

Hydrogen Isotopic (D/H) Composition of Organic Matter During Diagenesis and Thermal Maturation

Arndt Schimmelmann,¹ Alex L. Sessions,² and Maria Mastalerz³

¹Indiana University, Department of Geological Sciences, Bloomington, Indiana 47405-1405; email: aschimme@indiana.edu

²California Institute of Technology, Division of Geological and Planetary Sciences, Pasadena, California 91125; email: ALS@gps.caltech.edu

³Indiana Geological Survey, Indiana University, Bloomington, Indiana 47405-2208; email: mmastale@indiana.edu

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deuterium, fossil fuel, isotope exchange, isotope fractionation, catagenesis

Abstract

Changes in the D/H ratio of sedimentary organic matter (SOM) during thermal maturation have been difficult to interpret because the effects of hydrogen exchange and kinetic fractionations are confounded in natural samples. Recent analytical developments have significantly improved our understanding of the responsible mechanisms. In this paper, we review experimental and field data that document a progressive increase in the D/H ratio of most organic hydrogen at the bulk and molecular levels, and suggest that the transfer of hydrogen from water to organic matter is the most important mechanism leading to those changes. SOM and water in natural petroleum systems approach a pseudoequilibrium D/H fractionation of about -80 to -110% . D/H ratios of organic hydrogen can preserve quantitative information about paleoclimate throughout diagenesis, and some qualitative information through catagenesis.

1. INTRODUCTION: STABLE ISOTOPES OF HYDROGEN IN ORGANIC MATTER

Exploration for fossil fuels relies heavily on geochemical and isotopic characteristics that relate oil, gas, and coal to the biomass of ancient organisms and to the geological conditions of maturation. At the same time, many earth scientists are exploring the paleoenvironmental record that is captured by the isotopic composition of organic materials. Hydrogen is abundant in all natural organic materials, including sedimentary organic matter (SOM) and fossil fuels, and is usually the most abundant element. Yet studies of stable hydrogen isotopes in SOM and fossil fuels have lagged far behind those of carbon isotopes, a fact that reflects both analytical difficulties in measuring hydrogen isotopes and conceptual difficulties in interpreting the results. The latter situation arises in part because of the propensity of certain hydrogen positions—such as hydroxyl hydrogen—to undergo rapid exchange with external sources of hydrogen. Until recently, most hydrogen-isotopic measurements were of bulk organic samples, and thus could not distinguish primary isotopic signals preserved in organic matter from secondary signals resulting from isotopic exchange. Two recent technological developments have changed that situation. The first is the development of detailed protocols for controlling the isotopic composition of readily exchangeable hydrogen in bulk organic samples via laboratory exchange with isotopically defined waters (Section 2). This allows quantitation of the amount of labile hydrogen and correction for its contribution to the bulk D/H ratio. The second is the advent of methods for compound-specific isotopic analyses, which allow us to select specific molecular analytes that contain no exchangeable hydrogen. The combination of these two approaches provides a new understanding of hydrogen-isotopic changes accompanying the thermal maturation of organic matter. These developments are the subject of this review.

1.1. Physical Chemistry of Hydrogen Isotopes

Hydrogen has two stable isotopes, protium (^1H) and deuterium (^2H or D, $\sim 0.015\%$ natural abundance). To minimize confusion, we follow the convention of using H to represent the element hydrogen, including both isotopes (e.g., H_2O), whereas ^1H specifies the isotope protium and D specifies deuterium (e.g., ^1HDO). The sole exception to this rule is the D/ ^1H ratio, which we abbreviate as D/H following conventional usage.

The isotopes ^1H and D differ in mass by a factor of ~ 2 . This is the largest relative difference between any two isotopes of the same element (Criss 1999). The dissimilar masses of ^1H and D cause significant differences in the physical and chemical properties of compounds with different isotopic contents (i.e., isotopologues). For example, the boiling point of D_2O is 1.42°C higher than that of $^1\text{H}_2\text{O}$. Physical and chemical differences are also expressed in compounds with a natural abundance of deuterium, e.g., volatile hydrocarbon molecules containing at least one D have a slightly higher vapor pressure than their all- ^1H isotopologue (Wang & Huang 2001, 2003), and C- ^1H bonds are more reactive than otherwise equivalent C-D bonds. Such differences also extend to the ordering of isotopic substitution (i.e., isotopomers), such

that relative to methanol $C^1H_3O^1H$, $C^1H_2DO^1H$ has a higher vapor pressure and C^1H_3OD has a lower vapor pressure (Hopfner 1969). These differences arise because isotopic substitution fundamentally alters reaction equilibrium and rate constants, a consequence known formally as an isotope effect. Due to their extreme mass difference, isotope effects for 1H versus D can have a theoretical maximum of 18, i.e., $C-^1H$ bonds react 18-fold more rapidly than $C-D$ bonds (Bigeleisen & Wolfsberg 1958). In practice, such extreme isotope effects are rarely encountered, but effects of 2 or greater are common in many biologic reactions.

Isotope effects on physical processes and chemical reactions lead to differences among D/H ratios in natural products, known as isotopic fractionations, which we measure by mass spectrometry. Measured fractionations are sometimes—although not always—equal in magnitude to the causative isotope effect. The relationship between the two is described in detail by Hayes (1983) and Criss (1999) and depends on whether the system under consideration is open versus closed. Both isotope effects and fractionations are commonly classified as either equilibrium or kinetic, for reversible or unidirectional reactions, respectively. Significant confusion can result when geochemical studies measure variations in D/H ratio (fractionations) and incorrectly interpret the results as inherent isotope effects.

1.2. Stable Isotope Nomenclature

H-isotopic compositions are most accurately determined as D/H ratios relative to a standard, rather than as absolute isotopic abundances. The D/H ratio of a sample is conventionally reported as a delta value (δD or δ^2H) relative to the international standard Vienna Standard Mean Ocean Water (VSMOW) in units of permil (‰) or parts per thousand:

$$\delta D_{\text{sample}} = [(D/H)_{\text{sample}} - (D/H)_{\text{VSMOW}}] / (D/H)_{\text{VSMOW}} \times 1000\text{‰}. \quad (1)$$

The accepted D/H ratio of 155.76×10^{-6} for VSMOW serves as a defining anchor for $\delta D \equiv 0\text{‰}$. Another primary international standard is the strongly D-depleted Standard Light Antarctic Precipitation (SLAP) with a defined δD value of -428‰ . Both VSMOW and SLAP are typically used to normalize the attenuation of the δD -scale (Coplen 1996). The scale ranges from $\delta D = -1000\text{‰}$ (all 1H) to $+\infty$ (all D), and any compound with a D/H ratio smaller than that of VSMOW has a negative δD value. The δD scale is nonlinear with respect to D/H ratio, and because of the large fractionations affecting H, this feature of delta notation is more troublesome for H than for other stable isotopes (Sessions & Hayes 2005).

Isotopic fractionations can be described quantitatively in several ways (Table 1). The most accurate descriptions are provided by α and ϵ . $\Delta\delta D$ provides a relation that is more convenient to use, but one whose accuracy is poor when dealing with large fractionations. These measures of fractionation are commonly used to describe the difference in D/H ratio between two substances. As a concrete example, consider the fatty acids produced by a plant. The source of H for the plant is soil water, and the biochemical preference for utilization of 1H results in an isotope effect of about 0.850, that is, the fatty acids are depleted in D relative to the water by about 150‰.

Table 1 Definitions for several common representations of isotopic fractionation

Symbol	$\alpha_{A/B}$	$\epsilon_{A/B}^a$	$\Delta \delta_{A/B}^a$
Definition	$= \frac{\delta D_A + 1000}{\delta D_B + 1000}$ $= \epsilon/1000 + 1$	$= (\alpha - 1) \times 1000$ $= \left[\frac{\delta D_A + 1000}{\delta D_B + 1000} - 1 \right] \times 1000$	$= \delta D_A - \delta D_B$

^aExpressed in units of permil (‰).

This difference can be described by

$$\Delta \delta D = \delta D_{\text{water}} - \delta D_{\text{lipid}} = -150\text{‰} \quad (2)$$

$$\epsilon = \left[\frac{\delta D_{\text{lipid}} + 1000}{\delta D_{\text{water}} + 1000} - 1 \right] 1000 = -150\text{‰} \quad (3)$$

To demonstrate the approximation inherent in the former equation, if δD_{water} was 0‰, then the use of either equation would indicate that $\delta D_{\text{lipid}} = -150\text{‰}$. But if δD_{water} were -200‰ , then the former (approximate) equation would give $\delta D_{\text{lipid}} = -350\text{‰}$, whereas the latter (exact) equation would give $\delta D_{\text{lipid}} = -320\text{‰}$. A more convenient form of Equation 3 is given by Sessions & Hayes (2005):

$$\delta_A = \alpha_{A-B}(\delta_B + 1000) - 1000 \quad (4)$$

The simplicity of this mathematical expression is deceptive. The net fractionation that we observe (α_{A-B}) is the sum of many individual fractionations, some potentially of opposite sign, that accompany each physical transformation and chemical reaction (Hayes 2001). An example of the former would be enrichment of leaf water in D by evapotranspiration, whereas the latter is represented by the strong D depletion during biochemical transfer of water H into organic molecules (Sessions et al. 1999). The H attached to the carboxyl moiety of the fatty acid will also undergo exchange with ambient water, leading to enrichment of D at that position via equilibrium fractionation (Schimmelmann et al. 1999).

1.3. Hydrogen Exchange Nomenclature

Discussions of H-isotopic changes accompanying the maturation of bulk organic matter are often complicated by the superposition of many chemical processes. For example, the net increase in D/H ratio of organic matter during maturation (Section 5) is sometimes described as resulting from “exchange,” while implying merely that there has been a net transfer of water H to organic H, regardless of underlying mechanisms. In other cases, exchange is more properly used to imply a strictly reversible process accompanied by equilibrium fractionations.

