

## Chapter H

# **A Possible Deep-Basin High-Rank Gas Machine Via Water–Organic-Matter Redox Reactions**

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# A Possible Deep-Basin High-Rank Gas Machine Via Water–Organic-Matter Redox Reactions

By Leigh C. Price

## Abstract

Petroleum geochemistry is often portrayed as being well understood and capable of providing accurate predictions reflecting the reality of Nature. Nonetheless, important controlling parameters of organic metamorphism, including oil and gas generation, still go unrecognized. One such parameter is water, which plays especially pivotal roles in HC-generation reactions. Another is the origin of hydrocarbon gases and gas deposits, including deep-basin, high-rank, methane-rich gas deposits. The traditional view for the origin of HC gases—in-situ thermal cracking of oil deposits—has flaws which have been pointed out by different investigators. Consequently, alternate mechanisms for the origin of natural gas have independently been proposed. One such mechanism which is evaluated in this report is the hydrogenation of deep, high-rank spent kerogen by water, with subsequent generation of methane-rich HC gas.

Different investigators have presented data, from both the laboratory and Nature, which demonstrate that water, organic matter, and mineral phases take part in aqueous-based redox reactions in attempting to achieve or maintain a metastable equilibrium among themselves. This process has been termed “the hydrolytic disproportionation of organic matter.” Data sets presented and discussed herein support a previous proposal that water and high-rank, deeply buried, post-mature kerogen possibly undergo hydrolytic-disproportionation reactions with one another, resulting in the generation of a high-rank methane-rich gas. The most important implication of this reaction occurring in Nature is the possible creation of very large, basin-centered, deep-basin, methane-rich gas reserves in continuous reservoirs.

## Introduction

Organic metamorphism in Nature, including hydrocarbon (HC) generation, is traditionally portrayed (Tissot and Welte, 1984; Hunt, 1996) as being well understood and utilitarian in a predictive sense. HC-generation reactions are classically thought to occur by first-order reactions. Thus, geologic time and temperature are held as the only important controlling parameters of organic metamorphism, parameters which can be substituted for one another in first-order Arrhenius equations, which are thought to faithfully describe organic metamorphism in Nature. By these models, generation of HC gases is thought to occur mainly at elevated burial temperatures from a thermal destruction of oil, and perhaps  $C_{15+}$  hydrocarbons (HCS) residing in shales. Such thermal destruction is held to commence at a vitrinite reflectance ( $R_o$ ) value of 0.9 percent ( $150^{\circ}$ – $200^{\circ}C$ , depending on the geologic time of burial, and the model being

used). Complete  $C_{15+}$  HC thermal destruction is depicted as occurring by  $R_o=1.35$  percent, with the  $C_2$ – $C_4$  HC gases completely being converted to methane by  $R_o=2.0$  percent, and methane being thermally destroyed by  $R_o=4.0$  percent.

A minority opinion exists among different investigators that the traditional models of HC generation are far too simplistic, and have trivialized the complexity and ignored other important controlling parameters of organic metamorphism. Much of this alternate viewpoint is discussed in Price (1997a) and will not be detailed here with two exceptions: the mechanics of natural gas generation and the role of water, via redox reactions, in organic metamorphism. These topics are pivotal to this report because of their control on a possible unrecognized source of high-rank natural gas, generated at great depths ( $>15,000$ – $20,000$  ft;  $4,572$ – $6,096$  m) in petroleum basins. As such, I first review these two topics and then discuss evidence, from both the laboratory and the natural system, which appears to strongly support the possible operation in Nature of processes which could result in generation of a late-stage, high-rank, methane-rich HC gas.

## Natural Gas Generation Mechanisms

To repeat, thermogenic natural gas, especially methane-rich “dry gas,” has traditionally been thought to originate largely, or solely, from thermal destruction of oil at relatively low maturation ranks. Although this viewpoint is staunchly held by many petroleum geoscientists, there are major problems with the hypothesis: First,  $C_{15+}$  HCS exhibit remarkable thermal stability in fine-grained sedimentary rocks, persisting to maturation ranks of at least  $R_o=7$ – $8$  percent (Price, 1993, and references therein). Moreover, biogenically derived saturated HCS, with sediment-like characteristics, including sediment-like biomarkers, persist to high temperature in metamorphic and other crystalline rocks in moderate to low concentrations (Price and others, 1998) and even in mantle-derived rocks in low concentrations (Sugisaki and Mimura, 1994; Mimura and others, 1999). Numerous other investigators, including Kontorovich and Trofimuk (1976), Sagjò (1980), Guthrie and others (1986), Shock (1990), Mango (1990, 1991), Helgeson (1991), and McNeil and BeMent (1996) have either rejected the traditional view of the thermal instability of  $C_{15+}$  HCS or have provided telling evidence that this generally accepted hypothesis is unrealistic.

A second problem with the hypothesis of  $C_{15+}$  HC thermal instability is that the carbon-isotopic values of methane in dry-gas deposits are far too light (negative) to have originated from the thermal destruction of  $C_{15+}$  HCS (Price, 1995). Other

problems with the hypothesis of a pronounced thermal instability of  $C_{15}+$  HCS, and an exclusive, or even predominant, origin of HC gas from  $C_{15}+$  HC thermal destruction are presented in Price (1983, 1993, 1995, and 1997a and b) and will not be reviewed here. Whereas some thermal cracking of oil *may* take place in certain deeply buried oil reservoirs, it is now clear to some investigators that the thermal instability of oil has been greatly overstated. As such, alternate mechanisms for gas generation, and for the origins of methane-rich dry gas, have been proposed by different researchers.

For example, Price (1989a) pointed out that data from both the natural system and laboratory HC-generation experiments in closed water-wet systems demonstrate that  $C_1$ – $C_4$  HCS are cogenerated in large quantities with  $C_{15}+$  HCS. Moreover, these same data demonstrate that the  $C_1$ – $C_4$  HC gases are even generated in measurable amounts before mainstage  $C_{15}+$  HC generation commences. Price (1989a, b) also pointed out that, based on data from these laboratory experiments, the  $C_1$ – $C_4$  HC gas absolute and relative (to the sum of all generated products) concentrations continuously increase, with increasing experimental temperature, throughout mainstage  $C_{15}+$  HC generation.

Price and Schoell (1995) sampled oils and gases produced from the source rocks for the HCS (the Upper Devonian–Lower Mississippian Bakken Formation shales) in the North Dakota portion of the Williston Basin. Oils from this self-contained source-reservoir HC system, which had not migrated far from their generation sites (not more than 10 ft, 3 m), had gas-oil ratios averaging 1,100 standard cubic feet (SCF) of gas per barrel of oil. This observation conclusively demonstrated that large amounts of natural gas are cogenerated with oil in source rocks, thus corroborating the results of various laboratory experiments. In fact, I have calculated that 18.5 weight percent of the HC-generation potential of Bakken shale kerogen went toward  $C_1$ – $C_4$  HC gases (unpub. data, 2000). Thus, cogeneration of  $C_1$ – $C_4$  HC gases with oil probably represents the most significant source of wet ( $C_1$ – $C_4$ ) HC gases in the natural system.

The origin of significant deposits of methane-rich (“dry”) gas, with >98 percent  $C_1$  and  $\delta^{13}C$  ratios of  $-39$  to  $-50$ , is problematic. As Price (1995) pointed out, if such gases originated from the thermal destruction of  $C_{15}+$  or  $C_2+$  HCS, the methanes should have isotopic values of  $-38$  to  $-5$ . Although dry gases exist in Nature with such values, they are usually associated with plutonic or volcanic intrusions or have been sourced from coals (resulting in the more positive  $\delta^{13}C$  ratios). This observation suggests that  $C_2+$  HC thermal destruction is not a common occurrence in Nature. Moreover, Mango (1997) established that ethane is extremely thermally stable in Nature, with a half-life of billions of years at elevated temperatures. As an aside, dry gases with  $\delta^{13}C$  values of  $-45$  to  $-50$  reflect significant admixture of biogenic and thermogenic methanes (Price, 1995).

In light of the preceding considerations, different investigators have proposed alternate origins for these dry gases with light-isotopic values. For example, Mango and others (1994) were able to produce impressive exact examples of these gases in the laboratory using transition metals as catalytic agents during the thermal decomposition of longer-chained HCS. They thus proposed HC cracking, via transition-metal catalysis, to

explain the origin of deposits of isotopically light dry gas. In contrast, McNeil and BeMent (1996) strongly criticized the hypothesis advanced by Mango and others (1994), and proposed instead demethylation reactions in deep post-mature kerogens, which had gone completely through mainstage  $C_{15}+$  HC generation, to explain these methane-rich gas deposits.

Price (1995) and Price and Schoell (1995) proposed a migration and fractionation of  $C_1$ – $C_4$  wet HC gases generated by source rocks, to isotopically light methane-rich gases. Their mechanism centers on the fact that at significant burial depths, and therefore elevated fluid pressures, the  $C_2$ – $C_4$  HC gases condense into a liquid phase (Salisbury, 1968; Mark Beeunas, Chevron USA, oral commun., June 8, 9, 1999). Thus, Price (1995) and Price and Schoell (1995) proposed that in Nature, the  $C_2$ – $C_4$  HC gases in gas caps over deeply buried oil deposits condense into the oil phase, leaving a methane-rich gas cap riding over the oil deposit from buoyancy differences. As fluids continue to migrate into the trap, eventually the gas cap fills the trap to spill point, displacing the oil phase containing condensed  $C_2$ – $C_4$  HC gases updip to another trap or to commence long-lateral secondary migration (Gussow’s (1954) principle of differential entrapment). This process eventually would leave all deep-basin traps filled with dry gas, wherein the methanes would have isotopic signatures characteristic of cogeneration with oil, for example,  $\delta^{13}C$  values of  $-39$  to  $-50$ . Price (1995) termed this process “migration-fractionation.”

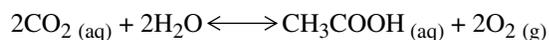
It is possible that all three of these mechanisms contribute to the formation of dry-gas deposits, or that other yet-unidentified processes are responsible. However, in my opinion, the thermal destruction of  $C_2+$  HCS, including  $C_{15}+$  HCS, plays only a minor role, if any, in the creation of dry-gas deposits. As an aside, some investigators have been reticent to accept the possibility of dry-gas formation via transition-metal catalysis, because it has not yet been demonstrated that the laboratory conditions that have resulted in such impressive experimental results are applicable to Nature.

Another possible origin for deep-basin HC gases (proposed by Seewald, 1994) is generation of high-rank methane-rich gas via oxidation-reduction (redox) reactions between water, spent kerogen, and mineral phases. Seewald’s (1994) proposal centers on the hydrolytic disproportionation of kerogen. An assessment of the feasibility of this generation path for high-rank natural gases from existing data from both the laboratory and the natural system is the purpose of this report. However, at the outset, we must define, characterize, and provide evidence for the hydrolytic disproportionation of organic matter (OM).

## The Hydrolytic Disproportionation of Organic Matter

In traditional oil and gas generation models, water and most forms of organic matter (OM), especially kerogen and naturally occurring HCS, traditionally are viewed as being completely unreactive. However, Shock (1988) and Helgeson and Shock (1988) proposed the existence of a metastable equilibrium between rocks, water, and reservoir oil in petroleum

basins, based on thermodynamic considerations. The different phases are linked by the reaction,



Helgeson and others (1993) termed the process, “the hydrolytic disproportionation of OM.” The overall reaction is thought to be irreversible; however, both reversible and irreversible intermediate reactions occur during the process. The end products are  $\text{CO}_2$  and  $\text{CH}_4$ . A strong theoretical foundation also exists for the formation of intermediate-step compounds, including low-molecular weight HCS and various species of oxygen-bearing (oxidized) HCS. Where the process has proceeded extensively, high concentrations of low-molecular weight ( $\text{C}_1$ – $\text{C}_6$  to  $\text{C}_1$ – $\text{C}_{10}$ ) HCS would result. The term “hydrolytic disproportionation of OM” results from the premise that water disproportionates into charged ions which then react with OM, which also disproportionates, to form an oxidized carbon species and a lower-molecular weight HC, compared to the molecular weight of the starting OM. Helgeson and others (1993) noted that when all phases (water, OM, and minerals) of a geologic system are in equilibrium with one another, hydrolytic disproportionation of OM would not occur. However, when these phases are out of equilibrium with one another, such reactions would proceed.

## Evidence for the Hydrolytic Disproportionation of Organic Matter

The hypothesis of the hydrolytic disproportionation of OM has strong supporting evidence from both the natural system and the laboratory. French (1964) carried out experimental siderite synthesis and stability studies, and inadvertently produced measurable amounts of oxidized HCS (alcohols, organic acids, ketones, among others), and most probably HCS themselves, starting only with water and  $\text{FeCO}_3$ . Palmer and Drummond (1986) and Bell and others (1994) also inadvertently produced HCS from water and acetic acid, while experimentally examining aqueous acetic-acid thermal stability. Hoering (1968, 1984) deuterated both shale kerogen and HCS with deuterated water, demonstrating that kerogen and HCS exchange hydrogen with water, a pivotal observation.

Seewald (1994) conducted experiments in gold bags containing water, ethane, ethene, and the naturally occurring mineral buffer of pyrite-pyrrhotite-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  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_2$  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 by exchanging hydrogen and (or) oxygen with one another, and thus provided convincing evidence of the existence

of the hydrolytic disproportionation of OM under laboratory conditions. Of pivotal interest to our discussion, considering his experimental results, Seewald (1994) proposed that water might hydrogenate spent, deeply buried, high-rank, post-mature kerogens, which could then generate significant amounts of deep-basin high-rank methane-rich HC gas. We will return to Seewald’s (1994) proposal after reviewing evidence that the hydrolytic disproportionation of OM is widespread throughout the natural system.

Price and others (1998) extracted low to moderate concentrations (0.5–200 ppm) of highly modified bitumens, compared to the bitumens found in sedimentary rocks, from crystalline metamorphic and ore-deposit rocks, with maximum “burial” temperatures of  $500^\circ\text{C}$ . These bitumens had high relative concentrations of oxidized HCS (ketones, esters, and aldehydes), and especially of 1,2-benzene dicarboxylic acid esters, and the aromatic-HC and resin fractions of the bitumens had been fundamentally chemically transformed to compositions never before reported in the literature. Pivotaly, the results of Price and others (1999) confirmed predictions previously made by Helgeson (1991) and Helgeson and others (1993) regarding the consequences of the hydrolytic disproportionation of OM: (1) high concentrations of oxygen-bearing (oxidized) HCS, (2) the presence of dicarboxylic acids, (3) high concentrations of light HCS, and (4) *highly extended* HC thermal stabilities. Price and others (1998) concluded that the hydrolytic disproportionation of OM was a previously unrecognized geologic agent of the first magnitude.

Price and others (1998) also concluded that the principal control of the hydrolytic disproportionation of OM is an open-fluid system, wherein water or OM flow past one another, resulting in the different phases of a given system being out of equilibrium with each other. In closed-fluid systems, the different phases would reach a metastable equilibrium with one another, and the process would halt. Price and others (1998) also provided a large body of evidence demonstrating the widespread existence of the process in, as well as results of the process from, many different geologic regimes, including petroleum basins. One of these lines of evidence specifically concerns us here: the hydrogen-enrichment of kerogen by water, via the hydrolytic disproportionation of kerogen, during HC generation, including gas generation, reactions. Price and others (1998) found strong evidence for this reaction between kerogen and water in the closed-system, water-wet, aqueous-pyrolysis experiments of Price (1989a, b), Wenger and Price (1991), and Price and Wenger (1992). The results of these experiments also have strong implications for the possible previously unrecognized high-rank, deep-basin, late generation of HC gases under discussion.

Key data in this report are derived from both ROCK-EVAL analysis and aqueous-pyrolysis experiments. Thus, perceived weaknesses of ROCK-EVAL, the experimental procedures of aqueous pyrolysis, and the validity of HC generation experiments carried out in the laboratory as a representation of HC generation in Nature are all discussed at length in an appendix. Suffice it to say that, as discussed in the appendix, the aqueous-pyrolysis experiments of Wenger and Price (1991) and Price and Wenger (1992) have a proven record of closely replicating

numerous aspects of HC generation in Nature, including important aspects which previously were unrecognized. As also discussed in the appendix, cross plots of ROCK-EVAL hydrogen indices to kerogen hydrogen to carbon ratios for our different sample bases demonstrate very good correlations.

