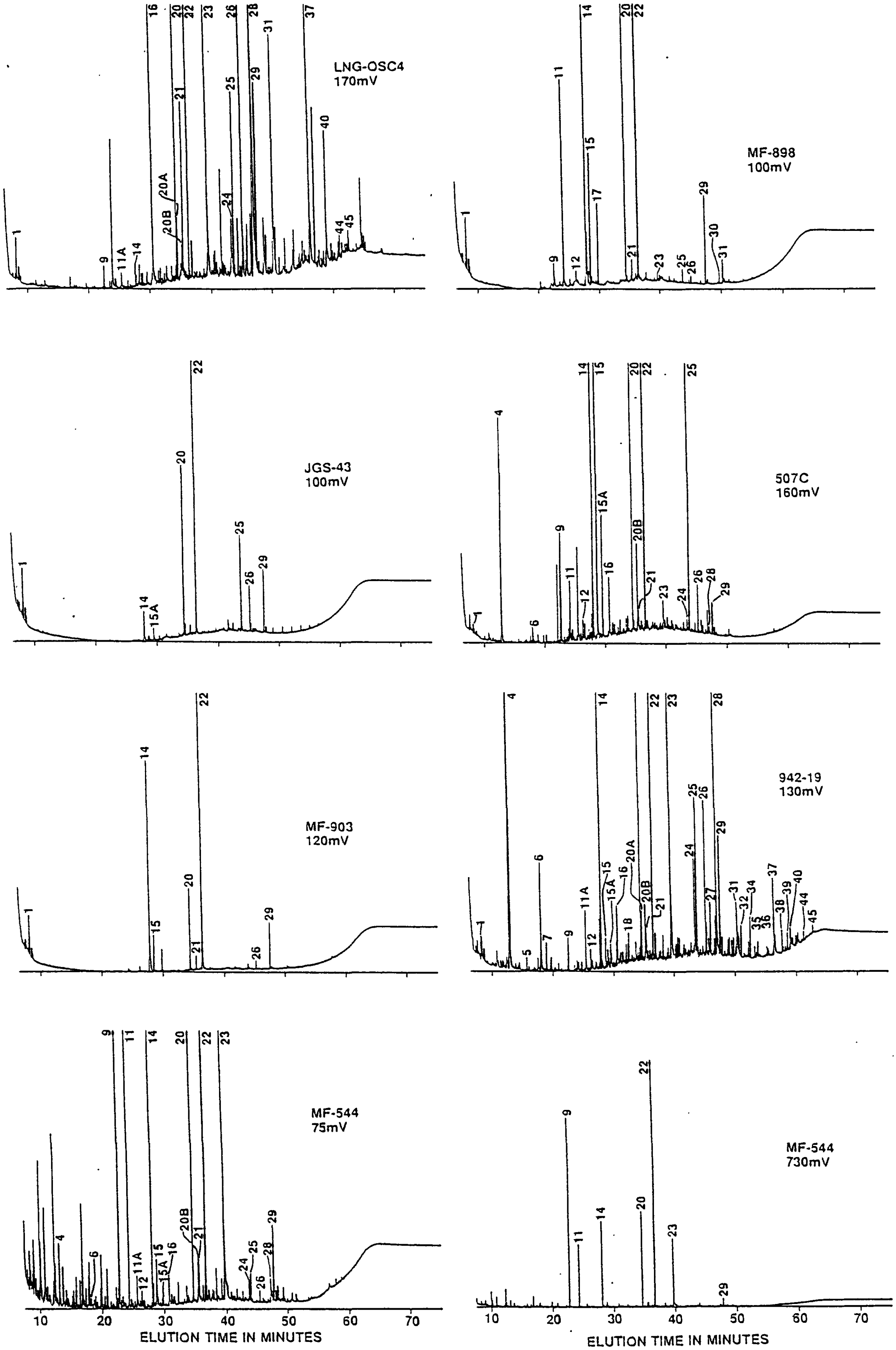


Figure 10. Gas chromatograms of the resins from 7 samples of this study (2 of which, MF-898 and 942-19) are shown in Figure 9. The chromatograms in Figure 10 have been attenuated (full-scale millivolts, mV shown for each chromatogram) to better show the smaller peaks in these samples. The numbers above the peaks refer to (unknown) compounds recurring in all samples. The sample MF-544 is the resin fraction of a Swiss Alp metamorphic rock from research subsequent (to this paper), wherein the resin fraction was not evaporated to dryness (discussed in text).

"grass" level. However, the differences between these two groups are in reality analytical artifacts:

Because most of the resin fractions are concentrated in 2 to 8 peaks (depending on the sample), these samples were rather difficult to perform gas chromatography on. This was because ascertaining the correct concentration to dilute the samples was troublesome. As such, gas chromatography had to be performed on these resin samples several times before acceptable results were obtained. In these multiple analyses, some of the resin samples had their characteristics reversed. To wit: samples which had few peaks evident in the "grass" portion of Figure 10 would have many peaks in the vertically-expanded "grass" portion of the chromatogram. Furthermore, some samples which had many "grass" peaks (Fig. 10) had none, or few, in the vertical expansions of other analyses. Thus we draw the conclusion that although 2 to 6 compounds make up most of the resin fraction (95 to 99%), a greater number of other compounds exist in much smaller concentrations in all these samples.

We followed our standard laboratory procedure in quantitatively analyzing the resins by taking the entire resin fraction to dryness to obtain weights for the resins. In doing so, we lost any lower-molecular weight resins which may have been present in our samples. In subsequent research (see "Related Work" section), we take only one-half of the resin fraction to dryness to obtain resin weights, and save the other half for "C_8+ " resin gas-chromatography. One of the chromatograms of Figure 10 (MF-544) is from the newer research. Although more lower-molecular weight resins are present in MF-544, the loss of lower molecular weight material in the resins of the samples of this study does not appear extreme.

Note that in Figure 10, the same 30 largest peaks recur in all samples, although relative peak heights vary between samples and several peaks may be present in only one sample or in only one sample suite. Nonetheless, the recurrence of most of the same large to moderate-sized peaks in the resins from all our samples, even though the samples are from widely-diverse geographic localities and different geologic settings, again strongly suggests to us that a strong drive towards thermodynamic-equilibrium exists in these samples.

Full-scan GCMS was run on six of our resin fractions, four total ion-current spectra of which are shown in Figure 11. We were able to identify only 5 peaks with surety in these fragmentograms (Table 5), peaks which were again oxygenated organic compounds. Two other peaks (1? and 2?) were only tentatively identified. Peaks 3-6 in Table 4 obviously are a homologous series, no doubt resultant from their reaction mechanism (discussed below). In subsequent research, we intend to effect identification of more of the smaller to moderate-sized resin peaks. From our present work, limited research by other investigators, and theoretical considerations (the latter two being discussed below), we believe that most of the organic compounds we eventually identify will be oxygenated compounds (acids, esters, ketones, ethers, etc.).

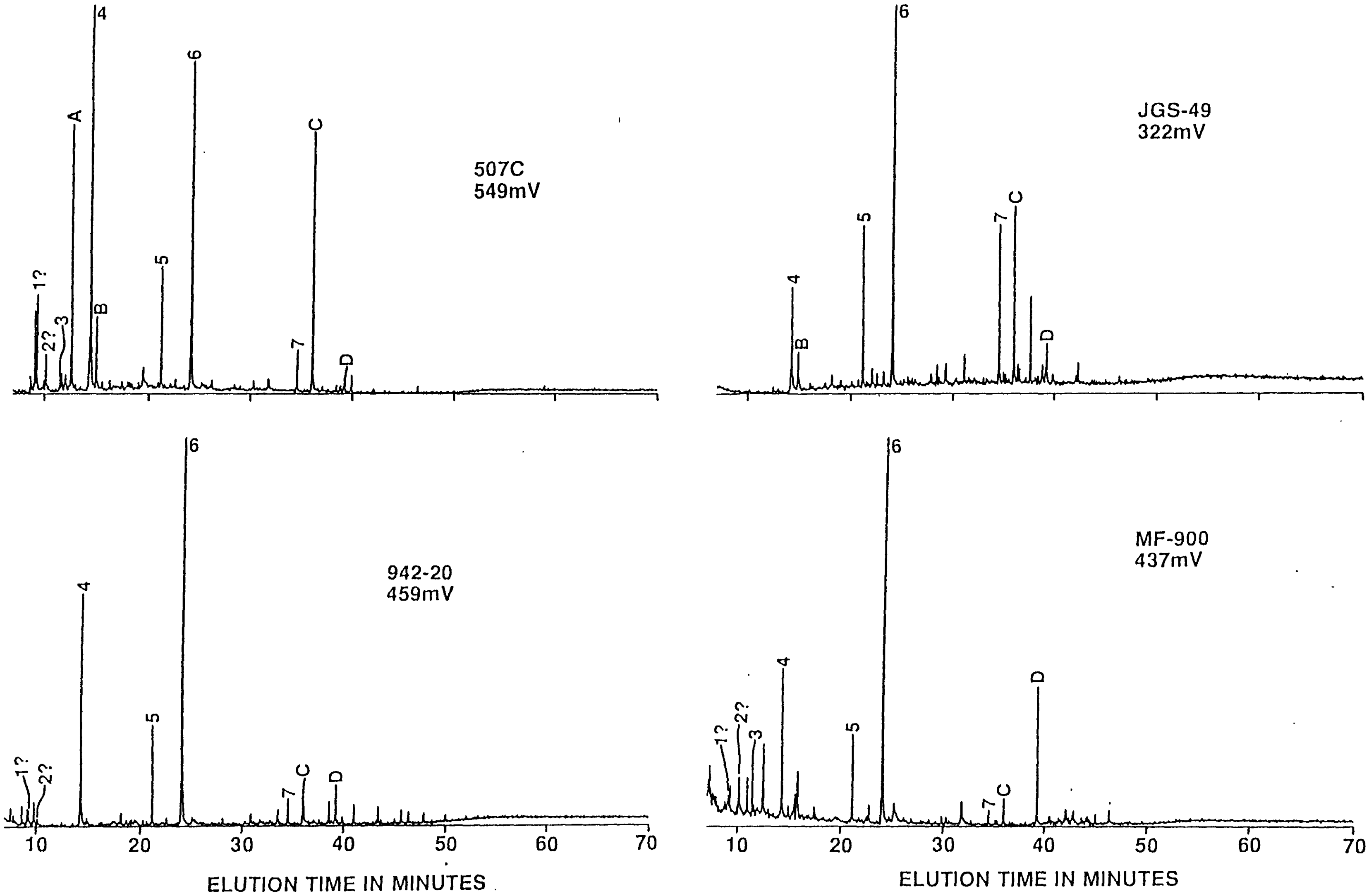


Figure 11. Whole-ion fragmentograms of four of the six resin fractions of this study on which whole-scan mass spectrometry was performed. Peak identification corresponding to the numbers in Figure 11 are in Table 5. Letters refer to unidentified recurring peaks. Full-scale attenuation are shown in millivolts (mV).

Table 5.

Compounds identified by whole scan mass spectrometry of the resin fractions from the samples of this study. Peak numbers and letters refer to Figure 11. Letters are unidentified peaks with the mass numbers of the most prominent fragments provided. MW is molecular weight. Structures of these compounds are given in Table 1 of the Appendix.

Peak	MW	Compound
1?	168.137496	1H,5H,7H,11H-Dipyrazalo 1,2-a:1',2'-d! 1,2,4,5! tetrazine-tetrahydro- (nitrogen bearing)
2?	140.156500	1-Decene
3	194.057910	1,2-Benzenedicarboxylic acid, dimethyl ester
4	222.089210	1,2-Benzenedicarboxylic acid, diethyl ester
5	278.151810	1,2-Benzenedicarboxylic acid, dibutyl ester
6	278.151810	1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester
7	370.308310	Hexanedioic acid, dioctyl ester

The resins from our samples, like our aromatic HCS , have been fundamentally chemically-transformed compared to resin compositions observed in sediment bitumens and oils. Moreover, at the least, a significant part of our resins are composed of oxygenated organic compounds and a strong tendency to thermodynamic equilibrium appears to be present in the resins from all our samples. The oxidation of OM and the drive towards thermodynamic equilibrium are both predicted by the theory of hydrolytic disproportionation of OM (Helgeson et al., 1993), thus strongly suggesting that the OM in our samples took part in this reaction.

4.05 BIOMARKERS

Biomarker analyses were run on 10 of our samples (MF-647 and -898; 942-20 and -24; JGS-43 and -49; the anthracite and meta-anthracite; 89C-10 502.8 and 506C). The biomarkers corresponding to numbers in the biomarker fragmentograms (Figs. 12-16) are given in Table 6 and various biomarker ratios and normalized percentages for all 10 analyzed samples are given in Table 7.

4.051 Steranes

All samples, except the anthracite, had high diasterane to sterane ratios (1.64 to 5.58, Table 7) compared to values commonly found in many oils and sediment extracts. Because of a strong facies dependency, diasterane/sterane ratios are not considered good maturity indices (Peters and Moldowan, 1993). However, high-rank oils and high-rank sediment extracts analyzed in our laboratory invariably have a predominance of diasteranes over steranes, a point also noted by Peters and Moldowan (1993). Classically, the increase in diasteranes over steranes at high ranks has been attributed to thermal conversion of steranes to diasteranes (Peters and Moldowan, 1993). Sterane

(M/Z = 219) fragmentograms for two Swiss Alps samples (MF-647, MF-898), and for two Williston Basin Bakken oils, are shown in Figure 12. The two Swiss Alps fragmentograms are very similar, peaks 20-29 being slightly higher in the MF-647 fragmentogram. The bars on peaks 20-29 in the MF-647 fragmentogram indicate the relative heights of these respective peaks in the MF-898 fragmentogram. Notwithstanding these differences, in spite of a temperature difference of 150°C between MF-647 and -898, the sterane fragmentograms from these two rocks are nearly identical. Thus, maturity has been frozen in these two rocks (e.g., HC thermal cracking has been suspended).

Except for peaks 20 and 22 (diasteranes), all the peaks with bars in the MF-647 fragmentogram are steranes. Thus we might hypothesize that these peak height differences are from conversion of steranes to diasteranes. However, two observations argue against this hypothesis, and suggest instead that the control is molecular-weight related. First, the diasterane peaks 20 and 22 are also reduced in MF-898 compared to MF-647. Second, the sterane peaks 15 and 16 are not reduced in MF-898 compared to MF-647.

The sterane fragmentogram for the NDGS-12779 Bakken oil (Fig. 12) appears to be that of a moderately-mature oil. However, the ROCK-EVAL hydrogen (535) and production (0.068) indices for the lower Mississippian-upper Devonian Bakken shales, which are both the source and reservoir for this oil, are those of only marginally-mature to moderately-immature shales. Note that the NDGS-12779 Bakken oil sterane fragmentogram is strikingly similar to those from the Swiss Alps metamorphic rocks. In fact, the similarity between the sterane fragmentograms of this oil and the two rocks is characteristic of that found both in oil families from one source rock or found between source rock to oil matches. Biomarkers with peak distributions comparable to those of only moderately-mature oils surviving in metamorphic rocks is inconceivable by accepted petroleum-geochemical paradigm, as is the fact that organic maturity has been frozen in these rocks, in spite of metamorphic-temperature differences of 150°C.

The sterane fragmentogram of a "post mature" Bakken oil is shown in Figure 12 (NDGS-1350). The ROCK-EVAL hydrogen indices of the Bakken shales which sourced this oil are 169 (Price and LeFever, 1994). The steranes demonstrate the typical "thermally-stressed" peak distribution expected for this maturity. However, the NDGS-1350 oil could not have been exposed to higher temperatures than MF-898 (400°C). That the sterane fragmentogram from a 400°C metamorphic rock could be so less mature than that of an oil is also completely unexpected by petroleum-geochemical paradigm and dictates that an unknown parameter has greater control than temperature in these metamorphic rocks.

As discussed, the anthracite has been strongly affected by gaseous solution. Thus we assume that this sample's sterane-peak distribution (Fig. 12) and the low (0.60) diasterane to sterane ratio for this sample (compared to other Table 7 values) both result from gaseous solution. The meta-anthracite sterane-peak distribution (Fig. 12) is different than that of the anthracite: more peaks, and the presence of several unidentified

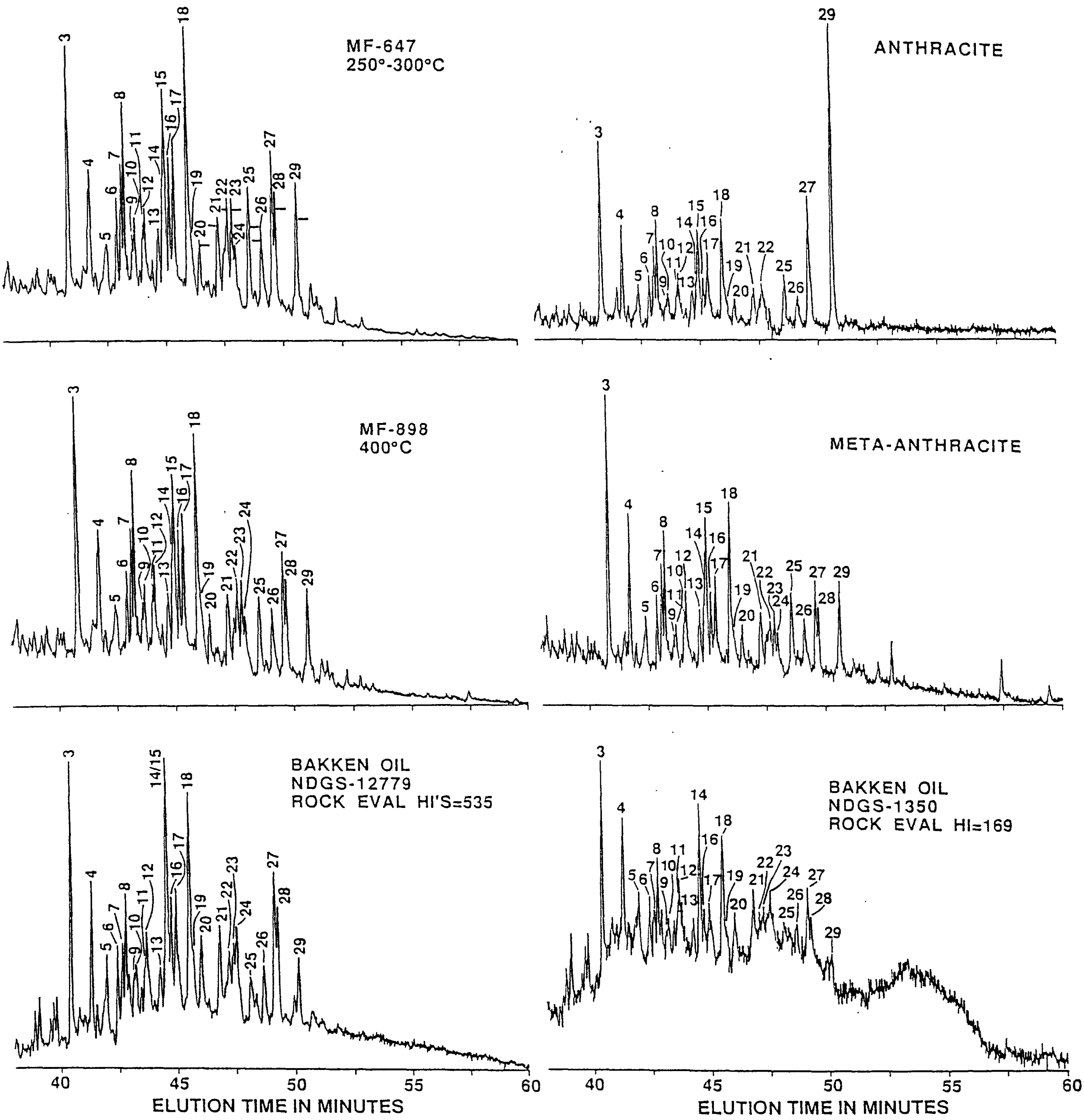


Figure 12. Sterane (M/Z = 219.1956 fragmentograms from four samples of this study and for two oils from the Williston Basin, North Dakota, U.S. Provenance of the oils in Price and LeFever (1994). Peak identifications corresponding to the numbers in Figure 12 are in Table 6.

Table 6. List of biomarkers identified in Figure 12-16.

STERANES (Figs. 12, 13).

Peak Number	Compound
3	13β,17α - (20S) diacholestane (C_{27})
4	13β,17α - (20R) diacholestane (C_{27})
5	13α,17β - (20S) diacholestane (C_{27})
6	13α,17β - (20R) diacholestane (C_{27})
7	13β,17α - (20S) 24-methyldiacholestane (C_{28},I)
8	13β,17α - (20S) 24-methyldiacholestane (C_{28},II)
9	Diacholestane (C_{27})
10	24-methyldiacholestane (C_{28})
11	13β,17α - (20R) 24-methyldiacholestane (C_{28},I)
12	13β,17α - (20R) 24-methyldiacholestane (C_{28},II)
13	24-ethyldiacholestane (C_{29})
14	13α,17β, - (20S) 24-methyldiacholestane (C_{28})
15	5α,14α,17α - (20S) cholestane (C_{27})
16	5α, 14α,17β - (20R) cholestane (C_{27}+ unknown C_{29} diasterane
17	5α,14β,17β - (20S) 24 cholestane (C_{27})
18	5α,14α,17α - (20R) cholestane (C_{27})
19	13α,17β - (20R) 24-methyldiacholestane (C_{28})
20	13β,17α - (20R) 24-ethyldiacholestane (C_{29})
21	5α,14α ,17α - (20S) 24-methylcholestane (C_{28}) + unknown C_{29} diasterane)
22	13α,17β - (20R) 24-ethyldiacholestane (C_{29})
23	5α,1β,17β - (20R) 24-methylcholestane (C_{28})
24	5α,14β,17β - (20R) 24-methylcholestane (C_{28})
25	5α,14α,17α - (20R) methylcholestane (C_{28})
26	5α,14α,17α - (20S) 24-ethylcholestane (C_{29})
27	5α,14β,17β - (20R) 24-ethylcholestane (C_{29})
28	5α,14β,17β - (20S) 24-ethylcholestane (C_{29})
29	5α,14α,17α - (20R) 24-ethylcholestane (C_{29})

TRICYCLIC TERPANES (Fig. 14)

Peak Number	Compound
30	C_{19} tricyclic terpane
31	C_{20} tricyclic terpane
32	C_{21} tricyclic terpane
33	C_{22} tricyclic terpane
34	C_{23} tricyclic terpane
35	C_{24} tricyclic terpane
36	C_{25} tricyclic terane
37	C_{28} (22S) tricyclic terpane
38	C_{26} (22R) tricyclic terpane
39	unidentified C_{24} tetracyclic terpane
41	C_{28} (22R) tricyclic terpane
42	C_{28} (22S) tricyclic terpane
43	C_{28} (22R) tricyclic terpane

PENTACYCLIC TERPANES (Fig. 15)

Peak Number	Compound
44	18α - trisnorneohopane (C_{27} Ts)
47	17α - trisnorneohopane (C_{27} Tm)
51	norhopane (C_{29})
52	18α - neonorhopane (C_{29})
56	hopane (C_{30}))
59	17β, 21α - moretane (C_{30})
62	22S homohopane (C_{31})
64	22R homohopane (C_{31})
65	gammacerane (C_{30})
66	17β, 21β hopane (C_{31})
67	22S bishomohopane (C_{32})
68	22R bishomohopane(C_{32})
71	22S trishomohopane (C_{33})
74	22R trishomohopane (C_{33}) + C_{36} (22R) tricyclic terpane

PENTACYCLIC TERPANES (Fig. 15)

76	22S tetrakishomohopane (C_{34}) + 17β, 21β - (22R) bishomohopane (C_{32})
78	22R tetrakishomohopane (C_{34})
79	22S pentakishomohopane (C_{35})
81	22R pentakishomohopane (C_{35})

TRI- AND MONO-AROMATIC STEROIDS

Peak Number	Compound
82	C_{21} monoaromatic steroid
83	C_{22} monoaromatic steroid
84	5β (-20S) monoaromatic steroid (C_{27})
85	5β (-20R) monoaromatic steroid (C_{27})
86	5α (-20S) monoaromatic steroid (C_{27}) + 5β (-20S) monoaromatic steroid (C_{28})
87	C_{27}+C_{28}+C_{29} monoaromatic steroid isomers
88	5α (-20S) monoaromatic steroid (C_{29})
89	5α (-20R) monoaromatic steroid (C_{82}) + 5β (-20R) monoaromatic steroid (C_{29})
90	5α (-20R) monoaromatic steroid (C_{29})
91	C_{20} triaromatic steroid
92	C_{21} triaromatic steroid
93	(-20S) triaromatic steroid (C_{26})
94	(-20R) triaromatic steroid (C_{26}) + (-20S) triaromatic steroid (C_{27})
95	(-20S) triaromatic steroid (C_{28})
96	(-20R) triaromatic steroid (C_{27}) (b)
97	(-20R) triaromatic steroid (C_{28})

higher-molecular-weight compounds present in the meta-anthracite compared to the anthracite. We assume that these differences are largely from more intense gaseous solution in the anthracite.

Two Homestake sterane fragmentograms (942-20, Ellison Formation; 942-24 Homestake Formation, Fig. 13) are very similar to one another, being characterized by a dominance of 13β17α20S diacholestane (C_{27}), peak 3. In fact, in all the analyzed samples, except the anthracite, this peak is either one of the two largest, or is the dominant peak, in the sterane fragmentograms (Figs. 12 and 13). The sterane fragmentogram of the 506C slate/schist is almost an exact match to that of the Homestake 942-20 sample and is very similar to that of the 942-24 sample in spite of having a different geologic provenance than the Homestake rocks.

The sterane fragmentograms of the JGS-43 and -49 Jerritt Canyon samples (Fig. 13) are mature in appearance and both are dominated by 13β17α20S diacholestane (C_{27}), peak 3. However, apart from this similarity, the peak distribution of these two Jerritt Canyon fragmentograms is otherwise moderately different. Very low sterane concentrations are in the Montana Precambrian Belt Series sample (89C-10/502.8, Fig. 13). As a consequence, the steranes had a "stressed" appearance, again with a dominance of 13β17α20S diacholestane (C_{27}). In fact, low concentrations of all biomarkers were present in this sample. As discussed above, both these rocks had very unusual saturated-HC peak distributions. Moreover, these samples were the least thermally and geochemically-stressed of all the samples in this study. Thus, the low biomarker concentrations in this Precambrian sample most probably are an original facies control.