Sessions et al. (2004) reviewed these issues with respect to compound-specific studies, and have suggested that the term hydrogen exchange be reserved for cases in which the reactant and product are true isotopologues (or isotopomers) produced by a reversible reaction, a convention that we follow here. In contrast, H incorporation

or transfer are more general terms that can be used to describe changes in the D content without implying specific chemical mechanisms. Further confusion can also be generated by imprecise descriptions regarding the potential for exchange by organic H. H that is nonexchangeable on laboratory timescales may well be exchangeable over geologic timescales or under different physical or chemical conditions. In this case, the usage should clearly indicate the timescale or conditions of interest.

2. ANALYTICAL TECHNIQUES FOR QUANTIFYING D/H IN ORGANIC MATTER

A wide array of methods for the analysis of D/H ratios in organic materials has been published and reviewed elsewhere (see references in de Groot 2005). Here we summarize those that are specific to SOM and fossil fuels.

2.1. Selection and Preparation of Organic Matter

Geolipids and especially *n*-alkanes with a high content of isotopically conservative alkyl H are preferred substrates for geochemical D/H investigations (Section 4). In contrast, kerogens and other humic compounds contain some organic H that can undergo rapid exchange with ambient water, even during laboratory procedures. Methods are now available to equilibrate labile organic H with water of known δD value in a reproducible fashion. Parallel equilibration of two aliquots of the same kerogen with two isotopically distinct water vapors, determination of bulk δD values, and subsequent isotopic mass balance calculations yield a quantitative measure of the readily exchangeable organic H (in percent of total organic H). When the equilibrium fractionation factor for reversible exchange between organic H and water is known, these data can also be used to calculate the δD value (hereafter δD_n) of organic H that is nonexchangeable under the chosen equilibration conditions (typically between 110°C and 120°C for ~12 h; Schimmelmann 1991, Wassenaar & Hobson 2000). δD_n values of kerogen avoid the spurious results caused by rapidly re-equilibrating H in many functional groups (e.g., -OH, etc.) and are strongly recommended.

Kerogen's insolubility and immobility guarantee that its properties reflect in situ geochemical and isotopic conditions. Unfortunately, the mineral matrix of rocks and sediments contains abundant inorganic H and must be dissolved in strong acids before remaining kerogen can be analyzed, a laborious procedure. There is also some potential for strongly acidic conditions to induce isotopic exchange in otherwise nonexchangeable organic molecules (Alexander et al. 1984), although this possibility has not yet been systematically examined for kerogen. As an alternative, geolipids from powdered whole rock or sediment can be easily extracted with organic solvents and separated into aromatic, aliphatic, and other compound classes prior to bulk analysis (e.g., references in Schimmelmann et al. 2004). This separation also serves as a useful first step toward compound-specific isotopic measurements. The primary disadvantage of working with extractable geolipids is that they are susceptible to subsurface migration, making their association with source rocks occasionally ambiguous.

Kerogen: the fraction of dispersed organic material in rocks and sediments that is insoluble in organic solvents. The organic matter initially deposited in sediments is gradually converted into kerogen by biological, chemical, and physical processes accompanying diagenesis

2.2. Dual-Inlet Mass Spectrometry

Preparative methods leading from organic matter to H₂ gas for determination of δD values are summarized by de Groot (2005). For example, H in organic matter can be combusted to water at 550°C to 800°C in a glass vacuum line or in sealed silica glass ampoules in the presence of copper (II) oxide. Water is separated from other combustion products (e.g., CO₂ and N₂) by freezing at -80°C and is subsequently converted to H₂ using a heated metal reducing agent (e.g., Zn, U, Mn, Cr). H₂ is collected in sealed glass ampoules and later admitted to the dual-inlet system of an isotope-ratio mass spectrometer (IRMS) for measurement of isotope ratios.

2.3. Continuous-Flow Mass Spectrometry

A second class of analytical procedures involves the continuous conversion of organic materials to H₂ in a stream of helium carrier gas. The carrier gas flows into the IRMS where ¹HD⁺ and ¹H₂⁺ ion beam currents are continuously monitored, allowing measurement of D/H ratios for each H₂ peak produced by the analytical stream. The conversion of organic to elemental H is typically accomplished by pyrolysis at temperatures >1400°C, either in a bare alumina tube or over glassy carbon (Burgoyne & Hayes 1998). The process is variously known as pyrolysis, thermal conversion (TC), and high-temperature reduction. The two most common preparative devices in continuous-flow analysis are the elemental analyzer for bulk samples (Kelly et al. 1998), and the gas chromatograph for compound-specific analyses (Hilkert et al. 1999).

Continuous-flow technologies for organic D/H analyses offer two significant advantages. For bulk organic analyses, the primary advantage is in speed and automation of analysis, a particular benefit when every sample must be equilibrated with several different waters. Compound-specific analyses have opened a new analytical window that was not previously available with off-line techniques, and are providing new information on fractionations at the molecular level (e.g., Li et al. 2001, Schimmelmann et al. 2004). The fact that we can now select various molecular structures for isotopic analysis is particularly beneficial with respect to studying the effects of exchange on the composition of the bulk material.

3. D/H RATIOS IN BIOLOGICAL MATERIALS

D/H ratios of meteoric waters, including precipitation and groundwater, span a range of more than 400‰ depending on latitude, altitude, moisture source regions, storm track patterns, and evaporative regimes (Sheppard 1986). In contrast, ocean waters are relatively well mixed and are isotopically close to VSMOW \equiv 0‰ (Criss 1999). Water is the only significant source of H for photoautotrophs, and the D/H ratio of autotroph biomass is thus directly correlated to the D/H ratio of environmental water (Estep & Hoering 1980, Sternberg 1988). However, the magnitude of the fractionation between water and biomass can vary significantly, depending on environmental conditions and biochemical pathways (see Sidebar: Biological Fractionation of Hydrogen Isotopes; Sauer et al. 2001, Chikaraishi & Naraoka 2001, Huang et al.

BIOLOGICAL FRACTIONATION OF HYDROGEN ISOTOPES

Biological fixation of water into organic hydrogen provides the starting point for subsequent isotopic changes in organic matter. Although biosynthetic fractionations between water and bulk organic matter are well characterized (e.g., Estep & Hoering 1980), studies at the molecular level using compound-specific D/H measurements are a current research frontier. As might be expected, different classes of biochemicals within individual organisms present a wide array of δD values. Carbohydrates are the most D-enriched class, possibly as a result of hydrogen exchange during isomerization and polymerization reactions. Lipids are more depleted, and fall into two groups. Straight-chain lipids are depleted in D by $\sim 150\text{‰}$ to 210‰ relative to water, whereas isoprenoid lipids such as sterols are typically depleted by $\sim 200\text{‰}$ to 300‰ . Phytol is even more strongly depleted, occasionally reaching δD values of -380‰ in higher plants (Sessions et al. 1999). Ongoing research is focused on (a) providing quantitative relationships connecting δD values of environmental water to those of biomarker lipids, (b) identifying specific biochemical reactions responsible for the array of organic δD values, (c) measuring fractionations in heterotrophic and chemoautotrophic microbes, and (d) exploring organismal and subcellular gradients in the D/H ratio of water utilized for biosynthesis.

2002, Smith & Freeman 2006). One direct result of the correlation between D/H of biomass and environmental water is that terrestrial SOM typically exhibits a much wider range of D/H ratios than does marine SOM (Schimmelmann et al. 2004). Heterotrophs derive their H from both food and body water (Hayes 2001), and there is some debate about which source is more important in setting the isotopic composition of heterotrophic biomass. One recent report (Valentine et al. 2004) suggests that chemoautotrophs utilizing H_2 may in some cases produce biomass with strongly negative δD values (-300‰ or lower) as a result of the strong D depletion in H_2 . Such biological variations in isotope ratio serve as the starting point for subsequent changes during the maturation of organic matter.

4. ISOTOPIC EXCHANGE OF ORGANIC HYDROGEN

H occupies diverse molecular positions in the complex organic structures that make up SOM. The rate of isotopic exchange between an organic H atom and other available H (e.g., water, mineral H) depends on the activation energy for exchange, and generally increases with temperature and decreasing bond strength. Alkyl H is covalently linked to carbon by a strong and nonpolar bond requiring high activation energy for exchange, making it the most isotopically conservative H moiety (Sessions et al. 2004). However, reduced bond strength and increased polarity of bonds can increase the acidity and hence exchangeability of other H positions. Structures that stabilize

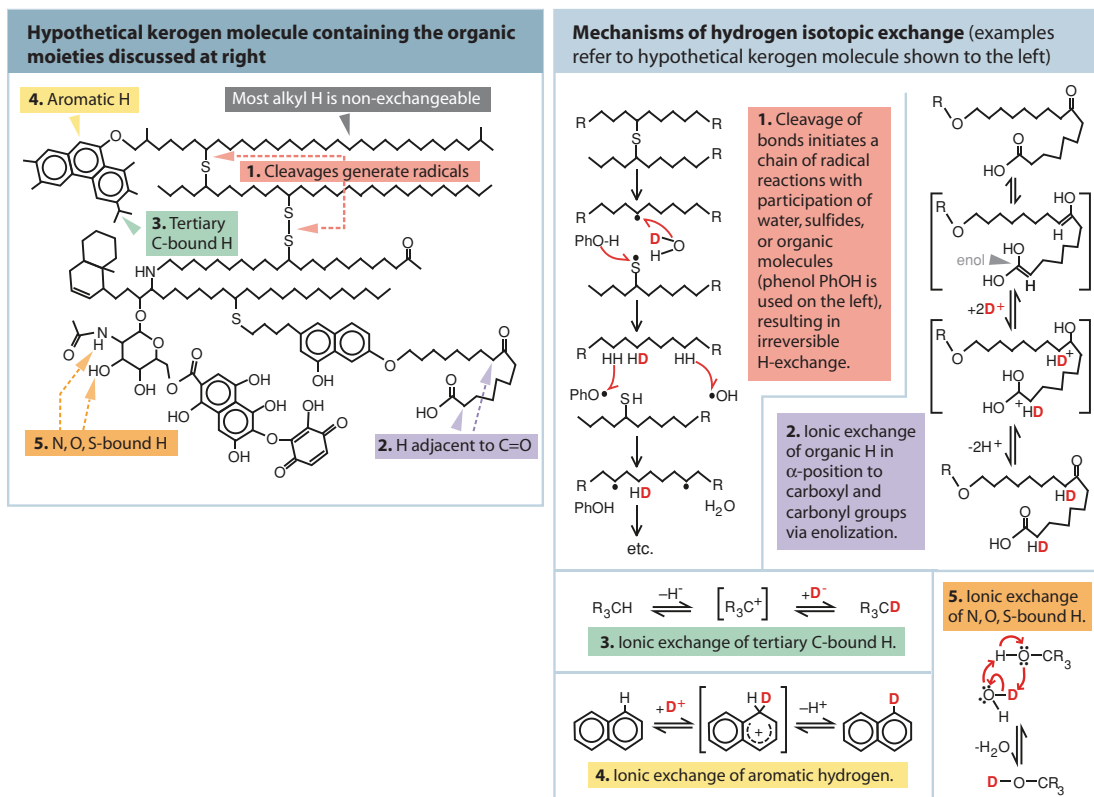


Figure 1

Summary of hydrogen exchange mechanisms affecting various organic moieties. (1) Irreversible H-exchange via radical reactions may proceed via chain reactions affecting several H-sites in one or more molecules. (2) Reversible ionic exchange of organic H in α -position to C=O and COOH via enolization. (3) Reversible ionic exchange of H bound to tertiary C atoms. (4) Reversible ionic exchange of aromatic H. (5) Reversible exchange of organic H bound to O, N, or S with H₂O. Redrawn from Schimmelmann et al. (1999).