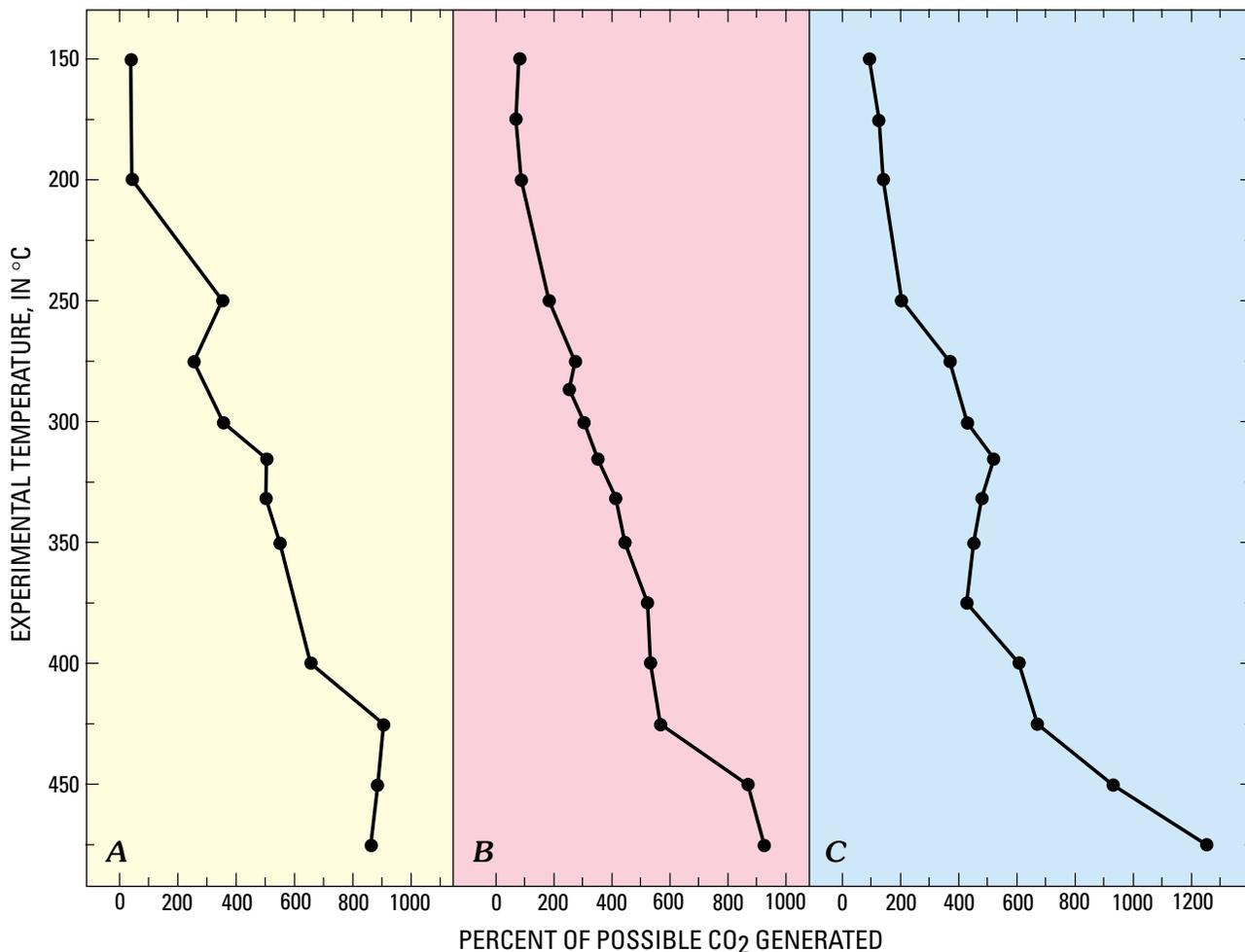
## Hydrogenation of Kerogen by Water in the Laboratory

### Excess CO<sub>2</sub> Production

In the aqueous-pyrolysis experiments carried out with six different rocks at variable temperatures (Price, 1989a, b; Wenger and Price, 1991; Price and Wenger, 1992), much more CO<sub>2</sub> was generated than possibly could be accounted for, considering the original oxygen content of the kerogens. Moreover, the same effect occurs in hydrous-pyrolysis experiments (Lundegard and Senftle, 1987; Barth and others, 1989; Lewan, 1992). This effect

appears to be present in all HC-generation experiments carried out in closed, water-wet systems. Examples of this excess CO<sub>2</sub> from the HC-generation experiments of Wenger and Price (1991) are shown in figures 1 and 2.

In figure 1, the amounts of CO<sub>2</sub> generated from three different OM types (Type-I, Eocene Green River Formation shale; Type-II-S, Lower Permian Phosphoria Formation shale; and Type-II/III, Middle Pennsylvanian Anna Shale Member of Pawnee Limestone) are shown. In all three cases, 100 percent equals the maximum amount of CO<sub>2</sub> possible, given the original oxygen content of the kerogen. Kerogen oxygen contents were determined by ROCK-EVAL oxygen indices. However, kerogen elemental analyses performed on these same samples yield the same results (L.C. Price and L.M. Wenger, unpub. data, 1991). For all experiments, carbonate-carbon determinations on the reacted shales were carried out by Huffman Laboratories, Golden, Colo., by acid dissolution of the carbonate minerals and measurement of the liberated CO<sub>2</sub>. These analyses were accurate to 0.5 percent of the reported value. Thus, we were able to subtract any CO<sub>2</sub> contributions from reactions of carbonate minerals during the experiments from the total CO<sub>2</sub> values,



**Figure 1.** Percent of CO<sub>2</sub> generated over what is possible, based on the original oxygen content of the kerogens, for three rocks (Eocene Green River Formation shale, Type-I OM (fig. 1A); Lower Permian Phosphoria Formation shale, Type-II-S OM (fig. 1B); and Middle Pennsylvanian Anna Shale Member of Pawnee Limestone, Type-II/III OM (fig. 1C)) on which 30-day, variable-temperature aqueous-pyrolysis HC-generation experiments were performed.

to obtain the figure 1 values. In the figure 1 rocks, mainstage pyrolytic HC generation commences at 250°C (275°C for the Green River shale) and is complete by 320°–333°C. Experimental temperatures of 350°C and higher represent mainstage C<sub>8</sub>+ HC thermal destruction. From figure 1, excess CO<sub>2</sub> is generated from all three rocks before mainstage HC generation commences and also during both the mainstage HC-generation and the HC-destruction phases.

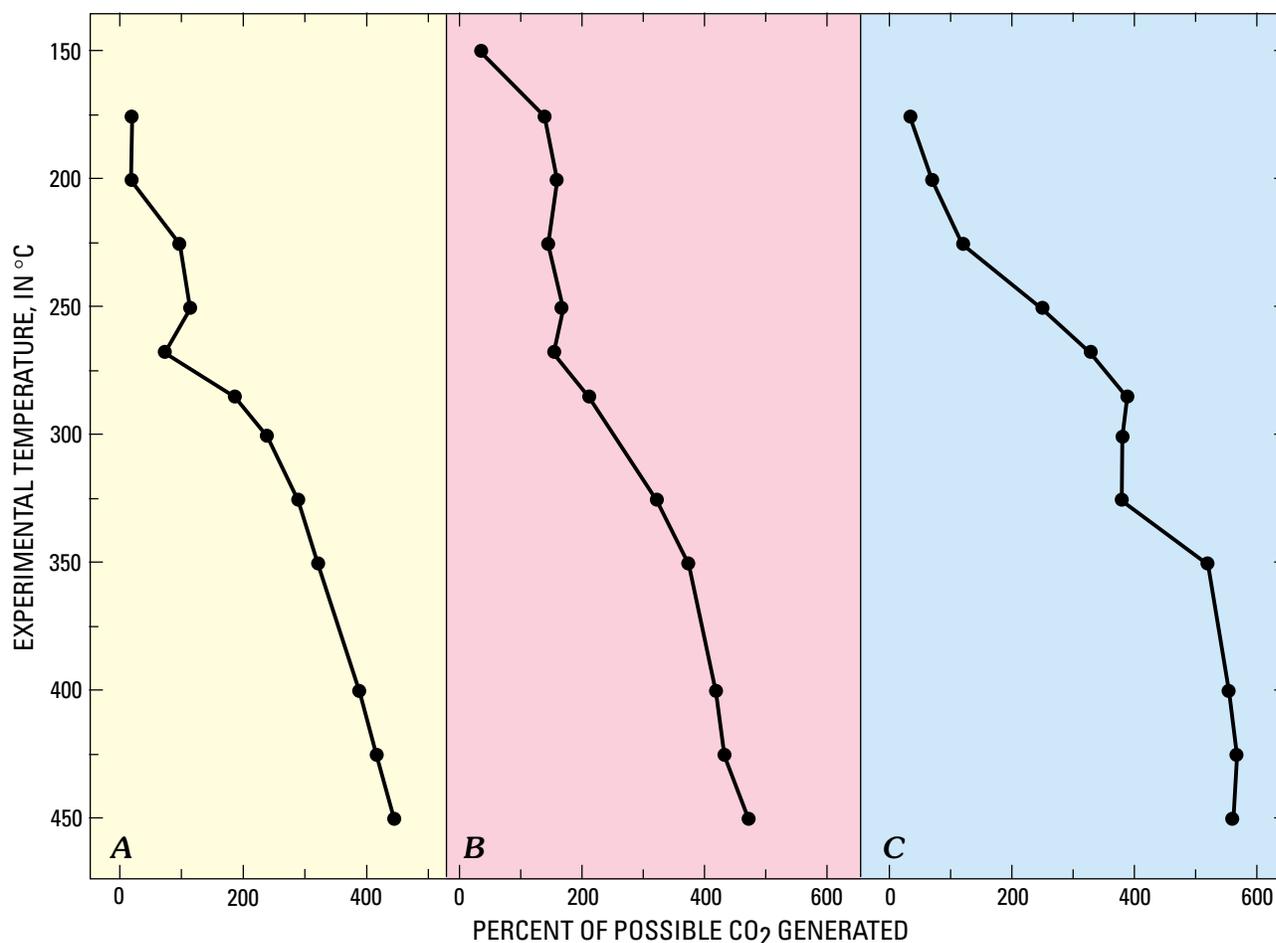
In figure 2, the same type of data is shown for the other three rocks on which variable temperature experiments were also performed: the Upper Devonian–Lower Mississippian Bakken Formation shale (fig. 2A, Type-II/I OM), the Eocene Rattlesnake Butte lignite (fig. 2B, Type-IV OM), and a composite of mid-Miocene Monterey Formation time-equivalent Los Angeles Basin shales (fig. 2C, Type-II OM). In all three cases, excess CO<sub>2</sub> is generated before, during, and after mainstage C<sub>15</sub>+ HC generation, which occurs from between 250°C and 275°C, to 333°C.

### Excess HC Production

Not only is excess CO<sub>2</sub> generated in these experiments, but also excess HCS are generated, based on the starting values of

the ROCK-EVAL S<sub>2</sub> peaks of all six rocks. At the temperatures exceeding 150°, 175°, and 200°C in figure 3A, the S<sub>2</sub> peak increases from a starting value of 96.6 mg/g, to values of 97.6 to 104.9 mg/g. The hydrogen index also increases from 451 to between 478 and 507. In other words, over the lower temperature (150°–200°C) experiments, the HC-generation potential of the rock is being increased.

In figure 3A, the HC-generation products (C<sub>1</sub>–C<sub>4</sub> HC gases, C<sub>5</sub>+ saturated and aromatic HCS (C<sub>5</sub>+ HCS), and resins plus asphaltenes, NSO+ASP) are plotted, along with the value of the S<sub>2</sub> peak measured for the Soxhlet-extracted shale for each experimental run, all in mg/g rock, for the aqueous-pyrolysis 30-day, variable-temperature experiments carried out with the Phosphoria shale. As is apparent from figure 3A, in the 150°, 175°, and 200°C experimental runs, the sums of the generated products, plus the S<sub>2</sub> value for the extracted shale of the particular experiment, all exceed the starting (and theoretically the maximum) value, which is 118.5 mg/g, of the extractable bitumen plus the HC-generation potential of the Phosphoria shale (dashed line, fig. 3A). In other words, at first glance, it appears that something is being made from nothing. Moreover, above 200°C, the sum of the S<sub>2</sub> peak and the generated products exceeds the theoretical limit of 118.5 mg/g by even greater amounts, reaching maximum values of between 162 and 169



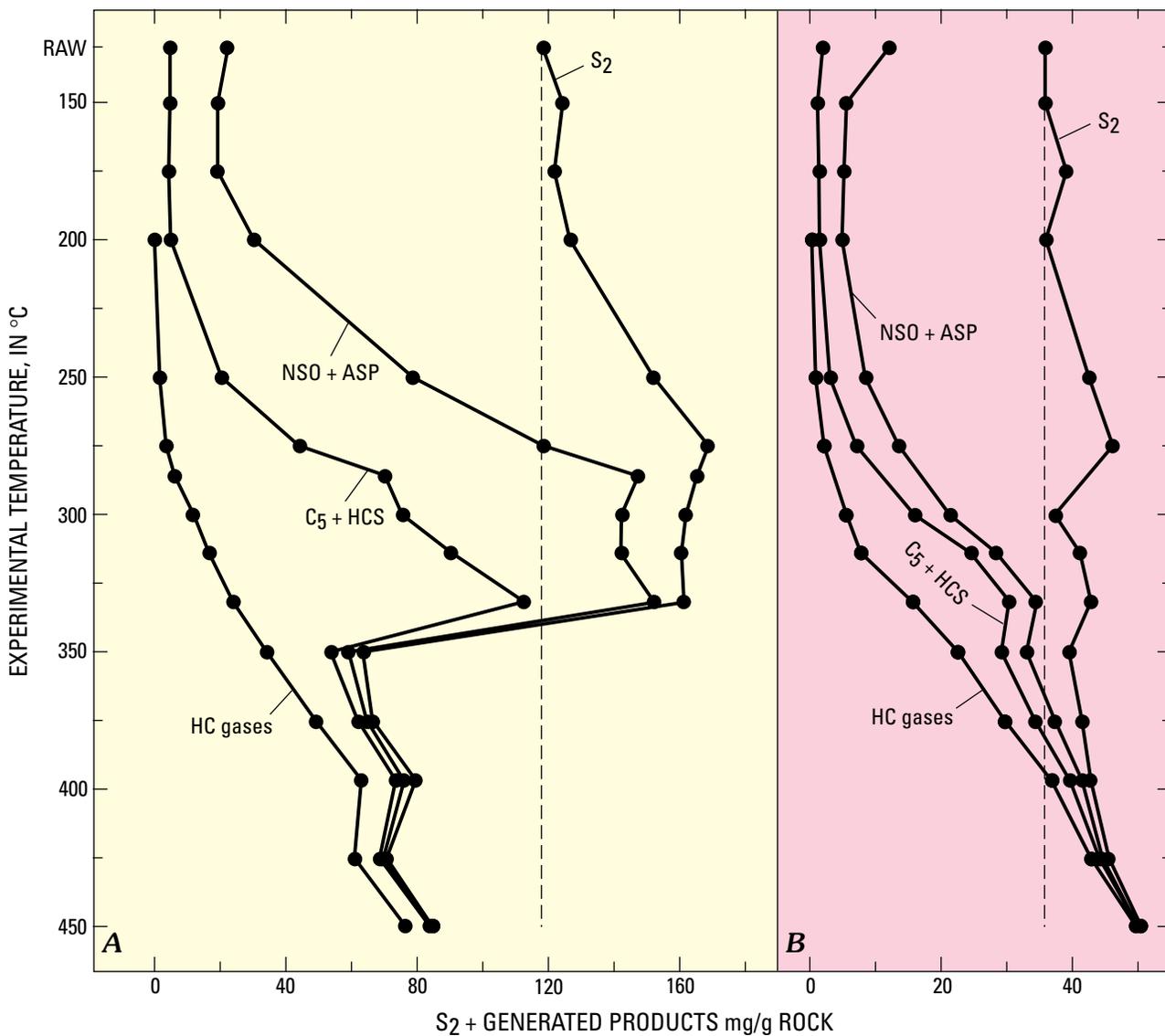
**Figure 2.** Percent of CO<sub>2</sub> generated over what is possible, based on the original oxygen content of the kerogens, for three rocks (Upper Devonian–Lower Mississippian Bakken Formation shale, Type-II/I OM (fig. 2A); Eocene Rattlesnake Butte lignite (fig. 2B); and composite of mid-Miocene Monterey Formation time-equivalent shales, Los Angeles Basin, Type-II OM (fig. 2C)) on which 30-day variable-temperature aqueous-pyrolysis HC-generation experiments were performed.

mg/g at 275°–333°C. I attribute the creation of excess generation potential in figure 3A to water undergoing redox reactions with kerogen, with the oxygen from the water being given off as excess CO<sub>2</sub>, and the hydrogen from the water hydrogenating the kerogen, thus increasing its generation potential.

Mainstage C<sub>15</sub>+ HC generation commences at 250°C in the Phosphoria shale experiments (fig. 3A). However, significant generation of resins and asphaltenes commences at lower temperatures, somewhere between 200° and 250°C. Between 333° and 350°C, mainstage C<sub>15</sub>+ HC thermal destruction commences and largely proceeds to completion. However, from 350° to 450°C, the amount of generated HC gases increases from 33.5 mg/g rock to 76.5 mg/g rock, a difference of 43.0 mg/g rock (fig. 3A), whereas the sum of the C<sub>5</sub>+ products and the S<sub>2</sub> peak decreases from 29.0 mg/g rock at 350°C to 8.5 mg/g rock at

450°C, a difference of only 20.5 mg/g rock. This leaves an increase in generated products of 22.5 mg/g, and again it appears that something is being made from nothing. We are most concerned with the data from the 350° to 450°C experiments, data we discuss in the section, “A Deep High-Rank Gas-Generation Machine?.”

In figure 3A, in proceeding from 333°C to 350°C during the wholesale destruction of C<sub>15</sub>+ HCS, significant charring occurred and carbon was added back into the Phosphoria shale sample. Thus the total organic carbon (TOC) content of the shale increased from 12.70 percent at 333°C to 15.54 percent at 350°C. However, charred carbon was also deposited on the stainless-steel walls of the reaction vessels, from where it could not be quantitatively recovered. The TOC values for the Phosphoria shale from experiments above 333°C are thus all minimal values.



