



Invited Review

Factors controlling the deuterium contents of sedimentary hydrocarbons



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ABSTRACT

The hydrogen isotopic compositions of sedimentary hydrocarbon molecules are now being used to address a range of scientific questions, from paleoclimate to environmental reconstruction to understanding of petroleum systems. Here I review the environmental, biological, and physical/chemical factors that influence the H isotopic compositions of sedimentary hydrocarbons. A hierarchy of four main controls can be recognized: (i) the composition of environmental water that serves as ultimate hydrogen source to the biosphere, (ii) physiologic and metabolic processes in organisms that fix water hydrogen into organic molecules, (iii) hydrogen exchange processes that alter D/H ratios slowly over time under geologic conditions, and (iv) kinetic fractionations that arise during the thermal conversion of sedimentary organic matter to liquid hydrocarbons. Variations in the terrestrial hydrologic cycle, and in biologic fractionations, create lipids with δD values spanning a huge range, and carrying abundant information about source organisms and environments. This information is gradually lost over geologic timescales due to hydrogen exchange, although the rates of this process appear to vary by orders of magnitude in clastic versus carbonate sediments. The H isotopes of hydrocarbons in many sediments of low to moderate thermal maturity may only be partially exchanged. Finally, additional kinetic fractionations are imposed during thermal cracking to generate mobile hydrocarbons. The δD values of sedimentary hydrocarbons are thus concluded to generally reflect a complicated combination of processes. Although it is tempting to view this as a failure of the isotopic record, there are numerous opportunities for understanding environmental, diagenetic, and catagenetic processes if we can learn to quantitatively disentangle the competing fractionations.

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1. Introduction and history

Quantitative analysis of the relative abundances of stable hydrogen isotopes, protium (^1H) and deuterium (^2H , or D), dates back more than 80 years to the earliest work of Urey and his students (Urey and Teal, 1935). However, most early studies of hydrogen isotopes were focused on environmental water, and the modern era of H-isotopic studies of organic matter arguably did not begin until 1967, when Zborowski measured the D content of fatty acids from sediments of the Mohole coring project (Zborowski et al., 1967). Shortly thereafter, Schiegl and Vogel (1970) and Smith and Epstein (1970) reported their respective surveys of the H-isotope ratios of extant plants, noting that they are universally depleted in D relative to the environmental water around them. The former authors also noted that coal and oil had similar D/H ratios as wood and marine algae, respectively, and that natural gas had a much lower ratio than either. Over the next 4 decades there appeared numerous measurements of the isotopic

composition of bulk organic matter, including the landmark 1980 contribution by Estep and Hoering “Biogeochemistry of the stable hydrogen isotopes.” Yet it seems fair to say that – with two main exceptions – such bulk measurements did not figure prominently in organic geochemical research. The two exceptions are cellulose (Sternberg et al., 1984; Feng and Epstein, 1995) and methane (Schoell, 1980; Whiticar et al., 1986), both pure compounds that can be isolated in sufficient quantity for “bulk” isotopic analysis.

The problem was – and still is – that many organic compounds contain hydrogen in functional groups where it is rapidly exchangeable with water and/or mineral H (Schimmelmann et al., 2006). Methane does not, so its isotope ratio was readily interpretable; similarly, cellulose could be nitrated to yield a non-exchangeable product. But for complex sedimentary organic matter, comprising a spectrum of compounds with widely varying propensity for H-isotopic exchange, interpretation of bulk D/H measurements was tenuous at best. Isotopic studies of whole oils could do little more than note the similarity in ^2H content to the presumed source organic matter (Rigby et al., 1981; Yeh and Epstein, 1981).

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The invention of compound-specific analytical techniques in the late 1990's was game-changing for the study of hydrogen isotopes in organic molecules (Summons et al., 2008). These techniques married the separation and specificity of gas chromatography with the continuous, online conversion to H_2 afforded by pyrolysis (Burgoyne and Hayes, 1998; Hilkert et al., 1999; Scrimgeour et al., 1999), allowing measurements of nanogram quantities of individual molecules isolated from sediments or crude oils. Obtaining 100's of nanograms of hydrocarbons is usually quite feasible, with the last major analytical hurdle being the separation of analytes from complex mixtures. Relevant analytical methodologies were reviewed by Sessions (2006b). The compound-specific approach to H isotopes has the dual benefits of both simplifying source/product relationships and avoiding exchangeable H. By the early 2000's commercial instruments were available and fueling a wave of renewed interest in organic D/H studies, in paleoclimate (Sauer et al., 2001), in Earth History (Dawson et al., 2004), and in petroleum systems (Li et al., 2001). These advances notwithstanding, our knowledge of hydrogen isotope behavior at the molecular level is based on little more than a decade of study, and so there remains much that is still incompletely understood.