charged transition states, such as aromatic rings and electron-withdrawing groups, also tend to increase the rate of exchange. **Figure 1** illustrates typical mechanisms of isotopic exchange for several organic H moieties. Even potentially exchangeable H can be deeply embedded in large macromolecular structures leading to steric hindrance of exchange, although the importance of this effect is not well documented.

Experimental and empirical data regarding rates of organic H exchange are scarce, even for simple laboratory systems. Alexander et al. (1982, 1983, 1984) conducted groundbreaking investigations of ³H-labeled aromatic compounds incubated with various mineral substrates, but there has been little follow-up to that work. When we account for variability in natural systems owing to changes in mineralogy, water/rock ratio, organic composition and structure, etc., the uncertainties grow even larger. *n*-Alkanes are the most resistant to exchange, with exchange half-times exceeding

a billion years in pure water and probably 10^6 to 10^8 years under typical geologic conditions (references in Schimmelmann et al. 1999, Sessions et al. 2004; **Table 2**). Aromatic H is more acidic and seems to be affected by exchange on timescales of 10^3 to 10^6 years at temperatures $<100^\circ\text{C}$ (Alexander et al. 1982, 1983). At the other extreme, hydroxyl, carboxyl, and amine-bound H can undergo exchange essentially instantaneously at room temperature. Methods for identifying H exchange in SOM are discussed in Section 6.

The approach to isotopic equilibrium is asymptotic and follows a familiar first-order rate law, i.e., 50% of H has exchanged after one reaction half-time, 75% after two, etc. (references in Sessions et al. 2004). The endpoint of continuing H exchange is that the two exchanging phases (e.g., organic H and water) differ in their D/H ratios by some temperature-dependent equilibrium fractionation. They will not have identical D/H ratios. The magnitudes of equilibrium D/H fractionations in organic compounds are very poorly known. Sessions et al. (2004) compiled estimates based on spectroscopic data, and showed that organic H could be depleted in D by between 50‰ and 300‰ relative to water in equilibrium at 25°C . Unfortunately, the uncertainties associated with these estimates of fractionation factors are almost equally large, typically $\pm 100\%$ (1σ). These data are crucial to our interpretation of diagenetic changes in organic D/H ratios, and there is considerable room for improvement based on experimental and theoretical approaches.

Finally, chemical changes during organic maturation can also affect the exchangeability of H atoms. For example, H adjacent to electron-withdrawing groups like carbonyl (ketone and aldehyde), carboxyl (carboxylic acid and ester), alcohol, or amino groups undergo exchange with ambient water over relatively short geologic timescales (e.g., Larcher et al. 1986). During the course of thermal maturation, electron-withdrawing groups are eliminated, effectively “locking in” the D/H ratio at the adjacent H positions. The net effect would, in hindsight, look like the rapid transfer of H into C-H positions that are not normally prone to significant exchange.

5. D/H CHANGES DURING THE DIAGENESIS AND MATURATION OF ORGANIC MATTER

Processes of isotopic exchange, H addition, H loss, cracking, etc., will all affect the D/H ratios of organic matter through maturation. Time-temperature paths, catalytic mineral components, and the chemical variability of SOM further complicate the picture. Laboratory maturation experiments (Section 5.1) provide a necessary ability to isolate and study individual mechanisms and effects under controlled conditions, but can be difficult to extrapolate to natural conditions. Field studies documenting natural maturation (Section 5.2) provide complementary information on net effects of maturation over geologic timescales.

5.1. Laboratory Maturation Experiments

Artificial maturation of kerogen by laboratory heating can be either “open” to permit the continuous exit of fluid reaction products during heating, or “closed” to trap

Cracking: a group of (mainly free-radical) reactions that cleave C-C bonds in organic molecules and form mobile hydrocarbons. Primary cracking is the breakdown of kerogen molecules, whereas secondary cracking is the breakdown of bitumen and oil

Diagenesis: the earliest stage of transformation of SOM. It is commonly defined as the time interval from deposition until the onset of thermal breakdown of kerogen ($< \sim 50^\circ\text{C}$)

Table 2 Chronological summary of published studies on organic D/H during laboratory-simulated maturation

Organic substrates	Water	Conditions	Conclusions	Reference
Crude oil ± calcium montmorillonite	D ₂ O	160°C, 200°C, 240°C; 0.7 h to 225 days	A small fraction of H in oil exchanges more rapidly than most H in oil. Ca-montmorillonite was catalytically inactive below 160°C.	Köpp 1979
Algal mat and peat	None	35°C–550°C; 1 h to 625 days	δD values of residual kerogen increased by 40 to 100‰.	Peters et al. 1980, 1981
Saturated and aromatic hydrocarbons, whole oil; no mineral substrate	D ₂ O	100°C, 200°C, and 240°C; exchange reaction time up to 250 days	An isotopic shift by 100‰ in the examined pure hydrocarbons at 100°C would require more than 10 ⁹ years. Some hydrogen in oil exchanges more rapidly than most hydrogen. Clay was catalytically inactive below 160°C.	Schoell 1981
Crude oil, no mineral substrate	δD = +2000‰	180 ± 20°C for 2 months	No detectable change in δD value of oil.	Yeh & Epstein 1981
Tritium-substituted naphthalenes, bentonites	With and without H ₂ O	23°C–275°C (dry), 70°C (wet); up to 34 days	Acidic clays promote exchange; exchange half-time at 50°C is 4500 years.	Alexander et al. 1982
Aromatic hydrocarbons, crushed shale and siltstone	H ₂ O	138°C, time unspecified	Exchange half-time for naphthalene is a few years to ~200 years.	Alexander et al. 1983
Kerogen from Messel shale	D ₂ O	330°C, 72 h	Hydrogen from water enters into newly forming organic hydrocarbons during hydrous pyrolysis of Messel shale.	Hoering 1984
Isopropyl-benzene and pristane, montmorillonite	None	160°C, up to 670 h	Ionic hydrogen exchange catalyzed by montmorillonite; 63% of total pristane H and 40% of methyl H exchanged after 670 h.	Alexander et al. 1984
Acyclic isoprenoids, D ₂ O-hydrated montmorillonite	None	160°C, up to 670 h	Rapid exchange between mineral H and α-position of isoprenoid acids.	Larcher et al. 1986
Chitin from crustaceans	None	Up to 275°C, 3 h in air or water vapor	δD of carbon-bound H in chemically intact amino sugar from chitin does not change.	Schimmelmann et al. 1986
Pure cellulose and cellulose in corn cobs	None	Up to 275°C, 1 h in air	δD _n in chemically intact cellulose does not change.	Marino & DeNiro 1987
Type-IIS kerogen from Monterey Fm.	None	Closed-system pyrolysis; 300°C for 2, 10, 100 h	Decreasing elemental H/C ratio and progressive D-enrichment of maturing kerogen, with maximum isotopic shifts ΔδD = 17‰ and 27‰.	Idiz et al. 1990

(Continued)

Table 2 (Continued)

Organic substrates	Water	Conditions	Conclusions	Reference
Coals from Wandoan and Datong	³ H-spiked H ₂ O	100°C–400°C; up to 6 h	≤40% of coal H exchanged with water after 2 h at 300°C.	Ishihara et al. 1993
Methanol, higher alcohols, and ketones	D ₂ O	200°C–300°C, up to 1 h	No exchange of C-bound H in alcohols, near quantitative exchange adjacent to carbonyl C in ketones.	Katritzky et al. 1996
Source rock chips	H ₂ O (δD varies)	300°C–381°C, 1 to 144 h	See text, Section 5.1.2.	Schimmelmann et al. 1999, 2001a
Messel shale ± alkenes, alkanes	H ₂ O, D ₂ O	330 or 350°C, 1–72 h	See text, Section 5.1.2.	Leif & Simoneit 2000
Whole oils	None	300°C to 430°C heating at 10°/hour	D enrichment of <i>n</i> -alkanes due to fractionation during cracking.	Gillaizeau et al. 2001; Tang et al. 2005

all evolving gas and liquid and continually expose them to high temperatures. Open systems reduce secondary cracking of fluid products (Behar et al. 2003). Although this should influence the H-isotopic mass balance among different organic molecules, especially fluid maturation products, differences in isotopic fractionation between open and closed systems have not been studied in detail. In contrast, much insight has been gained from experiments that fundamentally differ with regard to the absence versus the presence of water during maturation.