**Figure 3.** Plot of generated products: HC gases, C<sub>5</sub>+ saturated and aromatic HCS (C<sub>5</sub>+ HCS), and resins and asphaltenes (NSO+ASP), plus the S<sub>2</sub> peak (S<sub>2</sub>), all in milligrams per gram of rock (mg/g), for the starting rock (“RAW”) and for rock samples after 30-day aqueous-pyrolysis experiments on the Phosphoria Formation shale (fig. 3A) and the Rattlesnake Butte lignite (fig. 3B). The light-dashed vertical lines trace the theoretical maximum of HC-generation capacity and generated products for both rocks.

Figure 3B is a plot of all the HC generation products ( $C_1$ – $C_4$  HC gases,  $C_5+$  saturated and aromatic HCS, and resins plus asphaltenes) plus the  $S_2$  value measured for the Soxhlet-extracted rock for each experimental run, all in mg/g of rock, for the 30-day, variable-temperature, aqueous-pyrolysis experiments carried out with the Eocene Rattlesnake Butte lignite. The lignite has a starting ROCK-EVAL hydrogen index of 48.8 (Type-IV OM), with a low capacity for  $C_{15+}$  bitumen generation. At all experimental temperatures above 150°C, the sum of both the products and the HC-generation potential in the lignite exceeds the sum of the original products and the original HC-generation potential (the  $S_2$  peak), as traced by the light-dashed vertical line, albeit only slightly for some temperatures. Thus, as with the Phosphoria shale, mass appears to be added to the OM. The same results (excess generation products given the original organic richness of the shales) were also obtained for the 30-day aqueous-pyrolysis experiments performed on the other four rocks of figures 1 and 2.

Comparison of figure 3A with 3B reveals some differences. Relatively small amounts of  $C_{15+}$  HCS are generated by the lignite compared to Phosphoria shale, and the HC gases make up a much greater normalized percentage of the total products in the lignite. Mainstage HC thermal destruction commences in the lignite between 333° and 350°C. However, the significant decrease in  $C_5+$  generated products, so apparent over this temperature interval in the Phosphoria shale (fig. 3A), is much less apparent in the lignite (fig. 3B). This observation is largely valid because of a much smaller amount of  $C_5+$  generated products in the lignite experiments compared to those with the Phosphoria shale.

Another difference between the lignite and Phosphoria results is that in the lignite experiments, at temperatures above 150°C, there is an excess of generated products and HC-generation capacity over all experimental temperatures, including the highest experimental temperatures (fig. 3B). In contrast, in the Phosphoria experiments, excess products and HC-generation capacity appear to be present only between over 150° and 333°C (fig. 3A). Both rocks have a maximum in their excess products at 275°C (fig. 3A, 3B). However, the lignite has its greatest maximum in excess generated products at 450°C (fig. 3B), with a 40.0 percent excess, a number which is equivalent to the 42.5 percent excess of generated products and HC-generation capacity at 275°C in the Phosphoria experiments (fig. 3A).

The differences between the two rocks are almost certainly due in part to the vastly different OM types in the two rocks. The Phosphoria shale has hydrogen-rich Type-II-S OM, with a starting ROCK-EVAL hydrogen index of 451, a value which increases to a maximum of 507 in the 175°C experiment. In contrast, the lignite has hydrogen-poor Type-IV OM with a starting ROCK-EVAL hydrogen index of only 48.8, a value which increases to a maximum of 77.9 to 78.6 in the 175°–250°C experiments. These two different OM types no doubt followed different reaction paths in the aqueous-pyrolysis experiments.

Note in figure 3B that, as with the Phosphoria shale, there is a steady increase in the amount of HC gases generated by the lignite above 350°C. This observation has significant implications for the possible unrecognized deep-basin, high-rank gas-generation mechanism we are concerned with.

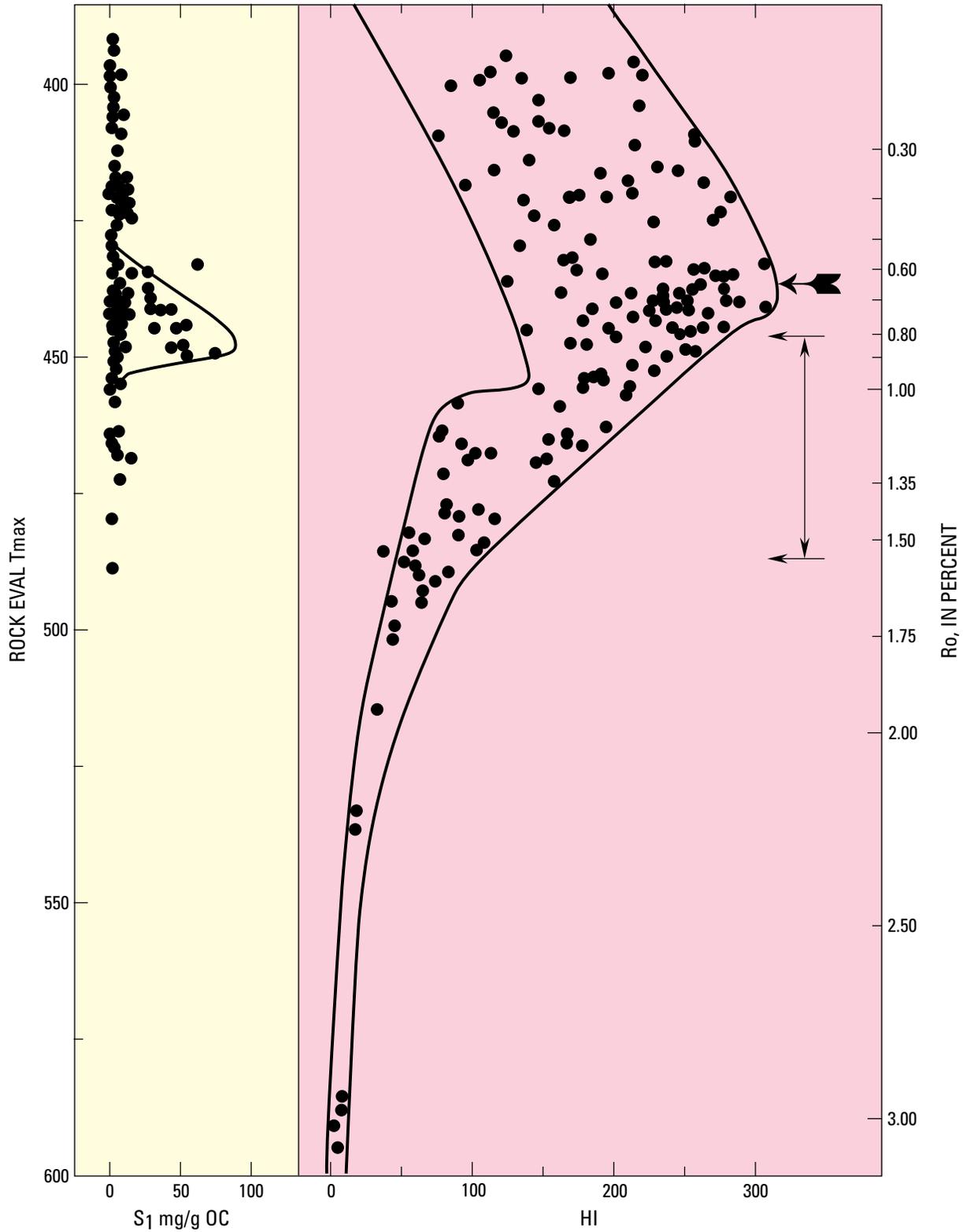
The lignite had the most hydrogen-poor OM of the six rocks on which aqueous-pyrolysis experiments were performed (Wenger and Price, 1991). Yet the lignite generated the highest percentages of methane and  $C_2$ – $C_4$  HC gases, as normalized to the total generated products. The HC gases, especially methane, are the most hydrogen-rich products generated by source rocks. That the most hydrogen-poor OM generates the highest relative amounts of hydrogen-rich product suggests that  $C_5+$  side chains are minimized, and  $C_1$  to  $C_4$  side chains are maximized, on hydrogen-poor kerogens, compared to hydrogen-rich kerogens. Although the lignite generates higher percentages of HC gases as normalized to total products, all five of the other rocks we studied generated far higher *absolute* amounts of HC gases as normalized to the TOC content in the starting rock. Thus, hydrogen-poor OM should not necessarily be considered as a prolific gas source.

The data from figures 1–3 are best explained, in my opinion, by water in the closed water-wet aqueous-pyrolysis experiments reacting with kerogen, and producing far more  $CO_2$  before and during HC generation (figs. 1, 2) than can be accounted for given the original oxygen content of the kerogen. Moreover, many other experimentalists have noted this same feature, including Lundegard and others (1984), Lewan (1992), and Stalker and others (1994). However, the aqueous-pyrolysis experiments of Wenger and Price (1991) also clearly demonstrate that the hydrogen from this water is being chemically incorporated into kerogen and coal, to increase their HC-generation capacity significantly beyond their starting values (fig. 3A, 3B). Hoering (1984) and Lewan (1991) have called upon free-radical mechanisms to account for the excess  $CO_2$  from water hydrogenating kerogen. In contrast, Siskin and Katritzky (1991), Ross (1992), Price and others (1998), and Larson (1999) have advocated ionic pathways. Price and others (1998) pointed out that the products of hydrolytic disproportionation reactions with OM were identical to those from classic organic-chemical ionic-based redox reactions, thus indicating that the reactions in Nature responsible for these products largely proceeded via ionic reaction pathways. The actual mechanism for this reaction is not important for our discussion, rather the critical observation is that the reaction clearly occurs in laboratory experiments. Moreover, this reaction is an oxidation-reduction reaction of the type envisioned by Shock (1988), Helgeson and Shock (1988), and Helgeson and others (1993)—in other words, the hydrolytic disproportionation of kerogen. Lastly, large data bases from the natural system demonstrate that the hydrogenation of kerogen by water occurs in Nature.

## Evidence for Kerogen Hydrogenation in Nature

### Coals

ROCK-EVAL analyses for Paleozoic to Tertiary coals from worldwide locations from Teichmüller and Durand (1983) are shown in figure 4. Note that between  $R_o=0.2$  and 0.7 percent, a



**Figure 4.** The ROCK-EVAL TOC-normalized  $S_1$  and  $S_2$  (hydrogen index) pyrolysis peaks plotted versus vitrinite reflectance ( $R_0$ ) and the ROCK-EVAL  $T_{max}$  for Paleozoic to Tertiary coals worldwide. Feathered arrow indicates the maximum in hydrogen-index data. Bracketed vertical arrows indicate maximum loss in the hydrogen index from HC generation. Data from Teichmüller and Durand (1983), whose original vitrinite reflectance data were given in  $R_m$  values;  $R_m$  was converted to  $R_0$  by  $R_m = 1.066 R_0$ .

dramatic increase in the hydrogen indices of the coals occurs, regarding minimum, maximum, and mean values. For example, the mean hydrogen-index value of 150 for the least mature coals

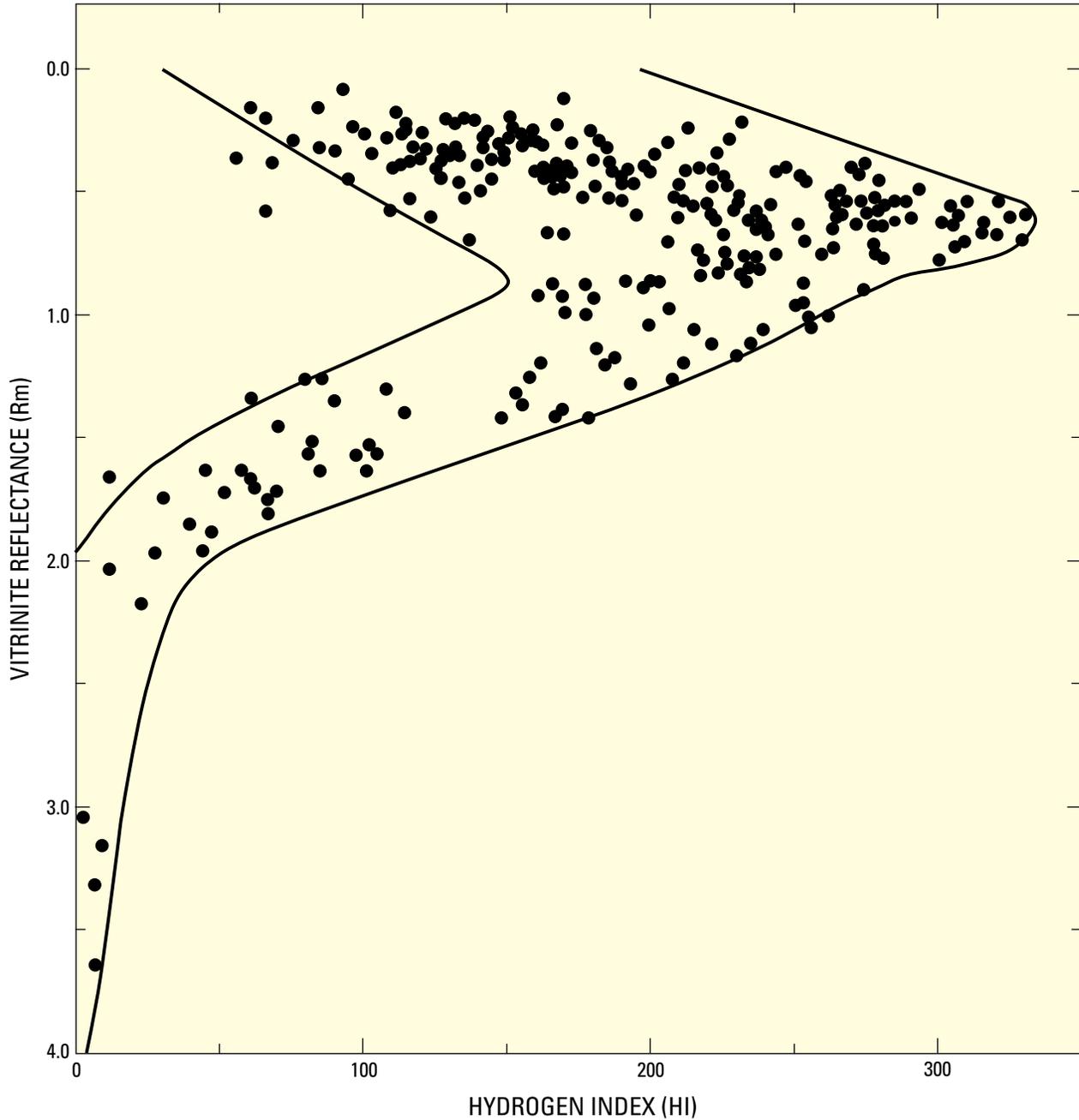
increases to 220 at  $R_0 = 0.7$  percent. The decrease in hydrogen indices at  $R_0$  values in excess of 0.7 percent is due to the commencement of intense HC generation. This is evidenced by the

increase in the  $S_1$  pyrolysis peak, which is equivalent to Soxhlet-extractable HCS (Price and others, 1984), at these same ranks.

A plot of the ROCK-EVAL hydrogen index versus mean vitrinite reflectance ( $R_m$ ) is shown in figure 5 for an entirely different set of worldwide coals from Bertrand (1984). We see the same dramatic increase in ROCK-EVAL hydrogen indices over  $R_o=0.2-0.7$  percent in Bertrand's (1984) data set as occurred in figure 4. The hydrogen-index increase in figure 5 appears to be more pronounced than that of figure 4; however, this is largely due to the compressed vertical scale in figure 5 as compared to figure 4. In actuality, the two data sets are very similar; for example, in figure 5 the mean hydrogen-index values at  $R_o=0.2$

and 0.7 percent are 150 and 230 (an increase of 53 percent) versus 150 and 220 (an increase of 47 percent) in the figure 4 data.

One may attribute the increases in the hydrogen indices of the coals of figures 4 and 5 to a loss of the original oxygen in the coals via  $CO_2$  loss. Such a loss of oxygen does occur from coals and kerogens at low ranks ( $R_o=0.2-0.8$  percent), and this  $CO_2$  loss would slightly increase hydrogen indices. However, given the range of original and final atomic oxygen to carbon ratios of coals, mass-balance calculations demonstrate that this oxygen loss could account for only a fraction of the increase in hydrogen indices in figures 4 and 5. No recognized mechanism can explain the hydrogen-index increases in figures 4 and 5. Thus, I



**Figure 5.** Mean vitrinite reflectance ( $R_m$ ) versus the ROCK-EVAL hydrogen index for coals worldwide and all geologic ages. Modified from Bertrand (1984).

attribute these increases as evidence from the natural system that the hydrogenation of coal by water, which occurs in closed, water-wet HC-generation experiments, also occurs in Nature.

