

Equilibrium $^2\text{H}/^1\text{H}$ fractionations in organic molecules. II: Linear alkanes, alkenes, ketones, carboxylic acids, esters, alcohols and ethers

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Abstract

Equilibrium $^2\text{H}/^1\text{H}$ fractionation factors (α_{eq}) for various H positions in alkanes, alkenes, ketones, carboxylic acids, esters, alcohols, and ethers were calculated between 0 and 100 °C using vibrational frequencies from ab initio QM calculations (B3LYP/6-311G**). Results were then corrected using a temperature-dependent linear calibration curve based on experimental data for H_α in ketones (Wang et al., 2009). The total uncertainty in reported α_{eq} values is estimated at 10–20‰. The effects of functional groups were found to increase the value of α_{eq} for H next to electron-donating groups, e.g. –OR, –OH or –O(C=O)R, and to decrease the value of α_{eq} for H next to electron-withdrawing groups, e.g. –(C=O)R or –(C=O)OR. Smaller but significant functional group effects are also observed for H_β and sometimes H_γ . By summing over individual H positions, we estimate the equilibrium fractionation relative to water to be –90‰ to –70‰ for *n*-alkanes and around –100‰ for pristane and phytane. The temperature dependence of these fractionations is very weak between 0 and 100 °C. Our estimates of α_{eq} agree well with field data for thermally mature hydrocarbons ($\delta^2\text{H}$ values between –80‰ and –110‰ relative to water). Therefore the observed $\delta^2\text{H}$ increase of individual hydrocarbons and the disappearance of the biosynthetic $\delta^2\text{H}$ offset between *n*-alkyl and linear isoprenoid lipids during maturation of organic matter can be confidently attributed to H exchange towards an equilibrium state. Our results also indicate that many *n*-alkyl lipids are biosynthesized with $\delta^2\text{H}$ values that are close to equilibrium with water. In these cases, constant down-core $\delta^2\text{H}$ values for *n*-alkyl lipids cannot be reliably used to infer a lack of isotopic exchange.

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1. INTRODUCTION

Compound-specific hydrogen isotope analysis has become widespread over the past decade and has led to a variety of studies using the H isotopic composition ($\delta^2\text{H}$ value) of sedimentary organic matter (SOM) and oils as paleoenvironmental proxies (Xie et al., 2000; Huang et al., 2002; Dawson et al., 2004; Sachse et al., 2006). However, such

applications implicitly assume the preservation of biosynthetic isotopic compositions over geological timescales, and therefore must address the exchangeability of C-bound H (Sessions et al., 2004). A recent review of field data (Schimmelmann et al., 2006) shows that, as thermal maturity increases, $\delta^2\text{H}$ values of individual hydrocarbons steadily increase while the typical 100‰ biosynthetic offsets between linear and isoprenoid structures (Sessions et al., 1999) steadily disappear. Furthermore, this systematic change in $\delta^2\text{H}$ values is negligible where the hydrocarbons are ^2H -depleted relative to water by 80–110‰ (typically associated with very high maturity) and is more apparent where the depletion is smaller or larger (dos Santos Neto and Hayes, 1999; Lis et al., 2006). These observations can

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potentially be explained by H exchange between hydrocarbons and sediment porewater and imply that the endpoint of exchange results in fractionations between hydrocarbons and water in the range of -80% to -110% (Schimmelmann et al., 2006). Testing this hypothesis requires quantitative knowledge of the equilibrium $^2\text{H}/^1\text{H}$ fractionation factors (α_{eq}).

Currently, accurate values of α_{eq} are not known for fractionations involving organic molecules larger than methane. This primarily reflects the difficulties involved in measuring equilibrium fractionations in organic materials: experimental studies suffer from very slow exchange rates of C-bound H (Koepp, 1978; Sessions et al., 2004), while theoretical calculations incorporate potential systematic errors that are particularly limiting for the H-isotope system (Richet et al., 1977). Knyazev et al. (1992) systematically calculated β factors for various H positions in major organic compounds. The results were later modified by Sessions et al. (2004) who incorporated the vapor pressure isotope effect to give α_{eq} values in aqueous phase at $27\text{ }^\circ\text{C}$, but the estimated systematic errors amount to $\pm 100\%$, far too large to be useful for studies of natural-abundance isotopic variations.