5.1.1. Anhydrous experiments. Anhydrous experiments do not accurately reproduce the natural oil generation process, and thus have received relatively little attention. Nevertheless, a significant benefit of anhydrous systems is that water is avoided as a source of reactive H. Important artificial maturation studies and their main results are summarized in **Table 2**; C-bound H can be isotopically conservative at quite high temperatures in the absence of water. For example, partial thermal destruction of cellulose-containing materials during air roasting does not alter the D/H ratio of C-bound H in the remaining, chemically intact cellulose (Marino & DeNiro 1987). The same is true for the poly-amino-sugar chitin (Schimmelmann et al. 1986). However, once breakdown of the carbon skeleton begins, significant fractionations generally ensue. Tang et al. (2005) demonstrated that anhydrous pyrolysis of a North Sea oil at 445°C to an equivalent vitrinite reflectance of $R_o = 1.5\%$ caused a ~50% D-enrichment of the remaining C₁₃-C₂₁ *n*-alkanes relative to the unheated oil, and generated a distinctive pattern of increasing δD value with chain length. Methane and higher homologues produced by anhydrous pyrolysis of organic matter at temperatures within the gas-window are depleted in D and ¹³C (Clayton 2003). The cause of these fractionations is thought to be kinetic isotope effects on oil cracking reactions. In other words, C-C bonds in all-¹H molecules have a lower activation energy (are

Vitrinite reflectance: a physical parameter measuring the percentage of incident light reflected from the surface of fossilized woody material (vitrinite). The reflectance increases systematically with thermal maturity, making it one of the most common maturity parameters for coal and SOM

Hydrous pyrolysis: an experimental method for simulating the thermal generation of petroleum and natural gas by closed-system heating of source rocks or kerogen submerged in water and in the absence of oxygen

easier to break) than those in molecules containing at least one D. The remaining reactants (high-molecular-weight compounds) become D-enriched, while the products (low-molecular-weight compounds) become D-depleted. The mechanistic details of these isotope effects are not clearly understood.

Although such experiments are useful for understanding fundamental processes, Peters et al. (1981) observed a large discrepancy in isotopic composition between anhydrous pyrolysis experiments and natural systems where water is present. Likewise, theoretical predictions of $\sim 200\%$ D-enrichment in remaining kerogen during the generation of thermogenic methane are at odds with actual observations of only 10% to 25% in natural wet systems (Redding et al. 1980). Clayton (2003) recognized the isotopic buffering effect of water H and judged the D/H ratios of thermogenic gases from anhydrous experiments to be “totally unrelated to natural gases.”

5.1.2. Hydrous experiments. The presence of water during laboratory heating mimics the natural conditions of SOM thermal maturation more closely (Lewan 1997), and hydrous pyrolysis experiments have been a mainstay of experimental organic geochemistry for at least two decades. Pioneering work by Hoering (1984) involved heating organic-rich, pre-extracted Messel shale with D_2O at temperatures up to $330^\circ C$ for 72 h. Subsequent analysis of the products demonstrated that extractable *n*-alkane molecules typically acquired 4 to 6 D atoms, and in some cases at least 14 D atoms. Possible radical and/or ionic chemical mechanisms of D-transfer remained speculative, however, until Leif & Simoneit (2000) conducted additional experiments using pure aliphatic compounds as probe molecules. Their data showed that in the absence of shale, the incorporation of D from D_2O occurred only in olefinic compounds via ionic, acid-catalyzed double-bond isomerization. The presence of Messel shale catalytically accelerated the incorporation of D into the olefins, caused a minor amount of D incorporation in the (newly generated) saturated *n*-alkanes, and resulted in the hydrogenation of olefins to saturated *n*-alkanes with concomitant oxidation of olefins to ketones. Leif & Simoneit concluded that the breakdown of kerogen generates *n*-alkanes and transient terminal *n*-alkenes by free-radical hydrocarbon cracking of the kerogen structure. Rapid ionic acid-catalyzed isomerization of *n*-alkenes to internal alkenes provides a mechanism for exchange of multiple organic H positions on a single molecule. Competing with the ionic reactions of olefins are rapid free-radical hydrogenation reactions that lead to saturated hydrocarbons, adding H to the molecule in the process but preventing further exchange via isomerization. The rate of these reactions is greatly enhanced by the presence of species that act as free radical shuttles, such as sulfides and H_2S .

The net result of these reactions is to transfer water-derived H into organic alkyl positions where isotope exchange is slow or negligible in the absence of free radical reactions. Thus, while the D/H ratio of aliphatic H may change substantially during cracking reactions, afterward the D/H ratio of expelled alkanes is virtually locked in. This expectation has been supported by field evidence showing a strong correlation between δD values of reservoir oils and their source rocks, whereas the same oils are uncorrelated with associated reservoir waters (Schimmelmann et al. 2004).

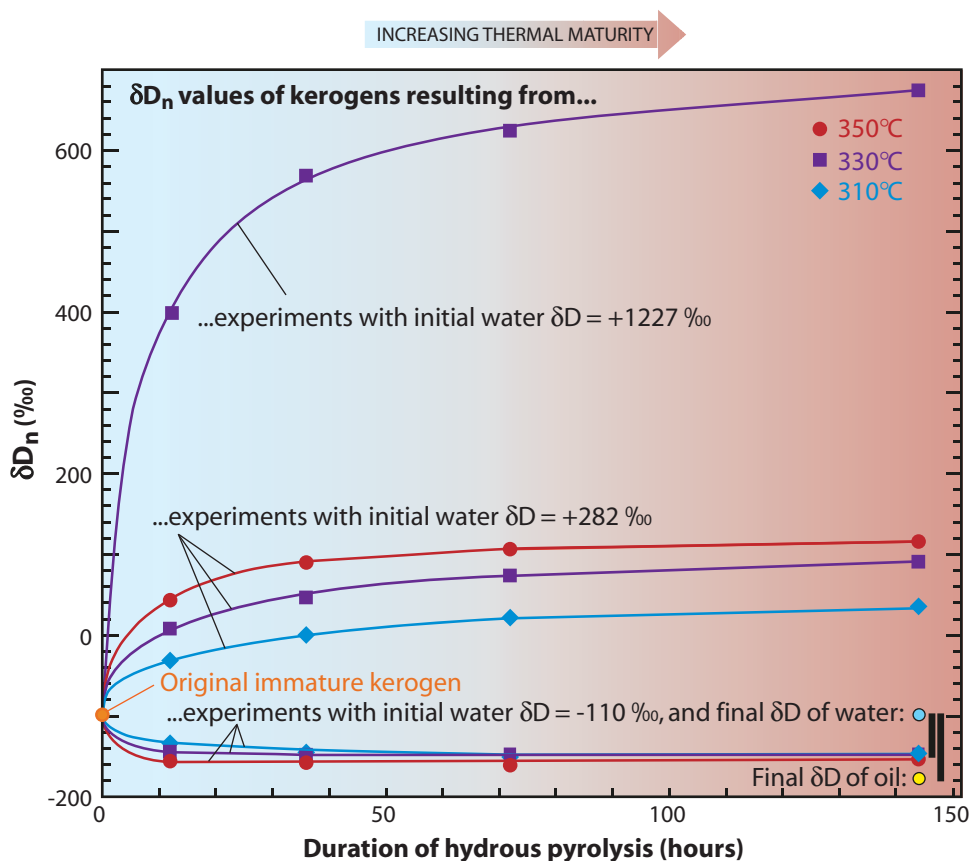


Figure 2

Shifts in δD_n values of type-II kerogen following hydrous pyrolysis in isotopically distinct waters at three temperatures. The δD values of final water and expelled oil are indicated for experiments with the closest approach to isotopic pseudoequilibrium. Black vertical bars represent the remaining fractionation between water and organic hydrogen in kerogen and oil. Redrawn from Schimmelmann et al. (1999).

Immature source rocks were heated by Schimmelmann et al. (1999) in waters with starting δD values ranging from -110‰ to $+1260\text{‰}$ (Figure 2). Isotopic mass-balance calculations indicated that 45%–79% of carbon-bound H in matured kerogens was derived from water. Estimates for bitumen and expelled oil were slightly lower (37%–78% and 36%–73%, respectively), with oil being the least affected. Experiments comparing source rocks containing different kerogen types showed that kerogen, bitumen, and expelled oil/wax contained less water-derived H in the order $\text{IIS} > \text{II} \approx \text{III} > \text{I}$. The predominantly aliphatic type-I kerogen, with its large pool of isotopically conservative hydrogen, is least affected, whereas the sulfur-rich and highly reactive type-IIS kerogen interacts most readily with water H. Water/rock

Bitumen: the dispersed organic matter in rocks and sediments that can be extracted with organic solvents. When bitumen accumulates in geologic reservoirs it is called petroleum

Kerogen types: Kerogen is classified as type-I, -II, or -III based on its elemental H/C and O/C ratios. Type-I has the highest H/C ratios, type-III has the highest O/C ratios, and type-II is intermediate. Type-IIS kerogen contains large amounts of organic sulfur and is the most reactive with respect to hydrocarbon generation and hydrogen exchange

Maturity: a term referring to the degree of thermal alteration of SOM resulting from the integrated influences of geologic time and elevated temperature with burial. Rocks in the oil window are considered mature, whereas those before and after are immature and overmature, respectively

Oil window: the interval over which SOM generates the largest amount of liquid hydrocarbons via thermal breakdown. It is commonly 60°C–160°C, but can vary with heating rate, burial history and kerogen type

ratios, rock permeability, and mineral grain size were also found to affect the rate and amount of water H incorporated into organic matter (Schimmelmann et al. 2001a). The precise chemical mechanisms that produce this net transfer of water H to organic molecules are not known, but presumably include both equilibrium exchange reactions and unidirectional reactions such as double-bond hydrogenation. Schimmelmann et al. (1999) estimated the net isotopic fractionation between new, water-derived organic H and ambient water as -47% to -53% for kerogen maturing at 330°C. Fractionations should be larger at lower temperatures, although it is not possible to quantitatively extrapolate their results.

Seewald (2001, 2003) demonstrated that at temperatures of 300°C to 350°C chain-shortening of *n*-alkanes in the presence of water and mineral buffers proceeds through a series of oxidation and hydration reactions that promote H exchange with water. It was concluded that the stability of aqueous hydrocarbons at elevated temperatures in natural environments is not a simple function of time and temperature but also depends on the mineralogical environment (buffering the oxygen fugacity) and the presence of catalytically active aqueous sulfur species.