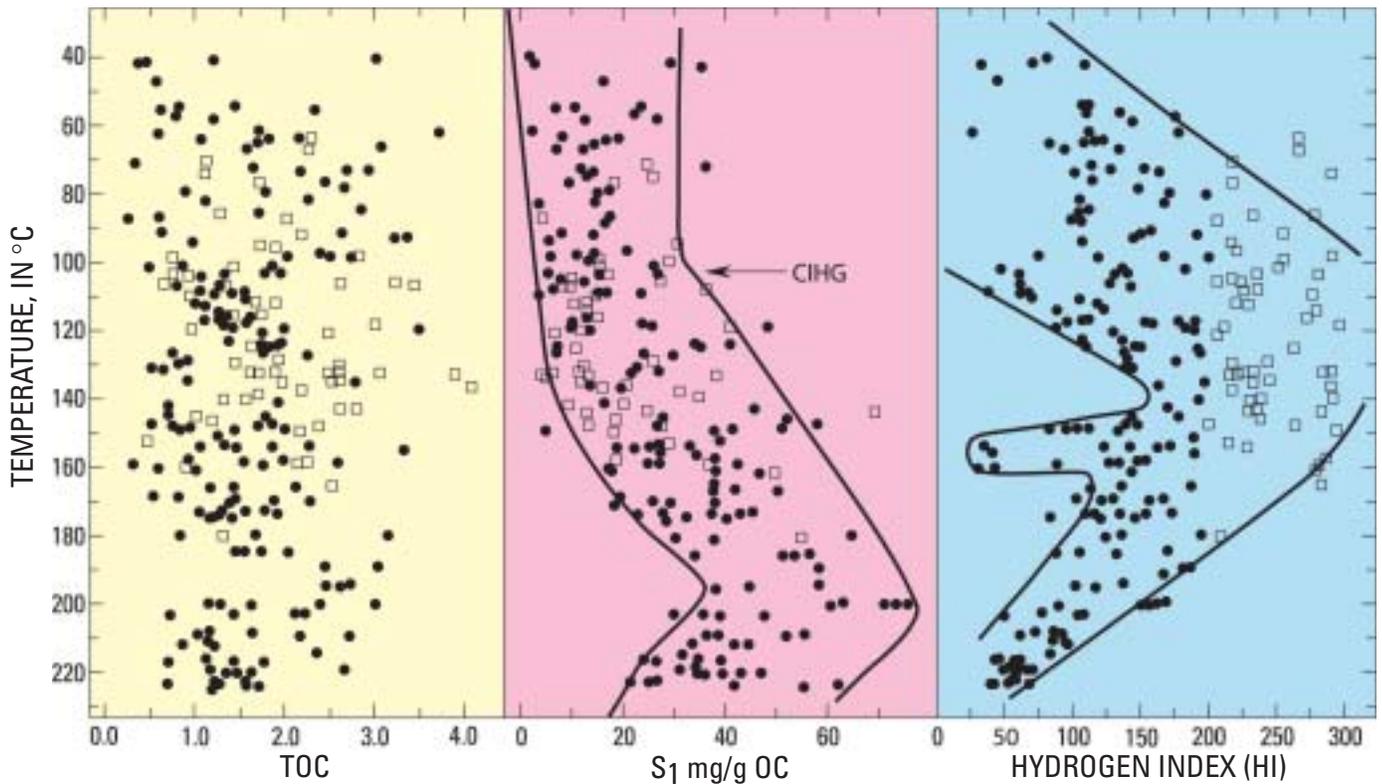
## Los Angeles Basin Upper Miocene Shales

The increase in hydrogen indices at low ranks before HC generation occurs is not limited to coals. Figure 6 shows a large number of ROCK-EVAL analyses versus burial temperature for upper Miocene siltstones and shales with Type-III OM (ROCK-EVAL hydrogen indices <300) from the Los Angeles Basin, Calif. Commencement of intense HC generation (CIHG) is evident from the increase in the TOC-normalized S<sub>1</sub> peak at a burial temperature of 100°C. In gure 6, before HC generation commences, as with both gures 4 and 5, minimum, maximum, and mean hydrogen-index values all dramatically increase. For example, in gure 6 at 80°C, the mean hydrogen-index value is around 150, and at 140°C, where the maximum hydrogen-index values occur, the mean value is about 225 (an increase of 50 percent).

As discussed in Price and others (1999), part of the increase in hydrogen indices in gure 6 at shallow depths of burial (corresponding to burial temperatures of 40°–80°C) is from vertical facies variations in the rocks that lead to significant decreases in organic richness in the shallowest rocks. Therefore, to best

gauge the extent of the contribution of kerogen hydrogenation to the increase in kerogen hydrogen indices, samples with burial temperatures less than 80°C in gure 6 are excluded from consideration.

The gure 6 data also demonstrate that kerogen hydrogenation is occurring in these rocks not only before, but also during, HC generation, as was the case in the laboratory experiments (gs. 1–3). Thus, in gure 6, HC generation commences at 100°C, but hydrogen indices continue to increase in spite of the loss in the hydrogen indices which must occur because of HC generation. Therefore from 100° to 140°C, kerogen hydrogenation is proceeding more rapidly than HC generation. At 140°C, HC generation finally overtakes kerogen hydrogenation, and hydrogen indices begin to decrease. The hydrogen-index trend of gure 6 is not due to changing depositional conditions, because visual-kerogen and extractable bitumen analyses demonstrate that the OM of gure 6 beyond 80°C is uniform. I have observed the same trend of increasing hydrogen-index values over lower maturation ranks in several large data sets from different sites in the U.S. onshore Gulf Coast, and this same trend has been observed in large data sets of rocks with Type-III OM in basins worldwide (Barry Katz, Texaco, oral commun., 8/99). All of the preceding examples of kerogen or coal hydrogenation are for hydrogen-poor Type-III OM. However, hydrogenation of kerogen by water also occurs with hydrogen-rich OM in the natural system.



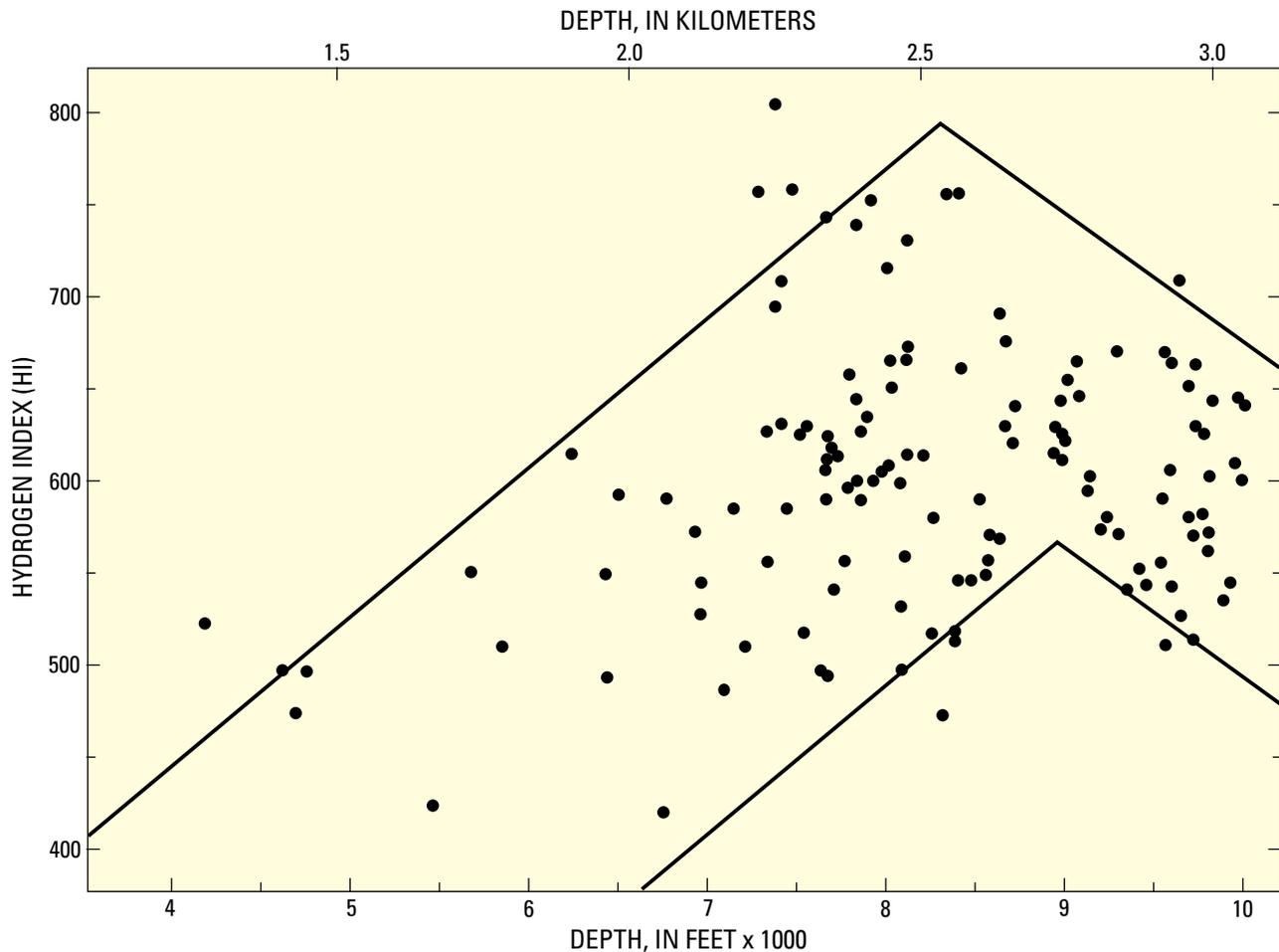
**Figure 6.** Plot of TOC (total organic carbon), and the TOC-normalized (milligrams per gram, mg/g OC) ROCK-EVAL S<sub>1</sub> and S<sub>2</sub> (HYDROGEN INDEX) peaks, all versus burial temperature in °C, for siltstones and shales with hydrogen-poor OM (hydrogen-index values <300) from the Los Angeles Basin. Solid lines in the S<sub>1</sub> and hydrogen-index plots define principal trends of the data. Circles represent samples with hydrogen-index values below 200; squares represent samples with hydrogen-index values of 200 to 300. CIHG in the TOC-normalized S<sub>1</sub> plot is commencement of intense HC generation by that measurement. Modified from Price and others (1999).

## Bakken Formation Shales

I have collected a very large sample base of Upper Devonian–Lower Mississippian Bakken Formation shales, including all available samples on the far eastern flank of the Williston Basin, where the Bakken shales are immature (see fig. 5 of Price and others, 1984). ROCK-EVAL analyses were performed on some 1,300 of these samples by Dow Geochemical Services Inc. (DGS), Houston, Tex. The analyses significantly enlarged a pre-existing ROCK-EVAL data base of more than 400 Bakken shales, previously run at the U.S. Geological Survey laboratories. The Bakken shales are an ideal candidate to check if water also hydrogenates hydrogen-rich OM, therefore increasing its hydrogen content, and thus ROCK-EVAL hydrogen-indices. This is because a large amount of work has already been carried out, and published, on the Bakken Source System (Price and Le Fever, 1992). Moreover, no other source rock worldwide, with high TOC contents and hydrogen-rich OM, has a rock-sample base equivalent to that of the Bakken shales, regarding both geographic coverage (complete coverage of North Dakota and Montana) and range of shale maturity (extremely immature (3,300 ft (1,006 m) of burial) to post-mature). The resulting data for both immature Bakken shales, and Bakken shales which have just commenced HC generation, are shown in figure 7.

Numerous investigators (including Webster, 1982, 1984; Price and others, 1984; Martiniuk, 1988; Le Fever and others, 1991; and Muscio, 1995) have documented that throughout almost all of the depositional area of the Bakken shales, both lithology and OM type of the shales are invariant. In other words, no detectable organic lateral-facies variations occur in the Bakken shales. However, concurrently, Price and others (1984) noted that as the depositional edge of the Bakken Formation is approached, facies variations do occur in the OM, presumably from variations in depositional conditions. Thus, both the initial TOC and hydrogen-index values decrease as the depositional edge of the Bakken shales is approached. Moreover, the extractable OM also changes, taking on slightly more Type-III OM characteristics. The extensive Bakken shale ROCK-EVAL data base I have compiled corroborates the previous conclusions of Price and others (1984) regarding OM variations as the Bakken Formation depositional edge is approached. To avoid these OM variations in the present considerations, only ROCK-EVAL data from Bakken shales whose thickness equals or exceeds 17 ft (5.2 m) were plotted in figure 7.

Three features are immediately apparent in figure 7: (1) the steep increase in hydrogen-index values versus depth from 4,000 to 8,300 ft (1,219 to 2,579 m), (2) the steep decline in hydrogen-index values deeper than about 8,300 ft (2,579 m),



**Figure 7.** Plot of the ROCK-EVAL hydrogen index versus burial depth in feet and kilometers, for immature upper and lower Bakken Formation shales, Williston Basin, and for Bakken shales which have just commenced HC generation where total shale thickness is 17 ft (5.3 m) or greater.

and (3) the wide range in hydrogen-index values at any given depth. Concerning this last observation, although lateral-facies variations do not occur within Bakken shales removed from the depositional edge, significant random variations in TOC and hydrogen-index values do occur both vertically in the shales at any given site, and from site to site. For example, in figure 7, from 7,500 to 8,300 ft (2,286 to 2,579 m), hydrogen indices vary from 475 (Type-II/III OM) to 803 (Type-I OM), although most values fall between 500 and 775. TOC values (not shown in figure 7) also exhibit large variations, ranging from 15 to 40 percent. Close-spaced (3 to 6 in., 7.6 to 15.2 cm), continuous-core samples of Bakken shale from single wells also demonstrate significant vertical variation in both TOC and hydrogen-index values. Price and others (1984) reported the same observation. Thus, the large range of hydrogen-index values in figure 7 at any given depth is due to random organic-richness variations within the Bakken shales themselves.

Because of the significant range of variation of organic richness vertically through the Bakken shales, analyses of core samples of this rock are not reliable for determining mean organic-richness values. Instead, cuttings chips of Bakken shale which have been cleaned, sieved to less than 100 mesh, and picked under a microscope to a 100 percent Bakken shale sample, are *much* more desirable. Such samples represent a homogenized cross section of the entire Bakken shale interval, thus best reproducing mean organic-richness values. Such cuttings chips samples made up the sample base for figure 7. Neither the trends in the figure 7 data nor the wide ranges in hydrogen-index values at any given depth can be attributed to lack of reproducibility or precision in either sampling or analysis. Seventeen random samples were inadvertently taken, cleaned, picked, and analyzed twice. The resulting ROCK-EVAL values from the paired analyses varied no more than 10 percent, and most were within 5 percent. Thus, the trends in the figure 7 data, including the large range of hydrogen-index values at any given depth, are indigenous to the shales themselves.

The strong increase in Bakken shale hydrogen-index values versus depth from 4,000 to 8,300 ft (1,219 to 2,579 m) in figure 7 is equivalent to the same trends shown in figures 4 and 5, versus  $R_o$ , and in figure 6, versus burial temperature. The only obvious cause of the hydrogen-index increase in figure 7 is from water hydrogenating Bakken shale kerogen, thus increasing both its hydrogen richness and its hydrogen indices. Lateral-facies variations are not responsible for the hydrogen-index increases of figure 7.

The significant decrease in hydrogen-index values deeper than about 8,300 ft (2,579 m) shown in figure 7 is due to the first detectable onset of intense HC generation, which commences at around that depth. Also note that at the onset of HC generation, the Bakken shales have *mean* hydrogen indices of 625, making this an extremely rich source rock. As shown in figure 7, a mean hydrogen-index value of 475 at shallow depths increases to a maximum mean value of 625 at 8,300 ft (2,579 m). This is an increase of 31.5 percent, somewhat less than the mean hydrogen-index increases in the coals of figures 4 and 5 (47 and 53 percent, respectively) and in the Los Angeles Basin shales of figure 6 (50 percent). However, all these hydrogen-index increases

from the natural system (31.5 to 53 percent) are in the same range as was observed for the excess products generated in the 30-day, variable-temperature, aqueous-pyrolysis experiments with the Phosphoria shale and the lignite (figs. 3A, 3B; 42.0 and 40.0 percent, respectively).

Data for the Los Angeles Basin mid-Miocene shales (fig. 6) provide evidence that kerogen hydrogenation was taking place not only before, but also during, HC generation. Other evidence of kerogen hydrogenation by water *during* HC generation exists in figures 4, 5, and 7. In the coals of figure 4, HC generation commences at  $R_o=0.6$  percent increase, yet minimum hydrogen-index values continue to increase, presumably from kerogen hydrogenation, until  $R_o=1.0$  percent, where they begin to decrease. In figure 5, minimum hydrogen-index values for the other coal suite also continue to increase past  $R_o=0.6$  percent, again presumably from kerogen hydrogenation, up to  $R_o=1.0$  percent, where they again begin to decrease. In the Bakken shales of figure 7, maximum hydrogen-index values demonstrate that HC generation commences at 8,300 ft (2,579 m), yet minimal hydrogen indices continue increasing in value to at least 8,900 ft (2,765.7 m).

## Conclusions and Implications from the Natural Data

An abundance of data from the natural system regarding kerogen hydrogenation by water confirms that our aqueous-pyrolysis experiments are replicating Nature. Moreover, the natural data also demonstrate that, as in the laboratory experiments, this kerogen hydrogenation occurs both before *and during* HC generation, and also occurs with all OM types. Because: (1) the lower temperature (150°–333°C) aqueous-pyrolysis experiments are replicating Nature in this regard, and (2) as discussed previously, these experiments have also replicated other formerly unrecognized characteristics of HC generation in Nature, it seems reasonable to assume that, with qualifications, possibly the higher temperature (>350°C) experiments may also be replicating natural HC generation processes.

In my opinion, the hydrogenation of kerogen by water can only be explained by redox reactions between water and OM, or in other words, the hydrolytic disproportionation of kerogen. The occurrence of this kerogen-hydrogenation reaction has profound implications for HC exploration and for both source-yield and resource-base assessments: To estimate the amount of oil a source rock can generate, typically ROCK-EVAL derived organic-richness values are used from immature samples of that rock. However, the preceding discussions demonstrate that those richness values could increase by a *minimum* of 30 percent before HC generation even commences, and most probably continue to increase by similar amounts during HC generation. Of even more interest to us in this discussion, is that the very low hydrogen indices of “spent” kerogen may not preclude the possibility that deeply buried kerogen could still generate significant amounts of HC gas.