4.052 Tricyclic Terpanes

Tricyclic terpane fragmentograms of 8 of the 10 samples analyzed are in Figure 14. Homestake 942-24 tricyclic fragmentogram was excluded because it was almost an overlay of the Homestake 942-20 tricyclic fragmentogram. The Montana Precambrian Belt series sample (89C-10-502.8A) was excluded in this, and subsequent figures, because of its low biomarker concentrations. All the tricyclic terpanes normally found in oils and moderately-mature to mature sedimentary rock extracts (Table 6) are present in varying concentrations in the Figure 14 fragmentograms. The C_{23} and C_{24} tricyclic terpanes (peaks 34 and 35), usually the dominant peaks in oils and extracts, are also the dominant peaks in all but one of our samples (MF-898). Moreover, some of the fragmentograms closely resembled those of oils and rock bitumens, especially the two Jerritt Canyon (JGS-43 and -49) samples and, less so, the two Homestake samples (942-20 being shown in Fig. 14). Conversely, other samples had tricyclic-terpane peak distributions atypical of those from oils and rock extracts, with moderate to large peaks not normally studied in petroleum geochemistry. These peaks are labeled U (unknown) followed by a number, or a number and a letter, (e.g., U13 or U13a, U13b, etc.).

The tricyclic-terpane fragmentograms of the two Jerritt Canyon samples (JGS-43 and -49, Fig. 14), although both oil-like, are moderately different from one another,

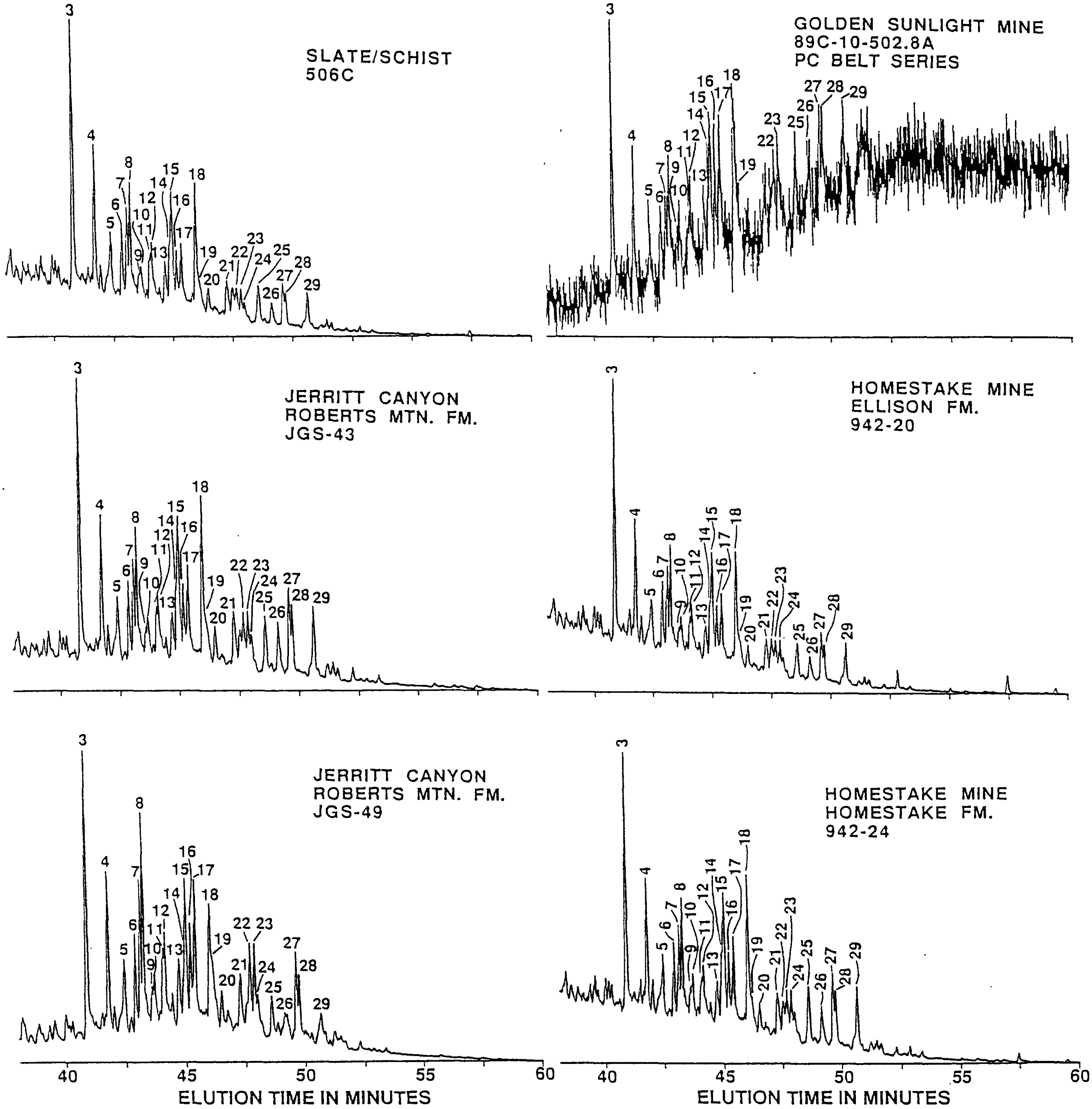


Figure 13. Sterane (M/Z = 219.1956) fragmentograms from the other six of our samples subjected to biomarker analysis. Numbers over peaks correspond to compounds in Table 6.

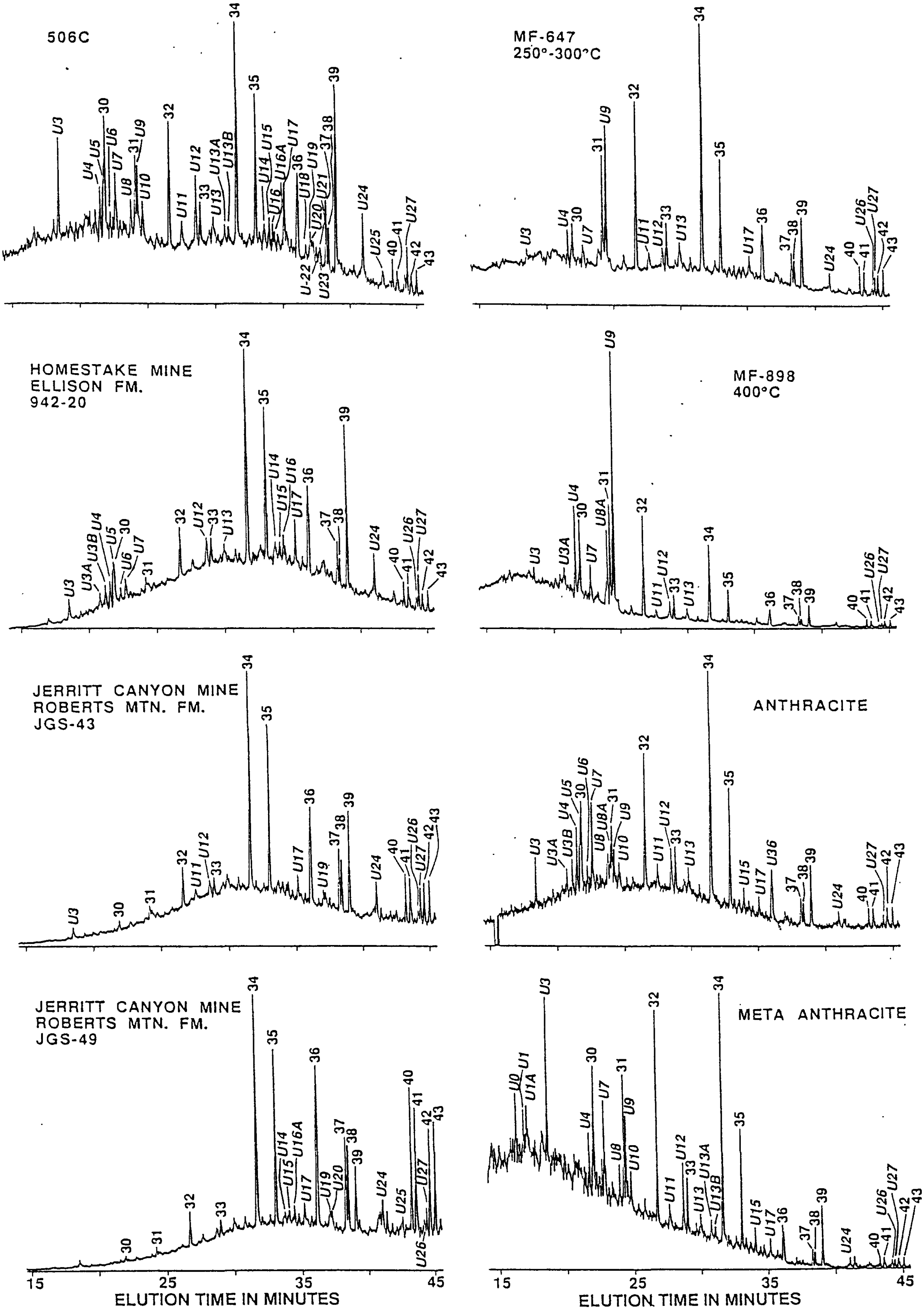


Figure 14. Fragmentograms of tricyclic terpanes (M/Z = 191.1800) for eight of the samples of this study. Numbers over peaks correspond to compounds in Table 6. Unknown compounds are designated by U and a number.

paralleling the differences in the steranes (Fig. 14) for these two samples. The tricyclic terpanes from the two Swiss Alps samples (MF-647 and -898, Fig. 14) are completely different from one another, contrasting with the almost exact sterane fragmentograms of these two samples. Peters and Moldowan (1993) note that the tricyclic terpanes are thermally resistant compared to other biomarker classes. We also have observed this in other studies. Thus, given the apparent moderate maturity of the steranes for the two Swiss Alps samples, the differences between the tricyclic terpanes could not have resulted from thermal processes.

We noted above that although the anthracite was high rank (R_0 = 3.56), the quantitative and qualitative characteristics of this sample's saturated and aromatic HCS were largely the result of gaseous solution and not HC thermal stability. The significant differences between the tricyclic terpanes of the anthracite and meta-anthracite, especially for peaks eluting before the C_{23} tricyclic terpane (peak 34), thus may be at least partly due to gaseous solution having been more intense in the anthracite.

4.053 Pentacyclic Terpanes

The pentacyclic terpane fragmentograms of the ten analyzed samples were somewhat similar (eight examples shown in Fig. 15), with hopane (peak 56) being dominant and norhopane (peak 51) usually being the second-highest peak. Peaks 44 and 47 (18α trisnorneohopane (C_{27} Ts) and 17α trisnorneohopane (C_{27} Tm), respectively were usually the next most abundant peaks, but could be dominant in some samples. Previous biomarker analyses, in our laboratory, of high-rank sediment bitumens and oils or of higher-temperature ("post mature") aqueous-pyrolysis experiments (Wenger and Price, 1991; Price and Wenger, 1992), demonstrate that hopane and norhopane are the dominant pentacyclic terpanes in those samples also.

The two Swiss Alps pentacyclic fragmentograms were very similar to one another, the extended hopane peak heights (peaks 62 to 81) being slightly higher in the MF-647 sample. The bars on these peaks in the MF-647 fragmentogram (Fig. 15) delineate the relative heights of these peaks in the MF-898 sample. Also peaks 44 and 47 were 40-50% greater in the MF-898 sample. The similar MF-647 and -898 pentacyclic fragmentograms contrast with the disparate tricyclic fragmentograms (Fig. 14) of these two samples. The two Homestake pentacyclic fragmentograms (942-20 and -24; Fig. 15) are almost exact overlays, except for the greater heights of peaks 44 and 47 in the 942-20 sample. The bars on peaks 44 and 47 in 942-20 represent the relative height of these two peaks in sample 942-24. Note the similarity of the 942-24 pentacyclic fragmentogram to that of the MF-898 sample, even though the samples are from completely different geologic environments.

The pentacyclic terpane fragmentograms of the two Jerritt Canyon samples (JGS-43 and -49, Fig. 15), like the sterane (Fig. 13) and tricyclic terpane (Fig. 14) fragmentograms, and aromatic HC gas chromatograms (Fig. 6), of these two samples, are significantly different. The JGS-43 pentacyclic fragmentogram is similar to those of other

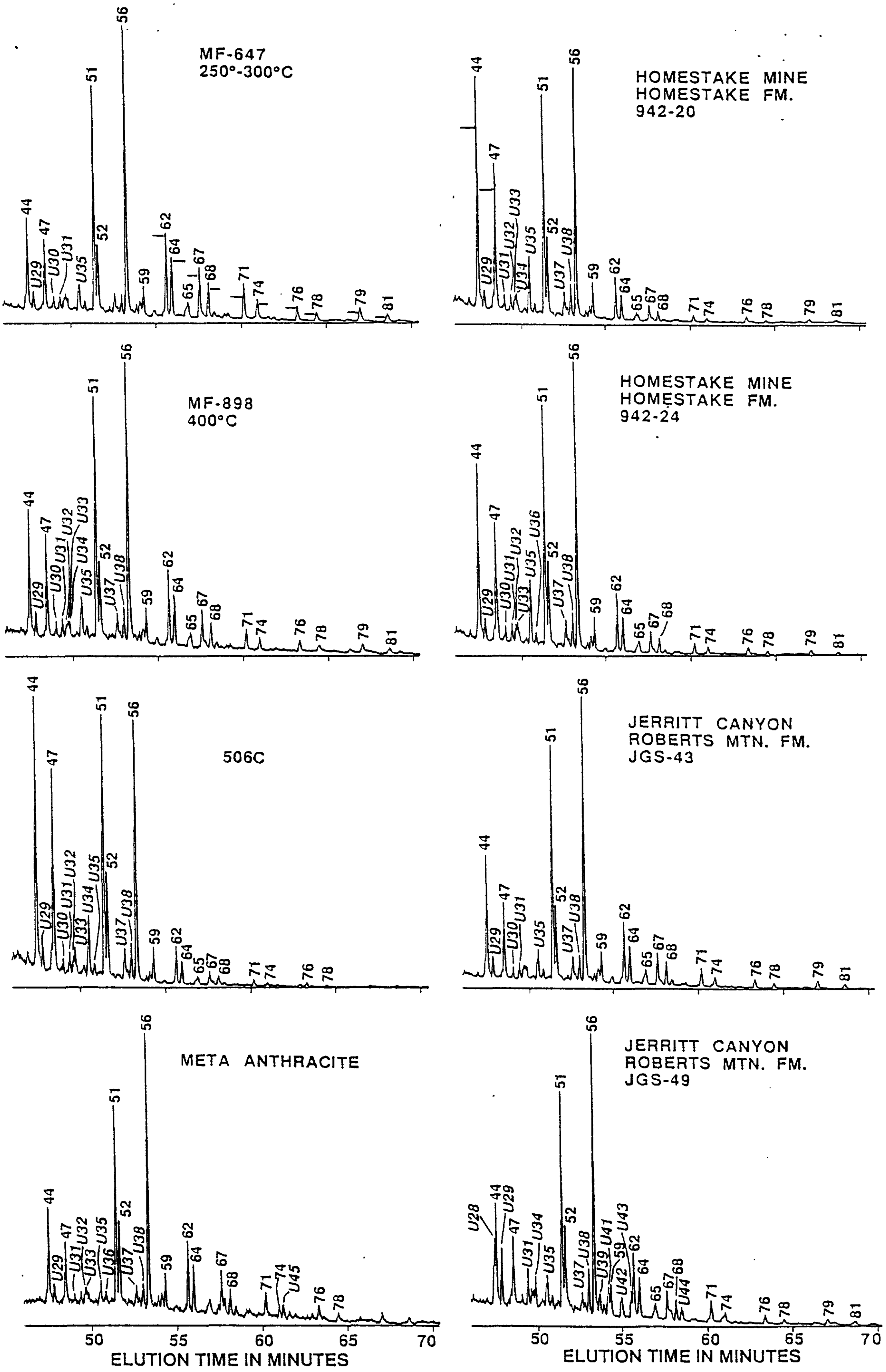


Figure 15. Fragmentograms of pentacyclic terpanes (M/Z = 191.1800) for eight of the samples of this study. Numbers over peaks correspond to compounds in Table 6. Unknown compounds are designated by U and a number.

samples in Figure 15. However, the JGS-49 fragmentogram has prominent unknown peaks ("U" and a number), which, though present, are smaller in the other Figure 15 fragmentograms. The anthracite and meta-anthracite pentacyclic terpane fragmentograms were near overlays of one another and thus only that of the meta-anthracite is shown in Figure 15. We surmise that gaseous solution did not affect the higher-molecular-weight pentacyclic terpanes in the anthracite compared to other lower-molecular-weight HCS and/or compound classes in this rock. The meta-anthracite and the Jerritt Canyon JGS-43 pentacyclic terpane fragmentograms are very similar, again despite the disparate geologic environments of these rocks.

4.054 Tri- and Mono-Aromatic Steroids

The conversion of monoaromatic to triaromatic steroids, which can be measured different ways, is a widely accepted maturity index, with the triaromatic steroids increasing from 0 to 100% with increasing maturity (Peters and Moldowan, 1993). Changes in this ratio have been hypothesized to result from the thermal aromatization of monoaromatic to triaromatic steroids (Peters and Moldowan, 1993). The U.S. Geological Survey Organic Geochemistry Laboratory measures this ratio as the sum of the triaromatic steroid peaks 91-97 (Table 6) divided by the sum of the monoaromatic peaks 82-90 (Table 6); however, other measures of this ratio are also given in Table 7. Excluding the Montana Precambrian Belt Series sample, our measure of this ratio ranges from 0.28 to 1.91 (TRI/MONO, Table 7). These are values characteristic of sediment extracts and oils. In fact, higher values for this ratio are present in sediment extracts and oils. Increases in this biomarker ratio have thus apparently been frozen in the rocks of this study, again suggesting a suspension of HC thermal cracking.

Representative fragmentograms of the tri- and monoaromatic steroids of four of the 10 analyzed samples are in Figure 16. Besides the known peaks (Table 6), unidentified peaks, some of which repeat in all samples, are also in the fragmentograms and are dominant in some fragmentograms. Such unidentified peaks are also in mono- and tri-aromatic steroid fragmentograms from oils and sediment extracts, wherein they also sometimes can be in high concentrations. Aside from the high concentrations of some of these unidentified peaks, the mono- and triaromatic steroid fragmentograms, with those of the coals being exceptions, were typical of those of oils and sediment extracts. The peak distribution of the anthracite fragmentogram is very unusual, being most likely originating from the intense gas solution that this sample experienced. The meta-anthracite fragmentogram is also unusual, with low concentrations of the known higher-molecular weight aromatic steroids and high concentrations of unidentified lower-molecular-weight aromatic steroids.

4.055 Biomarker Ratios

Various biomarker ratios, widely used as maturity indices in the petroleum industry, plus other maturity ratios used by the U.S. Geological Survey Organic Geochemistry Group, are presented in Table 7. The $5\alpha 14\alpha 17\alpha 24$ ethylcholestane (C_{29})

Table 7. Various biomarker ratios (all peak numbers are from Table 6): Normalized percentage/TRI PENT STER is the sum of the: tricyclic terpanes (Σ peaks 30-43), pentacyclic terpanes (Σ peaks 44-81), and steranes (Σ peaks 3-29), each divided by the sum of all three classes (Σ peaks 3-81). C31 HSR is the 22S/22S+22R ratio for the C31 hopanes (peaks 62 (22S) and 64 (22R); C29α SR (29ααα S/R) is the ratio of peaks 26/26+29. M/M+T is the mono to tri-aromatic steroid coversion of McKenzie et al (1981). TRIM is the Lewan et al (1986) triaromatic steroid cracking ratio (peaks 91+92/ Σ91-97). ααα STERANES NORMALIZED % is the proportion of the respective C27, C28, and C29 ααα sterane to the sum of all three (peaks 18, 24, and 29). GAM/HOP is the gammacerane/hopane ratio (peaks 65/56). DIA/REG is peaks 3/18. TRI/HOP is the ratio of the C23 tricyclic terpane (peak 34) to C30 hopane (peak 56). TET/TRI is the ratio of the C24 tetracyclic terpane (peak 39) to the C23 tricyclic terpane (peak 34). Ts/Tm is the ratio of C27 Ts (peak 44) to C27 Tm (peak 47). NOR/HOP is the ratio of norhopane (peak 51) to hopane (peak 56). NEO/HOP is the ratio of peaks 52/56. MOR/HOP is the ratio of the C29-C30 moretanes (peaks 52+59) to the C29-C30 hopanes (peaks 51+56). C32H SR is the ratio of the C32 S and R hopanes (peaks 67/67+68). C35/C34 is the ratio of the C35 hopanes (peaks 79-80) to the C34 hopanes (peaks 76+78). STER/PENT is the ratio of the identified steranes (Σ peaks 3-29) to the identified pentacyclic terpanes (Σ peaks 44-81). TMT is the ratio of peaks 95+97/peaks 95+97+86+89+88+90 (C28 tri-/C28 tri- + C28 mono- + C29 mono-aromatic steroids). TRI CR1 is the ratio of the C20/C20+C28 triaromatic steroids (peak 91/91+95+97). TRI CR2 is the ratio of the C20+C21/C27+C28 triaromatic steroids (peaks 91+92/ Σ 94-97). TRI/MONO is the ratio of the sum of the identified triaromatic steroids to the sum of the identified monoaromatic steroids (Σ 82-90/ Σ 91-97). TRI/STER is the ratio of the sum of the identified triaromatic steroids (Σ 91-97) to the sum of the identifiedsteranes (Σ 3-29). TRI/PENT is the ratio of the sum of the identified triaromatic steroids (Σ 91-97) to the sum of the identified pentacyclic terpanes (Σ 44-81).

	NORMALIZED %								ααα STERANES NORMALIZED %					
Sample	TRI	PENT	STER	C31H SR	C29α SR	C29βα	M/M+T	TRIM	C27	C28	C29	GAM/HOP	DIA/REG	TRI/HOP
89C-10 502.8A	29.4	35.7	34.9	ND	0.55	0.50	ND	ND	0.43	0.26	0.31	0.16	2.85	0.61
942-24	41.2	27.1	31.7	0.61	0.45	0.50	0.70	0.23	0.60	0.20	0.19	0.07	3.55	1.13
942-20	50.7	23.3	26.0	0.62	0.45	0.53	0.50	0.27	0.65	0.19	0.18	0.07	5.46	1.56
506C	58.0	17.6	24.4	0.62	0.40	0.49	0.63	0.08	0.65	0.18	0.18	0.06	5.58	1.43
JGS-43	28.4	36.7	34.8	0.59	0.48	0.52	0.77	0.21	0.63	0.18	0.19	0.11	3.36	0.52
JGS-49	23.0	23.2	53.8	0.59	0.46	0.62	0.61	0.41	0.70	0.18	0.13	0.11	5.18	0.71
MR898	67.6	13.4	19.0	0.59	0.51	0.52	0.75	0.23	0.62	0.19	0.19	0.12	2.81	1.52
MF647	38.7	27.8	33.5	0.56	0.45	0.50	0.32	0.04	0.55	0.22	0.23	0.12	1.64	1.02
ANTHRA.	52.2	21.3	26.5	0.57	0.18	0.40	ND	0.10	0.27	0.17	0.55	0.00	0.60	1.42
META-ANTHRA.	71.4	13.1	15.5	0.59	0.51	0.46	1.00	0.06	0.53	0.25	0.22	0.14	2.28	1.62

Sample	TET TRI	Ts Tm	NOR HOP	NEO NOR	MOR HOP	C32H SR	C35 C34	STER PENT	TMT	TRI CR1	TRI CR2	TRI MONO	TRI STER	TRI PENT
89C-10-502.8A	0.57	0.73	0.57	0.39	0.51	0.40	ND	0.93	ND	ND	ND	0.00	0.00	0.82
942-24	0.56	1.37	0.85	0.42	0.15	0.54	0.85	1.07	0.30	0.23	1.18	0.40	0.07	1.52
942-20	0.61	1.42	0.85	0.42	0.15	0.67	0.76	1.01	0.50	0.21	2.98	0.28	0.08	2.18
506C	0.72	1.47	0.95	0.45	0.15	0.47	0.31	1.24	0.37	0.85	3.55	1.72	0.51	3.30
JGS-43	0.40	1.72	0.78	0.37	0.13	0.64	1.12	0.87	0.23	0.42	1.00	0.44	0.04	0.77
JGS-49	0.25	1.08	0.76	0.55	0.12	0.48	0.99	2.16	0.39	0.42	5.52	0.40	0.01	0.99
MF-898	0.24	1.12	0.78	0.36	0.12	0.54	1.03	1.33	0.25	0.35	3.24	1.76	1.02	5.05
MF-697	0.28	1.49	0.70	0.44	0.12	0.62	1.04	1.14	0.68	0.53	0.70	1.91	0.29	1.39
ANTHRA.	0.25	2.90	0.73	0.44	0.18	0.48	ND	1.18	ND	1.00	ND	0.67	4.72	2.45
META ANTHRA.	0.25	1.33	0.67	0.52	0.13	0.55	0.74	1.10	0.00	0.57	3.59	1.18	2.11	5.45

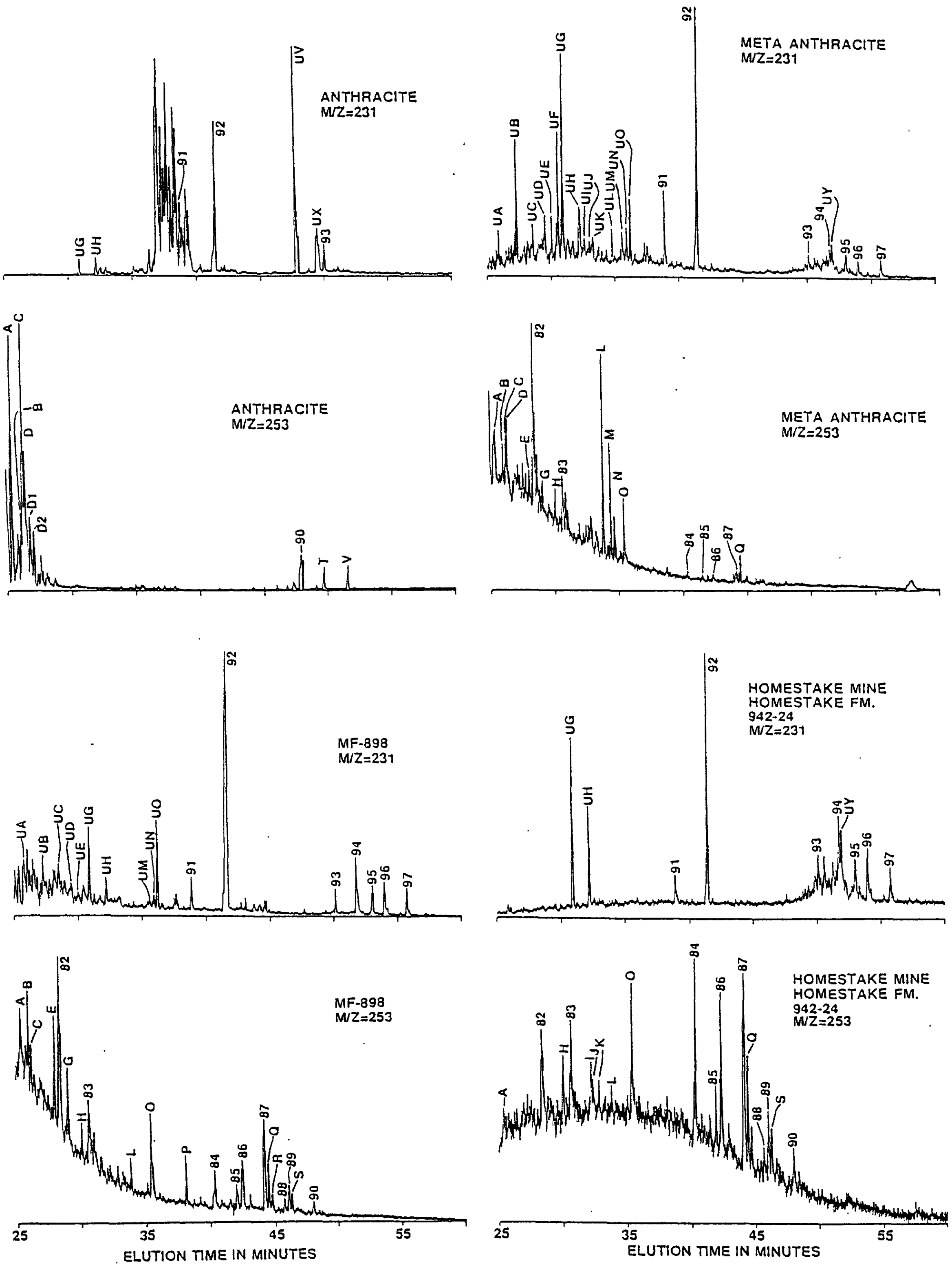


Figure 16. Fragmentograms of monoaromatic (M/Z = 253.1956) and triaromatic steroids (M/Z = 231.1174) for four of the samples of this study. Numbers over peaks correspond to compounds in Table 6. Unknown recurring compounds in the monoaromatic fragmentograms (MZ = 253) are designated by "U" and a letter UA through UY). Unknown recurring compounds in the triaromatic steroids (M/Z = 231) are designated by a letter (A through V).