5.2. Maturation in Natural Systems

More than 20 independent field studies provide mostly consistent evidence for gradual D-enrichment of organic matter with increasing maturity (summarized in **Table 3**). Although natural systems are complex and individual patterns of isotopic enrichment may be ambiguous, taken as a whole, the field studies paint a coherent picture in which the transfer of water-H to organic-H during maturation and oil-generating reactions leads to increasing δD values at both the bulk and molecular levels. Significant examples of field studies leading to this conclusion are described below.

5.2.1. Biodegradation and early diagenesis. Post-mortem D/H changes affect bulk biomass as various biochemical compound classes, each with slightly different D/H ratio, are biodegraded at different rates (Fenton & Ritz 1988). Decomposition experiments of macroalgae and seagrass over 60 days produced up to 50% D-enrichment in remnant bulk organic matter (Macko et al. 1982). In contrast, partial biodegradation of the biopolymer chitin does not fractionate H isotopes (Schimmelmann et al. 1986). Decaying organic matter can include a transient contribution from newly generated live microbial and fungal biomass.

Fractionations associated with aerobic biodegradation of alkanes have been studied at the molecular level by Pond et al. (2002). Short *n*-alkanes (*n*-C₁₄ to *n*-C₁₈) biodegrade quickly with a $\sim 12\%$ to 25% D-enrichment in residual alkanes, whereas longer *n*-alkanes biodegrade more slowly and are fractionated by $< 5\%$ (Pond et al. 2002). Biodegradation of petroleum under anaerobic conditions (e.g., within oil reservoirs) has not been reported to cause significant D/H fractionation at the bulk level (e.g., Schoell & Redding 1978, dos Santos Neto & Hayes 1999), although a $\sim 35\%$ D-enrichment in *n*-alkanes was recently reported for severely biodegraded petroleum (Sun et al. 2005).

Table 3 Chronological summary of published hydrogen-isotopic studies of natural SOM

Samples	Maturity range	Conclusions	Source
Crude oils, shale extracts, and chromatographic fractions	(Not available)	See text, Section 5.2.2.	Hoering 1977, Estep & Hoering 1978
Crude oils, C ₁₅₊ fractions, SHC, AHC	(Not available)	Broad increase in δD values with age (Tertiary to Ordovician).	Schoell & Redding 1978
Kerogen sequence from marine sediments	R _o from 0.25% to ~2.5%	δD values of kerogens increase 70‰ to 150‰ with increasing maturity.	Simoneit et al. 1978
Oils and alkane extracts from Australian coals	(Not available)	δD values of oils and alkane extracts increase with depth (see Figure 3c,d).	Rigby et al. 1981
Marine kerogen sequence	(Not available)	Kerogens near diabase intrusion are D-enriched.	Simoneit & Mazurek 1981
18 Australian coals, macrolithotypes, and extracts	R _o from <0.7% to 1.04%	δD values of coals and extracts converge with increasing maturity.	Smith et al. 1982
Coal sequence from Tertiary lignite seam (Hoher Meissner, Germany)	R _o from 0.29% to 2%	Contact-metamorphism by basalt flow increases δD values of coals from -120‰ to -94‰.	Redding et al. 1980; Schoell 1984b, pp. 23-24
Three kerogen sequences (types I, II, and III)	Mean R _o : type-I 0.7 to 1.39%; type-II 2.1 to 2.5%; type-III 0.35 to 2.81%	All kerogen types show D-enrichment with increasing maturity.	Redding et al. 1980; Schoell 1984b, pp. 28-32
5 crude oils from Viking Fm., C ₁₅₊ , SHC, AHC, and NSO fractions	(Not available)	Increasing δD values with depth for all samples except NSO fractions.	Schoell 1984b, pp. 57-59
Condensates from deep source rocks	R _o from 0.5% to 1.5%	Increasing δD values with maturity.	Schoell 1984b, pp. 62-64
Type-III kerogen, SHC, AHC, NSO fractions	T _{max} from ~414 to ~458°C	Increasing δD values with maturity within each fraction (see Figure 3a).	Schoell 1984a, Schoell et al. 1983
Type-II and -III kerogen, SHC, AHC, NSO fractions	(Not available)	Increasing δD values with maturity within each fraction (see Figure 3b).	Schou et al. 1985
Jurassic oils, SHC fractions	Biomarkers indicate increasing maturity	δD values of oils and SHC fractions covary around $-78 \pm 6\%$.	Baker 1987
Bitumen extracted from drill cores of Kupferschiefer	(Not available)	D-enrichment of bitumen near intrusive bodies.	Bechtel & Püttmann 1992
Oils, condensates, SHC, AHC fractions	Biomarkers indicate maturity within oil window	δD values increase with maturity except in aromatic fractions (see Figure 4a).	Waseda 1993
Oils from lacustrine, marine-evaporitic and mixed sources, Potiguar Basin, Brazil	Biomarkers indicate maturity within oil window	See text, Section 5.2.2. (Figure 4b).	dos Santos Neto & Hayes 1999; E.V. dos Santos Neto, personal communication

(Continued)

Table 3 (Continued)

Samples	Maturity range	Conclusions	Source
Oils, condensates, bitumens, asphaltenes, maltenes	“Across oil window”	δD values tend to increase in older, more mature SOM.	Lukin 1999
<i>n</i> -Alkanes in crude oils (CSIA*)	Across oil window; maturity data cited	δD values increase for all alkanes with maturity of oil.	Li et al. 2001
Type-IIS kerogens from Monterey Fm., 2 sections	R_o from 0.23 to 0.33% and 0.29 to 0.42% (Rullkötter et al. 2001)	More mature kerogens are D-enriched by ~40‰ relative to less mature section.	Schimmelmann et al. 2001b
Coal- and oil-derived thermogenic methane	Up to 200°C (oil-derived) and 300°C (coal-derived)	δD values increase with maturity due to isotopic exchange with water.	Clayton 2003
<i>n</i> -Alkanes and isoprenoids from sediments and oils, Perth Basin (CSIA)	Equivalent R_o from 0.53 to 1.13% based on biomarkers	δD values of isoprenoids increase by ~150‰ with maturity; <i>n</i> -alkanes increase only by ~42‰.	Dawson et al. 2005
<i>n</i> -Alkanes and isoprenoids from two sedimentary sequences	Equivalent R_o from 0.48 to 1.3% based on MPII index	δD generally increases with maturity, more rapidly for isoprenoids; rates of increase differ between the two sequences at equivalent maturity.	Radke et al. 2005
Type-II and -III kerogens	R_o from 0.3% to 3%	δD increases with maturity up to $R_o \sim 2\%$, rates of increase vary between basins (Figure 4c).	Lis et al. 2006
<i>n</i> -Alkanes, pristane, phytane, and kerogen from lacustrine sequence, Gabon Basin	R_o from 0.55% to 0.7%	Isoprenoid δD values increase rapidly, to equal the δD of <i>n</i> -alkanes at $R_o \sim 0.7\%$. Kerogen and <i>n</i> -alkanes change only slightly (Figure 5).	Pedentchouk et al. 2006
Type-III kerogens, Pennsylvania anthracite field, USA	R_o from 2.68% to 6.3%	No significant δD_n trend with maturity. Mean $\delta D_n = -90 \pm 4\%$ (n = 8).	A. Schimmelmann & J.P. Boudou, unpublished data
Type-III kerogens, Bramscher Massiv, Germany	R_o from 2.91% to 7.14%	No significant δD_n trend with maturity. Mean $\delta D_n = -97 \pm 9\%$ (n = 8).	A. Schimmelmann & J.P. Boudou, unpublished data

*CSIA: compound-specific isotope analysis, referring to the analysis of individual molecular species by coupled gas chromatography and IRMS.

5.2.2. Thermal degradation and catagenesis. Several studies have documented increases in D/H ratio of oils with increasing age. Hoering’s (1977) D/H ratios of eleven whole oils and oil fractions with source rock ages from Pliocene to the Precambrian showed that older samples tend to be progressively D-enriched. The Green River Shale, an unusually low-maturity rock, was a notable exception with more D-depleted

composition than expected. Similarly, Lukin (1999) showed that older bitumen, asphaltene, maltene, and heavy oils from the Dnieper-Donetsk Depression possess δD values of -40% to -80% , whereas younger oils and condensates have δD values of -85% to -165% . Interpretation of these data remains ambiguous. The conclusion drawn from both studies is that H-isotopic changes accumulate slowly over geologic time. An alternative, although not mutually exclusive, interpretation is that older rocks tend to be more thermally mature, and that the Green River Shale exception demonstrates that maturity is more important than absolute age.

Other studies clearly identify a trend toward increasing organic D/H ratio with increasing burial depth and heating. In Indonesia's Mahakam Delta, kerogen type-III, associated saturated hydrocarbon extracts (SHC), aromatic hydrocarbon extracts (AHC) and nitrogen-, sulfur-, and oxygen-containing extractable heterocompounds (NSO) all trend toward more positive δD values with increasing depth (Schoell 1984b; **Figure 3a**). At the same time, the δD values of kerogen, AHC, and NSO converge, whereas δD values of the isotopically more conservative SHC fraction remain offset from those of kerogen by a constant amount. Kerogen and extractable components from the Norwegian North Sea (Schou et al. 1985; **Figure 3b**) and extracts from Australian coals (Rigby et al. 1981; **Figure 3c, d**) show virtually identical patterns.

A study of 25 crude oils and their saturate and aromatic fractions by Waseda (1993) showed increases in δD values of whole oils and SHC fractions with increasing maturity (**Figure 4a**). The same relationship was not apparent for the aromatic fraction, perhaps owing to later overprinting by H exchange of the more labile aromatic H (Section 4; Schimmelmann et al. 2004). dos Santos Neto & Hayes (1999) measured δD values of oils and saturates from lacustrine, mixed, and marine-evaporitic paleoenvironments across a maturity gradient in the Potiguar Basin, Brazil (**Figure 4b**). At low levels of thermal maturity, the three different paleoenvironments are distinguished by their δD values (lacustrine $\delta D \sim -90\%$; mixed $\delta D \sim -110\%$; marine-evaporitic $\delta D \sim -120\%$ to -135%), presumably reflecting differences in the D/H ratio of water in these environments. With increasing thermal maturity, the hydrocarbon δD values all converge toward an average δD value of $\sim -110\%$. This study is unique in documenting a simultaneous increase in δD values of some oils and decrease in δD values of others.