## A Deep High-Rank Gas-Generation Machine?

Seewald (1994, p. 287), in his definitive paper which clearly demonstrated the existence of the hydrolytic disproportionation of OM in the laboratory, made the following statements and speculations:

That water may contribute hydrogen directly to hydrocarbon formation has important implications for oil and natural-gas generation because water is abundant in most sedimentary environments. Thus the initial atomic H/C composition of sedimentary organic matter may not limit the availability of requisite hydrogen for petroleum and natural-gas formation, especially at high temperatures in the deepest parts of sedimentary basins. Water may be particularly important during natural-gas generation owing to the substantial increase in the H/C ratio of CH<sub>4</sub> relative to the source organic material. Consequently, models that do not include water as a source of hydrogen during hydrocarbon formation may significantly underestimate the gas generation potential of organic matter.

Seewald's (1994) hypothesis about water possibly hydrogenating deeply buried, high-rank, spent kerogen, with low hydrogen to carbon ratios to manufacture a very late-stage HC gas is strongly supported by the same aqueous-pyrolysis experiments which have also indicated that hydrogenation of kerogen was occurring at lower ranks before and during mainstage C<sub>15</sub>+ HC generation.

### Lignite High-Temperature Experiments

Returning to figure 3B, at 350°C and higher, there is an excess of generated products (mainly HC gases) over what is possible, given the original organic richness (ROCK-EVAL S<sub>2</sub> peak plus extractable bitumen) of the lignite. Moreover, above 350°C, there is a continuous increase in these excess generated gases, versus increasing experimental temperatures. Furthermore, the most significant increases occur at the highest experimental temperatures where very little C<sub>5</sub>+ product remains in the system to thermally crack to gas, and also, very little HC generation potential is left in the lignite: the 425°C lignite sample had a hydrogen index of 0.39, and the 450°C sample had a value of 0.29. Clearly in these high-temperature lignite experiments, hydrogen from water must have been added to the lignite to manufacture the high-rank gases. However, from the CO<sub>2</sub> plot for the lignite in figure 2B, the oxygen from the water apparently was not being assimilated into the lignite between 333°C and 425°C, because CO<sub>2</sub> production is largely invariant over these temperatures. This hypothesis is supported by the fact that the ROCK-EVAL oxygen indices of the lignite are low, and are either constant or decrease between 350° and 450°C. However, at 450°C, where the largest jump in generated-HC gases occurs, a significant increase in the amount of excess generated CO<sub>2</sub> also occurs. Thus, from 333° to 425°C, the oxygen from the water which hydrogenated the lignite had to be sequestered in the inorganic (mineral) phase in these experiments. If mineral species are reacting with the excess oxygen from the

water hydrogenating the kerogen, the reaction paths would have to be ionic.

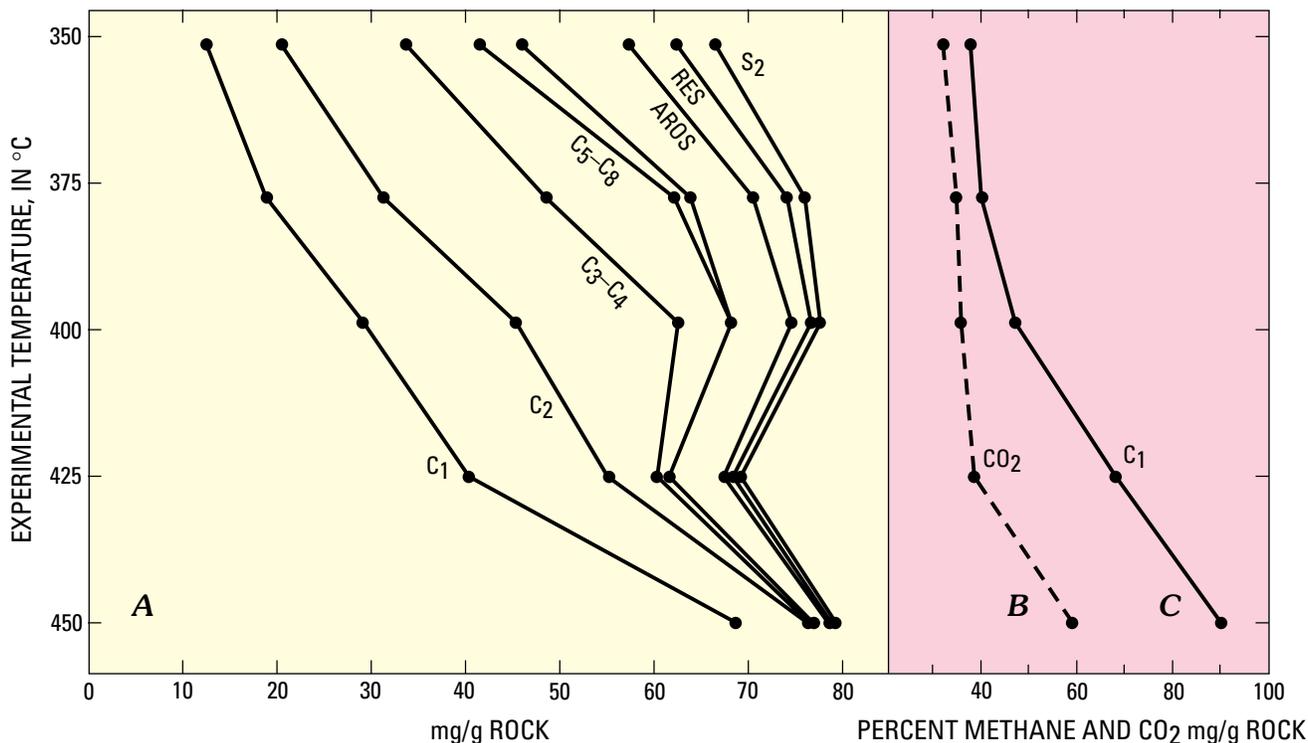
Seewald (1994) noted that a host of minerals with reduced iron, which would consume oxygen during oxidation of OM by water, exist in Nature. To reinforce the point, hydrolytic disproportionation of OM as envisioned by Shock (1988), Helgeson and Shock (1988), and Helgeson and others (1993) involves a metastable equilibrium between water, OM, and the minerals in a system—an equilibrium that is maintained via redox reactions between the different species. Such a metastable equilibrium affected the mineralogy of all six rocks used in our aqueous-pyrolysis experiments, because obvious mineral deposits were present in the upper reaches on the walls of our reaction, above the rock-water mixtures, for all our higher temperature experiments. Thus, mineral species in our experiments appear to be partly responsible for sequestering the oxygen from the disproportionated water.

One last line of evidence further supports the conclusion that water was being consumed not only by the lignite to make HC gas in the 400°C and higher temperature experiments, but also by all five of the other rocks. In the 375°C and lower temperature experiments, excess water always was present in the reaction vessels after the experimental runs were completed. However, in the 400°C and higher temperature experiments, no visible excess water was present after the experimental runs were completed for all six rocks.

### Phosphoria Formation Shale High-Temperature Experiments

In the case of the Phosphoria Formation shale, as previously discussed, pronounced C<sub>15</sub>+ HC thermal destruction occurred between 333° and 350°C, accompanied by significant charring (fig. 3A). Thus, to ascertain whether or not the HC gases being generated at the experimental temperatures of 375°C and higher are exceeding the remnant HC generation capacity of the system inherited from the 350°C experiment, I plotted the amount of generated products, plus the ROCK-EVAL S<sub>2</sub> peak, all in mg/g rock, for the high-temperature Phosphoria shale experiments (fig. 8A). From figure 8A, the total HC-generation capacity of the system at 350.5°C is 66.5 mg/g rock. At all experimental temperatures above 350.5°C, this number is exceeded, reaching a maximum of 79.2 mg/g rock in the 450°C experiment. Thus, even at these extreme experimental temperatures, excess HC generation capacity is being created by water hydrogenating the spent Phosphoria kerogen. This observation is corroborated by other data in figure 8.

Note that the percentage that methane makes up of the total generated product increases from 38 percent at 350.5°C to 90 percent at 450.3°C (fig. 8C, solid line). Methane (CH<sub>4</sub>) is the most hydrogen-rich organic compound in both Nature and in these laboratory experiments. Given the ROCK-EVAL hydrogen indices (and elemental kerogen analyses) of these high-temperature rocks, mass-balance calculations demonstrate that insufficient hydrogen is present in the organic moieties (including the kerogen) of the Phosphoria shale experiments to allow



**Figure 8.** Plot of generated products (in milligrams/gram (mg/g) of rock) for 30-day, variable-temperature aqueous-pyrolysis experiments at 350.5°C and higher for the Phosphoria Formation shale (fig. 8A). C<sub>1</sub> is methane; C<sub>2</sub> is ethane; C<sub>3</sub>–C<sub>4</sub> are the C<sub>3</sub> to C<sub>4</sub> HC gases; C<sub>5</sub>–C<sub>8</sub> are the C<sub>5</sub> to C<sub>8</sub> gasoline-range HCS; AROS are the C<sub>8</sub>+ aromatic HCS; the C<sub>8</sub>+ saturated HCS are unlabeled and are between “C<sub>5</sub>–C<sub>8</sub>” and “AROS”; RES are resins and asphaltenes; and S<sub>2</sub> is the ROCK-EVAL S<sub>2</sub> pyrolysis peak. Amount of generated CO<sub>2</sub> (in milligrams/gram of rock; CO<sub>2</sub> mg/g ROCK) versus experimental temperature shown by dashed line (fig. 8B). The weight percent methane makes up of the total generated product (PERCENT METHANE) is shown by solid line (fig. 8C).

absolute concentrations of the HCS and the relative concentrations of methane both to increase with increasing experimental temperature. Clearly, as was the case with the high-temperature lignite experiments, the water-driven, high-rank deep-basin gas machine envisioned by Seewald (1994) also appears to be simulated in our high-temperature aqueous-pyrolysis experiments with the Phosphoria shale.

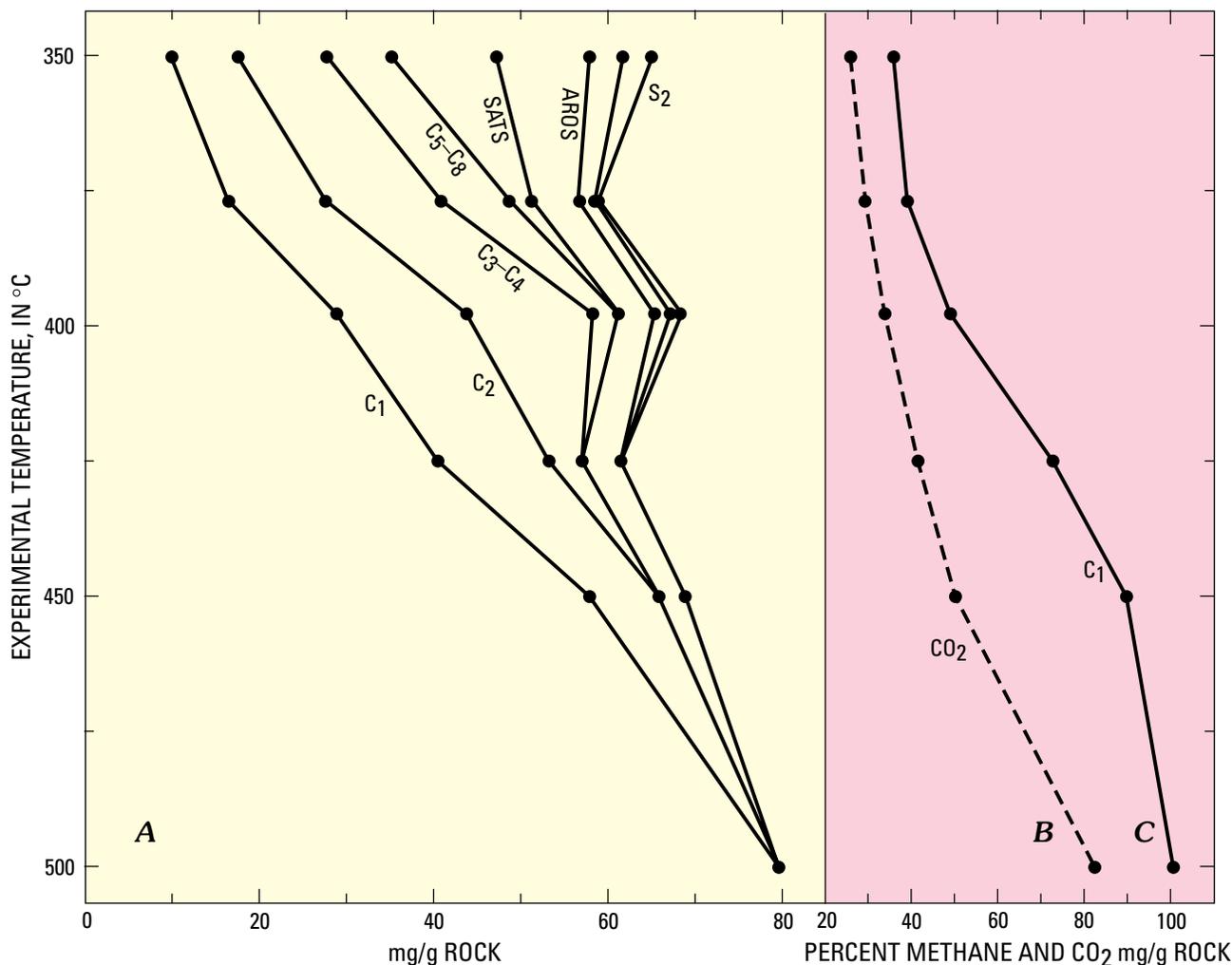
Note also that the amount of CO<sub>2</sub> production in figure 8B is not keeping pace with the excess HC generation. This observation dictates that, as with the lignite, the oxygen from the water hydrogenating the kerogen is also being sequestered in the inorganic phase in the Phosphoria experiments. Whatever that agent was, it appears to have been largely satiated by the 424.3°C experiment, given the significant jump in CO<sub>2</sub> production from 424.3° to 450.3°C (fig. 8B). Lastly, in figure 8A, note that at 424.3°C a second charring event occurs, besides the 350.5°C charring event of figure 3A, wherein significant amounts of the C<sub>5</sub>–C<sub>8</sub> gasoline range HCS and the C<sub>3</sub>–C<sub>4</sub> gaseous HCS are thermally destroyed.

### Anna Shale Member of Pawnee Limestone High-Temperature Experiments

Figure 9A is a mass-balance plot for the high-temperature experiments with the Anna Shale Member of Pawnee Limestone.

As in the case of the Phosphoria shale (fig. 3A), a massive charring event occurs between the 333° and 350.5°C Anna shale experiments (not shown), with a huge loss of C<sub>8</sub>+ saturated and aromatic HCS and resins and asphaltenes. The Anna charring event continues in the 377.3°C experiment, with a continuing loss of C<sub>8</sub>+ saturated and aromatic HCS (fig. 9A). In the 398°C Anna shale experiment, the amount of generated products (69.0 mg/g rock) exceeds the possible generation capacity of the system at 350.0°C (65.5 mg/g rock). As in the Phosphoria shale experiments, a second charring event also occurs in the Anna shale experiments at 425°C, wherein the C<sub>3</sub>–C<sub>8</sub> HCS are significantly reduced in concentration. With increasing experimental temperature to 500.5°C, the amount of generated products continuously exceeds the possible generation capacity of the system at 350.3°C (65.5 mg/g rock), reaching a maximum of 79.7 mg/g rock at 500.3°C.