20S/20S+20R ratio (29αααS/R, Table 7) is such an index, increasing from zero or near zero at immaturity, to maximum equilibrium values of 0.52 to 0.55 (Peters and Moldowan, 1993). All of the Table 7 values for this ratio, are, with one exception, mature values, although six samples had less than equilibrium values. The low value of the anthracite is probably due to gaseous solution. The 5α14β17β 20R 24 ethylcholestane (C_{29}) to 5α14α17α 20R 24 ethylcholestane (C_{29}) ratio (C_{29}ββαα, Table 7) is slower to come to equilibrium values than the previously discussed C_{29}ααα S/R ratio, and thus the C_{29}ββαα ratio extends to higher maturities. This ratio increases with maturity from near zero at immaturity to equilibrium values of 0.67 to 0.71 (Peters and Moldowan, 1993). The Table 7 values for this ratio follow expected behavior, generally being further from equilibrium than the values for the C_{29}ααα S/R ratio for the same samples.

The ratio of 18α trisnorneohopane (C_{27} Ts) to 17α trisnorneohopane (C_{27} Tm) is calculated both generally and in our lab as Ts/Tm, but can also be calculated as Ts/Ts+Tm. This ratio ranges from zero to near zero at immature ranks to 3 to 4 at elevated maturities. Excluding the anthracite and, for reasons discussed above, the Precambrian Belt Series sample, this ratio ranges from 1.12 to 1.72, values significantly below those we have observed for mature oils and sediment extracts. The moretane to hopane ratio (MOR/HOP, Table 7) can be measured using the C_{29} and C_{30} compounds alone or in combination. The U.S. Geological Survey laboratory measures the ratio as 17β21α normoretane (C_{29})+17β21α moretane (C_{30})/norhopane+hopane. Peters and Moldowan (1993) note that this ratio decreases with increasing maturity from values of about 0.8 in immature bitumens to less than 0.15 in mature bitumens and oils, with a minimum of 0.05. Excluding the two unapplicable (anthracite and Precambrian belt series) samples, this ratio ranges from 0.18 to 0.12 in our samples, mature numbers, but again not maximum maturity values.

Peters and Moldowan (1993) note that with increasing maturity, the C_{32} hopane 22S/22S+22R ratio increases from 0 at immature ranks to equilibrium values of 0.57 to 0.62. Moreover, values of 0.50 to 0.54 are characteristic of only the beginning of mainstage oil generation. This ratio ranges from 0.48 to 0.67 (Table 6). By this index, 2 of the Table 7 samples (506C slate/schist; Jerritt Canyon JGS-49) have not entered the oil generation stage, while 2 other samples (Homestake 942-24 and MF-898) would have just entered oil generation, clearly inapplicable interpretations. Moreover, the C_{32} 22S/22S+22R ratio of the MF-898 sample was 0.54, compared to the maximum equilibrium value of 0.62 for MF-647. This, in spite of the fact that MF-898 was 150°C hotter than MF-647.

Three other C_{32} 22S/22S+22R ratios in Table 7 are of interest: the 0.67 value of the Homestake 942-20 sample, the 0.64 value of the Jerritt Canyon JGS-43 sample, and the 0.48 anthracite value. Peters and Moldowan (1993, p. 228) state that values for this ratio greater than the 0.62 equilibrium value have never been observed. Thus, the 0.64 and 0.67 values (Table 7) are unusual. Philp and Gilbert (1982) reported an anomalously low

C_{31} hopane 22S/22S+22R ratio (less than 0.50) for a Gippsland Basin oil. The waxy oils of this basin are thought to have been sourced from coals, which would involve significant gaseous solution. The low ratio (0.48) for the anthracite (R_o = 3.56%) is also most likely due to gaseous solution.

In contrast to the C_{32} hopane 22S/22S+22R ratio, the C_{31} hopane 22S/22S+22R ratio provides expected values ranging from 0.56 to 0.62. The range of maximum equilibrium values for this ratio is 0.57-0.62. Moreover, as expected, MF-898 has a higher value for this ratio (0.59), than MF-647 (0.57); and the anthracite has a "normal" value (0.57). That these two similar hopane maturity indices (C_{31} and C_{32} 22S/22S+22R) exhibit such disparate behavior in our samples is surprising.

Several observations are germane. First, that any HCS at all are surviving in these high-temperature rocks is both surprising and unexpected, considering predictions of accepted petroleum-geochemical paradigm regarding HC thermal stability. That biomarkers, with the peak distributions routinely observed in oils and sediment bitumens, are also present in these rocks, is even more unexpected. Moreover, maturity indices of these biomarkers are often less than the maximum (equilibrium) values. This is yet more evidence that HC thermal cracking has been suspended in these rocks, and hence HC maturity trends have been frozen. We attribute the suspension of thermal cracking and thus the persistence of HCS, including normal-appearing biomarkers, to the extreme ranks to which our samples were exposed, to the metastable equilibrium proposed (Shock, 1988; Helgeson et al., 1993) to result from the hydrolytic disproportionation of OM in Nature. Certainly the persistence of our HCS to these, and even significantly more extreme ranks, has no other ready explanation.

4.06 $\delta^{13}C$ RATIOS

Carbon isotopic analyses of the saturated HCS of our samples yielded a narrow range of values (-27.14 to -28.47, Table 1). Because of the low extract concentrations, some samples were composited for an adequate sample weight for this destructive analysis. Thus, the Jerritt Canyon JGS-43 and -49 samples were composited to a single sample as were the Homestake 942-20, -24, and -32 samples. Carbon isotopic analysis was not attempted on any of the aromatic HCS because of their low recovered amounts.

The value of -27.77 for the MF-647 Guggenegg, Swiss Alps sample corresponds to the range of $\delta^{13}C$ ratios (-22.0 to -27.2, average around -25.5) which Hoefs and Frey (1976) measured for "kerogens" from rocks of equivalent metamorphic grade, and is close to the range of ratios (-25.4 to -26.9) they measured for kerogens from three different Guggenegg samples. The close ratios for the two anthracites (-27.66 and -27.49) may be expected because these saturated HCS were similar in appearance (Fig. 2) and were both derived from Pennsylvanian coals of moderate geographical proximity. The distinguishing feature of the Table 1 $\delta^{13}C$ ratios is that these ratios, along with other of our analyses, lead to the inescapable conclusion that the indigenous HCS of our rocks are sedimentary-derived HCS; *e.g. - these HCS are not abiotic HCS.*

4.07 SUBSEQUENT WORK - PRELIMINARY RESULTS

Separate research projects are ongoing with Martin Frey University of Basel, Switzerland; Philippa Black, University of Auckland, New Zealand; and Koichi Mimura (Nagoya University) and Ryuchi Sugisaki (Neijo University), Japan. Martin Frey's metamorphosed Swiss Alps Lisassic rock suite of this study was extended to lower amphibolite grade (about 550°C) plus two starting unmetamorphosed Liassic shales from the Molasse Basin, Switzerland - about 20 samples total. The study with K. Mimura and R. Sugisaki involves subjecting many of the samples from Sugisaki and Mimura (1994) to more detailed petroleum geochemical analyses than performed in the Sugisaki and Mimura (1994) study. In addition, K. Mimura and L. Price are analyzing two metamorphic rock suites from Sanbagawa and Royoke, Japan; large rock suites of different hydrothermal ore deposits; and a sample suite of blueschist Franciscan facies rocks, California.

The study with P. Black involves the high-pressure New Caledonia metamorphics of Diessel et al. (1978), from starting unmetamorphosed shales to the garnet-eclogite metamorphic grade, again about 20 samples total. Lastly a graphite gneiss from the Hooper Brother's graphite mine, Washington County, Whitehall New York is being analyzed. This rock was calculated to have been exposed to metamorphic conditions of between 700°C and 7 kb to 950°C and 11.9 kb (Montgomery, 1983). All these samples have been solvent extracted and gas chromatographic analyses performed on the C_8+ saturated-and-aromatic HCS and resin fractions. Extract concentrations were on the order of, or greater than, those reported in Table 1 of this study. The gas chromatograms of the different column fractions were largely similar to the examples of this study, although some differences could be present. Moreover, our newer analyses demonstrate that sedimentary-derived HCS are persisting in much higher-rank rocks than those reported on in this study. However, the data from these subsequent analyses must still be collated and further analyses remain to be done.

4.08 THE QUESTION OF CONTAMINATION

In discussing our results with different petroleum geochemists, most immediately have dismissed our data as due to contamination, even though these researchers had no or little background information on the samples. Their conclusion was drawn on the basis of a firm belief in accepted petroleum-geochemical paradigm concerning limited thermal stability of C_{15}+ HCS. It is likely that the data in this paper will also be immediately dismissed as contamination by many other petroleum-geochemists. Thus, we review why we conclude that the extractable OM of our rocks is indigenous to our rocks and is not due to contamination.

First, laboratory blanks were run separately by L. Price and K. Mimura, a year apart, using different organic-poor powdered rocks (bull quartz vein rock and Pennsylvanian meta-sedimentary iron-stained (red) sandstone), baked at 400°C for 24 hours and at 500°C for 5 days. The blanks were subjected to the complete and same analytical workup as our samples and no detectable HCS (or other organic compounds) were found in either case. These results demonstrate that the bitumen of these rocks did not arise from laboratory procedures. Nor can this bitumen be from surface contamination of the rocks, because all surfaces were cleaned. The saturated HCS, and especially the biomarkers, are moderately-mature to mature in appearance. Thus our bitumens could not have arisen from low-temperature microbial processes. A telling argument against contamination is the length of the extraction times for many of our samples. Shales (source-rocks and otherwise) from sedimentary basins typically are solvent-extracted for only 24 hours in many laboratories, and show color in the extract immediately on commencement of extraction. However, most of our samples demonstrated noticeable tints in the extracting solvent *only after* 4 to 7 days of extraction. This observation dictates that the bitumen was very tightly held in our rocks. However, any contamination which would have occurred late in the history of these rocks, could have only moved into these rocks along permeable pathways in the rock. Such contamination would have been easily-extractable, contrary to the observed situation. Moreover, these rocks have minimal permeability and minute porosities. Thus, movement of late-stage bitumen deep into the matrix interior of these rocks is quite impossible.

The most persuasive argument against contamination are the compositions of the aromatic-HC and resin fractions. These compositions have never been observed in oils, petroleum distillates, sedimentary-derived OM from petroleum basins, or low-temperature HC assemblages at the earth's surface. Thus, none of these sources could have served as a contaminant. The unique compositions in the resins and aromatic HCS could only have originated from processes occurring within the rocks themselves. Within a given suite of rocks, the compositions of the saturated HCS could be somewhat similar, but never exact. The aromatic HCS within a rock suite, in contrast, invariably had distinctly different compositions. Contamination of any of the rock suites should yield very similar to exact HC compositions for all the samples of that suite. Lastly, the samples which appear to be most likely stained by a petroleum distillate (Homestake and Jerritt Canyon) have widely different molecular-weight distributions between the saturated and aromatic HCS (Fig. 3). Also, two Jerritt Canyon samples, whose saturated HCS had humps, also had low concentrations of C_{14}- saturated HCS (Fig. 2), whereas the aromatic HCS of these two samples had moderate and high concentrations of lower-molecular weight alkylated benzenes. Again, this is not possible if a petroleum distillate were contaminating these rocks.

Given the above observations, it is much more difficult to justify our extracted bitumens as due to contamination, rather than accept their, at first improbable, origin as indigenous to the rock.

5.0 DISCUSSION

5.01 PREVIOUS WORK

5.011 Introduction

Much previous work has characterized OM from high temperature crystalline rocks, where this OM is either "carbonaceous material" (e.g. - kerogen, or metamorphosed kerogen tending to graphite) or HC gases in fluid inclusions. Representative studies on carbonaceous OM will only be briefly considered here and the fluid inclusion work will be briefly discussed below in the "Plutonic Rocks" section. Examples of studies of carbonaceous OM in metamorphic rocks are Gavelin (1957) on northern Swedish metamorphic rocks, Barker and Friedman (1969) on Precambrian metamorphics of southwestern Colorado, U.S.A., Andreae (1974) on southern Norway metamorphics, and Hoefs and Frey (1976) on Swiss Alps metamorphics. All four studies determined $\delta^{13}C$ ratios of the carbonaceous OM in these rocks. Fuex and Baker (1973) measured $\delta^{13}C$ ratios of the carbon in different granitic, mafic, and ultramafic rocks. Landis (1971) studied the tendency of carbonaceous OM towards graphitization by x-ray diffraction. Diessel and Offler (1975) examined changes in phytoclasts, and R_0 values thereof, in carbonaceous OM from metamorphic rocks from two areas in Australia. Diessel et al. (1978) carried out the same procedure for metamorphic rocks from New Caledonia. Izawa (1968) determined elemental composition for, and ran x-ray diffraction on, carbonaceous OM in Japanese metamorphics. Numerous studies on the alteration of sedimentary OM by basaltic intrusives (for example Perregaard and Schiener, 1979) will not be considered here, either.

The association of bitumen with hydrothermal ore deposition has also been long-studied and is discussed in some detail below. However, typically most past studies have not characterized the bitumens in analytical detail.

In discussing previous work, we concentrate on studies which have extracted, and performed analyses on, C_8+ bitumen in various types of crystalline and ore deposit rocks. These studies fall under two categories. First, "Prior investigations", which examined rocks from the same geographic areas as our study; and second, "Related Work", where the rock samples of those studies originated outside of our study areas.

5.012 Prior Investigations

Radtke and Scheiner (1970, p. 97) studied rocks from the East Carlin ore body and reported extracting 120 ppm high-molecular weight HCS from 100g of carbonaceous ore. However, they did not analyze the extracted bitumen. Their extracted-bitumen concentration is within the range (58.8 to 131.5 ppm) in Table 1 for the four Jerritt Canyon samples. Radtke and Scheiner (1970) also reported recovering another ill-defined group of organics from this sample they classed as humic acids. Those authors proposed that the extractable organics (HCS and other undefined organics), and the nonextractable carbon (kerogen), played pivotal roles in both the precipitation of gold from the ore-bearing solutions and in the recovery of gold from the ore in mining operations at Carlin. Friedman et al. (1982) made similar hypotheses related to Russian disseminated gold deposits.

Nelson et al. (1982) extracted 50g of Carlin carbonaceous ore for 96 hours and reported obtaining only sulfur with no detectable HCS, in contrast to the results of Radtke and Scheiner (1970) and of this study. Our Soxhlet-extraction technique involves using a polished copper strip in the solvent-boiling pot to remove elemental sulfur (a standard procedure). Three of our Jerritt Canyon samples had large amounts of sulfur in them, as judged by the heavily-blackened copper strips. In fact, one of our samples still yielded elemental sulfur in the extract, which had to be cleaned before extract weights could be obtained. Separating elemental sulfur from the bitumen during extraction makes the extracted bitumen much more obvious, in contrast to the approach of Nelson et al. (1982). Moreover, as discussed, we extracted our samples for 504 hours versus 96 hours, and in some of our other rocks, after 96 hours, significant amounts of bitumen were not yet recovered. Also, the bitumen in these rocks is both in significantly-reduced concentrations and is very light-colored compared to bitumen from sedimentary rocks with equivalent TOCS. The color in bitumen from sedimentary rocks is largely from resins and asphaltenes, compound classes which are missing in Carlin-type rocks. Thus, the lack of, or light, color of extracts from Carlin-type rocks predisposes one to assuming no bitumen exists in the extracts.

Leventhal and Hofstra (1990) also reported that no bitumen was recovered from solvent extraction of rocks, similar to those studied by Nelson et al. (1982), but from Jerritt Canyon, thus seemingly confirming Nelson et al. (1982) and negating Radtke and Scheiner (1970). Moreover, other analyses carried out by Leventhal and Hofstra (1990) were interpreted as demonstrating that the carbon in their rocks was "burned-out" (overmature) and incapable of either generating, or being associated with, HCS. For example, ROCK-EVAL analyses of their four Jerritt Canyon samples of Table 1 yielded hydrogen indices of 1, except for UP-1 which had a value of 0 (Joel Leventhal, U.S. Geological Survey, written communication 12/21/94). Leventhal and Hofstra (1990) carried out their extractions by allowing powdered rock to sit in a covered beaker of solvent for 96 hours. Because of the apparent clarity of the extract, no attempt was made to obtain extract weights (Joel Leventhal, U.S. Geological Survey, personal communication, 12/95). The Jerritt Canyon samples of Table 1 are splits from some of the same samples Leventhal and Hofstra (1990) analyzed. We conclude that the different results regarding solvent extraction of these four studies result from both inappropriate analytical approaches and from preconceptions regarding expected results.

However, the conclusions of Nelson et al. (1982) and Levanthal and Hofstra (1990) regarding the highly-metamorphosed "dead" nature of the organic carbon in the ore-bearing shales of Carlin-type gold deposits would appear to be supported by the data of both Dean et al. (1987) and Dean and Pratt (1987). Those studies presented ROCK-EVAL data of ore-bearing shales from various north central Nevada Carlin-type gold deposits. Those samples had no measurable S_1 or S_2 pyrolysis peaks, suggesting "dead" organic carbon. Nonetheless, three points negate this conclusion. First, small concentrations of extractable HCS, even if present in high-rank rocks, illicit little or no response from the ROCK-EVAL instrument, for several reasons. Also ROCK-EVAL derived TOC values in high-rank (metamorphic) rocks are always much lower than actual TOC values as measured by other methods (wet oxidation, LECO, etc.). The reasons for these ROCK-EVAL responses will not be considered here. However, as a result of these responses, ROCK-EVAL is ill-suited for analysis of high-rank rocks.

The third point involves the samples of the Dean et al. (1987) and Dean and Pratt (1987) studies. Hausen and Park (1986) note that north central Nevada experienced significant subtropical sublateritic weathering, such that the Carlin-type deposits there can be highly weathered and oxidized to as deep as 180m. This weathering destroys the shale organic matter. As a result, gold recovery during ore processing is much higher from oxidized-weathered ore than from unweathered ore. This is because the unweathered OM is "active" and complexes with gold in "pregnant" (gold-bearing) leachate solutions (e.g. - "preg-robbing", Hausen and Buckman, 1985), hindering gold recovery. In fact, completely different recovery processes must be used for unweathered versus weathered ore. Be all that as it may, the samples from the Dean et al. (1987) and Dean and Pratt (1987) studies were all collected by L. Pratt. These were either outcrop samples, which had recent geologic weathering, or were from the deeply weathered portion of ore bodies. Thus all OM in these samples was destroyed. These samples were inappropriate for studies of any possible relationship between ore genesis and the shale OM. Thus, inappropriate sampling and analytical techniques, and erroneous preconceptions, in our opinion, have all obfuscated the relationships between ore and OM in Carlin-type deposits.

Perry et al. (1996) ran ROCK-EVAL analysis on the two samples of this study from the Golden Sunlight mine and concluded that these rocks were "overmature" regarding potential oil generation. These then, constitute the previous organic-geochemical studies on any of the rocks of this study.

5.013 Related Work

5.0131 Metamorphic rocks

Baker and Claypool (1970) Soxhlet extracted 40 rocks exposed to "incipient rock metamorphism" and compared the extracts to those from 22 "unmetamorphosed" samples. "Incipient metamorphism" was considered as that rank between normal burial diagenesis and regional rock metamorphism, the latter involving mineralogical and rock-textural changes. Some of Baker and Claypool's (1970) "incipient metamorphic" rocks had developed slatey cleavage or were near plutonic or volcanic intrusives. From the locations given for Baker and Claypool's (1970) "unmetamorphosed samples", most of them were likely in the maturity range of R_0 = 0.4-0.6. Significant differences were present between the unmetamorphosed and metamorphosed rock suites. For example, the incipient-metamorphic rocks had: 1) lower absolute (ppm) and carbon-normalized HC concentrations, 2) much lighter-colored extracts, and 3) higher saturated HC to aromatic HC ratios (1.2 to 5.2 versus 0.3 to 2.4). However, the different extracts were not analytically characterized, beyond fraction separation by column chromatography.

5.0132 Mantle rocks

Mathez (1987) reported thin films of carbonaceous matter on the walls of cracks in mantle xenoliths from alkalic basalts and characterized these films by x-ray photoelectron spectroscopy (XPS). This analysis suggested that these films were partially composed of complex mixtures of HCS and other organic compounds. Mathez (1987) noted that these films are in mantle xenoliths of variable lithologies from worldwide localities (New Mexico, U.S.A.; western Germany; Alaska; and New South Wales). He hypothesized that such carbonaceous films were formed abiotically when new, hot, relative, silicate surfaces were formed from mineral contraction during cooling. These mineral surfaces then reacted with hot volcanic HC gases precipitating the carbonaceous films by a Fischer-Tropsch reaction.

Tingle et al. (1990) studied organic compounds on olivine crack surfaces in Arizona and Hawaiian basalts by surface analyses with laser ionization ("SALI"). They noted that these organics are in carbonaceous films existing on nearly all crack surfaces *and grain boundaries* in mantle-derived xenoliths. They found that healed cracks in their samples contained neither carbonaceous films nor organic compounds, leading to their conclusion that the organics were introduced into these xenoliths during basalt eruption and cooling. Tingle et al. (1990) also noted that stepped-heating carbon isotope measurements of mantle xenoliths below 600°C yield rather uniform $\delta^{13}C$ ratios around -26% for this OM. These are values characteristic of sedimentary-derived OM. Tingle et al. (1990) acknowledged the possibility of a Fischer-Tropsch-like reaction during cooling of the host rocks as a possible origin for these organics as hypothesized by Mathez (1987). However, they also noted that the origin of these organics remained an unsolved question.

Tingle et al. (1991) furthered research on this topic by examining a yet wider suite of mantle-derived rocks by x-ray photoelectron spectroscopy (XPS), thermal-desorption surface analysis by laser ionization (SALI), and low energy electron diffraction (LEED). Samples included websterites, a wehrlite, and dunites, all from Hawaii, a molten basalt sample (cooled on a chain) from the Puu Kahaualea active lava pond (Kilauea, Hawaii), 4 layered plutonic rocks from the Stillwater Complex, Montana, U.S.A., layered plutonic rocks from the Bushveld Complex, South Africa, and garnet and diopside megacrysts from the Jagersfontein kimberlite, South Africa. Organics were detected in all mantle xenolith and kimberlite samples, but not in the layered plutonics, and most importantly, not in the chain-cooled basalt samples. Tingle et al. (1991) also presented preliminary $\delta^{13}C$ ratios of -32% for carbonaceous films in cracks in olivine from San Carlos, Arizona, U.S.A.

Given these previous investigations, Sugisaki and Mimura (1994) collected 227 mantle-derived rocks and granites from worldwide locations and analyzed these rocks for indigenous HCS by solvent extraction. Certain types of mantle-derived rocks (unaltered mantle xenoliths and tectonized peridotites) contained *petroleum-like saturated HCS*, while other rocks (serpentinized peridotite tectonites, periodotite cumulates, gabbros, alkali and tholeiite basalts, and with one exception, granites) contained no HCS. $\delta^{13}C$ ratios of the recovered saturated HCS ranged from -23.4 to -28.9, clustering around -27. Sugisaki and Mimura (1994) (successfully, in our opinion) applied different tests to demonstrate that their detected HCS were not from contamination. For example, whereas mantle xenoliths had HCS, the basalts surrounding the xenoliths did not.

Pivotally, they also found pristane and phytane in all their recovered HCS. Moreover, some of these HCS had rather high pristane/n-C_{17} and phytane/n-C_{18} ratios. Given the presence of these isoprenoid HCS and the $\delta^{13}C$ values of the saturated HCS, they concluded that their HCS originated principally from recycling sedimentary-derived OM through the mantle. We agree.

Conversely, we disagree with the hypothesis of Mathez (1987) and Tingle et al. (1990, 1991) that some (or all) of these compounds may be formed abiotically from a Fischer-Tropsch-type reaction from volcanic HC gases interacting with active sites on fresh mineral cracks formed during basalt cooling. Analyses of basalts carried out by Tingle et al.. (1991) to substantiate this hypothesis failed to find even traces of such HC gases or their proposed products. Moreover, Tingle, et al. (1990, p. 477) noted that organic compounds "--- are correlated with the carbonaceous material that exists on nearly all crack surfaces and grain boundaries in mantle-derived xenoliths and basalts". That these organics are found *ubiquitously on grain boundaries* precludes an origin from the above-proposed Fischer-Tropsch reaction. The presence of these organics on grain boundaries suggests, rather, that the organics were excluded from growing crystals during crystallization, and subsequently flowed from grain boundaries, by capillary forces, into the expansive cracks formed during cooling.