D/H ratios of kerogen from the New Albany Shale (Illinois Basin) and the Exshaw Formation (Western Canada Sedimentary Basin) spanning a wide maturity range ($R_o \sim 0.3\%$ to 1.4% and 0.4% to 3.0% , respectively) were compared by Lis et al. (2006). Both series of rocks contain type-II kerogen and represent chemically similar, mainly marine-derived SOM that was deposited near the paleoequator. Where the two suites of kerogen exhibit comparable maturities ($R_o \sim 0.3\%$ to 1.4%), δD_n values for the New Albany Shale kerogen have increased roughly twice as much as equivalent Exshaw Formation kerogen (**Figure 4c**). The primary difference between these systems is that Exshaw Formation water is depleted in D by at least 40% relative to water in the New Albany Shale, and so is closer in δD value to its corresponding kerogen.

In contrast to these results, several studies have documented a lack of isotopic changes in bulk organic matter with thermal maturity. Baker (1987) examined a

Catagenesis: the second stage of transformation of SOM in which increasing temperatures lead to the thermal breakdown of kerogen and generation of hydrocarbons ($\sim 50^\circ\text{C}$ – 200°C)

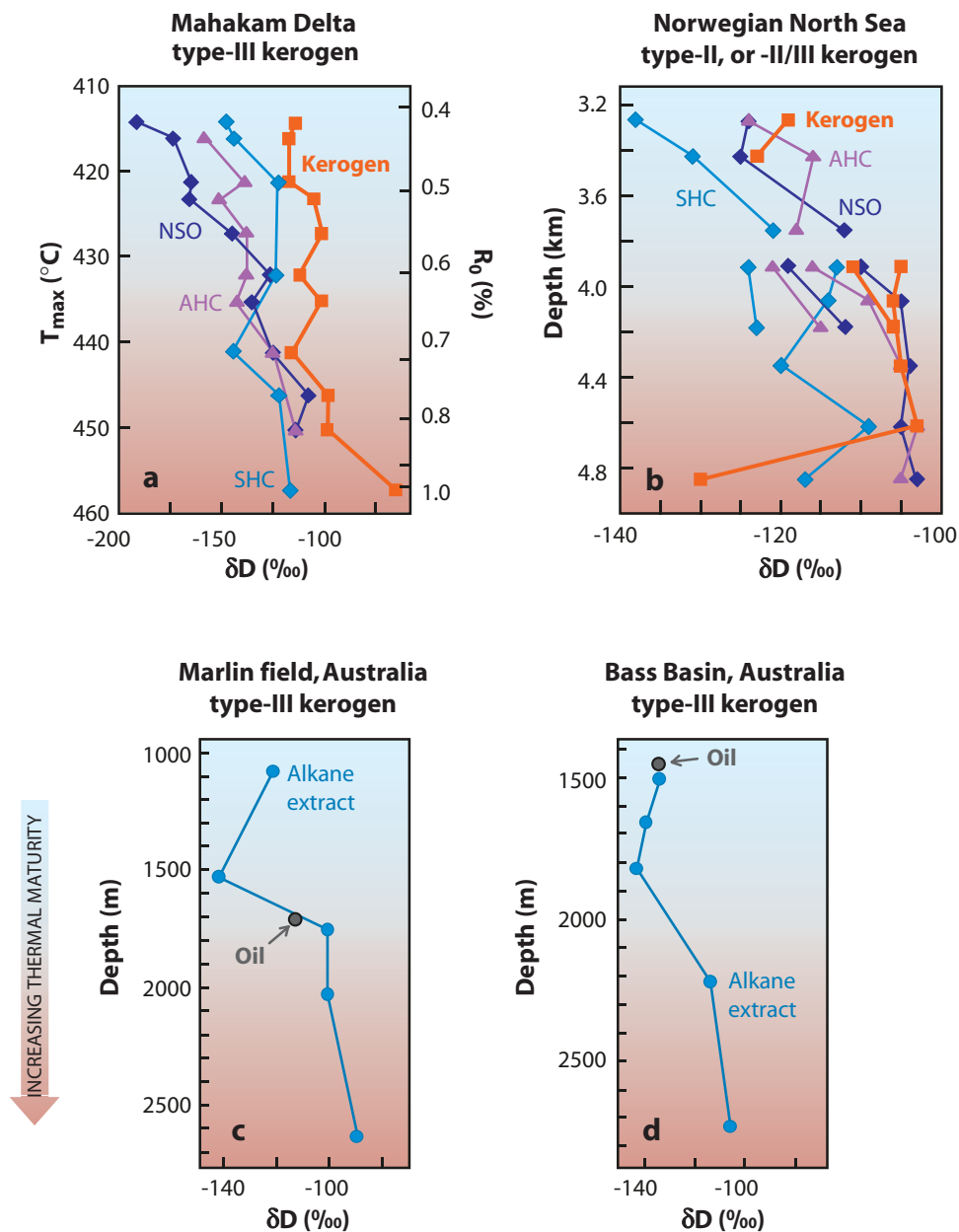


Figure 3

Changes in δD values of kerogen and oil fractions as a function of maturity or depth. The T_{max} and R_o vertical scales in panel *a* are maturity parameters. Data have been replotted from (*a*) Schoell (1984b) and Schoell et al. (1983), (*b*) Schou et al. (1985), and (*c*) and (*d*) Rigby et al. (1981).

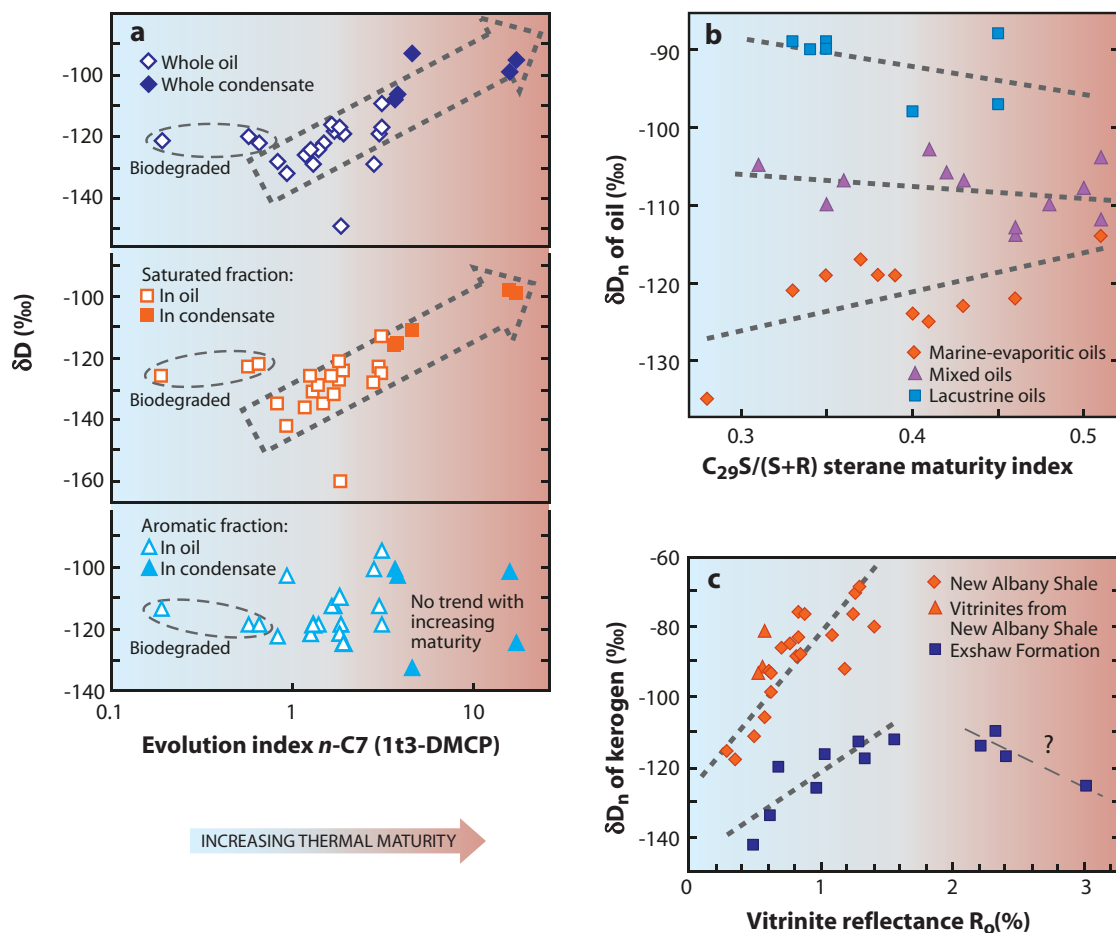


Figure 4

Changes in δD values of oils, oil fractions, and kerogen as a function of thermal maturity. Redrawn from (a) Waseda (1993), (b) dos Santos Neto & Hayes (1999), and (c) Lis et al. (2005).

sequence of Saudi Arabian oils and found that all oils and their subfractions covaried narrowly around a mean value of $\sim -78 \pm 6\%$ regardless of maturity. A similar result was obtained from a suite of eight relatively D-enriched kerogens from the Pennsylvania anthracite field spanning a maturity gradient of $R_o = 2.68\%$ to 6.3% . The δD_n values cluster tightly around $-90 \pm 4\%$ and exhibit no trend with maturity. Eight kerogens from the Bramscher Massiv (Germany) with $R_o = 2.91\%$ to 7.14% average $\delta D_n = -97 \pm 9\%$ and show no significant trend with maturity (A. Schimmelmann & J.P. Boudou, unpublished data). A common feature of these studies is that organic matter was relatively enriched in D prior to maturation (δD values $> -100\%$).