Unlike the case with the Phosphoria shale high-temperature experiments (fig. 8B), CO<sub>2</sub> generation continuously increases in the equivalent Anna shale experiments (fig. 9B), even over temperature intervals where charring is occurring. This observation has several implications. First, the oxygen-sequestering moiety present in the Phosphoria shale experiments was not present at equivalent concentrations, or if present, was not active, in the Anna shale experiments. Because the experimental vessels were equivalent in both cases, the difference must be due to different mineralogies between the



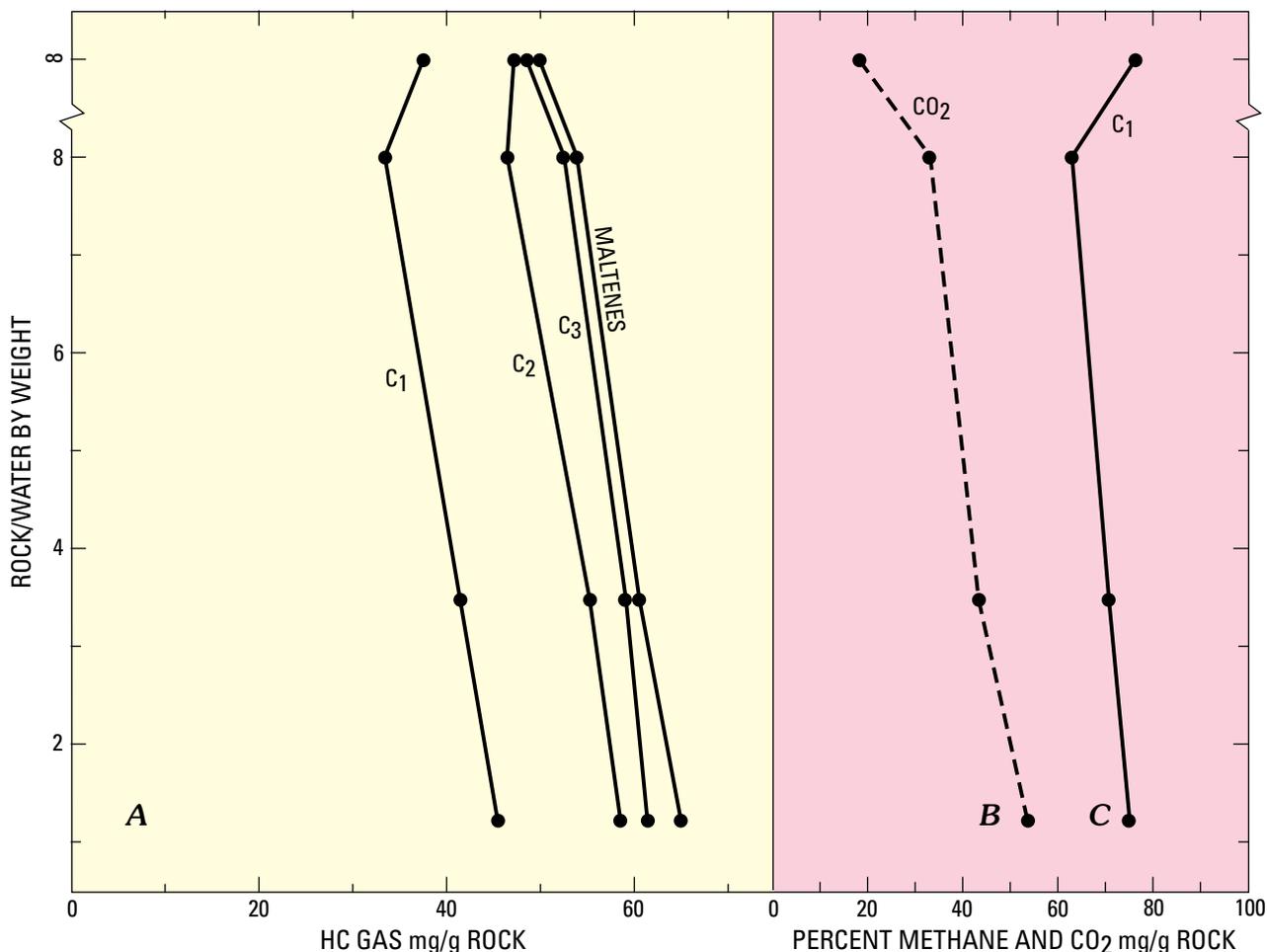
**Figure 9.** Plot of generated products (in milligrams per gram (mg/g) of rock) for 30-day, variable-temperature aqueous-pyrolysis experiments at 350.5°C and higher for the Anna shale (fig. 9A). C<sub>1</sub> is methane; C<sub>2</sub> is ethane; C<sub>3</sub>-C<sub>4</sub> are the C<sub>3</sub> to C<sub>4</sub> HC gases; C<sub>5</sub>-C<sub>8</sub> are the C<sub>5</sub> to C<sub>8</sub> gasoline range HCS; SATS and AROS are the C<sub>8</sub>+ saturated and aromatic HCS, respectively; and S<sub>2</sub> is the ROCK-EVAL S<sub>2</sub> pyrolysis peak. The resins plus asphaltenes are not labeled and are between "AROS" and "S<sub>2</sub>". Amount of generated CO<sub>2</sub> (in milligrams per gram of rock; CO<sub>2</sub> mg/g ROCK) versus experimental temperature is shown by dashed line (fig. 9B). The weight percent methane makes up of the total generated product (PERCENT METHANE) is shown by solid line (fig. 9C).

Phosphoria and Anna shales. Second, in the 425°C (charring) experiment with the Anna shale, thermal conversion of higher molecular weight material (with lower H/C ratios) to lower molecular weight materials (with higher H/C ratios) occurred, with an overall loss of mass in the system. Because excess CO<sub>2</sub> was produced in the 425°C experiment, hydrogen enrichment of the organic system took place by water hydrogenating the OM. Thus, not enough hydrogen was available from the charred OM to supply the hydrogen requirements for the lower molecular weight HC gases with higher H/C ratios. This observation demonstrates that even during the C<sub>15</sub>+ HC thermal destructive phase, hydrogen from water must be added to organic phases to create lower molecular weight HC gases. Lastly, not only do mineral phases help govern the reaction kinetics of these high-rank gas machines in laboratory situations, but also the starting kerogen type plays a role. This is because the high-temperature (>350°C) mass-balance plots (figs. 3A, 3B, 8A, and 9A) and CO<sub>2</sub> curves (figs. 1, 2, 8B, and 9B) for all three kerogen types are distinctly different from one another.

### Anna Shale Member 425°C Variable Water

Another set of experiments further corroborates that water hydrogenates spent kerogen to "manufacture" high-rank gases in water-wet, closed-system laboratory experiments. In figure 10A, the only generation products quantitatively analyzed, methane, ethane, the C<sub>3</sub>-C<sub>4</sub> HC gases, and the C<sub>13</sub>+ maltene fraction (aromatic HCS and resins), are plotted versus the rock/water ratios (grams to grams) for four different 30-day experiments carried out at 425°C with the Anna shale, versus increasing water content. On the vertical scale of figure 10, the sample at the infinity (∞) ratio was prebaked at 100°C for 2 days to remove loosely bound water from the sample before the 425°C experiment was performed. However, more tightly bound water (inner-layer clay water, water of hydration, for example) would have still remained.

As the amount of water in the experiments increases, the amounts of all the products increase, especially methane (fig.



**Figure 10.** Plot of generated products (in milligrams per gram (mg/g) of rock) for 30-day constant-temperature (425°C) aqueous-pyrolysis experiments with the Anna Shale Member of Pawnee Limestone as a function of variable rock to water ratios (fig. 10A). C<sub>1</sub> is methane; C<sub>2</sub> is ethane; C<sub>3</sub> is the C<sub>3</sub> to C<sub>4</sub> HC gases; and MALTENES is the sum of the C<sub>13</sub>+ aromatic HCS, resins and asphaltenes. Amount of generated CO<sub>2</sub> (in milligrams per gram of rock; CO<sub>2</sub> mg/g ROCK) versus the rock/water ratio is shown by dashed line (fig. 10B). The weight percent methane makes up of the total product (PERCENT METHANE) is shown by solid line (fig. 10C). The sample at infinity (∞) on the rock/water ratio axis had no added water and was prebaked at 100°C for 2 days before the 425°C run was performed on it.

10C). Also, the amount of CO<sub>2</sub> dramatically increases from 17.5 mg/g rock in the dry experiment to 53 mg/g rock in the wettest experiment (rock/water equals 1.221; fig. 10B). The figure 10 data clearly demonstrate that water is hydrogenating spent kerogen to produce a methane-rich generation product, with the oxygen from the water being given off as CO<sub>2</sub>.

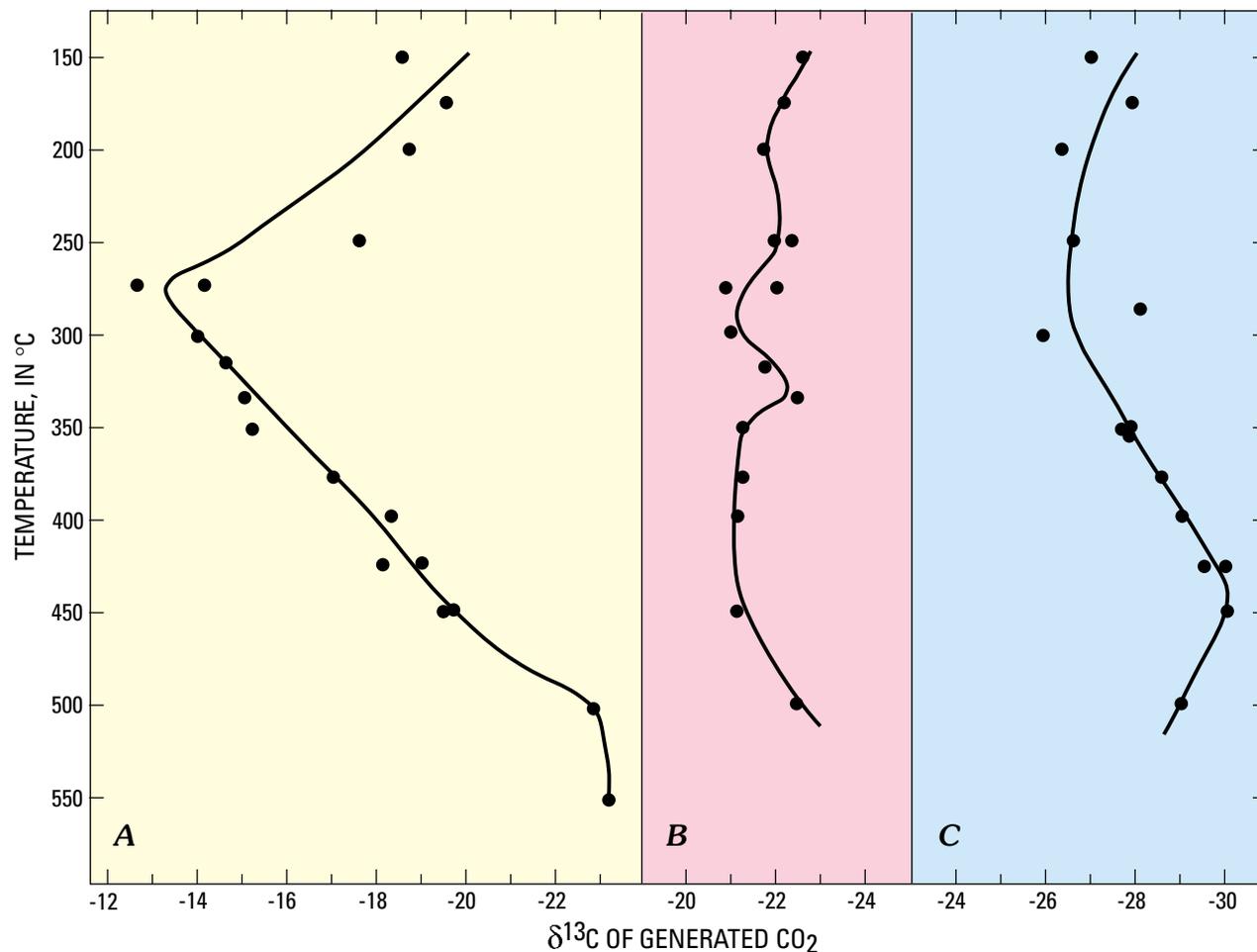
## CO<sub>2</sub> Carbon-Isotopic Values

Figure 11 presents  $\delta^{13}\text{C}$  values for the generated CO<sub>2</sub>, versus experimental temperatures, for the Anna and Phosphoria shales and the lignite. The negative  $\delta^{13}\text{C}$  values of figure 11 (−30.01 to −12.71) could only have been derived from substantial contributions of the biogenically derived carbon from the kerogen in these three rocks. Moreover, a cross plot of percent CaCO<sub>3</sub> for the starting rock versus the median and range of  $\delta^{13}\text{C}$  values for the generated CO<sub>2</sub> from all the experiments with a given rock demonstrates that the carbonate minerals in all six

rocks used in the aqueous-pyrolysis experiments were taking part in the reaction between water and the kerogens (fig. 12).

Figure 12 shows a pronounced relationship between heavier isotopic carbon in the generated CO<sub>2</sub> (less negative values) and increasing CaCO<sub>3</sub> content in the rocks. The data from the Los Angeles Basin shales seem to fall off the trend, but in reality this is probably not the case, because the carbon-isotopic value of the kerogen from this composite shale is −21.97, which is about 10 per mil heavier than that of the kerogens from the other marine shales. If this isotopic variance is taken into account by shifting the Los Angeles Basin shale data 10 per mil to the left, then the Los Angeles data lie directly on the trend.

As previously stated, quantitative carbonate-carbon analyses were run on all samples of all six rocks after each experiment, and these values for a given rock between the different experimental runs changed little, if any. Thus, any CO<sub>2</sub> contributed from the decrepitation of carbonate minerals would have been too small to materially affect the isotopic values in figures 11 and 12. Therefore, the pronounced trend in figure 12 can



**Figure 11.** Plot of carbon-isotopic values of CO<sub>2</sub> generated in 30-day variable-temperature aqueous-pyrolysis experiments, versus experimental temperature, for three different rocks: Anna Shale Member of Pawnee Limestone (fig. 11A), Rattlesnake Butte lignite (fig. 11B), and Phosphoria Formation shale (fig. 11C).

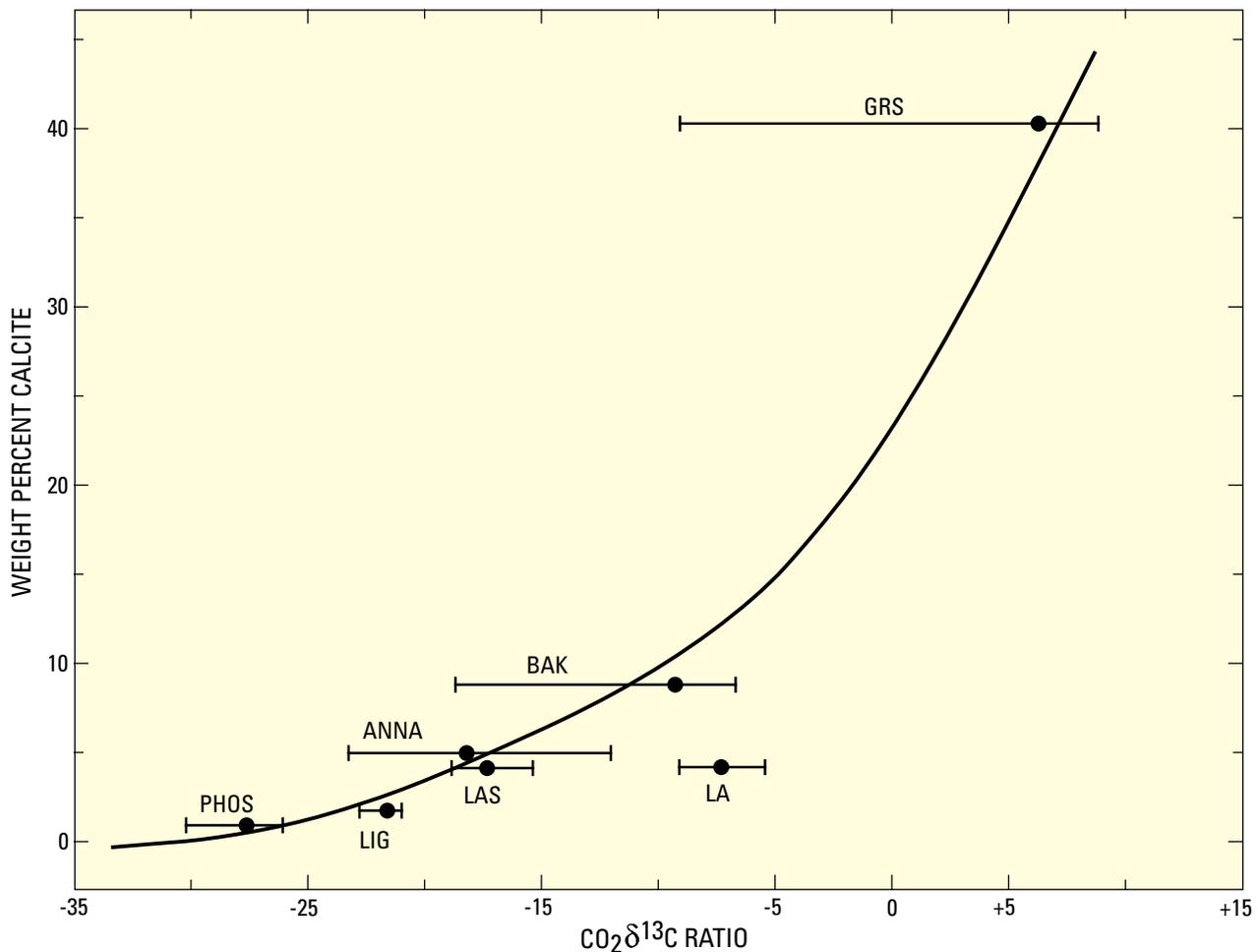
only be due to the carbon in the CO<sub>2</sub> generated from the kerogen-water reaction isotopically equilibrating with the carbonate carbon in the minerals. In other words, the water, OM, and minerals were either in a metastable equilibrium with each other or were attempting to reach such an equilibrium.

### Reservations and Ramifications of a Deep-Basin Gas Machine

The data from the various high-temperature experiments heretofore discussed conclusively demonstrate that water hydrogenates spent kerogen to produce a methane-rich isotopically light gas in laboratory situations. Can it be demonstrated that this same reaction is occurring in Nature? With the existing data from the natural system that I am familiar with, it can be neither proven, nor disproven, that this reaction occurs in Nature. However, kerogen hydrogenation by water occurs both in Nature and in our aqueous-pyrolysis experiments, both before and during mainstage C<sub>15</sub>+ HC generation. From this observation, it is reasonable to assume that hydrogenation of spent kerogen by water to produce a deep-basin methane-rich gas *might* also occur in

Nature, because this reaction occurs in our high-temperature aqueous-pyrolysis experiments. Moreover, the widespread occurrence of late-stage isotopically light carbonate cements (demonstrating the carbon was derived from OM) in deep-basin sediments (Price and others, 1998), shows that some form of OM redox reactions with water is occurring.