Lastly, two considerations contradict the hypothesis of Tingle et al. (1990) that the organics in mantle-derived rocks represent OM from the earth's surface introduced into these rocks during their eruptive phase. First, the chain-cooled basalt Tingle et al. (1991) collected and analyzed had no detectable OM. Second, Sugisaki and Mimura (1994) found no HCS in the numerous basalts that they analyzed.

Sugisaki and Mimura (1994) proposed that the HCS they detected were metastable under mantle conditions because of the very high pressures there. They cited work by Domine (1989, 1991) suggesting to them that under very high pressures, higher-molecular-weight HCS become more thermally-stable than lower-molecular-weight HCS, thus explaining only C_{17}-C_{29}+ material in their saturated HCS. However, this qualitative feature results from their analytical technique of removing their extraction solvent with a rotary evaporator in a water bath at 35°C. Calibrative evaporation experiments by L. Price for a previous study (Price, 1981) demonstrated that rotary evaporation alone, much less in a 35°C heated water bath, removes all of the lower molecular weight (C_{14}-) material, and some mid range (C_{14}-C_{23}) material, especially when the solute is in small concentrations. Sugisaki and Mimura (1994, p. 2529) assumed that their analytical technique would retain lower-boiling HCS. Quite the contrary, this technique effectively removes all lower-molecular HCS and much of the mid-range material. Thus, we do not believe that high pressures are the reason for these sedimentary-derived HCS surviving in the mantle.

Significantly more detailed organic-geochemical analyses, including biomarker analyses, than those performed in Sugisaki and Mimura (1994), have been performed by L. Price and K. Mimura on splits of six of the samples from Sugisaki and Mimura (1994). The results of these analyses will be presented in a future publication (Price et al., in preparation). However, we note here that the extracted bitumen from these six rocks had the same characteristics as the bitumens from this study, including most of the same peaks present in the aromatic-HC and resin gas chromatograms of this study. Thus, we attribute the persistence of biogenically-derived HCS in mantle-emanated rocks to a metastable equilibrium (as proposed by Shock (1988) and Helgeson et al. (1993) of these HCS via hydrolytic disproportionation of OM.

5.014 Plutonic Rocks

Indigenous HCS have also been reported in some plutonic rocks. Petersilie and Sörensen (1970) found moderately high concentrations of HC gases associated with bitumens in rocks of the Ilímaussaq alkaline intrusion, South Greenland. However, these bitumens were not analytically characterized by gas chromatography or mass spectrometry. HC gases in fluid inclusions of rock from the Ilímaussaq intrusion have been studied by Konnerup-Madsen et al. (1979, 1988) and Konnerup-Madsen and Rose-Hansen (1984). Laier and Nytoft (1995) extracted between 110 to 160 ppm bitumen from Ilímaussaq rocks and analyzed the saturated HCS thereof.

As referenced in Petersilie and Sörenson (1970), rocks from the Khibina and Lovozero alkaline massifs of the Kola Peninsula, and rocks from some of the alkaline massifs of Siberia, also contain considerable amounts of HC gases and bitumens (Petersilie, 1963, 1964; Ikorskii, 1967; Lyutkevich, 1967; Bazarova, 1969; and Petersilie et al. (1965). Ikorskii and Romanikhin (1964) concluded that the HC gases of nepheline granites of the Khibina alkaline massif were in fluid inclusions. Salvi and Williams-Jones (1992, 1997) observed high concentrations of HC gases, and detectable higher molecular weight HCS, in fluid inclusions in pegmatite quartz crystals of the Strange Lake peralkaline granite, Quebec/Labrador, Canada. Heinrich and Anderson (1965) found C_5 and C_6 HCS in the Goldie alkalic carbonatite of the McClure Mountain-Iron Mountain plutonic complex (Colorado, U.S.) by mass spectrometry. They concluded that these HCS were indigenous, and did not represent contamination from outside sources or sedimentary rocks. It is apparent that at least some silica-poor alkalic igneous rocks, from different worldwide localities, have associated indigenous

HCS. However, to date, in most cases, the C_6+ HCS in these rocks have not been well-analyzed and characterized.

Some of the above investigators assumed that these associated HCS were formed by abiotic (inorganic) processes. However, Laier and Nytoft (1995) demonstrated that this was not so with the Ilímaussaq rocks. Gas chromatography demonstrated that the saturated HCS from these rocks "resembled those of oils from marine source rocks". Pentacyclic terpane fragmentograms (from biomarker analyses) were also consistent with sedimentary-derived HCS as was the $\delta^{13}C$ value (-29) of an organic compound from these rocks (Konnerup-Madsen et al., 1988).

The presence of sedimentary-derived HCS in the Ilímaussaq rocks is of course unexpected by paradigm. Even more unexpected is that these HCS also exhibited no thermal stress; the saturated HCS having high pristane and phytane peaks (relative to adjacent n-paraffins) and large napththenic envelopes, and the biomarkers having normal sediment-like peak distributions. As was the case with the HCS from our samples and those of Sugisaki and Mimura (1994), all thermal cracking in these HCS has been suspended. Given the results of this study, and those of Sugisaki and Mimura (1994) and Laier and Nytoft (1995), we believe that the general *assumption* that HCS in high-temperature crystalline rocks always are abiotic, is incorrect. We believe that future adequate organic-geochemical analyses of such rocks will invariably demonstrate the HCS therein to be sedimentary-derived HCS.

Sugisaki and Mimura (1994) did not find detectable HCS in almost all of the granites they examined, in their study. However, they did find sediment-derived HCS in 9 s-type granites from the Ohsumi pluton, Japan. HCS indigenous to granites and granodiorites have never, to our knowledge, been previously reported, prior to Sugisaki and Mimura (1994).

Given the example of the results of different studies on carbonaceous rocks from Carlin-type gold deposits, the search for possible HCS in various crystalline rock types no doubt has been hampered by the preconceived conclusion that indigenous sedimentary-derived HCS cannot possibly exist in such rocks. Inadequate analytical approaches also have contributed. Moreover, the blanket assumption is without merit or foundation that such HCS in different crystalline rocks when found, must, a-prioi, have an abiotic origin. Only after the qualitative characteristics of such HCS have been delineated, will their origin become clear. To restate our position, in our opinion, future analysis will probably demonstrate that such HCS are invariably sedimentary-derived HCS, rather than abiotic HCS.

From the data of this study, and from studies of mantle-derived (and some igneous) rocks, petroleum-like sedimentary-derived HCS clearly enjoy a much richer life, in a wide variety of geologic settings, than has been portrayed by archaic and incorrect petroleum-geochemical paradigm. It appears that C_8+ petroleum-like HCS are thermally-unstable only in the minds of men. These HCS certainly do not have such thermal instability in the bowels of the earth.

5.02 ORIGIN OF OUR HCS: ABIOTIC?

We concluded above that the HCS of this study are biogenic HCS, from sedimentary rocks, surviving to much higher temperatures than predicted by accepted models. We recorded no detectable mantle-derived abiotic HCS in our rocks. Several lines of evidence support our conclusions of this matter. First, the ubiquitous presence of pristane and phytane (and other isoprenoid HCS) in all our samples dictates a biogenic origin. Second, higher-molecular weight biomarker compounds are present in all our rocks, biomarkers typical of sedimentary-derived OM. Third, the long extraction times necessary to remove the HCS in most of our samples demonstrate that the HCS are molecularly-dispersed throughout, and tightly held by, the rocks. An emplacement of abiotically-generated mantle HCS into our samples (by some unknown migration mechanism) would have occurred along permeable pathways in our rocks, and these HCS thus would have been much more amenable to solvent extraction than they were. Fourth, $\delta^{13}C$ values of our saturated HCS vary from -28.47 to -27.14, values characteristic of sedimentary-derived OM. Our $\delta^{13}C$ ratios are in the range of those that Sugisaki and Mimura (1994) found (-23.4 to -28.9) for the saturated HCS in their samples. As discussed, stepped-heating $\delta^{13}C$ measurements of mantle xenoliths demonstrate a relatively uniform $\delta^{13}C$ ratio around -26 to -28 for carbon liberated below 600°.

$\delta^{13}C$ ratios of the higher-temperature carbon liberated from mantle xenoliths (and basalts) in stepped-heating experiments cluster around -10 or slightly less (Pineau et al., 1976; Pineau and Javoy, 1983; DesMarais and Moore, 1984; Mattey et al., 1984, 1986; Sakai et al., 1984; Exley et al., 1986a,b; Nadeau et al., 1987, 1990; Pineau and Mathez, 1990). HCS derived from such OM would be expected to have $\delta^{13}C$ ratios of perhaps -10 to -16, in contrast to the reported ratios of -23 to -32 for HCS from these rocks.

Kenny (1995) proposed that Sugisaki and Mimuras' (1994) HCS were abiotic. He attributed the pristane and phytane of their HCS as due to such compounds having been found in carbonaceous chondrite meteorites, thus demonstrating that these compounds could be formed abiotically. The biogenic-like $\delta^{13}C$ values of those HCS were dismissed by Kenny (1995) as being due to Rayleigh fractionation and biological fractionation from near surface microbial activity. Gold (1992, 1993) has also dismissed biomarker molecules in any suite of HCS as being diagnostic of a biogenic origin. Gold (1992, 1993) proposes that high-temperature microbes can exist anywhere in the deep crust (up to 5-10 km of depth) of the earth and thus can contaminate an indigenous abiotic HC suite with biogenic HCS. As Sugisaki and Mimura (1995) pointed out, meteorite pristane and phytane is generally believed due to contamination, a conclusion also drawn by Cronin and Chang (1993) in their review article on the organics reported from the Murchison meteorite.

Even if pristane and phytane were in meteorites, it does not follow that those compounds are abiotic, because we would have no means to rule out their synthesis by extraterrestrial life forms (Mike Engel, Dept. Geology, Oklahoma University, Personal Communication 1/95). Moreover, pristane and phytane in meteorites have no bearing on the possible synthesis of these compounds by inorganic processes in the mantle, processes completely different from processes involved with meteorites.

As noted above, an abiotic origin of C_6+ HCS detected in various crystalline rocks has been called for by numerous investigators. However, no evidence has ever been presented that such HCS are really abiotic. The only data on this question currently available dictate a biogenic, sedimentary-derived origin for these HCS. Moreover, the very strong biologic imprints on these HCS cannot just be airily dismissed as meaningless and explained away by undocumented hypotheses, as some proponents of abiotic HC origin have done. Lastly, until C_6+ HC assemblages free of biologic-marker-type HCS and with $\delta^{13}C$ ratios of -6 to -12 can be documented, abiotically-derived C_6+ HCS can no longer be *assumed* to even exist.

5.03 SIGNIFICANCE OF HYDROLYTIC-DISPROPORTIONATION OF OM IN NATURE: HEAVY-METAL DEPOSITS

5.031 Introduction

Hydrolytic disproportionation of OM operating in the possible geologic environments from the near surface to the mantle would have profound consequences, many of which will be immediately apparent to the reader. In fact, widespread hydrolytic disproportionation of OM would be a geologic agent of the first magnitude. For example, OM acting through hydrolytic disproportionation of OM could be helping to set mineral stability fields during rock metamorphism. However, consideration of only a portion of these geologic environments in detail is outside the scope of this paper. Thus we will consider the possible effects of hydrolytic disproportionation only on heavy-metal deposition and oil and gas formation and occurrence.

5.032 The Heavy-Metal OM Association

Innumerable authors have noted and researched a strong, but ill-understood, association of heavy-metal deposits with OM. Disnar and Sureau (1990, p. 577) opened their comprehensive and insightful overview on the topic as follows:

> "Organic matter is often the principal stumbling-block to reconstructing the environment of metal deposition" (Krauskopf, 1955). The citation by Saxby (1976)--in the introduction of a review paper on the significance of organic matter in ore genesis--of this opinion expressed by Krauskopf 20 years before, stresses how difficult it is to assess the role actually played by organic materials in metal concentration and

> accumulation and how slowly knowledge has progressed in this field.---- Biological organic remains more or less altered by chemical, microbial and thermal diagenetic processes, can also interact with metals through their intrinsic reducing, acidic and chelating properties. Because of the complexity of natural media, most of these fundamental processes have been extensively studied in the laboratory. Geologists and geochemists must look for evidence of their influence in the field and evaluate the part they play in metal mobilization and concentration".

We emphasize two points from their quote. First, there is obviously a pronounced association of heavy metal deposits with OM. However, in spite of much research on the topic, a possible cause-effect relationship in this association has gone undelineated. Second, an understanding of this relationship is likely to result only if data from Nature are involved in the equation. In this paper, we have presented and discussed such data. Although similar data are also present in previous publications, the significance of these data has gone unrecognized, because the data were not related to a model or hypothesis which had a defined reaction mechanism.

The association of OM has been long observed with strataform lead-zinc (and copper) deposits (a.k.a., "Mississippi Valley Type (MVT) deposits"). For example, Siebenthal (1915) and Bastin (1926) noted significant occurrences of oil in the mid-continent (U.S.) Joplin and Tristate lead-zinc districts. The long-standing association of OM in MVT deposits has also been noted by Fowler (1933), Grogan and Schrode (1952), Barton (1967), Saxby (1976), Roedder (1976, 1984, and numerous other publications), Markios (1986), Spirakis (1986), Disnar and Sureau (1990, and references therein), and countless other studies. Numerous studies (including Rickard et al., 1975; MacQueen and Thompson, 1978; Hatch et al., 1986; Markios, 1986; MacQueen, 1986; Leventhal, 1990; Anderson, 1991; Henry et al., 1992; Niewendorp, 1993; to name but a few) have carried out organic-geochemical studies worldwide of various levels of sophistication, in attempting to establish a genetic relationship between various forms of OM and MVT deposits (e.g., the OM somehow caused the deposition of the ores).

The genetic relationship of OM having reduced oxidized-uranium species, thereby resulting in highly-oxidized OM while causing the precipitation of uranium in sandstone type deposits, is well-established and will not be reviewed here. Please see Disnar and Sureau (1990) for an overview of the topic.

Different studies have revolved around the pronounced association of large deposits of sub-microscopic gold in carbonaceous shales of northern Nevada ("Carlin-type" gold deposits) including Radtke and Scheiner (1970), Nelson et al. (1982), Hausen and Park (1986), Ilchik et al. (1986), Pasteris et al. (1986), Dean et al. (1987), Leventhal and Hofstra (1990), and Hofstra et al. (1991). Most of the publications concerning OM in Carlin-type gold deposits attempt to demonstrate that the carbonaceous OM of these shales caused the deposition of microscopic gold ore. However, as noted above, there is debate about this association, with some investigators maintaining no evidence of this genetic association exists (Nelson et al., 1982; Leventhal and Hofstra, 1990; and Hofstra et al., 1991). This difference of opinion, and the reasons for it, were discussed above.

The association of Carlin-type deposits with OM is not limited to northern Nevada, such deposits have been found worldwide. For example, a number of similar sub-microscopic gold deposits in carbonaceous shales have been found in China (Dean et al., 1988; Cunningham et al., 1988; Wang and Letian, 1993). Moreover, the possible genetic association of gold deposits with OM extends beyond Carlin-type deposits. Wilson and Rucklidge (1987) provide a "short list" (their Table 1) of gold deposits in carbonaceous units. Examples are: 1) the Witwatersand (Carbon Leader and Vaal Reef) deposits of South Africa (Zumberge et al., 1978; Button, 1979; Austin, 1986; and Disnar and Sureau, 1990); 2) the Pueblo Viejo gold deposit of the Dominican Republic (Kesler, et al., 1986); 3) the Aksu gold deposit of North Kazakhstan (Farfel et al., 1984); 4) gold deposits of the Abitbi belt of the Ontario and Quebec provinces of Canada (Springer, 1985); and 5) gold deposits of New Zealand (McKeag et al., 1989) and France (Gatellier and Disnar, 1989); to name but a few.

Black organic-rich shales long been thought to have high heavy-metal concentrations inherited from deposition. The Kupferschiefer of eastern Europe was previously the type example of such a shale (Eugster, 1985). However, Püttmann et al. (1988, 1989), and other investigators (see the references of Püttmann et al., 1989) have demonstrated that the Kupferschiefer is only locally mineralized where it contacts large faults which transported mineralizing solutions from depth. Away from such zones, the Kupferschiefer has only background concentrations of heavy metals. Moreover, Püttmann et al. (1989) demonstrate that the OM in the organic-rich Kupferschiefer shales was responsible for the deposition of the heavy metals in these shales.

Desborough et al. (1996) analyzed 80 Proterozoic to Tertiary black shales and found no enrichment of heavy metals in these rocks. For example, maximum gold concentrations in these rocks were 120 ppb and averaged 12 ppb. We have analyzed over 20 samples of high TOC Mississippian-Devonian Bakken shales from the Williston Basin and found no enrichment of heavy metals in any of these rocks. Moreover, in immature Bakken shales, increasing TOC content does not correlate with increasing metal concentrations. Nor was there a decrease in shale metal content with increasing Bakken shale maturity, as one might expect. In our opinion, the case has been overstated for high heavy metal concentrations in high TOC (black) shales over large regional areas, where these metals originated from syndeposition with the shales. We believe that shales with high metal contents are largely, but not exclusively, limited in areal extent and are chiefly associated, and in contact, with some avenue of fluid transport which allowed mineralizing solutions to interact with the OM in the shales, resulting in shale metal enrichment.

This is only a cursory overview of the possible genetic association of heavy metal deposits with OM.

5.033 Evidence for the Chemical Participation of the Hydrolytic-Disproportionation of OM in Ore Deposition

5.0331 Oxidation of OM

Hydrolytic disproportionation is characterized by the OM in rocks maintaining, or attempting to maintain, thermodynamic equilibrium between the rocks and aqueous solutions of the system they are present in (Helgeson et al., 1993; Seewald, 1994). Consequently, oxidized organic moities are the result. One overriding characteristic of the OM associated with heavy metal deposits (whether this OM is "carbonaceous" OM (degraded kerogen), degraded oils ("pyrobitumen"), or bitumen and HCS solvent-extracted from ore-bearing sedimentary rocks), is that the OM is always demonstrated to be highly oxidized, whenever elemental analyses are performed.

For example, as Disnar and Sureau (1990, p. 586) noted, the OM in sandstone uranium-type deposits is always highly-oxidized, often being referred to as "humic substances". However, to our knowledge, evidence, in the form of molecular analyses of exactly what these humic substances are has never been provided. Oxidized OM in uranium deposits is not limited to sandstone-type-uranium deposits. The Cluff Lake (Canada) deposit is an unconformity type uranium deposit, and graphite in the fractured ore body of the basement rocks (the Claude zone) has a "high content of oxygenated functions" (Disnar and Sureau, 1990, p. 585). Disnar and Sureau (1990, p. 585) also note that bitumen from the "D" zone orebody at Cluff Lake " has fixed uranyl species though free radicals and was oxidized in the course of metal reduction involving water." Oxidation of graphite and/or bitumen is *exactly* the expected consequences of hydrolytic disproportionation of OM.

Different investigators have demonstrated that the OM associated with the gold ore of the northern Nevada Carlin type deposits has been extensively oxidized. For example, Hausen and Park (1986) analyzed the "pyrobitumen" (now degraded, but once-mobile crude oil) associated with these gold ores and found it to be significantly oxidized, especially when compared to crude oils (Table 8). Hausen and Park (1986) also plotted $\delta^{13}C$ of the pyrobitumen versus elemental C/H ratios of the pyrobitumen (their Figure 25) and found an unexpected trend of decreasing C/H ratios versus less negative $\delta^{13}C$ values. This is exactly opposite the trend resulting from increasing thermal stress (increasing C/H (decreasing H/C) versus less negative $\delta^{13}C$ ratios). This observation demonstrates that there must be a process other than thermal maturation affecting the OM in these rocks. We believe that reaction to be hydrolytic disproportionation. As discussed above, other evidence of the oxidized nature of Carlin OM was provided by Radtke and Scheiner (1970). Lastly, oxidized organic compounds in carbonaceous shales hosting gold ore are not limited to northern Nevada. Kesler et al. (1986) found high concentrations of what they believed were a series of n-fatty acids and n-alkanols with progressively increasing carbon numbers, in the carbonaceous shales hosting gold ore in the large Pueblo Viejo gold deposit, Dominican Republic.

Table 8--Elemental analyses of Carlin pyrobitumen from Hausen and Park (1986), of an average crude oil from Hunt (1979), and of a Red Sea kerogen from Saxby (1976). C is carbon, H is hydrogen, N is nitrogen, O is oxygen, S is sulfur. NA is not available.

C	H	N	O	S	
81.072	2.037	1.493	0.3577	NA	Carlin pyrobitumen
84.5	13	0.5	0.5	1.5	Crude oil
66.0	0.65	3.1	21.4	3.0	Red Sea kerogen

The OM of Mississippi-Valley-Type (MVT) deposits is invariably found to be oxidized when appropriate analyses are performed. For example, Leventhal (1990) ran Rock-Eval analysis on bitumens from the Milliken mine (Viburnum Trend, U.S.) and found these bitumens to have relatively high oxygen indices (e.g., to be relatively oxidized relative to most crude oils). Henry et al. (1992) in a study of the entire Viburnum trend (U.S.) found that the kerogens of rocks associated with the deposits of this district had been significantly oxidized. Moreover, they plotted elemental H/C and O/C ratios of their altered kerogens on van Krevelen diagrams and found that their data fell in fields not occupied by the three OM types making up van Krevelen diagrams (their Figure 12). (van Krevelen plots (elemental H/C versus O/C ratio plots) are a petroleum-geochemical tool which allow the tracking of chemical changes of the three OM types (types I, II, and III), versus rock maturity increases). That the altered OM of the Viburnum trend does not fall within established fields on these diagrams again demonstrates some process, other than classical organic metamorphism, is at work in ore-depositional settings.

In point of fact, whenever any OM, associated with any type of ore deposit is analyzed, that OM is found to be oxidized. For example, Germanov and Bannikova (1972) and Germanov et al. (1972) found significant concentrations of oxidized organic compounds in the bitumen from Lower Cretaceous shales hosting pyrite-cinnabar mineralization in the northwestern Caucasus (then U.S.S.R.). Bitumen in the unaltered sedimentary rocks away from the deposits was unoxidized. Germanov (1965) earlier had documented extensive oxidation of the OM in sedimentary carbonate rocks hosting polymetalic ore deposits in the Kansay district (southwestern Karamazar, then Tadzhik, U.S.S.R). McKeag et al. (1989) found that graphite had been replaced by calcite in a graphite-schist-hosted gold-tungsten deposit, Macraes, New Zealand. Their analyses demonstrated that graphite had reduced the ore-bearing solutions and become oxidized to carbon dioxide in the process, thus resulting in the calcite. Saxby (1976) plotted the kerogens from sedimentary rocks hosting eleven different ore deposits on a Van Krevelan diagram (his Figure 4, not shown here). In all cases, these kerogens were oxidized compared to the trends of sedimentary OM on this diagram. Saxby (1976) also presented an elemental analysis of kerogen from an organic-rich heavily-mineralized, Red Sea shale, Table 8. Kerogen with 21.4% oxygen is unheard of from normal sedimentary environments.

We, in only a cursory literature search, found 14 other papers describing oxidized OM, both kerogen and bitumen. However, we will not detail those studies here. We do propose, however, that wherever ore deposits are hosted in OM-bearing rocks (whether the OM is graphite or sedimentary-OM), then appropriate analyses will reveal that OM to be oxidized.

5.0332 Severe bitumen compositional modifications

Besides the general oxidation of OM associated with ore deposits, other strong compositional changes (equivalent to those reported in this study) have been sporadically identified in past studies. For example, aromatic HCS have been noted as significantly quantitatively and qualitatively modified. Germanov et al. (1972) found in their study (discussed above) that aromatic HC concentrations were significantly decreased relative to saturated HCS in bitumens from mineralized sedimentary rocks. We found the same trend in the rocks of this study.

Püttmann et al. (1989) in their study of the Kupferchiefer mineralization of southwest Poland, found aromatic-HC compositions similar to those found in this study: In their mineralized rocks, methyl-, dimethyl-, and trimethyl-naphthalene concentrations were all very low, while dibenzothiophene, dibenzofuran, biphenyl, and fluoranthene concentrations were all high (top two chromatograms,). However, aromatic HCS from unmineralized Kupferschiefer samples had the distributions normally observed in sedimentary rocks (e.g. - high concentrations of alkylated naphthalenes and phenanthrenes). This is the only published study we have found where the aromatic HCS of mineralized OM were analyzed in detail. We believe that appropriate analyses of aromatic HCS from samples of carbonaceous ore-deposit and metamorphic (and other) rocks will eventually demonstrate that the highly-altered aromatic-HC compositions reported both here and by Püttmann et al. (1989) to be invariably present.

Püttmann et al. (1989) also ran gas chromatography on their resin fractions and did not find the large unresolved hump with no peaks typical of unmineralized sedimentary rocks (Fig. 9). Instead, they found a series of aromatic ketones, as sharp peaks, and no hump (bottom chromatogram, Fig. 17). We presented similar chromatograms for the resin samples of this study (Figs. 9 and 10). Püttmann et al. (1989) also found high concentrations of biphenyl in their samples (as we have in our samples).