Four recent studies using compound-specific isotopic analyses have documented D-enrichment at the molecular level. Li et al. (2001) observed a $\sim 40\%$ D-enrichment

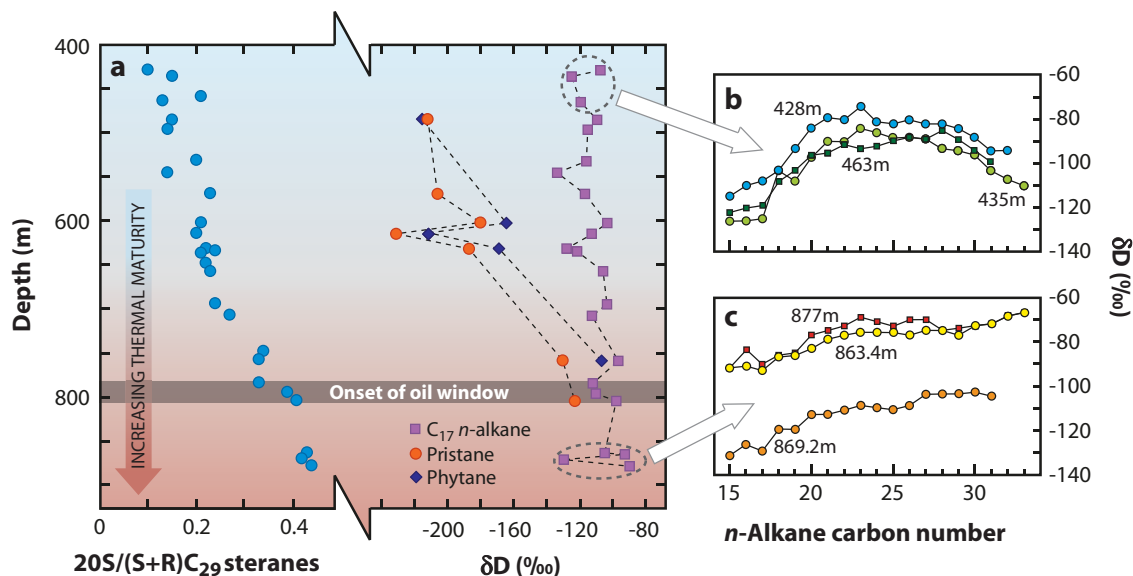


Figure 5

Changes in δD values for kerogen, *n*-alkanes, pristane, and phytane with depth in a core from the Gabon Basin of West Africa. Note the rapid increase in isoprenoid δD value with only minor change in the C_{17} *n*-alkane δD value. Panels b and c show profiles of δD value versus *n*-alkane chain length for the circled samples in panel a. Redrawn from Pedentchouk et al. (2006).

in *n*-alkanes with increasing thermal maturity from the Western Canada Sedimentary Basin. Li et al. suggested that δD values of *n*-alkanes can serve as maturity indicators for highly mature oils, a concept that appears promising but has not yet been rigorously tested in other petroleum systems. Radke et al. (2005) found that *n*-alkane and isoprenoid fractions from Kupferschiefer and Posidonia shales become D-enriched with increasing maturity. The increase in δD value was larger for isoprenoids than for *n*-alkanes, and was consistently larger in Kupferschiefer shales relative to Posidonia shales of comparable maturity. Dawson et al. (2005) measured strong D-enrichments of pristane and phytane in the northern Perth Basin, Australia, corresponding to an increase in thermal maturity, whereas δD values of *n*-alkanes increased only moderately through late maturity. Finally, Pedentchouk et al. (2006) documented significant increases in δD values of pristane and phytane with depth from a lacustrine sedimentary sequence in the Gabon Basin of West Africa (Figure 5). *n*-Alkanes and kerogen from the same samples showed little change in δD value with depth, although the pattern of δD versus chain length for the *n*-alkanes does become more steeply sloped.

Taken as a whole, these studies describe the following pattern. Organic matter D/H ratios often, though not always, increase systematically throughout thermal maturation. The increase is larger in systems where δD values of water and organic H differ more widely, and is negligible in systems where they differ by 80‰–110‰.

Catagenetic changes in aromatic and isoprenoid molecules are larger and more rapid than in *n*-alkanes.

Two mechanisms have been proposed to explain these changes. Peters et al. (1980, 1981) and Schoell (1984b) attributed δD increases at the bulk level to a progressive loss of D-depleted gaseous hydrocarbons, particularly methane. This is equivalent to invoking kinetic fractionations during petroleum generation (Section 5.1.1). There are, however, several problems with this explanation. Light hydrocarbons such as methane are also strongly depleted in ^{13}C , and the loss of thermogenic gases cannot adequately account for observed D enrichments in the absence of parallel ^{13}C enrichments. Moreover, this process should produce an equivalent enrichment in all kerogens of similar thermal maturity regardless of their original δD value, in direct contradiction to several of the studies described above. Finally, the mechanism does not account for the more rapid increases in D content of isoprenoid molecules relative to *n*-alkanes.

Schimmelmann et al. (1999, 2001a) proposed an alternative explanation involving the transfer of D-enriched H from water to organic compounds during cracking reactions. This mechanism adequately explains all of the results summarized above and in **Table 3**. In particular, the lack of changes in relatively D-enriched oils—and decreases in D content measured by dos Santos Neto & Hayes (1999)—can be ascribed to attainment of isotopic pseudoequilibrium between hydrocarbons and water. If this idea is born out, then the “equilibrium” fractionation between hydrocarbons and water must lie in the range of -80% to -110% . Differential changes in isoprenoid versus *n*-alkane molecules can be explained as resulting from the increased propensity of tertiary carbon centers in isoprenoids to undergo H exchange (Dawson et al. 2005). Given these observations, we suggest that incorporation of water H is likely a more important process controlling the H-isotopic composition of SOM during catagenesis than is loss of thermogenic gases, although the two mechanisms are not mutually exclusive.

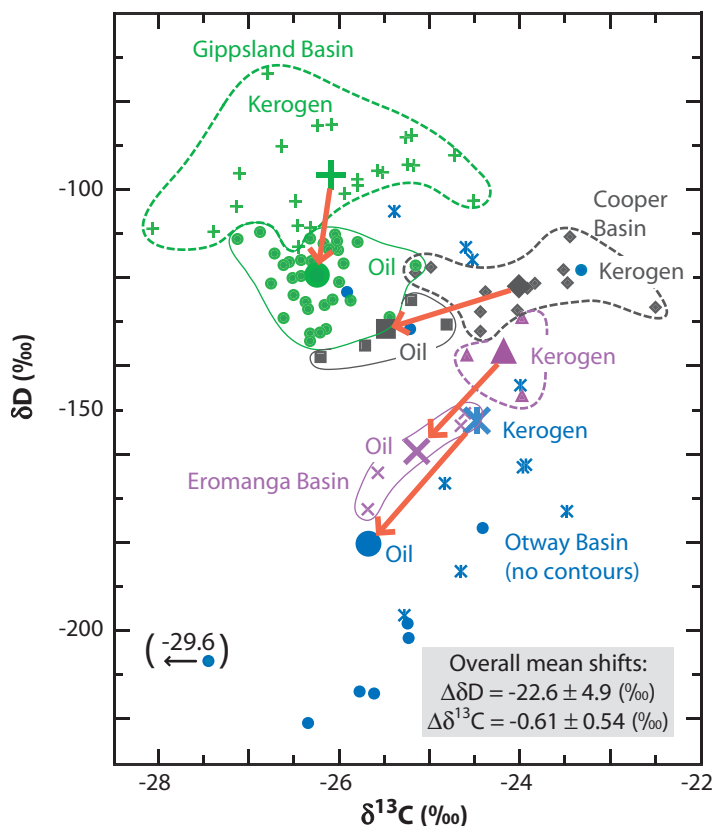
Despite the successes of this explanation, many mechanistic details remain beyond our understanding. For example, the transfer of H from water to organic matter could represent a true thermodynamic equilibrium, but could equally result from the irreversible incorporation of an approximately constant fraction of water H. The effects of temperature on this transfer also are not understood—will equivalent maturity levels resulting from different time-temperature paths lead to the same fractionation?

The concept of H transfer from water into maturing SOM can be used to explain many features of Clayton's (2003) compilation of δD values for thermogenic methanes. Early-formed methane from coal and petroliferous sources typically possesses δD values near -250% and is correlated with the source organic D/H ratio. At higher maturity, the D/H ratio of thermogenic methane becomes progressively dominated by exchange with water as δD values of methane from coals converge at -120% at temperatures of 250°C to 300°C. Methane accumulations associated with oils converge at δD values of -140% to -150% at temperatures of 170°C to 200°C, comparable to an advanced stage of oil to gas cracking (Clayton 2003). Variations in methane δD with increasing maturity approximate a Rayleigh fractionation curve, but the lower-than-expected fractionation indicates that water H is buffering the system with respect to H-isotopic composition.

5.2.3. Fractionations between kerogen and evolved hydrocarbons. The hypothesis that isotopic changes in maturing organic matter result from interactions with water does not negate the importance of kinetic fractionations during hydrocarbon generation. Indeed, H exchange with water, selective degradation of certain molecular classes, and kinetic fractionations during cracking may all play important roles in determining the isotopic composition of fossil fuels. To assess the net effects of all these processes, Schimmelmann et al. (2004) measured δD and $\delta^{13}C$ values of source-rock kerogens and derived oils from four different Australian basins in which the links between oil and kerogen were well established from biomarker data (**Figure 6**). The overall weighted-average isotopic shifts of $\Delta\delta D_{oil-ker} = -22.6 \pm 4.9\text{‰}$ and $\Delta\delta^{13}C_{oil-ker} = -0.61 \pm 0.54\text{‰}$ are useful for correlating oils to their likely source rocks, and could potentially be used to quantify the volume of oil expelled by using a Rayleigh-type distillation model. In this context, it is advantageous that oil migration does not seem to alter petroleum D/H ratios (Li et al. 2001).

Figure 6

Comparison of δD_n and $\delta^{13}C$ values for source-rock kerogens and their derived oils from four Australian basins of differing ages: Cooper Basin (Permian), Eromanga Basin (Middle Jurassic), Otway Basin (Early Cretaceous), and Gippsland Basin (Late Cretaceous/Early Tertiary). Small symbols indicate data from individual kerogen and oil samples, large symbols represent mean values for each basin. Dashed and solid contours are intended to aid visualization of the data. Redrawn from Schimmelmann et al. (2004).