In this review, I attempt to summarize our current understanding of the processes controlling hydrogen-isotopic compositions of hydrocarbon molecules, with reference both to the biomarkers of interest to Earth historians and the oil-forming compounds of interest to petroleum geochemists. In doing so, I have confined myself largely to studies examining the composition of individual molecules, as these afford the greatest insight. Bulk oils and kerogens are of course collections of individual molecules, so many of the same insights are relevant. However, I do not review the extensive (and generally older) literature on bulk D/H measurements of hydrocarbons and kerogen. The reader is referred to Schimmelmann et al. (2006) as a starting point for that subject. I have also largely sidestepped the extensive literature on D/H fractionations in plant leaf waxes, of interest to paleoclimatologists, as that subject has been recently reviewed by Sachse et al. (2012). Sections 3–6 of this review take a process-based approach, looking at the environmental, biological, and physical/chemical processes that influence D/H ratios along the path from environmental water to lipids to sedimentary hydrocarbons to produced oils. Section 7 takes a more phenomenological approach, summarizing observations of hydrocarbon isotopic composition from several major petroleum basins and attempting to reconcile those with what is known about process. Although the factors controlling the deuterium contents of sedimentary hydrocarbons are complex, I conclude that there are numerous possible applications for D/H measurements. For the biogeochemist, paleoenvironmental and hydroclimate reconstruction, terrestrial vs marine source apportionment, distinguishing microbial metabolic pathways, and understanding diagenetic pathways all appear promising. For the petroleum geochemist, compound-specific δD measurements could potentially be used in assessing organic matter sources, differentiating source rocks, correlating source rocks with oils, and perhaps even in organic matter thermal maturity studies.

2. Hierarchy of controls

A hierarchy of four main controls on the H-isotopic composition of hydrocarbons can be recognized. They are (i) the composition of environmental water that serves as ultimate hydrogen source to the biosphere, (ii) physiologic and metabolic processes in organisms that fix water hydrogen into organic molecules, (iii) hydrogen exchange processes that alter D/H ratios slowly over time under geologic conditions, and (iv) kinetic fractionations that arise during the thermal conversion of sedimentary organic matter to mobile

hydrocarbons. These processes are not mutually exclusive, and the relative importance of each depends strongly on the circumstances of a particular environment. For example, terrestrial organic matter deposited at high latitude will be strongly influenced by (i), whereas marine organic matter would be more strongly affected by (ii). (iii) is obviously more important for older deposits, but also depends strongly on temperature history, mineralogy, and other factors, while (iv) may vary more strongly with thermal maturity. These processes can interfere both positively and negatively, yielding exaggerations or cancellations of changes in isotopic composition. For example, increasing H isotope exchange tends to yield more positive δD values, whereas kinetic effects associated with cracking tend to produce more negative values, and both are evident in active petroleum systems. A δD value being a scalar quantity, it cannot be uniquely diagnostic for all combinations of processes.

A convenient starting point for considering hydrogen isotopes in sedimentary organic molecules is environmental water, which varies in its isotopic composition as a result of fractionations in the hydrologic cycle. Water is obviously the sole source of hydrogen to all plants, but also (and less obviously) the main source for most heterotrophic microbes. Biology harnesses a variety of energy sources, including both sunlight and a variety of chemical redox couples, to “fix” inorganic hydrogen (water) into organic hydrogen (lipids and other biomolecules). This feat is accompanied by a wide range of isotopic fractionations, and a full appreciation of them requires understanding the biologic conservation of energy and reducing power, as well as the synthesis of relevant biomolecules. Once these molecules are deposited in sediments, they are subject to a variety of processes that can lead to the exchange of hydrogen atoms with other molecules in the environment – including water – without alteration of the parent carbon skeleton. This process is somewhat unique to hydrogen, and is necessarily accompanied by changes in isotope ratios. The timescales for such hydrogen exchange in the natural environment range from seconds to billions of years, with rates being strongly influenced by temperature and mineral catalysis. They are thus one of the hardest parts of this system to grapple with. Kinetic fractionations occurring during kerogen (and oil) cracking are liable to be similarly complicated, but have not yet been thoroughly studied. Nevertheless, some broad trends have been recognized, particularly the progressive depletion of D in the products of cracking.

3. Origins of the signal: hydrogen isotopes in environmental waters

Environmental water serves as the primary source of hydrogen to photosynthesis, thus its isotopic composition exerts first-order control over the δD values of organic H. For marine organisms, this is a relatively stable starting point, with seawater being well-mixed with an average δD value close to $\sim 0\text{‰}$. Small variations, $<5\text{‰}$ in δD , are driven by evaporation and freshwater inputs (Craig and Gordon, 1965), whereas more extreme departures are rare. The δD value of seawater has likely been quite stable over most of Earth's history (see Section 3.4). In contrast, terrestrial vegetation draws on meteoric waters that are highly variable in isotopic composition over time and space, making it difficult to pin down a reference point for organic H. Nevertheless, a number of broad geographic patterns in water D/H do exist and can be observed in sedimentary organic matter.

Isotopic variability in the hydrologic cycle is driven almost entirely by fractionations accompanying the physical conversion of water between the solid, liquid, and vapor phases. Precipitation can vary markedly in δD , often by tens of permil, between seasons. Different hydrologic reservoirs, including the atmosphere, surface

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