Recall the "rounded" n-paraffin profiles in the saturated-HC gas chromatograms of Fig. 2 (samples 942-14, JGS-43, and JGS-49). Kesler et al. (1986) reported this effect at Pueblo Viejo. Moreover, saturated-HC gas chromatograms of samples from outside the commercially-mineralized zones at Pueblo Viejo did not exhibit this rounding. We believe that the intensity of this rounding is directly proportional to the intensity of hydrolytic disproportionation which affected a given rock. Hatch et al. (1986) found similar rounding in the n-paraffin profiles of saturated-HC gas chromatograms (Fig. 18) from the Thompson-Temperly mine, an MVT deposit in the Upper Mississippi Valley

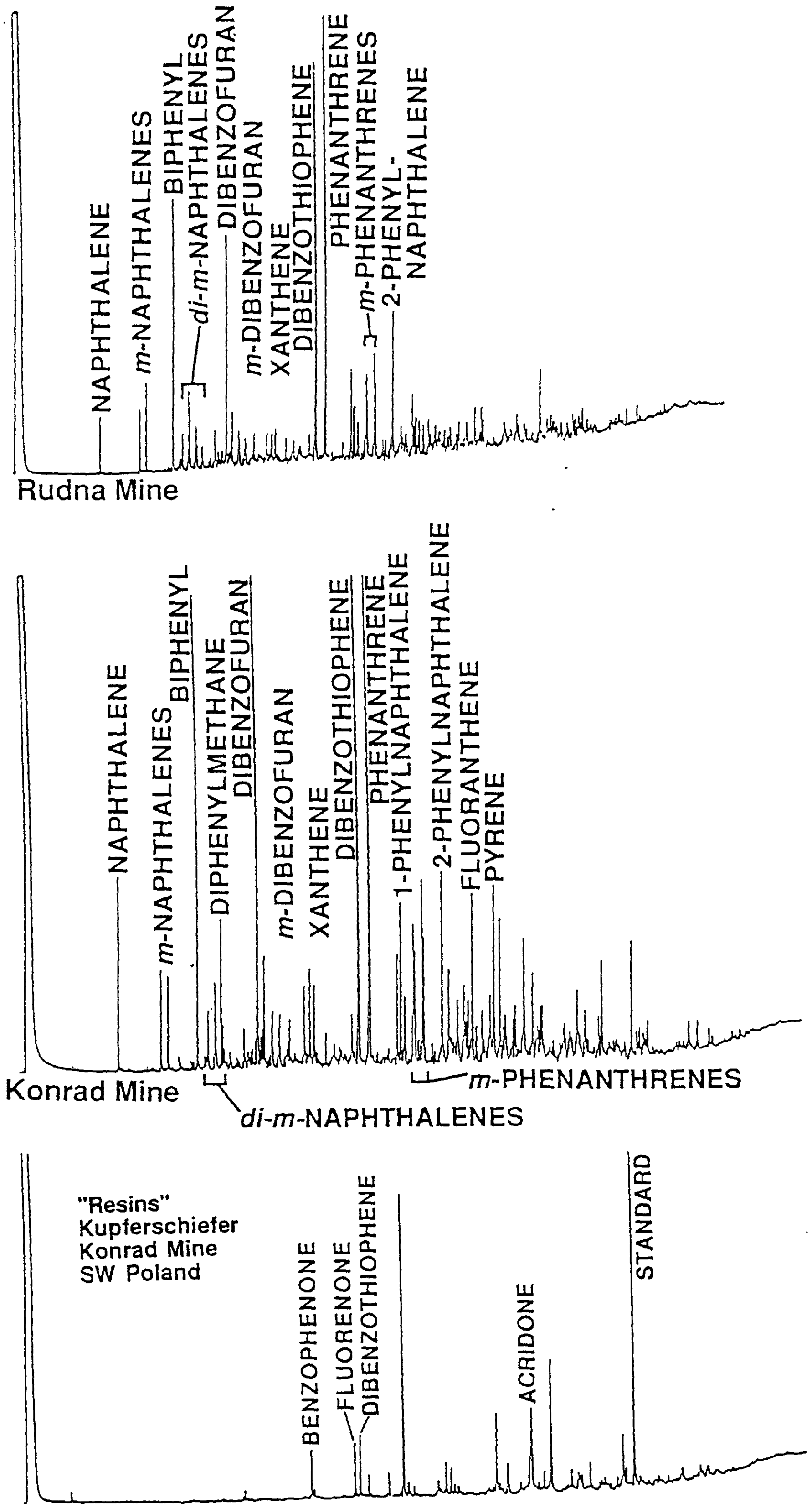


Figure 17. Gas chromatogram of a resin fraction (bottom chromatogram) and of two aromatic-HC fractions from bitumens extracted from Kupferschiefer mineralization (SW Poland). After Püttmann et al. (1989).

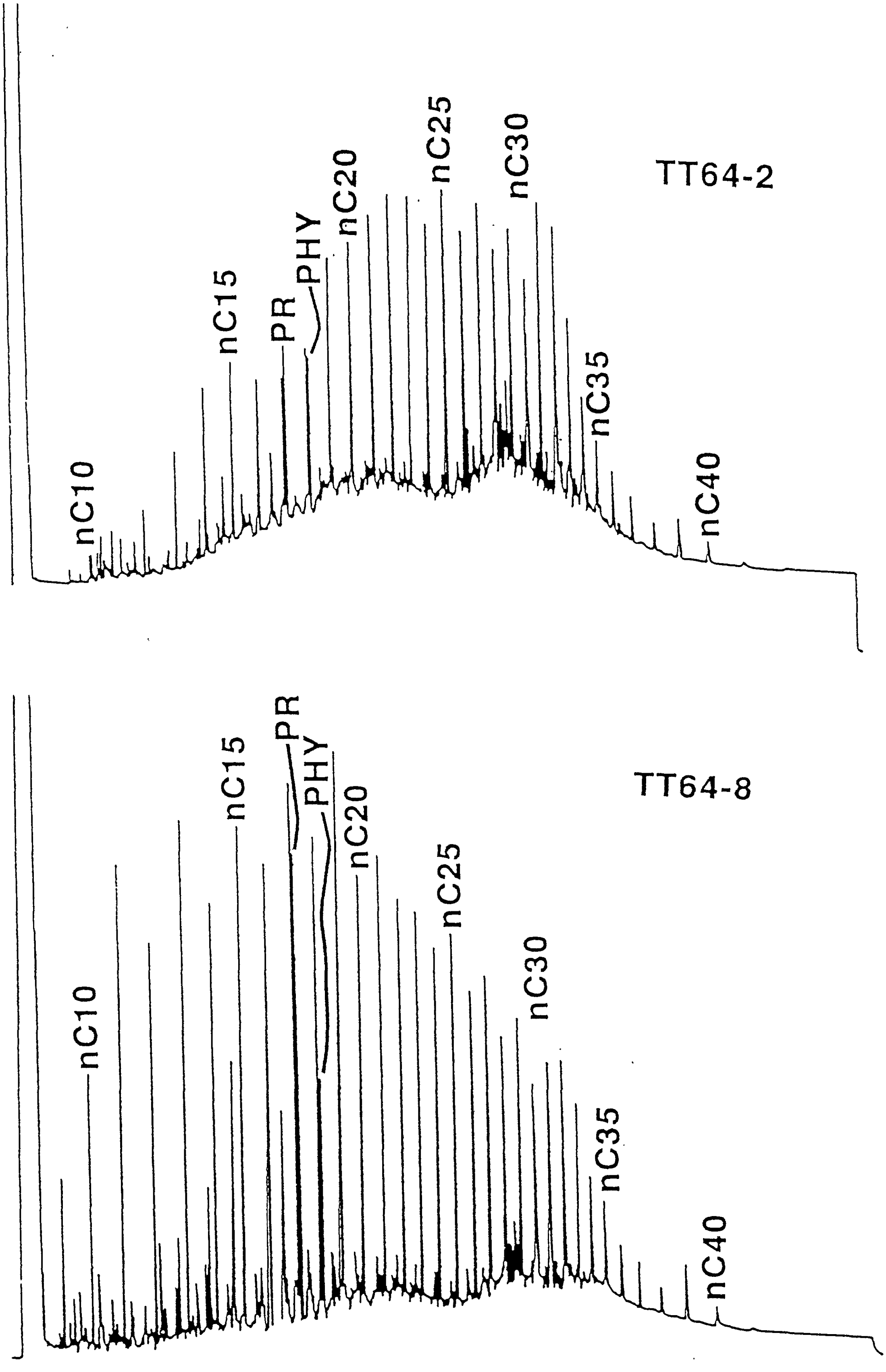


Figure 18. Two saturated-HC gas chromatograms from Thompson-Temperly mine host rocks. TT64-8 is slightly altered host rock and TT64-2 is from the Thompson ore body. PR is pristane and PHY is phytane. After Hatch et al. (1986).

District of southern Wisconsin and Northern Illinois, U.S. Hatch et al. (1986) noted that this rounding arose from a significant loss of C_{25}- n-paraffins, and attributed this loss to one of two causes: 1) a chemical reaction of C_{25}- material with the mineralizing brine, or 2) aqueous solution (based on the aqueous solubility data of Price, 1976). Mass balance calculations (not presented here) suggest the second possibility to be most unlikely, based on the solubility data of Price (1976, 1981), because ore deposition occurred between 125°-175°C at this locality. However, we agree with the first possibility raised by Hatch et al. (1986): a chemical reaction between C_{25}- saturated HCS and the mineralizing brine.

We hypothesize that the loss of C_{25}- saturated HCS (a loss which escalates with decreasing carbon number, down to about n-C_{12} to n-C_{14}) is from increasingly preferential oxidation of these HCS by hydrolytic disproportionation. Thus, n-C_{12} to n-C_{18} saturated HCS appear to be selectively oxidized compared to higher-molecular weight saturated HCS. In fact, by our data, higher-molecular saturated HCS do not appear to be measurably affected, because high-molecular-weight saturated-HC biomarkers with oil-like, even immature-oil-like, compositions exist in all our samples.

We would expect to invariably observe such rounding of saturated HCS in all OM-bearing mineralized rocks. However, there is a caveat to this expectation: The ability to observe this rounding depends on analytical techniques. Many petroleum-geochemical laboratory methods result in the complete loss of C_{15}- material, and some methods even result in substantial loss of C_{19}- material. Unless steps are taken to preserve C_8+ HCS, the presence, or absence, of this rounding will go undetected.

The last bitumen compositional modification to be discussed is the observation of Wilson and Rucklidge (1987) of elevated chlorine levels within the OM of Canadian Archean gold deposits. Recall the chlorinated aromatic HCS we identified in our samples (Table 4). Mineralizing fluids are commonly high in Cl^- concentrations. Thus, it is not completely unexpected by us that chlorine would be incorporated into OM during hydrolytic disproportionation of OM associated with ore deposition. We believe that future analyses will demonstrate the common occurrence of chlorinated HCS in these systems.

The data and discussion in this section demonstrate that various forms of OM appear to take part in the chemical reactions involving ore deposition. Further evidence of this participation exists within the deposits themselves. Many of these deposits are in carbonaceous rocks with very low porosity and permeability. Fluid flow is difficult through rocks if there are no paths for fluid transmission. One explanation for the paradox of fluids having clearly passed through such aquitards is that the ore-bearing solutions chemically ate the host rocks. Existing solid phases (including OM) were chemically-dissolved, and ore and gangue minerals were precipitated in their place. Some of these deposits faithfully track these carbonaceous aquitards, to the exclusion of immediately adjacent, and sometimes more porous and permeable rocks (except for perhaps the immediate edges of other units bordering the carbonaceous rocks). These textural relationships, and the fact that OM appears to be chemically-participating in the ore-deposition reactions, both combined, are strong evidence supporting the hypothesis that the OM is a, or the, parameter controlling ore deposition in some cases.

5.0333 Regional TOC loss and correlation of TOC to mineralization

Measurable decreases in the TOC values of sedimentary rocks (especially carbonaceous shales) around ore deposits, compared to regional background values, have been noted by different investigators studying different mineral deposits. For example, Wang and Letian (1993) observed that the host carbonaceous shales of the Chinese Carlin-type gold deposits had original carbon values of n.0% TOC which were reduced to 0.n% TOC within the deposits (e.g., 3.1% to 0.8%). Saxby (1976) found a "loss of a considerable amount" of OM from ore deposition at the Cobar polymetallic (Pb, Zn, and Cu) deposit, New South Wales, Australia. Germanov (1965) found losses of up to 0.5% TOC from ore deposition in sedimentary rocks. Kesler et al. (1986) documented a loss of TOC in mineralized carbonaceous shales (compared to non-mineralized shales) at Pueblo Viejo. Bechtel and Püttmann (1991) demonstrated strong decreases in both TOC and extractable bitumen in passing from unmineralized, or slightly-mineralized, Kupferscheifer rocks, into the strongly-mineralized Rote Fäule zone. These examples demonstrate a clear loss of OM in the host rocks during ore deposition.

Different investigators worldwide have looked for, and found, no positive correlation of TOC content in carbonaceous rocks hosting ore. This has led these investigators to conclude that TOC cannot be a controlling parameter in ore deposition in the case under consideration. For example, Leventhal et al. (1990, p. A37) discussed the possible association of ore deposition and OM at the Jerritt Canyon (northern, Nevada, U.S.) gold deposit: "-----there is no correlation between the gold content and carbon content of these rocks. Carbon was not a favorable substrate for gold and was probably not a direct contributor to gold deposition." However, if OM is taking part in the ore-deposition reactions, and being destroyed in these reactions, then there is no reason to expect a positive correlation of increasing OM content with increasing ore concentration, in fact, quite the opposite would be expected. Saxby (1976, p. 119-120) noted:

> "Under metamorphic conditions graphite is not stable in the presence of pure water but can coexist with a gas phase rich in carbon dioxide. Thus, under oxidizing or aqueous conditions at high temperatures, graphite may be effectively eliminated from an ore, particularly if carbon dioxide can be removed either as a gas or as a carbonate....".
>
> "Under these conditions, the initial association of metals with organic carbon is either partially or completely destroyed. It is thus conceivable that at least some metamorphic ore bodies which now how no evidence of

organic carbon, were originally formed with carbonaceous matter playing a major role."

We stress that the above examples demonstrate that both the extractable bitumen and the solid OM (kerogen/graphite) are taking part in these ore- deposition via rock-water-OM reactions.

5.0334 The carbonate association

Saxby's (1976) observation about the CO_2 derived from the oxidation of OM possibly being precipitated as carbonate requires amplification. Saxby's (1976) point is well taken: the only paths of escape for CO_2 from oxidized OM are 1) removal by through-flowing fluids, or 2) precipitation as a carbonate. Carbonates are often associated with ore deposits, even if only in small quantities. However, in ore deposits where oxidation of OM would be the principal parameter causing ore deposition, then, assuming an adequate supply of appropriate cations, carbonate minerals should be in high concentrations in the deposit. Even barring an adequate supply of appropriate cations, carbonate minerals should be in at least moderate concentrations in the deposit. In any case, any carbonate minerals in such deposits should show the influence of OM by exhibiting a wide range of carbon-isotopic ratios with more negative values than normally present. For example, carbonate minerals in ore deposits in crystalline rocks with no influence of OM, invariably have a distribution of $\delta^{13}C$ values between +2 to -6. However, most sediment OM typically has $\delta^{13}C$ values somewhere between -30 to -20, with most being between -24 to -29. These two expectations (a large volume of carbonate minerals and a strong modification of carbonate $\delta^{13}C$ values) are both borne out by reality.

Consider the U.S. midcontinent MVT deposits. Since these ores were first discovered, the large volume of carbonate minerals (mainly calcite and dolomite) associated with these deposits has been noteworthy. In fact, these deposits have produced, and still are producing in quantity, some of the finest museum-quality calcite specimens in the world. Notwithstanding, these deposits are commonly hosted in carbonate sediments. Thus, it may be argued that these carbonate minerals have simply resulted from a dissolution of the carbonate host rock. However, $\delta^{13}C$ ratios of these carbonate minerals often have a wider range than that of the host carbonate rocks, with significantly more negative values. For example, Hall and Friedman (1969) found that unaltered limestones at the Thompson Temperly mine (southern Wisconsin, U.S., discussed above) were 0 to -2, whereas carbonate host rocks in the ore body had values of -5 to -10. Altered limestones, spatially between the ore and unaltered limestones, had $\delta^{13}C$ values intermediate between the two extremes. These $\delta^{13}C$ values support the findings of Hatch et al. (1986) that the OM participated in the ore deposition at Thompson Temperly (discussed above).

Bechtel and Püttmann (1991, p. 12) noted that, "One of the common features of carbonate minerals in sediment hosted sulfide deposits is a large variation in $\delta^{13}C$, with a predominance of negative values---- indicating the contribution of organic carbon (Ohmoto, 1986)." Such modifications of $\delta^{13}C$ ratios in carbonate minerals are not limited to MVT deposits. Kríbek (1989) presented $\delta^{13}C$ analyses of carbonates associated with uranium deposits where graphite in the host rocks was thought to have caused deposition of the uranium, by oxidation of the graphite. The unaltered graphite $\delta^{13}C$ ratios varied between -24.2 to -26.8. Carbonates in unaltered host rocks had $\delta^{13}C$ ratios of -2 to +2. Carbonates in the uranium-bearing (altered-host) rocks in contrast, had $\delta^{13}C$ values of -7 to -16 (Fig. 19), indicating a clear contribution of carbonate carbon from the organic matter. Further discussion, and examples of this topic, will not be presented here. However, altered $\delta^{13}C$ ratios of carbonates from ore deposits hosted by carbonaceous rocks are one more line of evidence demonstrating a participation of the host OM in the ore deposition reactions.

5.034 The MVT Deposition Mystery

Numerous investigators, including MacQueen (1986), Spirakis (1986), Trudinger et al. (1985), Disnar and Sureau (1990), Anderson (1991), and Ming-An et al. (1995), have discussed and acknowledged the serious unanswered question concerning the controlling parameter(s) of MVT ore deposition. Reduction of sulfate to sulfide is universally acknowledged as causing the actual precipitation of the ore. However, the mechanism responsible for reducing the sulfate has not been delineated. The temperature range of MVT ore deposition is from perhaps 75° to 225°C. Two mechanisms of sulfate reduction have been proposed. First, bacterial reduction of sulfate to sulfide, as bacteria degrade associated OM while utilizing it as a food source. The second is thermochemical-sulfate reduction. However, microbial activity at low fluids pressures is thought to cease by 100°C; although we may speculate that perhaps it extends to 120°. Thermochemical-sulfate reduction has been *documented* as only occurring at temperatures of 200°C and higher in petroleum basins, although the process has been hypothesized to occur at lower temperatures (discussed immediately below). Thus, both proposed mechanisms are operable only at the minimum and maximum temperature extremes of MVT deposition, with no mechanism generally accepted as operable between 120° to 200°C, the temperature range over which most MVT ore is deposited.

Our data to date strongly suggest that hydrolytic disproportionation occurs over a huge temperature range (including 75° to 225°C). The process is a natural consequence of water (a commonly-occurring substance with one of the highest oxygen concentrations in nature) in an open-fluid system, flowing past OM (a commonly-occurring substance with one of the lowest oxygen concentrations in nature). Because of this chemical disequilibrium, water oxidizes OM, in turn causing a reduction of the sulfate ion (and other species). Note that the extractable OM of both the metamorphic

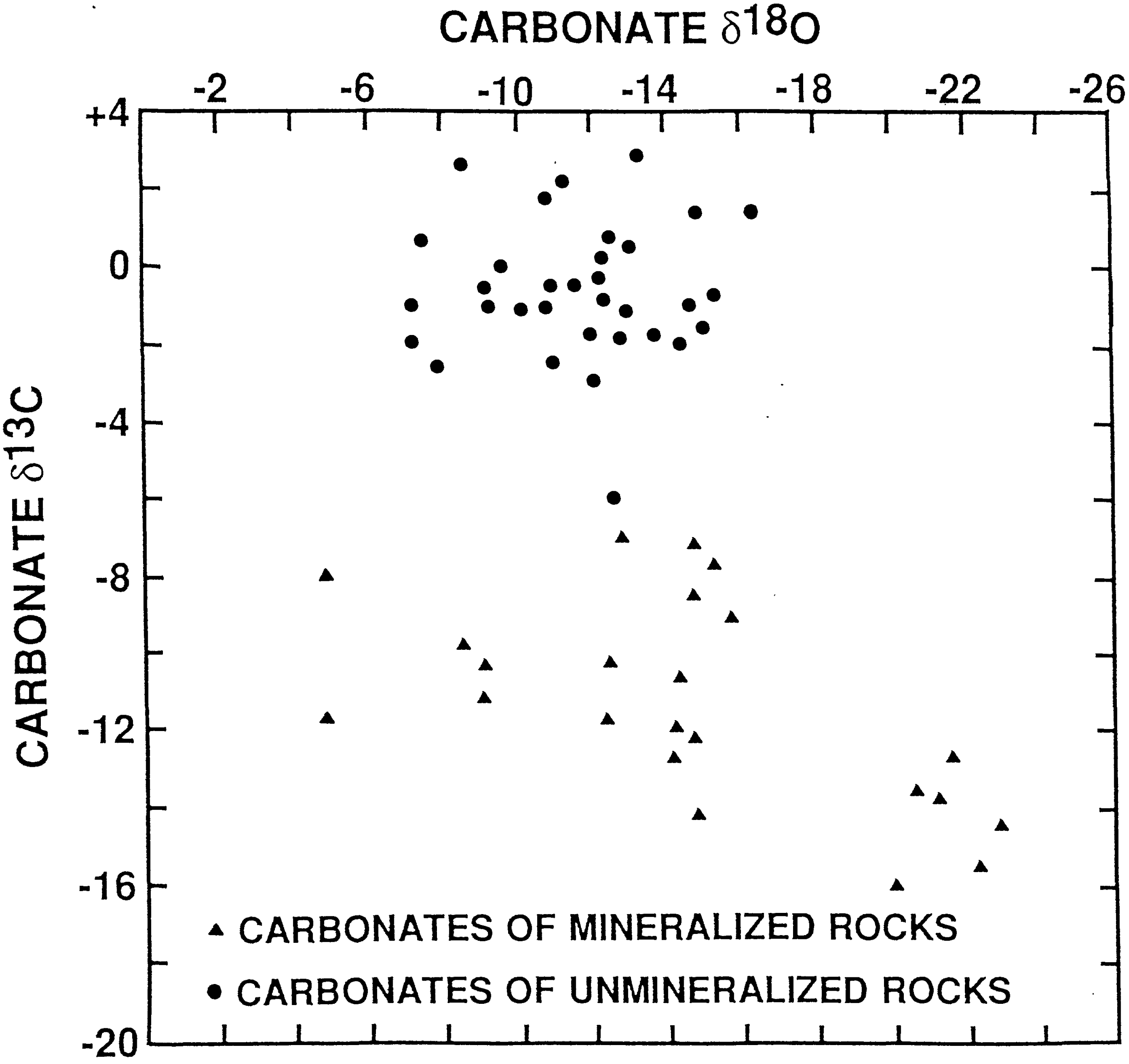


Figure 19. Carbonate $\delta^{13}C$ and $\delta^{18}O$ values for carbonates from uranium deposits in high grade carbonaceous metasediments of the Moldanubicum of the Bohemian Massif. After Kríbek (1989).

and ore-deposit rocks of this study share many of the same chemical features. Hydrolytic disproportionation is not the result of *ore-bearing* waters contacting OM. For example, there were no ore-bearing waters in the metamorphic systems which resulted in the metamorphic rocks of this study. However, hydrolytic disproportionation still proceeded in these rocks. We repeat, the principal variable causing significant hydrolytic disproportionation is water or OM flowing past each other in open-fluid systems at chemical disequilibrium. When the waters are carrying metal ions (or metal complexes, etc.), by changing (and therefore destabilizing) the chemistry of the aqueous phase from the OM-water reaction, metals are precipitated as ore. In this light, some ore deposition is simply a secondary consequence of hydrolytic disproportionation of OM.

Although this section on the possible control (and evidence for) hydrolytic disproportionation on ore deposition is extended, we have only broached the subject. From this discussion, we may conclude that OM, via hydrolytic disproportionation, clearly may be a major causal agent of ore deposition.

5.035 Thermochemical-Sulfate Reduction

A brief expansion of the discussion concerning the minimum temperature occurrence of thermochemical-sulfate reduction is warranted, because substantial confusion and contradiction exist in the literature concerning the process. Price (1997, p. 199-203) discussed development of the theory of thermochemical-sulfate reduction, including unaddressed problems: Orr (1974) first proposed the theory in an elegant presentation centering on the Big Horn Basin. However, he made three assumptions concerning the Big Horn Basin and the oils therein, which are actually in antithesis to the observed, and generally-accepted, data. Thus, the original hypothesis of thermochemical-sulfate reduction is founded on flawed assumptions. As also discussed in Price (1997), Orr (1974) specifically detailed reaction schemes and expected products for thermochemical-sulfate reduction; however, later investigators invoking the mechanism, call for reaction schemes and products anthithetic to Orr's (1974) original scheme. Moreover, different investigators (Sassen and Moore, 1988; and Claypool and Mancini, 1989) working in the same geographic area have drawn different conclusions regarding thermochemical-sulfate reduction and its products from both each other and from Orr (1974), regarding the mechanism and its reaction products (Price, 1997). Furthermore, there is no agreement among investigators regarding the threshold temperature for commencement of intense thermochemical-sulfate reduction. To quote Worden et al. (1995, p. 859):

> "Studies of gas composition vs. temperature generally have led to the conclusion that the threshold for thermochemical sulfate reduction lies between 80°C and 120°C (Le Tran et al., 1974; Orr, 1974, 1977; Krouse, 1980; Machel, 1987, 1988; Krouse et al., 1988; Sassen, 1988; Wade et al., 1989) although most accept that the threshold temperature may be much higher than this.

> Conversely, most experimental studies of thermochemical sulfate reduction generally have indicated a threshold temperature of greater than 200°C (Toland, 1960; Kiyosu, 1980; Trudinger et al., 1985). However, Orr (1982) produced evidence from his experimental work that thermochemical sulfate reduction may commence at a temperature as low as 175°C. Theoretical considerations with a review of all relevant experimental data suggested a thermochemical sulfate reduction onset temperature of 149-150°C (Anisimov, 1978; Siebert, 1985)".

There are statements in the literature calling for a lower-temperature (80°-140°C) onset of thermochemical-sulfate reduction. However, please note the last phase in the first paragraph of the above quote by Worden et al. (1995; this author's parentheses ".....most (investigators) accept that the threshold temperature may be much higher than this (80°-120°C)". As Worden et al. (1995) note, all of the lower temperatures can be explained by the mobility of gas, with H_2S migrating from its in-situ generation site to shallower, lower-temperature reservoirs.

The experimental temperatures have been generally dismissed as too high, because thermochemical-sulfate reduction is thought to be a first-order reaction (Orr, 1982; Goldhaber and Orr, 1995; Heydari, 1997). Thus, it is *assumed* that the same reaction will proceed much further over geologic time at lower temperatures given that time may be substituted for temperature in the *hypothesized* first-order reaction. Note that no proof has ever been forwarded that thermochemical-sulfate reduction is a first-order reaction, it is merely assumed as such because all HC-based maturation reactions are thought to be first-order reactions. However, Price (1983) provided a large body of evidence strongly suggesting that HC maturation reactions are not first-order at all, while demonstrating that the concept originated because petroleum-geochemical studies found advanced HC maturities in geologically-old basins which clearly had been much hotter in the past. However, the present-day burial temperatures in these basins were quoted in these studies as being responsible for the observed levels of organic maturation, as opposed to the much higher paleo-burial temperatures, which actually caused the organic metamorphism. The surprising thermal stabilities of the HCS in the rocks of this study (and other studies) clearly demonstrate that even if first-order reactions occur at all in organic metamorphism, under certain conditions first-order reactions are *completely* suspended. In any case, it is not valid to disregard the higher experimental temperatures of the thermochemical-sulfate-reduction reaction, solely on the *assumption* that this is a first-order reaction.

From the above discussion, the problem of thermochemical-sulfate reduction in sedimentary basins can hardly be considered as resolved. Nor can the minimum burial temperatures for the mechanism be considered to be well delineated.