If it is assumed for discussion that such a reaction does occur in Nature, what would be some of the qualifications and implications of its occurrence? As proposed by Shock (1988), Helgeson and Shock (1988), Helgeson and others (1993), and Seewald (1994), water, OM, and minerals can reach a redox-buffered metastable equilibrium. When this metastable equilibrium is reached, the hydrolytic disproportionation of OM ceases until system conditions are further changed. The possible controlling parameters that could vary during deep-basin methane generation via hydrolytic disproportionation reactions with kerogen are temperature, pressure, and fluid flow (open-fluid systems). Continuously increasing sediment burial results in continuously increasing burial temperatures and pressures (burial diagenesis). However, the pressure and temperature changes over geologic time would be slight, and theoretically, OM, water, and mineral phases would never be far from equilibrium in closed-fluid systems. As opposed to burial diagenesis,



**Figure 12.** Plot of range (bars) and average (dots) of carbon-isotopic values for  $CO_2$  generated during 30-day variable-temperature aqueous-pyrolysis experiments carried out with six rocks versus weight percent  $CaCO_3$  in the starting rock. PHOS, Phosphoria Formation shale; LIG, Rattlesnake Butte lignite; ANNA, Anna Shale Member of Pawnee Limestone; BAK, Bakken Formation shale; GRS, Green River Formation shale; LA, composite of mid-Miocene Los Angeles Basin shales; LAS, LA sample data shifted 10 per mil to the left to take into account its isotopically heavy kerogen.

punctuated diagenesis is caused by a sudden abnormally high heat flow, which can be due to any number of geologic events (Price, 1983; Morton, 1985). As discussed in Price (1983), punctuated diagenesis is rather common in sedimentary basins. In cases of punctuated diagenesis, sudden dramatic increases in burial temperatures in the deep basin could throw the system water, OM, and minerals far out of equilibrium. This would result in kerogen, pore water, and mineral phases entering into strong redox reactions with one another, thus theoretically producing methane-rich HC gases, and  $CO_2$ .

Price and others (1998) concluded that the principal drive for the hydrolytic disproportionation of OM was an open-fluid system (such as is found in heavy-metal ore deposition or rock metamorphism), where many volumes of pore water flow past a given site. In such cases, OM, water, and the mineral phases can never attain equilibrium with one another, and the hydrolytic disproportionation of OM achieves significant reaction extents. Thus, if the hydrogenation of spent kerogen to produce significant amounts of high-rank deep-basin methane occurs at all in Nature, it would have to take place in open or semi-open fluid systems in the deep basin.

As discussed in Price (1997b), petroleum basin depocenters traditionally have been considered to be open-fluid systems, because source-rock HC expulsion is considered to be an efficient process, which requires an open-fluid system. Thus, we may expect that deep-basin hydrogenation of spent kerogen by water could readily proceed. However, as discussed in Price and LeFever (1992), and Price (1994b, 1995, and 1997b), the position that the deep basin is an open-fluid system with efficient source-rock HC expulsion occurring from basin depocenters appears to have been significantly overstated. Additionally, the presence of abnormal fluid pressures and compartmentalization in petroleum basin depocenters worldwide (Powley, 1990; Ortoleva, 1994; Price, 1997b) clearly dictates that petroleum basin depocenters are semi-closed to closed-fluid systems. When basins are young and evolving, substantial cross-strata fluid flow does occur in basin depocenters. However, even in these cases, the depocenters may hardly be considered open-fluid systems. Otherwise, the high abnormal fluid pressures therein would not exist. Moreover, when fluid flow does occur in these young dynamic basins, it occurs in periodic bursts over geologic time, as opposed to continuous flow.

Meaningful expulsion of oil and (or) gas from source rocks or source systems appears to depend greatly on significant physical disruption of source rocks. Such disruption occurs from intense structural activity, faulting, or salt or shale diapirism, and thus results in a much more open-fluid system. As basin evolution proceeds to the mature stage, with the inevitable cessation of structuring and decline of heat flows, basin depocenters become semi-closed to near perfectly closed fluid systems. At that time, all fluid flow in the basin depocenter ceases, basin compartmentalization occurs, and the resulting fluid compartments can remain sealed for extremely long periods of geologic time. The Anadarko Basin depocenter serves as the type example of a mature “dead” deep basin. However, rejuvenation of high heat flows, and (or) significant structuring, would accompany resurgent basin evolution.

Almost all basin evolution and fluid flow, especially in basin depocenters, occur when basins are young and dynamic. Thus, this is the time when the most significant extents of hydrolytic disproportionation reactions involved with OM would correspondingly occur. This is also the time when the most HC gas would be generated by hydration of deep high-rank kerogen by water, if the reaction occurs at all. Such reactions cannot conceivably occur in stagnant mature basins, such as the Anadarko Basin depocenter, with near perfectly closed fluid systems, wherein pore fluids long ago achieved metastable equilibrium with their surrounding OM and mineral phases.

There is an important caveat to the preceding discussion. The hydration of spent kerogen by water and resulting generation of methane-rich HC gas and CO<sub>2</sub> is a volume-expansive reaction, wherein the products (gases) take up a *much* greater volume than the reactants. If this reaction did occur in Nature, it would be occurring in a semi-closed fluid system. Volume expansion in a constant volume system generates abnormally high fluid pressures. Thus, the kerogen hydration reaction might be self-driving, because the fracturing resulting from the reaction could expand the semi-closed fluid system, allowing an even greater localized volume of rock to take part in the reaction.

The reaction we have proposed herein for a high-rank late-stage generation of an isotopically light methane-rich gas from ultra-mature kerogen is similar to the reaction scheme proposed by McNeil and BeMent (1996). In their scheme, short-chained alkyl groups on the aromatic rings of ultra-mature kerogens preferentially cleave between the first and second carbon atoms next to the aromatic ring. This results in two free radicals: (1) the cleaved alkyl group, and (2) the CH<sub>2</sub> group remaining on the aromatic ring. McNeil and BeMent (1996) called for hydrogen to be shuttled between the kerogen and alkyl groups to satisfy the two free-radical sites, one of which is thus converted to a methyl group. The resulting methyl group still attached to the aromatic ring then preferentially cleaves off the ring if the carbon-carbon bond is a C<sub>12</sub>-C<sub>12</sub> bond, rather than a C<sub>12</sub>-C<sub>13</sub> bond, producing isotopically light methane. The significant difference between our reaction scheme and that of McNeil and BeMent's (1996) is that our hydrogen, which satisfies the open bonds, is derived from an external source (pore water) and not from the kerogen. Because of the limited amount of hydrogen available in high-rank kerogen, only limited amounts of methane can be generated by McNeil and BeMent's (1996) scheme.

However, if water is supplying the needed hydrogen, much greater amounts of methane could be generated. Other than the hydrogen source, the two schemes are similar, especially when compared to other mechanisms proposed to account for isotopically light high-rank methane-rich natural gas.

As previously discussed in the section, “Natural Gas Generation Mechanisms,” much confusion exists concerning natural gas generation. However, let us *assume* that deep-basin hydrogenation of spent kerogen significantly contributes to the natural-gas volumes generated by other likely, or possible, mechanisms (cogeneration of HC gas with mainstage C<sub>15</sub>+ HC generation with migration-fractionation, late-stage HC generation rich in HC gases, transition-metal catalysis, and demethylation reactions). In that case, what would be some of the consequences? One consequence would be that significantly more HC gas would be generated than expected, given the original kerogen hydrogen to carbon ratio or the original ROCK-EVAL hydrogen indices of the rock. In fact, one may expect to commonly find high-rank, basin-centered, continuous-reservoir gas deposits in the depocenters of deep petroleum basins.

To review a point hereforeto discussed in the section, “Natural Gas Generation Mechanisms,” at the fluid pressures in the depocenters of deep basins, almost all C<sub>2</sub>+ HC gases will condense into a liquid phase which may be under a methane-rich gas cap. According to Gussow's (1954) principle of differential entrapment, if the trap becomes filled to spill point, continued migration of methane-rich gas into the trap would cause all C<sub>2</sub>+ liquids to be displaced updip. If the trap continues filling, eventually methane would also be displaced from the spill point. At the elevated pressures and temperatures in basin depocenters, water has substantial solubilities in methane gas (Price and others, 1983). Thus, significant amounts of deep-basin pore water would go into gaseous solution in deep-basin methane-rich gas deposits. Therefore, with continued migration of methane into deep traps, and displacement of water-bearing methane out of the trap at the spill point, the deep basin could become partially, or even largely, dewatered. Moreover, of all the possible methane-generating mechanisms discussed herein, both hydration of deep-basin spent kerogen and hydration of kerogen during late-stage HC generation would consume significant amounts of pore water. In fact, it is possible that around very rich source rocks and (or) coals, all the pore water from the adjacent rocks could be consumed by the organic-rich rocks as they generate HCS, as was the case in our high-temperature aqueous-pyrolysis experiments.

Several important implications follow if parts, or even the entire depocenters, of deep petroleum basins are water-free. For example, a gas-only phase would exist in deep-basin gas-bearing reservoirs. All drilling fluids, even oil-based drilling fluids, contain water. Thus, drilling through gas-only reservoirs with water-based, or mixed water- and oil-based, drilling fluids would most likely create severe permeability blocks around the wellbore. These permeability blocks could significantly damage, or totally destroy, the productive capacity of the formation around the wellbore. Such permeability blocks would arise from the presence of two or more fluid phases around the wellbore (gas, oil, and water) and the Jamin effect. (See Price, 1995, p. 345–346, and 1997b, p. 193–194, for

further discussion.) If such permeability blocks were established around the wellbore during drilling, then drilling or completion techniques would have to be designed which would effectively eliminate the formation damage. Moreover, propped fracture treatments would not be the cure, they would only add to the problem.

The last consequence of deep-basin water-free gas reservoirs would be the possible absence of the permeability-blocking authigenic mineral phases which plague tight-gas sands. Tight-gas sands either are water- and gas-bearing now, or if only gas-bearing now, they contained water and gas when they were at maximal burial temperatures. Basins cool as they mature during progressive basin evolution. As a result of such cooling, a host of authigenic minerals precipitate from solution in the pore waters of coarse-grained rocks, slightly decreasing porosity, but dramatically decreasing permeability. If deep-basin reservoirs are now water-free, and were water-free when maximal burial temperatures existed, such late-stage deposition of authigenic minerals could not occur. Thus, water-free deep-basin gas reservoirs may not have the very low permeabilities which afflict tight-gas sands.

Even if hydrogenation of deep-basin spent kerogen by water does not occur in Nature, as discussed in Price (1995, 1997b), very deep, water-free, basin-centered, continuous-reservoir methane-rich gas accumulations of monstrous size could still exist in deep-basin depocenters. In my opinion, it is of utmost importance to determine the gas/water ratios for the few producing gas wells that have tapped these ultra-deep (>18,000 ft, 5,486 m) gas deposits. Accurate knowledge of such gas/water ratios may allow us to: (1) better assess the origin of the gas in these deposits, (2) design appropriate drilling and completion practices for such gas-resource bases, and (3) possibly better assess the size of the in-place reserves of such gas-resource bases.

Lastly, given the possibility that very large gas deposits exist in deep-basin, basin-centered continuous-reservoirs, as has been previously advocated (Price, 1995, 1997b), it is paramount to avoid the conclusion that the resource base does not exist, or cannot be commercially produced, because of disappointing results obtained from drilling and completion techniques which are inappropriate for the unique characteristics of the resource base. All unconventional resource bases, including energy-resource bases, before they become commercial, go through a time period when they are either not recognized, or if recognized, cannot be commercially produced because inappropriate production methods are being applied to them. Moreover, unconventional resource bases, when they become commercial, always do so because of a change in, or innovation of, technology. Historical retrospection of the development of any given unconventional resource base reveals that a new technological approach always addressed a then-unrecognized problem which was prohibiting efficient production of the resource base. If very large in-place deep-basin gas-resource bases do exist in most petroleum basins, which, based on firm scientific analysis, I have concluded is most likely the case (Price, 1995, 1997b), then the characteristics of these resource bases must be delineated. In this manner, appropriate drilling and completion techniques may be designed for these resource bases.

## Further Research

Certain laboratory and field research could add significant insight into whether or not water is hydrogenating deep-basin, high-rank, spent kerogen to generate methane-rich HC gas in the natural system:

1. Further high-temperature (>350°C) aqueous-pyrolysis experiments should be performed using variable-water contents with larger rock sample sizes (15–20 grams), compared to previous experiments with 4–5 gram sample sizes. In this way, changes in mineralogy versus experimental temperature could be examined. Moreover, post-experimental residual water contents (if any) should be determined. Deuterated water should be used in some experiments, with deuterium analyses performed on the HC products. Carbon-isotopic analyses should be performed on all products, including CaCO<sub>3</sub> in the mineral phase. Rocks with different OM types should also be used. Lastly, ultra high-temperature (550°–650°C) experiments should be carried out.

2. Some of the same experiments in (1) should be carried out using high-rank (R<sub>o</sub>>5 percent) rocks with high TOC contents (>4 percent TOC) and low (<50) hydrogen indices.

3. Gas/water ratios should be determined for ultra-deep (>18,000 ft; 5,486 m) high-rank (R<sub>o</sub>=2.5 percent) gas wells.

4. Carbon-isotopic analyses should be carried out on deep, late-stage, crosscutting CaCO<sub>3</sub> veins, to ascertain the contribution of organic carbon in such calcite cements.

5. Analysis of the gases in inclusions of late-stage isotopically light carbonate cements should be undertaken.

## Conclusions

1. The traditional view that organic metamorphism in Nature is well understood, with burial temperature and geologic time as the only two controlling parameters, is unrealistic. Other important controlling parameters have gone unrecognized. One such unrecognized parameter—water—plays key roles in organic metamorphic reactions, especially in HC-generation reactions.

2. Recent research by different investigators strongly suggests that water, minerals in rocks, and all forms of OM take part in a metastable equilibrium with each other, via aqueous-based redox reactions. This process has been termed the hydrolytic-disproportionation of OM.

3. Different investigators have compiled large bodies of data both from Nature and the laboratory, data which support the conclusion that the hydrolytic disproportionation of OM takes place in many different geologic environments and appears to play key roles in many different geologic and geochemical processes.

4. Historically, C<sub>2</sub>+ rich natural gas (“wet gas”) has been thought to result primarily from the thermal destruction of the C<sub>15</sub>+ HCS in reservoir oil. Moreover, high-rank, deeply buried, methane-rich “dry” gas has been held to result exclusively from thermal destruction of C<sub>2</sub>+ HCS, and especially of reservoir oil. The thermal cracking of C<sub>15</sub>+ HCS has been

portrayed as occurring over fairly moderate burial temperatures, 150°–200°C, depending on the model being used and sediment-burial time.

5. Large data bases from Nature, including but not limited to isotopically light methane-rich (“dry”) gases and *extreme* thermal stabilities of C<sub>15</sub>+ HCS, demonstrate that the hypothesis of a pronounced thermal instability of C<sub>15</sub>+ HCS for the origin of wet and (or) methane-rich gases is unrealistic.

6. As such, different investigators have proposed other generation mechanisms for both wet and methane-rich HC gases: transition-metal catalysis; late-stage demethylation of post-mature kerogens in shales; cogeneration of HC gases with C<sub>15</sub>+ HCS; late-stage generation of increasingly rich C<sub>8</sub>- HCS, including the C<sub>4</sub>- HC gases during the evolution of mainstage C<sub>15</sub>+ HC generation; C<sub>1</sub> to C<sub>4</sub> HC-gas fractionation during migration; and late-stage hydrogenation of spent kerogen by water, via the hydrolytic disproportionation of kerogen.

7. In Nature, HC generation occurs in closed, or semi-closed, water-wet, pressurized systems, where product escape is difficult and oxygen fugacities are low. Thus, dry, open-system pyrolysis techniques, such as ROCK-EVAL pyrolysis, with moderate oxygen fugacities, low pressures and where product escape is immediate, are not good replications of HC generation in Nature. This conclusion is corroborated by the fact that products from these types of pyrolysis are not found in Nature.

8. Different water-wet, closed-system, pressurized, experimental pyrolysis approaches to HC generation replicate Nature much better than dry open-system pyrolysis. However, even the water-wet pyrolysis approaches do not completely replicate Nature. Thus, results from water-wet closed-system pyrolysis experiments must always be compared to data from Nature to verify that the experimental result applies to the natural system.

9. Amounts of carbon dioxide far in excess of what are possible, given the original oxygen contents of kerogens or coals, are generated in water-wet closed-system HC-generation pyrolysis experiments.

10. Mass-balance calculations of 30-day, variable-temperature aqueous-pyrolysis HC-generation experiments demonstrate that in addition to excess CO<sub>2</sub>, generation potential plus generation products significantly in excess of what is possible, given the starting organic richness of the rocks, also result in these experiments. Moreover, hydrogen indices from post-experimental rock samples, for 150°–200°C pre-HC-generation aqueous-pyrolysis experiments for six different rocks, significantly increase over the starting values of the rocks. Thus, in addition to excess CO<sub>2</sub>, the coals and kerogens in these experiments are also becoming more hydrogen-rich and are acquiring excess HC-generation capacity.