6. LIMITATIONS ON THE USE OF D/H IN PALEOENVIRONMENTAL RECONSTRUCTIONS

The utility of organic D/H ratios as paleoenvironmental and paleoclimatic proxies relies on the preservation of isotopic information from the time of biochemical synthesis. The preceding section clearly demonstrates that this is not the case for high levels of thermal maturity, but at what point is all useful paleoclimatic information lost? Definitive answers are not yet forthcoming, but some rough guidelines can be established based on existing data (**Figure 7**).

In the earliest stages of diagenesis ($R_o < 0.4\%$), δD values of most lipid biomarkers appear to be unaffected. Large D/H offsets between isoprenoid and *n*-alkyl lipids are established during biosynthesis (Sessions et al. 1999), and the preservation of these offsets serves as a useful diagnostic. For example, Andersen et al. (2001) documented $\sim 100\%$ offsets between δD values of 5α -cholestane and *n*-docosane in a Messinian sapropel and concluded that there had been little or no isotopic changes. Yang & Huang (2003) demonstrated the preservation potential of lipid δD values in Miocene lacustrine sediments and plant fossils at Clarkia, Idaho by measuring downcore variations in *n*-alkane δD values in closely spaced samples. Other examples of excellent preservation during early diagenesis are provided by Xie et al. (2000), Huang et al. (2002), Sachse et al. (2004), and Xiong et al. (2005). Paleoclimatic information can also be preserved in nonlipid biopolymer molecules such as cellulose and chitin, provided that the material remains chemically intact (Marino & DeNiro 1987, Roden et al. 2000, Schimmelmann et al. 1986, Tang et al. 2000). In some settings, a convincing case can be made that even bulk organic matter preserves quantitative H-isotopic information (Krishnamurthy et al. 1995).

With the onset of catagenesis ($0.4\% < R_o < 1.0\%$) the biosynthetic fractionation between isoprenoid and *n*-alkane molecules progressively disappears, and a pattern of increasing *n*-alkane δD value with chain length begins to appear (**Figure 5**; Pedentchouk et al. 2006, Schimmelmann et al. 2004, Dawson et al. 2005). The quantitative paleoclimate utility of bulk organic matter and many specific biomarkers diminishes at this point, but useful qualitative information may still be preserved. For example, Pedentchouk et al. (2006) observed little change in *n*-alkane δD values at equivalent maturities up to $R_o = 0.7\%$, and argued that the preservation of subtle differences in δD of these compounds between successive horizons indicates little overall exchange of H. Dawson et al. (2004) showed that *n*-alkanes from low-maturity Late Carboniferous to Late Permian torbanites (derived mainly from a single algal source *Botryococcus braunii*) preserve δD values that correlate with the paleolatitude/paleoclimate at the time of SOM deposition.

Useful paleoclimatic data can also be obtained from bulk organic matter of moderate thermal maturity. Schimmelmann et al. (2004) measured differences of $\sim 80\%$ between kerogens from the same formation in a single borehole in the immature to mature Otway Basin of southeastern Australia, a difference they attribute to changing geographic conditions at the time of deposition. Type-III kerogens that have thermally matured to coals retain D/H ratios useful for estimating the paleolatitude of

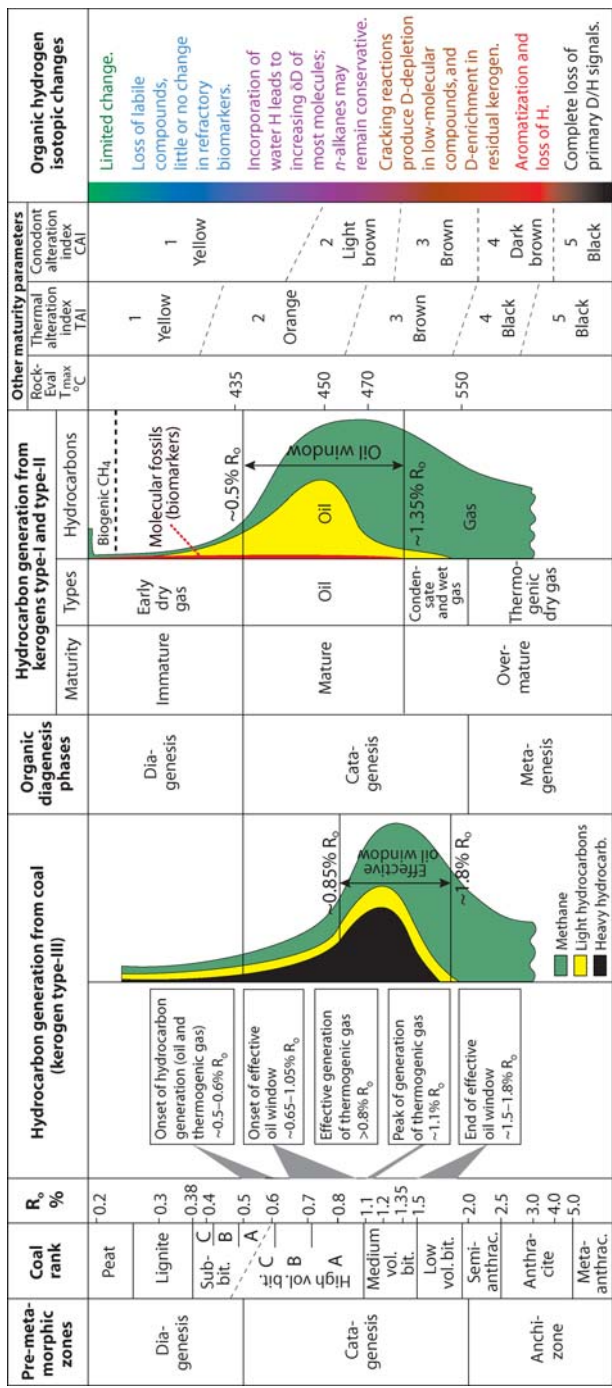


Figure 7

Relationships between metamorphic zones, coal rank, diagenetic and maturity phases, hydrocarbon generation, and organic D/H changes. TAI: Thermal alteration index, a relative scale of organic maturity based on the color of preserved organic matter. CAI: Conodont alteration index, a relative scale of maturity based on the color of preserved skeletal remains from specific marine fauna (conodonts). Compiled and modified after Tissot & Welte 1984; Murchison 1987; Teichmüller 1987; Boreham & Powell 1993; Taylor et al. 1998, p. 127; Petersen 2002; Petersen et al. 2000, 2004; Sykes & Snowdon 2002; and Faiz 2004.

deposition (Smith et al. 1983) and for constraining paleoclimatic changes across the Cretaceous/Tertiary boundary (Schimmelmann et al. 1984). Miocene type-IIS kerogens from California's Monterey Formation contain D/H variability that is correlated to changes in paleoceanographic conditions, although kerogens from the more mature Lion's Head section are enriched in D relative to less mature Naples Beach kerogens (Schimmelmann et al. 2001b). δD_n values of coal kerogens from the Pennsylvanian Illinois Basin and Appalachian Basin appear to reflect paleoenvironmental isotopic gradients that are preserved at low to moderate levels of maturity (R_o 0.54% to 1.28%; Mastalerz & Schimmelmann 2002).

At the highest levels of maturity ($R_o > 1.0\%$), several factors conspire to severely limit paleoclimatic interpretations of organic D/H ratios. First, biomarkers become thermally unstable and can undergo degradation, isomerization, and carbon-skeletal rearrangements leading to extensive H exchange (Sessions et al. 2004). More resilient but less specific *n*-alkanes are generated from kerogen, obscuring any primary isotopic signal. Second, SOM suffers an overall H loss (Baskin 1997) accompanied by isotopic fractionations. Third, an increasing percentage of remaining organic H will be in the form of readily exchangeable aromatic H (e.g., Boehm 1994).

SUMMARY POINTS

1. Some hydrogen in sedimentary organic matter (SOM) is weakly bonded and can exchange with water hydrogen on laboratory timescales. Analytical methods should either avoid or compensate for the influence of this labile hydrogen.
2. Variability in the D/H ratio of environmental water represents the first-order control on δD values of biomass and SOM. Biosynthetic fractionations produce offsets in δD between different classes of biomolecules, and selective degradation of certain components can alter D/H ratios of bulk SOM.
3. Anhydrous pyrolysis experiments suggest that kinetic fractionations accompany hydrocarbon cracking. Products with low molecular weight are depleted in D, leaving residual SOM enriched in D and producing a characteristic pattern of increasing δD with chain length in *n*-alkanes.
4. Hydrous pyrolysis experiments with D-labeled water suggest that 36–79% of the organic H in kerogen, bitumen, and expelled oil may be derived from water at moderate levels of thermal maturity. D/H fractionations of 40‰–50‰ between organic H and water are measured at a temperature of 330°C.
5. Studies of natural SOM indicate a general, although not ubiquitous, increase in δD value with increasing maturity. Changes in organic D/H ratio are greatest when the difference between δD values of SOM and water are largest, and are minimal when water and organic δD values differ by 80‰–110‰.

6. Incorporation of water hydrogen by SOM during catagenesis provides the most complete explanation for observed patterns of D enrichment in SOM. Kinetic fractionations during hydrocarbon generation contribute to fractionations between kerogen and generated fluids.
7. Quantitative paleoclimatic information can be preserved in organic D/H ratios throughout diagenesis. Primary isotopic signals are diminished during catagenesis, but qualitative paleoclimate information may still be preserved. *n*-Alkanes offer the best preservational potential but limited source specificity.
8. The complexity of D/H information recorded in fossil organic matter reflects a dynamic and continuously evolving system that can provide valuable information about biogenic precursor materials, geologic conditions of preservation, and maturation processes.

FUTURE ISSUES TO BE RESOLVED

1. Rates of hydrogen exchange between organic molecules, water, and mineral hydrogen, and the temperature-dependent equilibrium fractionation factors for that exchange.
2. Effects of time-temperature path on isotopic fractionation in maturing SOM.
3. Relative importance of water hydrogen versus fractionations associated with cracking in differing geologic conditions.

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