5.04 SIGNIFICANCE OF HYDROLYTIC DISPROPORTIONATION OF OM IN NATURE: PETROLEUM GEOCHEMISTRY

5.041 Introduction

Many processes in petroleum geochemistry take place in semi-closed, or closed, fluid systems. For example, HC generation takes place in low-porosity, low-permeability organic-rich source rocks, where indigenous shale fluids are expelled (most likely by overpressuring and fracturing), but external fluids essentially never pass through the shales. HC reservoirs must be, at the very least, semi-closed systems. Otherwise, the trapped HCS would be quickly lost over short periods of geologic time, which is clearly not always the case (Price and McNeil, 1997). As stated above, the principal control of hydrolytic disproportionation of OM is flow of water past OM (or OM through water), where the two species are not equilibrated. Thus, the effects of the hydrolytic disproportionation of OM should be minimized in petroleum-geochemical systems, compared to more open-fluid systems such as ore-deposition or rock-metamorphism. Nonetheless, hydrolytic disproportionation of OM still appears to play dominant petroleum-geochemical roles in some processes. We will consider four such possible processes: 1) the origin of dry gas deposits, 2) the incorporation of water into kerogen during HC generation, 3) the possible sealing capability of hydrolytic disproportionation of OM regarding fluid movement, and 4) the generation of secondary porosity.

5.042 Origin of dry-gas deposits

According to accepted petroleum-geochemical paradigm, one of the principal sources of dry-gas deposits is thought to be thermal cracking of reservoired-oil deposits to methane at only moderate burial temperatures (150° to 200°C), which are believed to be equivalent to R_o = 0..9-1.35% (Tissot and Welte, 1984). However, as discussed in Price (1993), much published data from the natural system contradicts this model of C_8+ HC thermal instability. This data is in the form of high HC concentrations in fine-grained sedimentary rocks at ranks of R_o = 2.0-5.0%, and moderate to low HC concentrations in rocks up to R_o = 8.0%. The data of this study, data from subsequent related, but yet unpublished, analyses we have performed, and published data from other investigators (discussed above), all also contradict the hypothesis of a thermal instability of C_8+ HCS at moderate burial temperatures. It is most difficult to explain C_8+ HCS concurrently being thermally cracked at 150°-200°C and surviving in high grade metamorphic rocks, high temperature ore deposition, plutonic intrusions, or being recycled through the mantle. All these data suggest that another origin, or origins, of dry-gas deposits must exist, besides thermal destruction of C_8+ HCS.

Both data from the natural system (Price, 1989b; Price and Schoell, 1995) and from laboratory experiments (Price, 1989a), demonstrate that large amounts of gases are cogenerated with C_8+ HCS during all HC generation stages. In addition, methane carbon isotopic ratios ($\delta^{13}C$ = -40 to -50) of Anadarko Basin dry gas deposits demonstrate that the methane of these deposits originated from co-generation with C_8+ HCS and not from the destruction of C_8+ HCS (Price, 1995). Where data are available, the methanes of dry gas deposits invariably have $\delta^{13}C$ ratios of -40 to -50 (Price, 1995). Relatively few examples exist worldwide of the heavier (more positive) $\delta^{13}C$ ratios (-38 and greater) expected from true C_8+ HC thermal cracking (Sacramento and Val Verde Basins; Price, 1995). In light of these data, Price (1995) proposed that the dry-gas deposits of the deep Anadarko (and other) basins originated by physical processes occurring after generation of the gases (condensation, and differential entrapment from buoyancy during primary and secondary migration). He termed these processes migration-fractionation.

Natural gas will increasingly make up greater percentages of the world's energy mix. Only by understanding the origin of natural gas deposits may we most effectively explore for them. The data of this study demonstrate that C_8+ HCS have surprising and unexpected thermal stability. This extended thermal stability: 1) is both predicted, and appears caused, by the metastable equilibrium resulting from the hydrolytic disproportionation of OM; and 2) makes an origin of dry gas deposits from C_8+ HC thermal cracking at only moderate burial temperatures most improbable. Both Helgeson (1991) and Giggenbach (1997) predicted extended HC thermal stability via redox reactions of HCS with water and the minerals of their environment. These predictions are corroborated by the data of both Price (1993) and this study.

5.043 Water Reacting with Kerogen during HC Generation

Aqueous-pyrolysis HC-generation experiments (Price, 1989a,b; Wenger and Price, 1991; Price and Wenger, 1992) generate much more CO_2 than can possibly be accounted for, considering the original oxygen content of the kerogen. Moreover, the same effect occurs in hydrous-pyrolysis experiments (Lundegard and Senftle, 1987; Barth et al., 1989; Lewan, 1992). It appears that this effect is present in all HC generation experiments carried out in closed water-wet systems. Examples of this excess CO_2 from the HC generation experiments of Wenger and Price (1991) are shown in Figure 20.

In Figure 20, the amounts of CO_2 generated from three different OM types (Type I, Green River shale; II-S, Phosphoria shale; and II/III Anna shale) are shown. In all three cases, 100% equals the maximum amount of CO_2 possible, given the original oxygen content of the rock. Kerogen oxygen contents were determined by ROCK-EVAL oxygen indices. However, kerogen elemental analyses performed on these same samples yield the same results (unpublished data, L. C. Price). In all cases, any CO_2 contributions from carbonate minerals during the experiments have been subtracted

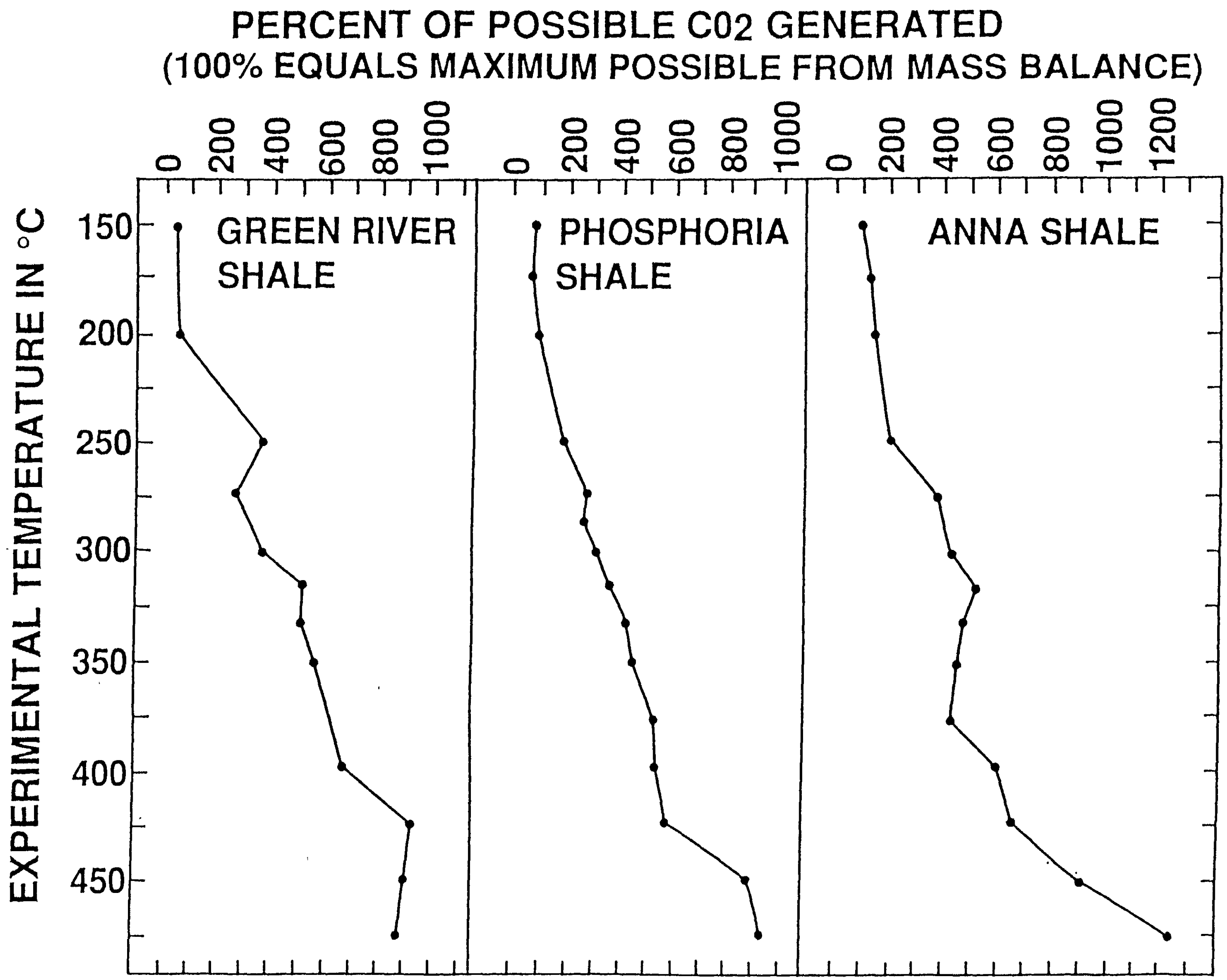


Figure 20. Percent of CO_2 generated over what was possible, based on the original oxygen content of the kerogens, for three rocks on which aqueous pyrolysis experiments were performed.

from the Figure 20 values. In the Figure 20 rocks, mainstage pyrolytic HC generation commences at 250°C (275°C for the Green River shale) and is complete by 320°C. Experimental temperatures of 350°C and higher represent mainstage C_8+ HC thermal destruction. From Figure 20, excess CO_2 is generated before mainstage HC generation even commences and during both mainstage HC generation and the HC destruction phase.

These results can only be explained by water disproportionating and reacting with kerogen (or somehow being otherwise incorporated into kerogen), with the oxygen from the water going to CO_2 and the hydrogen from water hydrogenating the kerogen. The kerogen after such hydrogenation would end up with more HC generation potential than suggested by original ROCK-EVAL or elemental-kerogen analyses. ROCK-EVAL analyses of all six of the rocks studied by Wenger and Price (1991) confirm this suggestion: Hydrogen indices of reacted rocks increase over those of the starting samples, where the experimental temperatures are below those of the commencement of mainstage HC generation. The experimental results of Hoering (1968, 1984) are also explained by hydrolytic disproportionation of OM and thus also support the Figure 20 data. Moreover, other investigators have called for water hydrogenating kerogen, and producing excess CO_2, based on their respective experimental results (Lewan, 1992, 1997; including oxygen-isotope labeling, Stalker, et al., 1994).

5.044 Hydrolytic Disproportionation of OM as a Seal

Based on theoretical considerations and a small natural data base, we hypothesize that hydrolytic disproportionation of OM acts as a sealing mechanism to preserve both conventional oil and gas deposits and basinal scale pressure compartments, over geologic time. Moreover, limited data from Nature support this thesis.

HCS leaking from a reservoir, through a caprock fracture, would be expected to encounter pore waters with a distinctly different chemistry, compared to that of the reservoir pore waters. If this were true, hydrolytic disproportionation between the HCS and aqueous phase would commence, because the leaking HCS and the newer pore waters would be out of equilibrium with one another. As discussed above, one of the principal end products of hydrolytic disproportionation of OM is CO_2; and under the proper pH conditions carbonates might precipitate, plugging the fracture, and thus preserving the deposit. Of course, intense structural activity would still override this process, resulting in trap destruction and loss of all reservoired HCS.

5.0441 Conventional HC-Deposit Trap Seals

Late-stage crosscutting carbonate veins are apparently common in all petroleum basins. However, published carbon isotopic analyses of such late-stage crosscutting carbonate cements are, to our knowledge, not readily available. We believe that isotopic analyses of such late-stage crosscutting vein carbonate cements may reveal, in many cases, a significant contribution of organic carbon to the carbonate carbon. Donovan (1974) has provided evidence supporting this hypothesis. He studied surficial expressions of the giant Cement oil field in the southern Anadarko Basin. It is relevant to note that the southern Anadarko Basin has been intensely structurally deformed (Landes, 1970). In spite of this structural deformation, this area contains a continuous string of large to giant oil deposits, deposits which were emplaced at least 220 million years ago, and perhaps as long as 300 million years ago, during the principal structural deformation in the basin. In spite of the long geologic time, and the intensely deformed structural terrain, these highly-structured anticlines still retain substantial amounts of oil. We believe it is not a coincidence that high concentrations of carbonate cement, with isotopically-light carbon, fill cracks and choke sandstone porosity at the crest of the Cement anticline. In fact, Donovan (1974) both demonstrated that carbonate cements, with increasingly isotopically-lighter carbon, ring the anticlinal crest in a bullseye fashion, and documented this isotopically-light carbonate cement occurring at least as deep as 762m (2,500 ft) at Cement. Donovan (1974, p. 434) noted, "Heavily mineralized rock along the anticlinal crest commonly is oil stained and emits a strong petroleum odor when freshly broken. Solid hydrocarbon deposits around grains and partly filling interstices are present in some thin sections. Hydrocarbon deposition appears to have preceded carbonate mineralization". Besides having derived part of their carbon from OM, these carbonate cements were also intimately associated with oil. Both observations strongly suggest a cause and effect relationship.

Donovan and coworkers (Donovan et al., 1974; Donovan and Dalziel, 1977; and Henry and Donovan, 1978) found the same patterns over other oil fields in the southern Anadarko Basin (Fox-Graham, Wheeler, and Velma fields) and over other oil fields in New Mexico, Texas, and California. In all these publications, "oxidized hydrocarbons" were called upon to provide the CO_2 with isotopically light carbon found in the carbonate cements. Bacterial degradation of oil could be called upon to explain these observations. However, as discussed in Price (1986), in HC microseepage and macroseepage situations, such bacterial degradation is principally a surficial process. The depths to which these pore-plugging cements extend would seem to preclude wide spread microbiologic involvement. Donovan and coworkers believed that some process other than, or in addition to, microbial HC ingestion was causing the HC oxidation they observed. However, no recognized process can account for such widespread HC oxidation. We note that hydrolytic disproportionation of OM explains these observations.

Leith and Fallick (1997) studied the organic geochemistry of cap-rock HCS of the Snorre field, Norwegian North Sea. They found that the carbonate cements in the Snorre caprocks, from $\delta^{13}C$ measurements, showed clear indications of a significant contribution from organic-carbon (e.g., the reservoired HCS). From this isotopic evidence, Leith and Fallick (1997, p. 131) noted, "This opens the possibility that vertical cap-rock leakage, may in fact, enhance the sealing capacity of a structure under certain conditions". Thus, Leith and Fallick (1997) from observations in the natural system, have independently proposed the same sealing mechanism which is under discussion here. However, Leith and Fallick (1997) did not provide the reaction pathway wherein leaking reservoired HCS might be oxidized to carbonate. Hydrolytic disproportionation of OM would be that pathway.

The question if hydrolytic disproportionation of OM plays the, or a, major role in providing seals for HC traps over geologic time is not academic. As noted by Price and McNeil (1997), traps and seals for the last 5-7 years have been one of the major research thrusts in petroleum geology. Models exist (Miller, 1992) wherein HC deposits are held to be very transitory in geologic time, with the only reason for the existence of the deposit being that the HC infill rate exceeds the HC leakage rate. As pointed out by Price and McNeil (1997), the existence of HC deposits in various basins for periods of 200 to 300 million years (or longer), especially the oil deposits in the southern Anadarko Basin, strongly contradicts such transitory models. Clearly, a more correct understanding of HC deposit traps and seals, and the mechanisms of seal formation, would have significant exploration implications.

5.0442 Basin Compartment Seals

Basin compartmentalization, or hydraulic isolation of very large (basinal-scale) volumes of rock, with very different fluid chemistry and fluid pressure regimes (e.g., "pressure compartments", Bradley (1975), Powley (1990), and Tigert and Al-Shaieb (1990), from one another has recently been recognized as a phenomenon occurring worldwide in petroleum basins (Hunt, 1990). Martinson (1994, p. 33) listed some of the characteristics of the seals surrounding such pressure compartments: 1) Such seals consist of interbedded permeable and non-permeable layers. The permeable layers can be HC bearing and the nonpermeable layers are carbonate or silica cemented, such that the seal sequence has a banded appearance. 2) Whereas the overpressured compartments can have open unmineralized fractures, seals have calcite filled fractures. 3) A resistive shale cap overlies abnormal pressure zones; and the sediments in this cap are carbonate-rich compared with adjacent intervals.

Whelan et al. (1994, p. 97) analyzed the rocks comprising pressure seals in three wells from two areas (the deep Anadarko Basin and the Tuscaloosa gas trend, southern Louisiana; both U.S.) and found that:, "---very tight associations of carbonate cements, fine pyrite, asphaltenes, and micrinite (generally considered to be a residual product of hydrocarbon generation) were observed in the general zone of pressure seals, suggesting that interactions of organic and inorganic materials may be required for pressure seal formation and maintenance...". Whelan et al. (1994) found that bitumen could coat quartz grains that were in turn encased by a subsequent phase of secondary silica overgrowths, thus mirroring the close association of oil and cementation which Donovan (1974; and coworkers) documented (as discussed above). The presence of pyrite in these seal assemblages studied by Whelan et al. (1994) is also noteworthy, suggesting an origin by reduction of sulfate to sulfide as the HCS undergo oxidation-reduction reactions via hydrolytic disproportionation. This association of sulfides with carbonate cements is not unique. Land et al. (1987) note that galena, and sphalerite, are associated with late cements in Mesozoic sands in the Gulf Coast. Lastly, Weedman et al. (1996) performed $\delta^{13}C$ analyses of the late dolomite and calcite cements of the seal rocks for the Tuscaloosa pressure compartment, finding values of -9.5 to -12.7, again indicating a strong contribution of carbon from sedimentary-derived OM.

Drzewiecki et al. (1994) and Winter et al. (1995) both studied dolomite seal cements in the Ordovician St. Peter sandstone of the Michigan Basin, and found that the dolomites were isotopically light and got lighter with increasing depth. Both groups of investigators concluded that these isotopically light carbon values demonstrated a major contribution of carbon from OM to the carbonate cements. Al-Shaieb et al. (1994) examined carbonate cements in the Ordovician Simpson sandstone seal of the deep Anadarko Basin and concluded that the range of $\delta^{13}C$ values (-5 to -9) for the carbonate carbon indicated that part of the carbonate carbon had been derived from OM, mirroring the situation in the Michigan Basin.

Chen et al. (1994) hypothesized a model wherein seals could heal themselves. Elements of this model have also been called upon by other investigators. Chen et al. (1994) note that the seals around pressure compartments must last tens to hundreds of millions of years. Over such time periods, tectonism and overpressuring would breach these seals, and thus, they reason, there must be a mechanism for healing these seals. As noted by Martinsen (1994) most investigators researching seals and pressure compartmentalization agree on these points, to repeat: the seals (and the resultant pressure compartments) are remarkably long lived, the seals must occasionally breach, or leak, over geologic time, and therefore, the seals must repair themselves. The model hypothesized by Chen et al. (1994) centers on waters with a given chemical balance escaping through a fracture in the seal. As the waters move into another chemical environment, the changing chemistry (especially decreases in pressure) causes mineral precipitation which heals the fracture. Surdham et al. (1994) called upon such a mechanism to precipitate carbonate due to the decrease in the partial pressure of CO_2 which would occur during such a breach, to possibly explain the maintenance of the Powder River Basin Cretaceous fluid compartment. MacGowan et al. (1994) presented geochemical models which suggested the boundary conditions for such a mechanism. They also presented a photomicrograph of a Cretaceous Muddy Sandstone sample from near a seal, wherein this rock sample had calcite-filled fractures.

We note that the observed characteristics of, and explanations for, the formation of pressure seals all correspond to the results to be expected from the hypothesis of hydrolytic disproportionation of OM, to wit: A HC phase, or HCS dissolved or entrained in an aqueous phase, move through a fracture in a pressure seal, from an abnormally-pressured fluid compartment, into waters in another fluid compartment. If the HCS were not in metastable equilibrium with the aqueous fluids in their new environment, hydrolytic disproportionation between water and the HCS would be expected to commence. One of the major end products of the process is isotopically lighter CO_2, which under the proper pH conditions, could lead to the precipitation of carbonate in the breach of the seal. The association of oil, or degraded oil, with the cements forming these seals, as observed by Donovan (1974) and Whelan et al. (1994), is evidence supporting the hypothesis of a cause and effect relationship between the oil and cements. We note that it is most difficult to explain the origin of such large volumes of late-stage carbonate cement with isotopically-light carbon in petroleum basins, wherein much of this carbon clearly originated from OM. This is because there is no known process or reaction in petroleum geology and geochemistry which can account for this isotopically-light carbonate carbon in all these different, and anhydrite-free, geologic environments, where thermochemical-sulfate reduction cannot be called on as a source of the isotopically-light carbonate. Hydrolytic disproportionation of OM solves this paradox.

5.045 Secondary Porosity

The occurrence of secondary porosity at depth in sedimentary basins is of pivotal economic importance; however, the processes responsible for the formation of secondary porosity are largely unknown. As Surdham et al. (1994, p. 127) note: "The discovery of secondary porosity in sandstone has been the most significant advance in the study of clastic diagenesis in the past decade". However, the mechanism leading to the formation of secondary porosity is an unknown. Franks and Forester (1984, p. 63) note: "Despite the importance of the concept of secondary porosity development in sedimentary basins, the actual physical and chemical processes for its development are poorly understood". Surdham et al. (1984, p. 127), and numerous other authors, make similar observations.

5.0451 Origin of Early Calcite

Three significant problems exist with the concept of secondary porosity. The first of these is the origin of the calcium in the calcite which is often precipitated early in the diagenetic history of sandstones, and then is dissolved later to create secondary porosity. Much of the earliest work on secondary porosity was carried out in U.S. Gulf Coast sediments, some of which involved mass balance considerations. The source of the early porosity-plugging calcite cements is agreed to be from shales interbedded with the sands; and different studies (including Hower et al., 1976; Land et al., 1997) have documented large losses of calcite from Gulf Coast shales with increasing burial depth. However, the source of the acid to dissolve and remove the calcite from the shales has gone unrecognized.

As Land et al. (1987) noted, there is not enough OM in Gulf Coast shales (which contain an average less than 0.5% total organic carbon, Galloway et al., 1982) to generate enough CO_2 (during the HC generation reactions) to create enough hydrogen ions (via the bicarbonate reaction) to dissolve the calcite in the shales for transport from the shales to the sandstones. Land and Fisher (1987) and Land et al. (1997) amplify on this problem. Land (1984, p. 60) observed: "The acid volume problem" together with the relatively ^{13}C-rich Gulf Coast carbonate cements indicates that reactions other than oxidation and decarboxylation must be involved. The reaction: kerogen $+H_2O \text{-->} CO_2+CH_4$ is an attractive possibility...". Land et al. (1987, 1997) invoked the same reaction to circumvent the acid problem and explain the relatively depleted $\delta^{13}C$ isotopic ratios of Gulf Coast carbonate cements. (Note that in the quote directly above, Land (1984, p. 60) meant ^{13}C-depleted not "^{13}C-rich" Gulf Coast carbonate cements).

In our opinion, Land and coworkers were correct in assuming this type of a reaction to explain the excess acid required to dissolve carbonate from the shales, and moved it to adjacent sands to form the shallow "carbonate curtain" in Gulf Coast sediments (Schmidt and McDonald, 1979). Unfortunately, there is no such reaction recognized in petroleum geochemistry. On the other hand, the hydrogenation of kerogen via hydrolytic disproportionation of OM with the huge resultant excess of CO_2, as discussed above, is exactly the reaction which Land and coworkers have invoked. Thus, hydrolytic disproportionation of OM could be the answer to the "acid problem" in moving $CaCO_3$ from shales to sandstones at shallower depths.

5.0452 The Acid Problems

Two other problems remain with the creation of secondary porosity: 1) the dissolution of plagioclase grains during this event, and 2) another acid problem regarding the dissolution of pore-plugging calcite from the sandstones to create secondary porosity. Regarding the first point, Surdham et al. (1984) note that solution of plagioclase grains, and transport of the dissolved aluminum, cannot be accomplished by "known solutions" in sedimentary basins. Solutions with elevated CO_2 levels, and the resulting species thereof, cannot dissolve plagioclase and move aluminum. To address this problem, Surdham et al. (1984) performed two-week experiments at 100°C, wherein they dissolved plagioclase grains using carboxylic acid solutions. They found extensive solution of plagioclase grains with these solutions, with the resultant partially-dissolved grains having the same morphology as partially-dissolved, naturally-occurring grains. However, the acid concentrations they employed, appeared to be uncharacteristically high compared to values found in Nature. On the other hand, these investigators apparently did not perform equilibrium approach experiments, as such experiments were not discussed in their paper. Thus longer experimental times at lower acid concentrations may result in similar levels of plagioclase solution as observed in the Surdham et al. (1984) experiments.

Surdham et al. (1984) also carried out the same experiments with dicarboxylic acids and found them to be much more effective than carboxylic acids in the dissolution of plagioclase. They concluded that carboxylic, and especially dicarboxylic acids, may play a key role in the formation of secondary porosity. However, Surdham et al. (1984, p. 135) qualify that: "A key element in building diagenetic models that include organic diagenesis is the determination of the organic acid generative potential of kerogen. To our knowledge there is no experimental evidence available that allows this determination to be made directly". Surdham et al. (1984, p. 145) proposed: "The reduction of mineral oxidants and consequent oxidation of organic matter may be more effective in releasing peripheral disfunctional carboxylic acid groups than thermal degradation". Franks and Forester (1984, p. 76) also call for the possible oxidation of OM to explain their observations and conclusions regarding the development of secondary porosity. We note, as with Land and coworkers who (directly above) called for oxidation of OM, that there is no recognized process in sedimentary basins which results in such widespread oxidation of OM. Hydrolytic disproportionation of OM would result in such an oxidation (and concurrent reduction) of OM. We further relate the observations and hypotheses of Surdham et al. (1984) to hydrolytic disproportionation of OM below.

The last problem to discuss concerning secondary porosity is a second acid-volume problem, to wit: Where does the acid, which actually creates the secondary porosity in sandstones by dissolving calcite (not to mention plagioclase), actually come from? Lundegard (1983) concluded, based on mass balance considerations, that CO_2 formation during HC generation in Gulf Coast (Frio Formation) shales was insufficient to account for the development of secondary porosity. Other investigators have drawn the same conclusion, including Franks and Forester (1984).

We note, as discussed above, that, CO_2 is one of the principal end products of hydrolytic disproportionation, the other being low molecular weight organic compounds, especially methane. From Tables 4 and 5, ester-bearing carboxylic acids, and especially dicarboxylic acids, are also significant products of hydrolytic disproportionation. We have not yet extracted and analyzed the C_4-C_9 HCS from our rocks. However, we suspect that lower-molecular-weight carboxylic and dicarboxylic acids make up a significant portion of this fraction by weight. Experiments are being designed to test this hypothesis. Be that as it may, we note that the principal chemical agents called upon by numerous investigators for the creation of secondary porosity are the principal products of hydrolytic disproportionation.