11. The excess generation products observed in our aqueous-pyrolysis experiments and the increases in the hydrogen indices of our rocks are both due to water hydrogenating our coals and kerogens via aqueous-based redox reactions, that is to say the hydrolytic disproportionation of kerogen (and coal). The oxygen from the water is given off as excess CO<sub>2</sub>.

12. Carbon-isotopic values of the CO<sub>2</sub> from these aqueous-pyrolysis experiments conclusively demonstrate that the excess CO<sub>2</sub> in these experiments is derived from the organic carbon in the coals or kerogens.

13. Large ROCK-EVAL data bases from Nature (two coal suites, and Los Angeles Basin upper Miocene and Williston Basin Bakken shales) all demonstrate strongly increasing hydrogen indices with increasing burial depth, before, and during, mainstage C<sub>15</sub>+ HC generation.

14. The strong increases in hydrogen indices in these rocks with increasing burial can only be due to water hydrogenating kerogen in the natural system, thus corroborating the results of our aqueous-pyrolysis experiments.

15. Mass-balance calculations for 30-day, variable-temperature, aqueous-pyrolysis, high-temperature (>350°C) experiments demonstrate that water is hydrogenating the kerogens of all six experimental rocks to make a progressively more methane-rich gas. Moreover, the amounts of generated products in all cases exceed that which is possible, given the starting organic richness of the systems at 350°C.

16. In some experiments, spanning certain temperature ranges, the oxygen from the water hydrogenating the kerogen was sequestered by mineral phases in the rock samples, instead of being produced as CO<sub>2</sub>. Thus, in these experiments, the mineral phases, water, and OM were all reacting with one another in an attempt to reach metastable equilibrium in the system.

17. A cross plot of CO<sub>2</sub> isotopic-carbon values versus CaCO<sub>3</sub> content in the starting rock also demonstrates that the carbon from the OM in the CO<sub>2</sub> was being isotopically exchanged with the carbon in the CaCO<sub>3</sub> of the rocks. This observation corroborates that the OM, water, and mineral phases in these experiments were all reacting with one another.

18. Constant-temperature (425°C), 30-day, aqueous-pyrolysis Anna shale experiments with varying water content also demonstrated that water hydrogenates spent kerogen to make a methane-rich HC gas.

19. Ascertaining whether or not hydrogenation of spent kerogen by water occurs in Nature is presently not possible. However, based on the concurrence of our experimental data with comparable data from Nature regarding kerogen hydrogenation at lower ranks, it is reasonable to assume that hydrogenation of high-rank kerogen by water may possibly occur in Nature. This assumption is supported by the widespread occurrence of late-stage carbonate cements with isotopically light carbon in the depocenters of deep basins.

20. If the late-stage kerogen hydrogenation reaction does occur in Nature, certain qualifications and ramifications follow:

A. Open, or semi-open, fluid systems are the key prerequisite for significant reaction extents in hydrolytic disproportionation reactions with OM, including reactions involving hydrogenation of spent kerogen by water.

B. In basins whose depocenters are closed-fluid systems and which are maturing by burial diagenesis, it is unlikely that the extent of the reaction producing high-rank methane by kerogen hydrogenation would be large.

C. The hydrogenation of deep, high-rank spent kerogen, with consequent methane production, could likely be significant in basins maturing via punctuated, rather than burial, diagenesis.

D. This reaction would primarily occur during the youthful stages of basin evolution, such as the present-day (Neogene) U.S. Gulf Coast, when maximum cross-basin fluid flow occurs.

E. The reaction should not occur during the mature stages of basin evolution when deep-basin depocenters are closed-fluid systems, with pronounced and unchanging compartmentalization over geologic time, the Anardarko Basin being an excellent example.

F. Because the reaction kerogen + water  $\rightarrow$  CH<sub>4</sub> + CO<sub>2</sub> is volume-expansive, in some situations this reaction may be self-driving by creating high fluid pressures that cause fracturing in the containing rocks, resulting in a more localized open-fluid system.

G. If the preceding reaction does occur, then significantly more deep-basin gas may be generated in certain situations than would be the case given the original hydrogen-richness of the OM in deep-basin rocks.

H. Thus, the depocenters of certain deep petroleum basins may contain continuous-reservoir, basin-centered, high-rank, methane-rich gas deposits.

I. Such deep-basin gas deposits may be water-free, because of both solution of water into gas volumes migrating out of the deep basin and deep-basin spent kerogen consuming water to make a methane-rich gas.

J. If gas-only phases exist in deep-basin reservoirs, it is probable that significant formation damage would occur to these reservoirs during drilling through them. Thus, the existence of these reservoirs may not be apparent.

K. If deep-basin gas reservoirs exist and are water-free, they could possibly contain minimal amounts of authigenic minerals. Thus, the low permeabilities typical of tight-gas sands may not be present in these reservoirs.

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## Appendix. Replication of HC Generation in the Laboratory

### Open versus Closed-System Methods

HC generation in Nature occurs over abbreviated or long geologic time periods, in water-wet, pressurized, closed or semi-closed fluid systems, where product escape is difficult, or at least retarded, and oxygen fugacities are low. In the last 10 years, HC generation, and organic metamorphism in general, have been primarily mathematically modeled from the results of open-system pyrolysis, particularly ROCK-EVAL analyses. This pyrolysis approach occurs instantly in open, dry, low-pressure systems, where product escape is immediate, and oxygen fugacities are moderate. Although ROCK-EVAL is a powerful screening tool to determine source-rock organic richness and maturity, a more inappropriate instrument with which to model natural HC generation could hardly be designed (Price, 1994a). Moreover, predictions concerning organic metamorphism, made on the basis of ROCK-EVAL derived kinetics, contradict large data bases from Nature (Price, 1993; 1997a). Lastly, as noted by Price and McNeil (1997), dry open-system pyrolysis, including ROCK-EVAL pyrolysis, yields generation products not found in Nature. These observations demonstrate that dry, open-system pyrolysis is not an acceptable replication of HC generation in Nature.

In contrast, results from closed-system water-wet pyrolysis experiments have been demonstrated to mimic aspects of natural HC generation. For example, Lewan and others (1979) and Lewan (1997) have simulated natural source-rock expulsion in their hydrous-pyrolysis experiments. Based on aqueous-pyrolysis experiments (Wenger and Price, 1991; and Price and Wenger, 1992), Price (1989a) reported that small concentrations of HC gas were generated before mainstage C<sub>15</sub>+ HC generation commenced in their experiments. Moreover, large quantities of C<sub>1</sub>–C<sub>4</sub> HC gases were cogenerated with C<sub>15</sub>+ HCS during mainstage C<sub>15</sub>+ HC generation in these same experiments. Price (1989a) presented evidence that these same events occurred in Nature, an observation since corroborated by numerous other investigators, including Price and Schoell (1995). Lastly, Price and Wenger (1992) demonstrated, again from aqueous-pyrolysis experiments, that fluid pressure was an unrecognized controlling parameter in organic metamorphism, with increasing fluid pressure retarding all aspects of organic metamorphism, including HC generation. Their results have been replicated in the laboratory by other studies, including Michels and others (1992), and have also been demonstrated to occur in Nature (Hao Fang and others, 1995, 1996; McTavish, 1998).

Many variants of closed-system pyrolysis experimental techniques are available with which to study HC generation. Such experiments may be carried out on a micro-scale in sealed

glass tubes (Horsfield and others, 1989), or in sealed gold bags (Monthieux and others, 1985) using only milligram amounts of source rocks, or on a much larger scale by submerging several hundred grams of rock under a water phase (“hydrous pyrolysis”) to simulate natural source-rock expulsion (Lewan and others, 1979; Lewan, 1997). In contrast, in aqueous-pyrolysis experiments, 4 to 25 grams (g) of source rock are reacted with added water, usually equivalent to 11 weight percent of the rock (Price, 1989a; Wenger and Price, 1991). Proponents of each of the different closed-system experimental approaches may claim that theirs is superior to others, and each has certain advantages, and deficiencies, with respect to the others. Be that as it may, all share significant common strengths over dry, open-system pyrolysis. Thus, compared to open-system pyrolysis, closed-system experiments: (1) occur over much longer time periods, tens of hours to months, (2) are all water-wet, with either added water or water indigenous to the sample, (3) have much lower oxygen fugacities (higher-hydrogen fugacities), and (4) retain all their generation products.

However, none of these closed-system approaches replicate natural HC generation exactly, one on one. For example, in all water-wet, closed-system pyrolysis experiments, much higher relative concentrations of resins and asphaltenes are generated with respect to the saturated and aromatic HCS, as compared to the case with natural HC generation. Thus, it is paramount in assessing the possible validity of a newly recognized facet of HC generation from such closed-system experiments that one compare the experimental results to similar data from Nature. In this manner, one may gauge if the experimental result in question is actually replicating the natural system, or instead is merely an experimental artifact. Aspects of HC generation, or organic metamorphism in general, hypothesized on the basis of experimental results but not corroborated by supporting data from Nature, are simply unsubstantiated hypotheses.

## Rock-Eval Pyrolysis

For those unfamiliar with the details of the ROCK-EVAL analysis, the  $S_2$  peak measures the milligrams (mg) of HCS, from the HC gases to heavy HCS, which can be generated from a gram (g) of shale (the analysis is normalized to mg/g values). For example, the Phosphoria shale used in the figure 3A experiments has an  $S_2$  value of 96.6 mg/g rock for starting Soxhlet-extracted rock. The ROCK-EVAL hydrogen index (HI) is equal to the ROCK-EVAL  $S_2$  peak divided by total organic carbon in weight percent ( $S_2/TOC$ ). The starting Soxhlet-extracted Phosphoria shale of figure 3 has a hydrogen index of 451.

As stated, the ROCK-EVAL analysis is held by many investigators, including Braun and Burnham (1991), as an acceptable replication of HC generation *and source rock expulsion* in Nature, an unrealistic viewpoint in my opinion. Concurrently, ROCK-EVAL has come under significant criticism as not even being able to fulfill the purpose for which it is best suited: providing reasonable estimates of organic richnesses of source

rocks. As an aside, these two viewpoints could not be more diametrically opposed to one another. Some investigators (Baskin, 1997) advise pronounced caution in using ROCK-EVAL hydrogen indices as a measure of kerogen HC-generation potential, or at the very least a good correlation between ROCK-EVAL hydrogen indices and kerogen hydrogen to carbon ratios should be demonstrated, which is a point well taken. Because much of the data from this study is derived from ROCK-EVAL analysis, some discussion is warranted of its analytical strengths, weaknesses, and limitations.

Significant problems do exist with the ROCK-EVAL instrument regarding accuracy and reproducibility of analyses. Moreover, I have repeatedly voiced concerns on this subject (Price and others, 1984, 1999), and still consider the variance in the reproducibility of  $T_{max}$  unacceptable, except in the case of coals where  $T_{max}$  is more reproducible and has an excellent correlation with  $R_o$  (Tissot, 1984). Poor correlations of kerogen H/C ratios with ROCK-EVAL hydrogen indices do exist, as pointed out by Baskin (1997). The reasons for this lack of correlation have been discussed by Horsfield and Douglas (1980), Peters (1986), and Larter (1988), and largely are attributed to erroneous ROCK-EVAL analyses. The lack of correlation between kerogen H/C and hydrogen indices thus far is limited to two cases. One of these involves very immature source rocks with hydrogen-rich OM from the California petroleum basins, where ROCK-EVAL hydrogen indices vary between 200 and 700, whereas kerogen H/C ratios for the same samples vary between 1.00 and 1.40 in cross plots of these two parameters, which thus are little more than scatter plots. This problem was discussed by Price and others (1999), and was largely attributed to the fact that these California immature mid-Miocene shales can, but do not always, have very high bitumen coefficients (200–400), most of this bitumen being composed of resins and asphaltenes, entities which are lost during kerogen isolation procedures. However, this material is present during the ROCK-EVAL analysis, which records this material as the  $S_2$  peak—and rightfully so, because it is HC-generation potential. Thus, the lack of correlation in this instance is due to the fact in some cases, kerogen maceration decreases the HC-generation capacity of the *rock*, which is what the ROCK-EVAL instrument is measuring. As such, Price and others (1999) made the point that the lack of correlation between the two parameters in this instance is actually more due to the kerogen maceration procedure than to the ROCK-EVAL instrument. Price and others (1999) presented a cross plot of kerogen H/C ratios versus ROCK-EVAL hydrogen indices for California source rocks, a plot which had an excellent correlation between the two parameters.

The other case of a lack of correlation between kerogen H/C ratios and the hydrogen index involves rich ( $TOC > 7.0$  percent) source rocks, with hydrogen indices  $> 450$ , where hydrogen-index values flatten out versus H/C ratios which thus become almost invariant versus hydrogen-index values (Baskin, 1997, his figs. 1, 2, not shown here). The lack of correlation in this case is due to faulty calibration of the ROCK-EVAL instrument with inappropriate standards. Flame-ionization detectors,

which are the HC detectors on the Rock-Eval instrument, are notoriously nonlinear for large sample sizes, which is demonstrated in plots of response (millivolts) versus sample size. ROCK-EVAL is typically calibrated using standards with  $S_2$  peak values of 5–10. However, in a large yet-unpublished costudy with Dow Geochemical Services Inc. (DGSI), we found with very rich source rocks, specifically the Upper Devonian–Lower Mississippian Bakken Formation shales, which have  $S_2$  values of 100–200, that standards with such low  $S_2$  values (5–10) resulted in abnormally low TOC and  $S_2$  values being reported for the sample being analyzed. We obtained appropriate values only after calibrating the instrument with a rock with similar organic richness to that of the rock being analyzed. As part of the study with DGSI, we also examined other variables affecting the ROCK-EVAL analysis, including grain size of the powdered rock and the sample size for analysis. We found that the optimum sample size varied as a function of the rock's organic richness, and that rocks had to be ground and sieved to 100 mesh or less to optimize the analysis.

I present large ROCK-EVAL data bases in this report from analyses of samples from both Nature and from laboratory experiments. The hydrogen indices from the ROCK-EVAL data bases in this study all exhibited excellent correlations in cross plots with kerogen H/C ratios. Moreover, all samples were properly calibrated, ground and sieved, with optimum sample sizes employed. Within all sample sets, the operating parameters of the ROCK-EVAL instrument, including heating rates, were held constant. Thus, the results reported here are due entirely to variances within the samples themselves, and in no manner should be considered as analytical artifacts. In my opinion, the argument that ROCK-EVAL cannot adequately measure source-rock HC generation potential is as overstated as the argument that ROCK-EVAL closely mimics HC generation in Nature.

## Aqueous Pyrolysis

In aqueous-pyrolysis HC-generation experiments, between 4 and 25 g of finely powdered source rock are reacted with variable amounts of added water. In most experiments, the added water makes up 11 weight percent of the rock, which is estimated to be the maximum amount of water available to a source rock in Nature. The samples are reacted for variable times, 30 days for most experiments, in stainless-steel “pipe bombs,” sealed by a high-pressure, high-temperature valve. With the sealing valve inside the heating furnace, the experimental vessels may be taken to maximum temperatures of 500°C.

However, much higher temperatures are possible if the sealing valve extends out of the furnace, and is thus not heated. Maximum pressures of 60,000 psi (4,136.8 bars) may be obtained with these vessels; however, most experiments are carried out in the range of 2,000–5,000 psi (137.8–344.7 bars). When the desired reaction time has been reached, the vessels are cooled and the sealing valve on the pressure vessel is opened allowing the generated gases to be vented into a glass round-bottom flask, of known volume. This flask is sealed by a compressed half-hole septum (Alltech Assoc.) in a Swagelok fitting which is attached to the metal tube of a glass-metal Kovar seal. Quantitative and qualitative analyses, including carbon-isotopic analyses, can be carried out on the trapped gases. The high-temperature sealing valve is then removed and quickly replaced by another high-pressure fitting terminating in another compressed half-hole septum in a Swagelok fitting, which once again seals the reaction vessel. The vessel is heated to 80°C in a convection oven, and a head-space sample is removed from the reaction vessel by a gas-tight syringe with a Minerett valve, via the half-hole septum, for quantitative and qualitative  $C_4$ – $C_7$  HC analyses. After the reaction vessel is cooled from the 80°C heating, the vessel is opened, and its contents (reacted source rock and generated products) are quantitatively transferred to a thimble in a Soxhlet extractor for extraction using dichloromethane.

The resulting extracted bitumen is filtered and passively evaporated (to preserve  $C_8+$  HCS) to 1 milliliter (mL) and the dichloromethane is replaced by hexane to precipitate asphaltene, which are filtered from the sample. The remaining maltene fraction of the bitumen is then separated into saturated and aromatic HCS and resins by silica-gel/alumina column chromatography. After passive evaporation of the saturated and aromatic HCS, they are transferred to 10 mL volumetric flasks, and splits are taken of both fractions. One split is used for gravimetric weight determination and  $C_{13}+$  gas chromatography, and the other split is used for  $C_8+$  gas chromatography and isotopic determinations. Electronic integration of the  $C_8+$  and  $C_{13}+$  saturated- and aromatic-HC gas chromatograms allow quantitative determination of  $C_8+$  HCS for both fractions. Resin and asphaltene weights are determined gravimetrically. ROCK-EVAL analyses and kerogen maceration are carried out on the reacted shales, with elemental analysis being carried out on the recovered kerogen. In this manner, all products and reactants from these experiments are qualitatively and quantitatively analyzed, and mass balance calculations between generated products and original and remaining source-rock generation potential may be carried out. Experimental runs may be carried out as a function of many different parameters, including reaction temperature or pressure, water content, starting source rock, reaction-headspace volumes, and so on.