Shebl and Surdam (1996) carried out pivotal experiments whose results are both predicted and explained by the theory of hydrolytic disproportionation of OM. They reacted hematitic Pennsylvanian Tensleep Sandstone samples both with water and Tensleep oil in various combinations at variable temperatures. Oil-water and rock-water experiments served as baseline companions for the results from the rock-oil-water experiments, wherein by far the most striking results were obtained.

In these latter experiments: 1) The iron oxides in the sandstones were reduced to pyrite and sandstone color thus turned from red to gray. Shebl and Surdam (1996) noted that the measured Eh values from the waters, after the experiments, demonstrated that the waters from all the rock-water-oil experiments were very reducing. They also noted that in most core samples of Tensleep sandstone reservoir rocks from the natural system, extensive bleaching had occurred and pyrite was the common iron species. 2) Excess CO_2 was produced (compared to the baseline experiments) along with both low and high molecular weight organic acids, the acids not being present in the original oil. 3) Significant increases in porosity also occurred in these experiments from dissolution of feldspars, volcanic rock fragments, and mainly carbonate cements. 4) The crude oil was significantly oxidized, going from a pre-experiment 0.11 weight-percent oxygen to a post-experiment value of 0.92%. 5) The altered oil became preferentially enriched in C_7-C_9 HCS at the expense of a decrease in C_{10}-C_{25} HCS. This last characteristic was also observed in the saturated HC gas chromatograms of this study (Figs. 1 and 2, especially 979-1 in Fig. 2).

5.0453 Secondary Porosity from Hydrolytic Disproportionation of OM

We propose that as oil and/or gas is expelled from its source rock, to begin secondary migration towards a trap, the HC phase progressively encounters aqueous fluids with which it may not be in thermodynamic equilibrium. If so, hydrolytic disproportionation between the HCS and waters would commence, resulting in an acidic front (from CO_2 and carboxylic acids) being created at the front of the migrating HC phase, as the HCS and water attempt to bring themselves into thermodynamic equilibrium. When the migrating HCS encounter a possible reservoir unit with pore-plugging calcite cement, the acidic front of the migrating HC phase dissolves the calcite, and some silicates. Thus a significant part of the migrating HCS may be "self cannibalized" via hydrolytic disproportionation of these HCS to create their own reservoir porosity.

Secondary porosity appears to be inferred as a process which has simultaneously affected large volumes of sandstone, regionally, or subregionally. However, most sandstone core for study comes from HC productive intervals. Thus, our view of secondary porosity may be biased, and secondary porosity may not be so widespread at all, but instead may be largely limited to the rock volumes in which the HCS reside, or through which they have passed. This viewpoint is supported by the observation of Shebl and Surdam (1996) that the minerals in oil-bearing Tensleep sandstone in Nature have been preferentially reduced, e.g., taken part in hydrolytic disproportionation reactions. If hydrolytic disproportionation of OM plays a major role in the creation of secondary porosity, which we envision it may do, then a simplified model of secondary porosity presents itself, because the HCS are creating their own porosity.

5.05 REACTIONS

5.051 Introduction

Attempting to write chemical reactions to account both for the observed distributions of compound classes and for the compounds of Tables 4 and 5 carries some qualifications. First, we have identified only a limited number of oxidized organic compounds in the aromatic-HC fractions of only three samples (Table 4) and only five peaks from the resin fractions (Table 5). Many prominent peaks are still unidentified in both fractions. Moreover, the lower-molecular-weight (C_{10}-) compounds have not been examined at all, and it is likely that compounds that would provide key insights into reaction pathways are present in this molecular weight range. Second, it is probable that intermediate products in the reactions are no longer present in our bitumens, again obfuscating reaction pathways. Third, hydrolytic disproportionation involves equilibrium between water, OM, and mineral phases. We have no way of determining what changes in mineral phases have occurred in most of our samples, and thus can not consider how minerals may have participated in the reactions. Lastly, our samples were at one time at elevated temperatures and pressures. Under such conditions, the aqueous solubilities of oxygen-bearing organic compounds would be quite high (Price, 1976). Because all our samples were from open-fluid systems, loss of the most water-soluble organic compounds is a strong possibility, yet further obfuscating reaction pathways. However, in spite of these limitations, some insights do exist into the organic-chemical reactions responsible for the bitumens of our study.

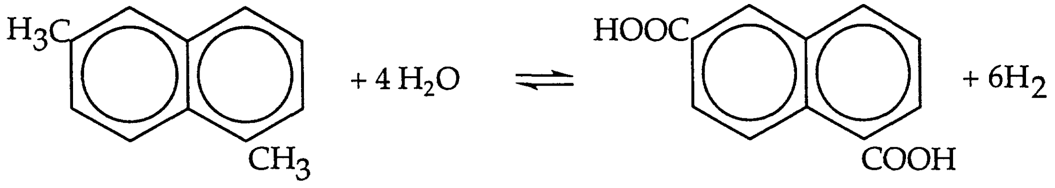
5.052 Relative Reactivities-Aromatic HCS

Several compositional observations of our bitumens are relevant. First, methylated benzenes are in higher concentrations than all other classes of aromatic HCS in our samples. Second, the methylated naphthalenes are in the lowest concentrations of all the aromatic HC compound classes. Third, the methylated phenanthrenes while in significantly higher concentrations than the methylated naphthalenes, are in low relative concentrations in many of our samples and missing completely in others. It is noteworthy that the relative abundances of the aromatic-HC compound classes in our samples inversely correspond to the relative reactivities of the three compound classes in well-documented organic-chemical oxidation-reduction reactions (Brewster, 1949; Roberts and Caserio, 1964; Morrison and Boyd, 1975; and McMurry, 1996). For example, Morrison and Boyd (1975, p. 384) note, "...benzene and alkanes are quite unreactive toward the usual oxidizing agents....". Morrison and Boyd (1975, p. 970) also note, "Naphthalene undergoes oxidation or reduction more readily than benzene, but only to the stage where a substituted benzene is formed; further oxidation or reduction requires more vigorous conditions". They also observe that the resonance energy for naphthalene is 61 kcal/mole versus 36 kcal/mole for benzene. Thus, 25 kcal/mole of resonance energy is sacrificed to break the first benzene ring in naphthalene versus 36 kcal/mole for the second benzene ring. Regarding the phenanthrenes, Morrison and Boyd (1975, p. 989) state, "Anthracene and phenanthrene are even more resistant toward oxidation or reduction than naphthalene". Thus, the relative concentrations of the methylated-benzenes, -naphthalenes, and -phenanthrenes in our samples are explained by the relative reactivities of the three compound classes.

5.053 Naphthalene Oxidation

Although single benzene rings, or even benzene rings in polynuclear aromatic HCS, are fairly resistant to oxidation, alkyl side chains on benzene rings are not: "....the benzene ring renders an aliphatic side chain quite susceptible to oxidation. The side chain is oxidized down to the ring, only a carboxyl group (-COOH) remaining to indicate the position of the original side chain.", Morrison and Boyd (1975, p. 384).

Thus, alkyl side chains on benzene, naphthalene, and phenanthrene rings might be easily oxidized to carboxylic acid groups, for example:

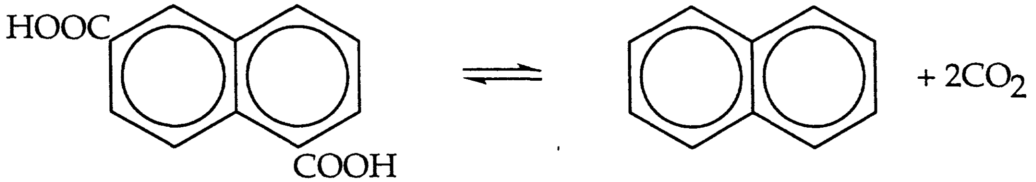


(6).

4, 7-Dimethylnaphthalene

4, 7-Naphthalene dicarboxylic acid

In turn, the dicarboxyclic acid could undergo decarboxylation to naphthalene,

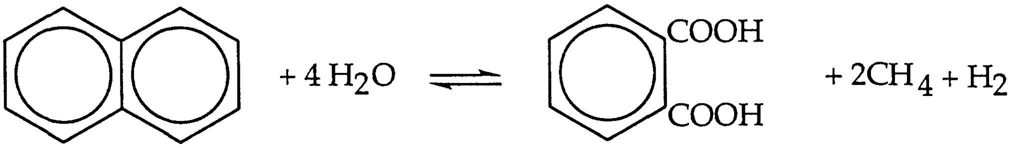


(7).

4,7-Naphthalene dicarboxylic acid

Naphthalene

As Morrison and Boyd (1975, p. 584-585) note, "The most important of the carboxylic acids, benzoic acid and the phthalic acids, are prepared on an industrial scale by....oxidation of alkylbenzenes.....; another precursor of phthalic acid (the ortho isomer) is the aromatic hydrocarbon naphthalene....".
Thus,

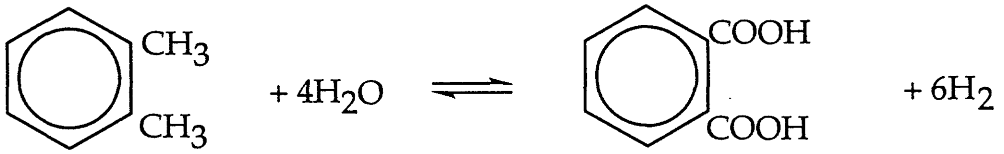


(8),

Naphthalene

1,2 Benzenedicarboxylic acid

or



(9).

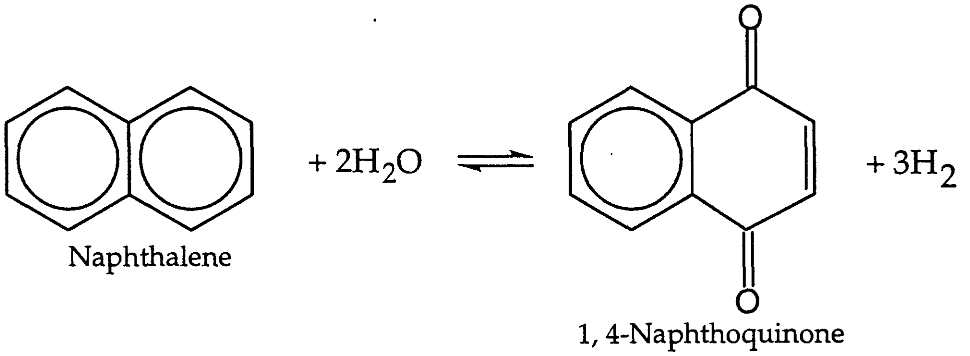
Orthoxylene

1,2-Benzenedicarboxylic acid

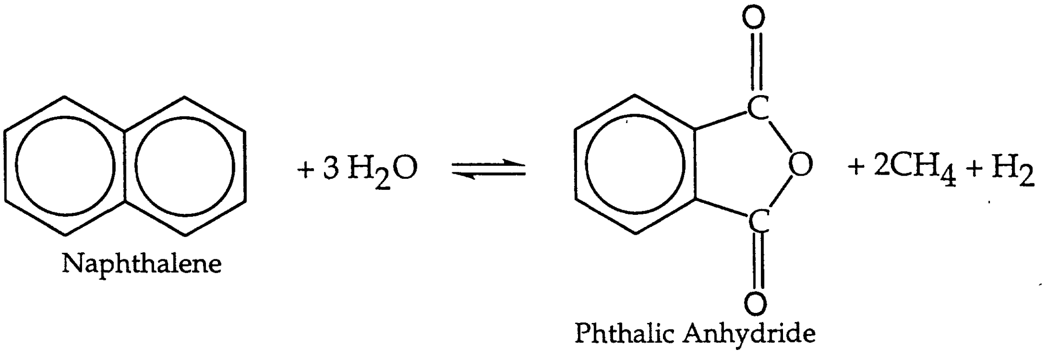
Note that three of the four large peaks in the resin fraction whole-ion fragmentograms of Figure 11 are 1,2-benzene dicarboxylic acid esters (Table 5), compounds which are also present in the aromatic-HC fraction (Table 4). Recall that the resin fractions of our samples make up the largest, or second largest, compound group of our bitumens by weight. Thus, the 1,2-benzenedicarboxylic acid esters make up an inordinate relative amount of the bitumens. These compounds could have originated from either oxidation of 1,2-dimethylbenzene (ortho xylene) or naphthalene.

Note that in Figures 5 and 6, in samples where significant evaporation has not occurred (such as in samples MF-647 and MF-898), in all but one sample (507C, Fig. 5), naphthalene (peak 44) is a larger peak than all the methylated naphthalenes. Moreover, in the one exception, only one methylated naphthalene (2-methylnaphthalene, peak 73) is slightly larger than naphthalene. This observation is exactly the opposite of the situation in oils and bitumens from sedimentary rocks, as represented by Figure 4, wherein naphthalene (peak 44) by far is a much smaller peak than all the other methylated naphthalenes (methyl-naphthalenes, peaks 73, 77; dimethylnaphthalenes, peaks 99-106; and trimethyl-naphthalenes, peaks 123-129). These two observations suggest to us that in our samples naphthalene is either being preferentially preserved relative to the methylated naphthalenes, or is being created, by reactions 6 and 7, as an intermediate product to the 1,2-benzenedicarboxylic acid esters. We favor the second possibility. The small relative concentrations of ortho xylene in our samples (peak 3, Figs. 5 and 6) does not suggest formation of ortho xylene as an intermediate product to the dicarboxylic acid esters. Moreover, only a limited amount of ortho xylene would originally have been present in our samples to be converted to the 1,2-benzenedicarboxylic acid esters. Thus, we conclude that the disappearance of the methylated naphthalenes and the very high relative concentrations of various 1,2-benzenedicarboxylic acid esters in our samples are due to variants of reactions 6-8. The conversion of the product of reaction 8 (1,2-benzenedicarboxylic acid) to the acid esters of Tables 4 and 5 is discussed below.

Morrison and Boyd (1975, p. 971) note that two other major reaction pathways exist for the oxidation of naphthalene, with the products being 1,4-naphthoquinone and phthalic anhydride. Thus,

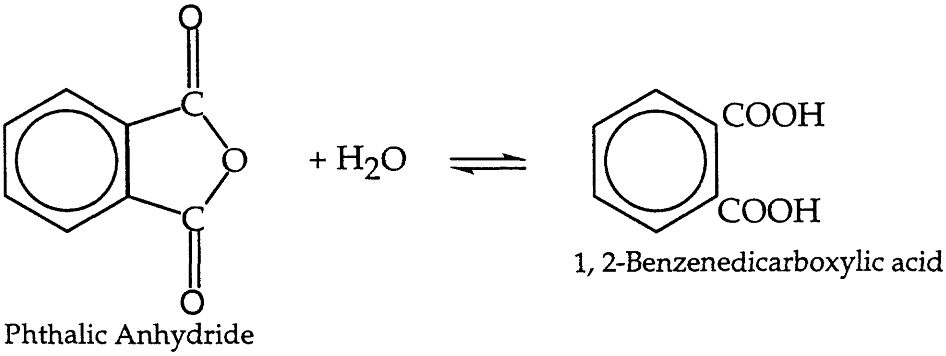


(10); and



(11).

Anhydrides can be converted into acids by hydrolysis (Morrison and Boyd, 1975, p. 668),

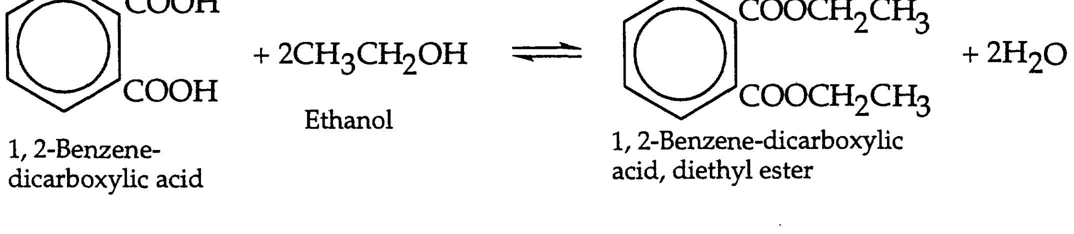


(12).

1,4-Naphthoquinone was not identified in our assemblage of oxidized hydrocarbons (Tables 4 and 5) in our cursory first-pass attempt at qualitative analysis. However, as discussed below, the presence of 9,10-phenanthrenedione (9,10-phenanthrene quinone; peak 18, Table 4) in our samples suggests to us that 1,4-naphthquinone will also eventually be identified in our bitumens. The presence of peak 8 (Table 4), 2,5-cyclohexadiene-1,4-dione-bis (1,1-dimethylethyl)-, which is 2,6-tertiary butyl substituted para-benzoquinone, suggests that benzoquinone, and other substituted variants thereof, may also be present in our bitumens. Thus, the benzene, naphthalene, and phenanthrene quinones may all be important components of our bitumens.

5.054 Ester Formation

"Esters are usually prepared by the reaction of alcohols or phenols with acids or acid derivatives, Morrison and Boyd (1975, p. 672). Thus, the 1,2-benzenedicarboxyclic acid esters (peaks 11, 23, 31 of Table 4; and peaks 3-6 of Table 5) could be derived by reaction of 1,2-benzenedicarboxylic acids with the respective alcohols, for example,



(13).

"If an organic chemist were allowed to choose ten aliphatic compounds with which to be stranded on a desert island, he would almost certainly pick alcohols. From them he could make nearly every other kind of aliphatic compounds: alkenes, alkyl halides, ethers, aldehydes, ketones, acids, esters, and a host of others.", Morrison and Boyd (1975, p. 497). Those authors also note that hydration of alkenes and fermentation of carbohydrates are the two principal methods to obtain alcohols. The latter reaction would not have been possible in our samples. However, Seewald (1994) demonstrated reversible metastable equilibrium between ethane and ethene in his experiments;

$$\underset{\text{ethane}}{C_2H_6} \Leftrightarrow \underset{\text{ethene}}{C_2H_4}+H_2 \qquad (14).$$

Hydration of the ethene could then produce the alcohol:

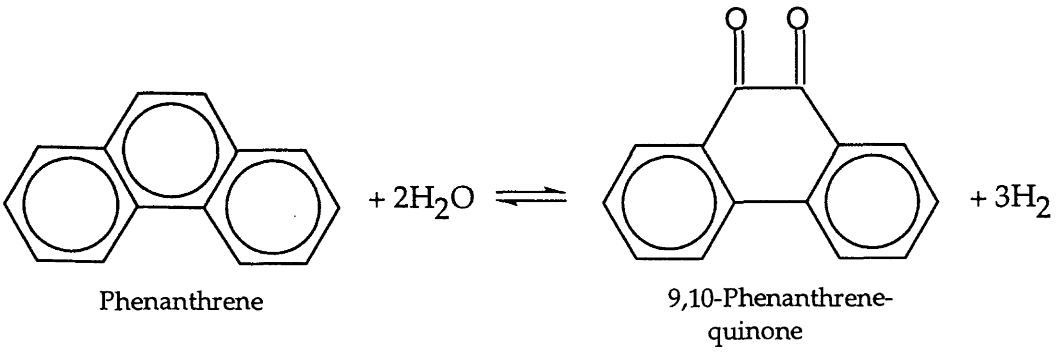
$$\underset{\text{ethene}}{C_2H_4}+H_2O \Leftrightarrow \underset{\text{ethanol}}{CH_3CH_2OH} \qquad (15).$$

Alkene-bearing aliphatic HCS, and other organic compounds with alkene bonds, exist within the compounds we have identified (peaks 15, 32, and 34, Table 4; and peak 2, Table 5), suggesting alkene formation in the bitumens of our samples via variants of reaction 14.

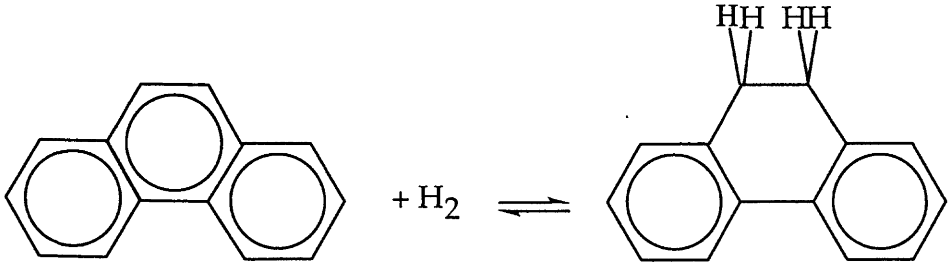
Another possible example of an acid-alcohol reaction to produce an ester within the compounds we have identified, would be benzoic acid and benzl alcohol going to the respective phenyl methyl ester (peak 16, Table 4).

5.055 Phenanthrene Oxidation

As discussed above, both anthracene and phenanthrene are more resistant to oxidation than naphthalene. However, as Morrison and Boyd (1975, p. 989-990) note, both three-ring compounds can be oxidized to the 9,10 quinones or reduced to the 9,10-dihydro compounds:



(16),

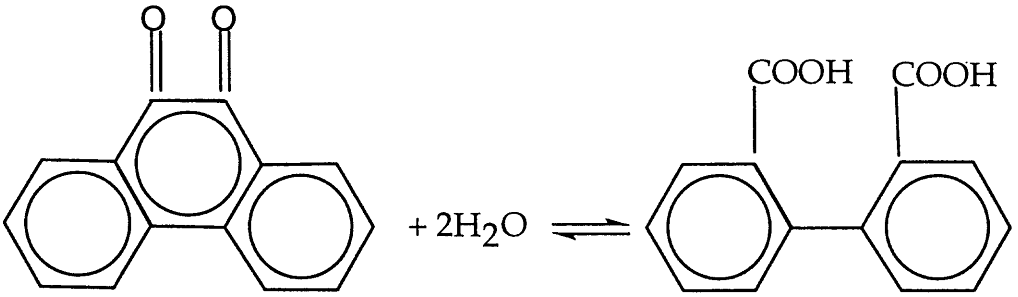


Phenanthrene 9, 10-Dihydrophenanthrene

(17).

Morrison and Boyd (1975, p. 989-990) also observe that attack at the 9,10 position of phenanthrene leaves two benzene rings intact, with a sacrifice of only 20 kcal of resonance energy, leaving 72 kcal of resonance energy intact. We identified 9,10-phenanthrenequinone in our bitumens (peak 18, Table 4), strongly suggesting to us that reaction 16 occurred, via hydrolytic disproportionation, within our samples. Two octahydro-phenenanthrene-based compounds were also identified in our bitumens (peaks 27 and 28, Table 4), one an aldehyde, the other an acid ester, suggesting that concurrent reduction and oxidation of phenanthrene group compounds took place in our samples.

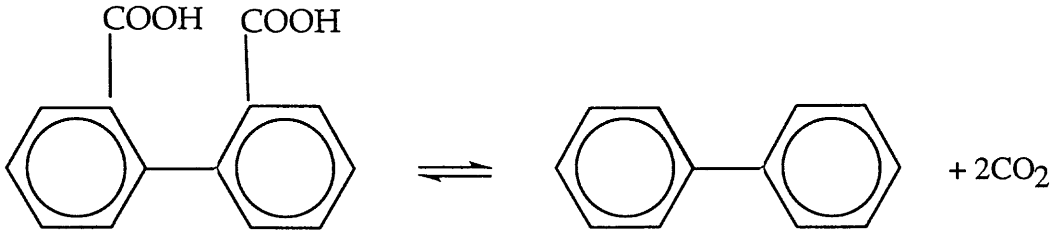
Brewster (1949, p. 699) notes that oxidation of 9,10-phenanthrenequinone yields diphenic (dicarboxylic) acid. Thus,



9, 10-Phenanthrene-quinone Diphenic acid

(18).

Subsequent decarboxylation of diphenic acid would yield diphenyl (biphenyl),



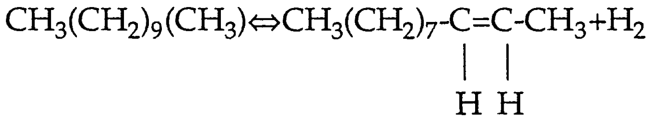
Diphenic acid Diphenyl

(19).

Biphenyl was either the, or one of the, major peaks in all our aromatic-HC gas chromatograms (Figs. 5 and 6, peak 95). Moreover, various biphenyl derivatives were also identified in our bitumens (Table 4). The different methylated variants of phenanthrene (peaks 196-200 and 218-224, Table 3) could undergo oxidation to carboxylic or dicarboxylic acids, with subsequent decarboxylation to phenanthrene, via reactions similar to reactions 6 and 7. Also, the methylated phenanthrenes could undergo direct oxidation to methylated 9,10-phenanthrenequinones with subsequent conversion to a methylated diphenic acid and thence to a methylated biphenyl via reactions similar to reactions 17, 18, and 19. That this latter reaction pathway may have been viable, at least in some cases, is suggested by the presence of alkylated biphenyls in our bitumens (peaks 9 and 13, Table 4). Püttmann et al. (1989) also explained the high biphenyl concentrations they observed in their bitumens from Kupferschiefer mineralization in SW Poland as due to phenanthrene oxidizing to 9,10-phenanthrenequinone, which in turn oxidized to biphenyl acid, which then underwent decarboxylation to biphenyl (reactions 17, 19, and 20). They noted that this was a well-established organic-chemical reaction pathway.

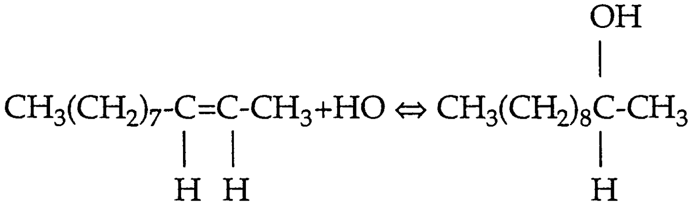
5.056 Ketones

Morrison and Boyd (1975, p. 529) note that secondary alcohols can be oxidized to ketones. Several aliphatic ketones with the ketone bond in the number 2 position were identified in our bitumens (peaks 8, 12, and 17, Table 4). In the case of 2-undecanone, the reaction sequence might be



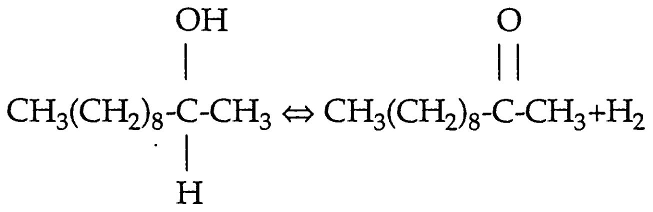
$$CH_3(CH_2)_9(CH_3) \Leftrightarrow CH_3(CH_2)_7\text{-}\underset{H}{\underset{|}{C}}{=}\underset{H}{\underset{|}{C}}\text{-}CH_3+H_2 \quad (20),$$

Undecane 2-undecene



$$CH_3(CH_2)_7\text{-}\underset{H}{\underset{|}{C}}{=}\underset{H}{\underset{|}{C}}\text{-}CH_3+HO \Leftrightarrow CH_3(CH_2)_8\overset{OH}{\overset{|}{\underset{H}{\underset{|}{C}}}}\text{-}CH_3 \quad (21),$$

2-undecene 2-undecanol



$$CH_3(CH_2)_8\text{-}\overset{OH}{\overset{|}{\underset{H}{\underset{|}{C}}}}\text{-}CH_3 \Leftrightarrow CH_3(CH_2)_8\text{-}\overset{O}{\overset{||}{C}}\text{-}CH_3+H_2 \quad (22).$$

2-undecanol 2- undecanone

Although only three aliphatic ketones have been thus far identified in our samples, we suspect that homologous series of these compounds exist within our samples.

Moreover, as discussed above, Püttmann et al. (1989) identified aromatic ketones (Fig. 17) in their study of Polish Kupferschiefer samples. Variants of reactions 21 to 23 could be responsible for the preferential loss of the n-C_{10} to n-C_{20} n-paraffins observed in many of our samples (Fig. 2).

5.057 Phthalates

Phthalate is a general term to designate various oxygen-bearing derivatives of the phthalic acids (aromatic carboxylic, or poly-carboxylic acids). Various phthalic acids, including dicarboxylic acids, are used in the manufacture of plastics and also as plasticizers to keep plastics from becoming brittle (Morrison and Boyd, 1975; Roberts and Caserio, 1964; McMurry, 1996). Various phthalates can arise as contaminants in organic-chemical or geochemical laboratory procedures, wherein organic solvents come in contact with some form of plastic. Hence, any phthalate delineated by organic-geochemical analyses, historically, immediately has been attributed to contamination. Some high-boiling esters (e.g., octyl phthalates) are manufactured specifically as plasticizers, and are indicative as contaminants. However, other phthalic acids, and derivatives thereof, can also be naturally-occurring materials. Doubtless, some (many?) investigators will immediately attribute the phthalic acid derivatives in our samples to contamination from plastic. However, to immediately attribute the existence of phthalates in our samples to contamination from plastic can be likened to attributing the presence of C_{22}+ n-paraffins in bitumen from natural samples solely to contamination from wax. The hallmark of hydrolytic disproportionation of OM is redox reactions of OM with water. Oxidation of aromatic HCS yields products that are dominated by phthalates.

The same phthalic-acid ester derivatives we report on are present in all the samples we have analyzed thus far, including over 80 samples not in this report. However, repeated laboratory background contamination checks, wherein blank samples are/have been subjected to the full analytical workup, have never yielded these same peaks. Thus, if contaminants, these phthalic acid esters would have to have originated as contaminants *within* the interior of our samples, because the outsides of our samples were thoroughly rinsed with solvent in all cases. That the same 6 or 7 phthalic acid esters, out of all those possible, would repeatedly arise as major contaminants interior to our samples would appear as prohibitively improbable. Lastly, other investigators have also reported phthalate occurrences. Rickard et al. (1975) in their study of the OM at the MVT lead-zinc deposit at Laisvall, Sweden, found phthalates in their samples which they attributed to contamination. Püttmann et al. (1989) in their Kupferscheifer study found a phthalate in their samples and hypothesized its occurrence due to contamination from storage and handling of samples.

However, a telling phthalate occurrence was reported by Bechtel and Püttmann (1991) in another study of the Kupferscheifer, wherein they found a whole series of phthalates in the saturated HCS of their samples. Moreover, the relative phthalate concentrations were proportional to the degree of alteration of their samples (Fig. 21). Thus, phthalate concentrations were highest in the highly-mineralized Rote Fäule zone and decreased as one moved away from this zone. In Figure 21, by aligning the phthalate peaks in the Rote Fäule gas chromatogram with the peaks in the other two chromatograms using a straightedge, it becomes evident that the same phthalate peaks are in the other two gas chromatograms, only in reduced concentrations. That these phthalate concentrations increase with increasing intensity of ore deposition (Fig. 21), strongly suggests that the phthalates have originated from the ore-deposition process, and thus are indigenous to the rock, as opposed to being contamination. Bechtel and Püttmann (1991) did not attribute these phthalates to contamination.

5.058 Water-Organic-Compound Reactivity

Siskin and Katritzky (1991) provided an insightful overview of increasing reactivity of water with organic compounds, with increasing temperature, and the geochemical and technological implications thereof. They noted that by conventional wisdom, most organic compounds are not thought to react with water; but when system temperatures are raised to 250° to 350°C, reactions thought not to occur, proceed facilely. As they observe, when system temperature rises from 25° to 300°C, water density decreases from 0.997 to 0.7813 gm/cc, the dielectric constant falls from 78.85 to 19.66, the solubility parameter decreases from 23.4 to 14.5 $(\text{cal/cc})^{1/2}$, and the dissociation constant increases from $10^{13.99}$ to $10^{11.30}$. Siskin and Katrisky (1991) remark that these changes in physical properties make the solvent properties of water at 300°C roughly equivalent to acetone at 25°C, thus increasing the favoribility of ionic reactions of organics in water. Moreover, the increase in the disassociation constant of water will increase the rate of acid- and base catalyzed reactions in water far above the effect from just the increase in temperature.

Pivotally, Siskin and Katrizky (1991, p. 232) state, "Ionic chemistry predominates as high-temperature water opens reaction pathways that are alternate to and preferred over thermal (free radical) routes. This ionic chemistry is often facilitated in brine". Roberts and Caserio (1964, p. 178) discuss carbonium ion formation and reactivity, wherein a positively charged unstable carbon cation is formed within a HC, or other organic compound. Because the carbonium ion is unstable, it will quickly react with a negatively charged species. Carbonium ions thus provide a pathway wherein covalently-bonded organic compounds may react with ionic species. Siskin and Katritsky (1991) give numerous examples of elevated-temperature (100°-350°C) reactions of organic compounds in water carried out in the laboratory and discuss application of their observations to various aspects of petroleum geochemistry, especially to oil and gas generation via kerogen degradation. For example, they note that even in high-temperature water, biphenyl type linkages in kerogen are unreactive. Biphenyl was one of the major constituents of our bitumens, suggesting that it is a stable end product of the hydrolytic disproportionation reactions responsible for our bitumens. The observations of Siskin and Katrisky (1991) concerning ionic-based reactions between water and OM at elevated temperatures in both laboratory and

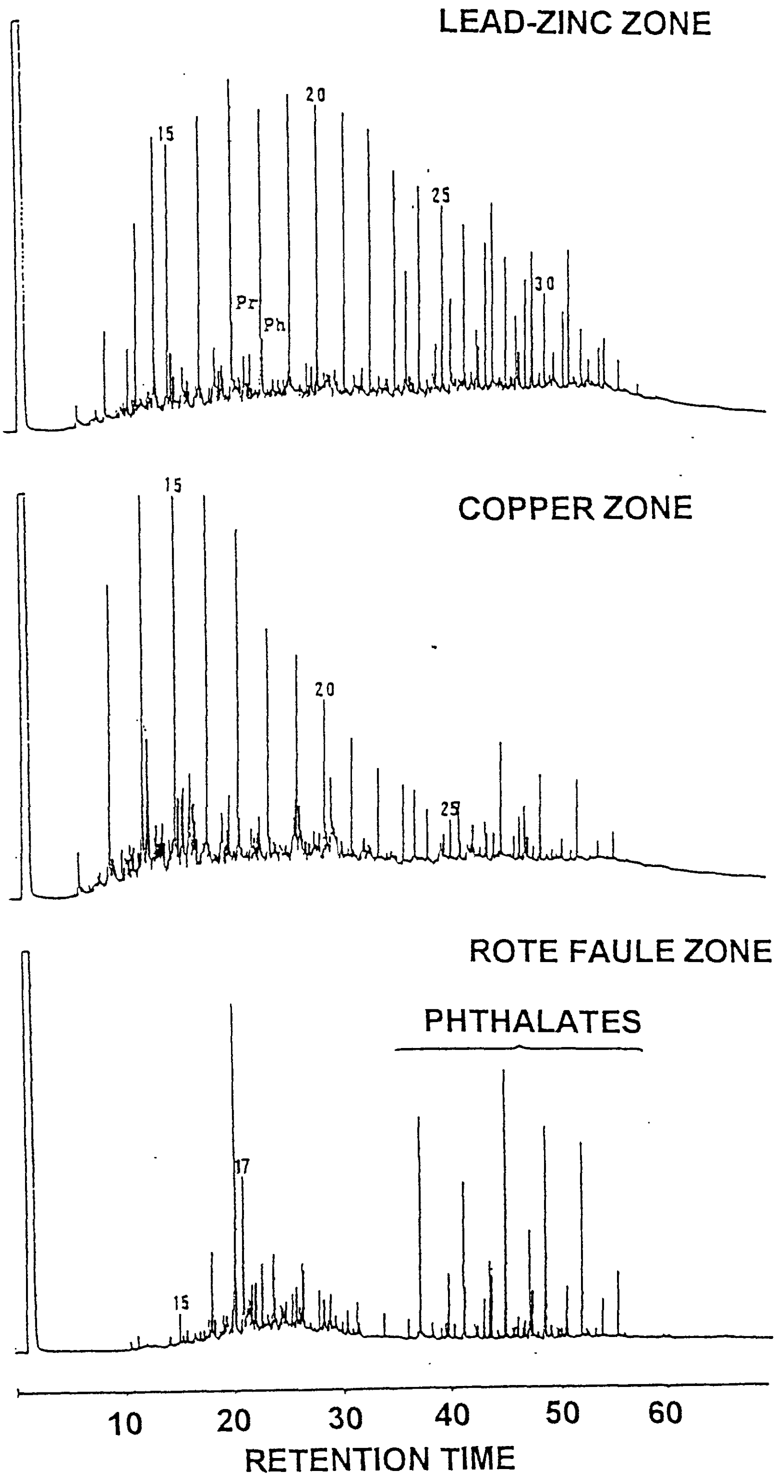


Figure 21. A series of saturated-HC gas chromatograms from Kupferscheifer mineralization, with increasing mineralization intensity downward. Numbers on the peaks are n-paraffins; PR is pristane; PHY is phytane.

petroleum geochemical situations is strong support of the hypothesis of hydrolytic disproportionation of OM (Helgeson et al., 1993).

The above discussion on reaction pathways demonstrates that the limited number of unusual compounds we have identified in our bitumens are formed by well-established ("mainstream") organic-chemical reactions, most of which are ionic-based redox reactions. That ionic-based reactions between water and HCS, and other organic compounds, easily proceed in high-temperature salty water (Siskin and Katritsky, 1991) leads us to hypothesize that hydrolytic disproportionation of OM takes place via ionic-based reactions. These observations, and the fact that oxidized HCS are predicted by the hypothesis of hydrolytic disproportionation of OM, strongly support our contention that our bitumens are both the result of, and provide evidence for, the widespread operation of hydrolytic disproportionation of OM in Nature. Moreover, research is underway to identify a much greater number of the organic compounds, including C_2-C_{10} compounds, in both the bitumens of this study, and from subsequently-extracted samples. With such identification, a much better understanding of the reaction pathways involving hydrolytic disporportionation of OM should be possible.

5.06 REVIEW - CHARACTERISTICS OF AND EVIDENCE FOR THE HYDROLYTIC DISPROPORTIONATION OF OM NATURE

5.061 Bitumens of This Study

Petroleum-like saturated HCS, including biomarker compounds, exist in: 1) the rocks of this study, some of which have been as high as 480°C, 2) subsequent rocks we have analyzed, which have been at much higher temperatures, and 3) the samples of both Sugisaki and Mimura (1994) and Laier and Nytoft (1995), both suites of which have been at extreme temperatures. None of the C_{15}+ saturated HCS from samples of any of these studies exhibit signs of thermal stress. The HCS in our Swiss Alps samples demonstrate no maturity variations versus large temperature differences, and the full suite of oil-like biomarkers, some of which are equivalent to those in moderately immature oils, are in all our samples. All these observations are completely unexpected and have no apparent explanation by existing paradigm. Moreover, these observations dictate that HC thermal cracking has been suspended in all these samples. In other words, these HCS appear to have been at equilibrium in their systems. By the hypothesis of hydrolytic disproportionation of OM, C_{15}+ HCS are predicted (Helgeson, 1991) to be metastable to far greater temperatures than expected by accepted paradigm (Hunt, 1979; Tissot and Welte, 1984). Giggenbach (1997) also proposed that HCS could be stabilized to unexpectedly high temperatures by redox reactions with minerals and water.

The aromatic-HC compositions in the samples of this study are most unusual. Such compositions have never been reported from sedimentary rocks from petroleum basins. Many prominent peaks in our aromatic-HC gas chromatograms are either unidentified or have been identified as compounds never prominent, if even present at all, in aromatic HCS from sedimentary rocks. Moreover, the dominant aromatic HCS, always present in oils and sediment bitumens (methylated-naphthalenes and phenanthrenes), were always in low relative concentrations, or missing altogether, in the bitumen of our rocks. Even when present in our samples, these compounds have unusual peak distributions not present in oils and sediment bitumens. These observations, in our opinion, can only be explained by very selective chemical reactions, examples of which were discussed above. Even more telling, oxidized saturated and aromatic HCS are in high relative concentrations in our aromatic-HC fractions and may completely make up the resin fractions, in all our samples. The compounds we have identified may be present in oils and sediment bitumens in low concentrations; however, they have not previously been identified therein to our knowledge. Their presence, in high relative concentrations, demonstrates that the chemical equilibria of the C_{10}+ fraction of our bitumens has fundamentally shifted from the reduced state of sediment bitumens and oils to a more oxidized state. Oxidation of the C_{10}+ fraction of bitumens, with an increase in the relative concentrations of the more reduced C_{10}- fractions of rock bitumens, is predicted by the hypothesis of hydrolytic disproportionation (Helgeson et al., 1993). The presence of high relative concentrations of oxidized HCS in our sample is compelling evidence, in our opinion, supporting the hypothesis of the hydrolytic disproportionation of OM (Helgeson et al., 1993).

Within our HCS, the alkylated benzenes remain in decidedly higher concentrations than the methylated phenanthrenes. The methylated naphthalenes are often missing altogether. This observed distribution of compound groups can be attributed to the relative reactivity of the aromatic rings to redox reactions, with the naphthalenes being the most reactive, followed by the phenanthrenes, and the single-ring benzenes being the least reactive (Morrison and Boyd, 1975). Bitumens from samples analyzed subsequent to those of this study, wherein the bitumens have been most severely modified, as judged by the compound distributions normally observed in sediment bitumens, have only small relative concentrations of, or no, high-molecular weight aromatic HCS. Thus, we surmise that polynuclear-aromatic HCS with four or more rings are also relatively susceptible to oxidation-reduction reactions, and thus will be largely absent in rocks subjected to strong instances of hydrolytic disproportionation of OM. We surmise that the relatively high concentrations of 1,2-benzenedicarboxylic acid esters (peaks 11, 23, 31, Table 4; and peaks 3-6, Table 5) are due to redox reactions of the methylated naphthalenes to yield naphthalene (reactions 6 and 7), which then oxidizes to 1,2-benzenedicarboxylic acid (reactions 8, or 10-12).

High relative concentrations of biphenyl exist in our samples. Püttman et al. (1989) found the same feature in their samples. They, as we here, attribute these high biphenyl concentrations to the oxidation of phenanthrene to 9,10-phenanthrenequinone (reaction 17), which is then oxidized to diphenic acid (reaction 19), which in turn decarboxylates to biphenyl (reaction 20).

Our data demonstrate that within the saturated HCS, the C_{11} to C_{20} n-paraffins appear to be markedly more reactive via hydrolytic disproportionation than higher, or lower, carbon-numbered n-paraffins. A maximum in reactivity occurs over n-C_{13} to n-C_{14}. Within samples which have undergone significant levels of hydrolytic disproportionation: 1) high relative, and absolute, concentrations of C_{10}- HCS can exist (confirming predictions of Helgeson et al., 1993, p. 3323); and 2) high naphthenic envelopes can be present (Figs. 2,3). This latter observation suggests that polynuclear naphthene rings, which are significantly more reduced than aromatic HCS, are relatively unreactive during hydrolytic disproportionation of OM. The relative unreactive nature of the naphthene ring during hydrolytic disproportionation is also manifested by sediment-like peak distributions within the sterane, tricyclic, and pentacyclic biomarkers in our (Figs. 12-15) and other samples, even though these samples have been exposed to very high to extreme burial temperatures.

Analyses of both the samples of this paper, and of subsequent samples, demonstrate that within the major compound groups fractionated by column chromatography, the resins (and asphaltenes) are most reactive during hydrolytic disproportionation of OM, followed by the aromatic HCS, with the saturated HCS, especially the C_{20}+ saturated HCS, being by far the least reactive. We attribute the relative reactivity of the first three compound groups to the preponderance of polynuclear aromatic HCS therein.

From the data of Tables 4 and 5, and from the work of Püttman et al. (1989), it appears that ketones, esters, and aldehydes are the stable "end-member" oxygen bonds which the redox reactions involved with the hydrolytic disproportionation of OM strive towards.

5.062 Previous Studies

Evidence for, and characteristics of, hydrolytic disproportionation of OM exists within previous publications from different fields of study. As discussed above, there is a long-standing recognition of a pronounced associated of OM with ore deposition. Whenever any form of OM associated with an ore deposit is analyzed, that OM is found to be oxidized, from kerogens in uranium deposits (Disnar and Sureau, 1990), MVT deposits (Henry et al., 1992), and cinnabar deposits (Germanov et al., 1972); to bitumen in gold deposits (Radtke and Scheiner, 1970; Kesler et al., 1986; Hausen and Park, 1986; this study); even to graphite in an Au-W deposit (McKeag et al., 1989). Saxby (1976) earlier documented the widespread oxidation of OM associated with ore deposition. Hydrolytic disproportionation of OM during ore deposition provides the only pathway, of which we are aware, for the oxidation of this OM, thus causing the reduction of the ore-bearing solutions, and hence precipitation of the ore.

Hydrolytic disporportionation of OM during ore deposition also explains the chemical modification of OM associated with ore deposits as documented in this and previous studies. This includes the decrease in aromatic HCS compared to the other compound classes in bitumen (Germanov et al., 1972); the severe chemical modification of the aromatic HCS and resins (Püttman et al., 1989); the n-paraffin "rounding" of saturated-HC gas chromatograms (Hatch et al., 1986; Kesler et al., 1986); and the elevated chlorine contents of the OM associated with Canadian Archean gold deposits.

Lastly, one of the principal end products of the hydrolytic disproportionation of OM is CO_2. The association of carbonate gangue minerals with isotopically-light carbon in many ore deposits, carbonate which only could have originated from the oxidation of OM, is strong evidence of significant reaction extents in the hydrolytic disproportionation of OM during ore deposition. Concurrently, in numerous (all?) petroleum-bearing basins, late-stage isotopically-light carbonate cements exist under a wide variety of circumstances. Previous investigators recognized that these cements could have only originated from the oxidation of OM, although the pathway for that oxidation was unclear to them. Hydrolytic disproportionation of OM provides that pathway. Moreover, the general occurrence of these late-stage isotopically-light cements in petroleum basins is further evidence of possible widespread significant reaction extents of the hydrolytic disproportionation of OM under a variety of geologic circumstances.

Giggenbach (1997, p. 3779) commented on hydrolytic disproportionation (and metastable equilibrium) of OM as a possible explanation for the redox reactions he observed among HC gases, CO_2, rocks and water:

> "Unless at least some attempt is made to provide information on the nature of catalysts active in geochemical systems, or some mechanistic justifications, the concept of metastable equilibrium, rather than "requiring a new way of thinking" (Shock, 1990) should be used with great caution. Computational diversions based on this concept (Helgeson et al., 1993) are as yet unlikely to bear much semblance to geochemical reality. The above examples may also serve to illustrate the danger of pushing thermodynamic reasoning too far, without due regard to the nature of species actually involved in a reaction and to realistic mechanisms facilitating their interactions. An early warning sign for over-reliance on thermodynamic arguments is the indiscriminate use of inappropriate variables, such as fo_2, fs_2, or even pH (Giggenbach, 1992)".

In our present paper, we have provided what Giggenbach (1997) requested concerning "mechanistic justifications", "the nature of the species involved in the reactions", "realistic mechanisms facilitating" the reactions, what some of the end products are of hydrolytic disproportionation of OM, and evidence of the widespread occurrence of the process in different geologic environments. We are in complete disagreement with his summary dismissal of hydrolytic disproportionation of OM as a viable naturally-occurring process. Giggenbach's (1997, p. 3779) statement about "computational diversions" bearing no "semblance to geochemical reality" is erroneous. A number of predictions made by Helgeson (1991) and Helgeson et al. (1993) solely on the basis of "thermodynamic reasoning" have been corroborated by our data. Lastly, fo_2, fs_2 and pH, to us , hardly appear to be "inappropriate variables". We maintain that Giggenbach's (1997) observation of methane and CO_2 being in equilibrium with one another and the mineral species of their environments, is, in point of fact, due to, and strong evidence of, the hydrolytic disproportionation of OM.

5.063 Preliminary Controls of Hydrolytic Disproportionation of OM

The question obviously arises, under what conditions does hydrolytic disproportionation of OM occur? Our studies thus far indicate that the key control is open-fluid systems, where water either flows past OM or vice versa. For example, open-fluid systems are requirements for both heavy-metal deposition and rock metamorphism (so that ionic transport can take place resulting in mineral-phase recrystallization). We stress that passage of water out of chemical equilibrium with both the system through which it flows, and the OM in that system, appears to be the principal parameter causing hydrolytic disproportionation of OM and the extensive chemical changes, thereof. Hydrolytic disproportionation of OM would only proceed at very low levels, if at all, in closed-fluid systems where pore waters remain in chemical equilibrium with their system over geologic time. The effects of hydrolytic disproportionation of OM will thus not be detectable in such systems. Petroleum source-rock systems, and shales in general, are an example of a closed-fluid system, where new water never or rarely enters the system. Consequently, source-rock or shale bitumen never exhibits detectable consequences of hydrolytic disproportionation of OM. For example, aromatic-HC compositions similar to those from the rocks of this study have never been reported from shales of petroleum basins despite uncounted aromatic-HC gas-chromatographic and mass-spectrometric analyses in laboratories worldwide.

Published studies demonstrate that the temperature range over which hydrolytic disproportionation of OM occurs is enormous. As discussed below, it occurs during the formation of Mississippi-Valley type (MVT) heavy metal deposits as low as 75°C. The data of Sugisaki and Mimura (1994) and Laier and Nytoft (1995) both suggest upper temperature occurrences of over 1000°C.

6.0 CONCLUSIONS

1) Low concentrations of solvent-extractable bitumen have been found in suites of ore-deposit and metamorphic rocks analyzed in this study from widely-separated worldwide localities. These preliminary results have been replicated by over 80 subsequent, but yet unreported, analyses we have also performed on crystalline rocks, also from widely-spaced worldwide localities.

2) These assemblages of organic compounds, at least in most cases, are molecularly-dispersed throughout the rocks; moreover, detailed contamination checks, and other considerations, preclude the possibility that the extractable OM from our rocks arose from contamination.

3) Isoprenoid HCS and biomarkers in, and the saturated-HC $\delta^{13}C$ values of, our samples demonstrate that the extractable OM of our samples originated as sedimentary-derived OM. Other investigators studying the solvent-extractable OM in crystalline rocks previously exposed to extreme temperatures have reached the same conclusion.

4) No trend of increasing maturity in the extractable OM versus increasing rock rank has been observed in any of the rock suites we have thus far analyzed, and in fact immature characteristics have been retained in the extractable OM of all our rocks.

5) The aromatic HC assemblages of our study are most unusual and are unlike anything ever before observed, either in the extractable OM of sedimentary rocks or in reservoired oils or condensates. The near, to total, absence of the methyl-, dimethyl-, and trimethyl-naphthalenes, and the presence of high concentrations of biphenyl and oxygenated-organic compounds within our aromatic HCS are both especially unusual observations.

6) The resin fractions of our samples are also highly unusual, being completely unlike resins found in sediment extracts and oils. Our resins are dominantly (>99%) composed of 6 to 8 discrete compounds which largely appear to be oxygen-bearing compounds (benzene dicarboxylic acids with ester bonds). Because the resins make up the dominant compound fraction from most of our samples, a strong drive to thermodynamic equilibrium is suggested to us.

7) The analytical data of this study, the results of our yet unpublished subsequent analyses, and the data of many other studies all strongly conflict with the petroleum-geochemical theory of a thermal destruction of HCS at burial temperatures of 150° to 200°C.

8) Controls, other than C_{15}+ HC thermal stability, are clearly responsible for the quantitative (and qualitative) characteristics of the extractable OM in our rocks.

9) Many of the analytical observations of this study are predicted by, and thus support, the theory of hydrolytic disproportionation of OM (Helgeson et al., 1993), wherein water and OM (including HCS), when out of chemical equilibrium with one another, exchange oxygen and hydrogen in a series of oxidation and reduction reactions (with respect to oxygen and hydrogen), via disproportionation of water to reach chemical equilibrium between both themselves and the mineral species in the system. The hypothesized end products of this process are CO_2 and CH_4. Our data are the first evidence, from the natural system, of the widespread occurrence of hydrolytic disproportionation of OM in the natural system.

10) We propose that hydrolytic disproportionation of OM is a major unrecognized geologic agent of the first magnitude. For example, this mechanism operating in Nature could help set mineral stability fields during rock metamorphism by helping to set eH and pH conditions of the total system.

11) Theoretical considerations also suggest that hydrolytic disproportionation of OM would also be a major cause of heavy-metal ore deposition, from OM entering into redox reactions with the ore-transport brines and thus changing the eH and pH of these brines, causing ore precipitation. Much data from ore deposits in the natural system strongly support these considerations.

12) Likewise, other data from both laboratory experiments and the natural system strongly suggest that hydrolytic disproportionation of OM plays critical roles in a number of petroleum-geochemical and geologic processes, examples being: A) the hydrogenation of kerogen by water before and during mainstage HC generation, B) the formation of secondary porosity, C) the maintenance of cap-rock seals of conventional oil and gas deposits through geologic time, and D) the formation and maintenance of the pressure seals responsible for fluid compartmentalization in petroleum-basin depocenters.

13) The data from this study strongly suggest that widespread redox reactions occur, via hydrolytic disproportionation of OM, between water, OM, and mineral species in varied geologic environments. We believe that these redox reactions occur via ionic/carbonium-ion pathways. Equilibria between water, mineral species, and the various forms of OM thus result.

14) We have identified a limited number of unusual compounds not normally present in sediment bitumens or oils, at least in detectable concentrations. Most of the compounds thus far identified are products of well-established organic-chemical redox reactions, strongly suggesting that the reactions responsible for these compounds followed natural reaction pathways, pathways significantly facilitated in hot salty waters.

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