To address these issues, we developed a calibration based on α_{eq} values measured via isotope exchange experiments to correct theoretical estimates using frequencies calculated by the B3LYP/6-311G** method. Details of that calibration are provided in a companion paper (Wang et al., 2009), where we show that α_{eq} values for H_α in various linear ketone molecules can be calculated with uncertainties $< 8\%$ for temperatures between 0 and $100\text{ }^\circ\text{C}$. Here we apply the same computational methods and calibration to systematically estimate α_{eq} values for H positions in other common organic compounds, including alkanes, alkenes, carboxylic acids, esters, alcohols, and ethers. In doing so, our goal is to provide a modular dataset for equilibrium $^2\text{H}/^1\text{H}$ fractionations in organic moieties common to sedimentary organic matter, in a form that can be used to piece together estimated fractionation factors for any complete molecule without resorting to further molecular modeling. As a demonstration of this approach, we calculate α_{eq} values for n -alkane and linear isoprenoid molecules and discuss the implications of those values to paleoenvironment and petroleum studies.

2. METHODS AND NOMENCLATURE

Methods for ab initio calculations are described fully in the companion paper (Wang et al., 2009) and only briefly here. Complete vibrational frequencies for selected organic molecules were calculated for the optimized geometries using the hybrid Hartree–Fock and Density Functional Theory (DFT), B3LYP/6-311G** method, with solvation effect treated by the Polarizable Continuum Model (PCM). Values of the reduced partition function ratio (β factor) for ^2H -substitution at individual organic H positions were then calculated from vibrational frequencies based on the theoretical method of Urey (1947) and Bigeleisen and Mayer (1947). The β factor for liquid water was obtained by first calculating the β factor for gaseous mole-

cules using the same method, which was then multiplied by the experimental liquid–gas fractionation factor measured by Horita and Wesolowski (1994). The complete dataset of calculated β factor values are provided as the online Electronic Annex.

Equilibrium $^2\text{H}/^1\text{H}$ fractionation factors (α_{eq}) were then calculated as the ratio of β factors between the organic molecule in aqueous phase and liquid water:

$$\alpha_{\text{eq}} = \frac{\beta(\text{CH})_{\text{aqueous}}}{\beta(\text{H}_2\text{O})_{\text{liquid}}}$$

The value of α_{eq} was then corrected using a linear calibration curve based on experimental data for ketones (Wang et al., 2009) with slope = $1.081 - 0.00376T$ and intercept = $8.404 - 0.387T$, where T is the temperature in degrees Celsius. Application of the ketone-derived calibration curve assumes the same calculation error for other organic compounds as that for ketones. We have shown that the dominant error in the calculation of β factors is the omission of anharmonicity, which is of similar size for C-bound H in most other linear compounds as in ketones (Wang et al., 2009). Therefore errors resulting from the application of ketone-derived calibration are generally expected to be small ($4\text{--}8\%$).

Fractionation factors were calculated over the temperature range $0\text{--}100\text{ }^\circ\text{C}$ for molecules in several major classes, including alkanes, alkenes, acids, esters, alcohols and ethers. In each compound class, the value of α_{eq} was calculated for every H position in 4–10 different molecules with carbon numbers between C_5 and C_{11} . In order to compactly summarize data for a large number of compounds, we average data for analogous positions (i.e. methyl group, methylene group, etc.) in different molecules to report a single α_{eq} value. Reported uncertainties for that value then combine the uncertainty of the calibration curve with true variations in α_{eq} for analogous H positions in different molecules (typically $1\text{--}7\%$). This approach gives a total uncertainty in the estimated α_{eq} values in the range of $10\text{--}20\%$.

It is important to realize that the calculated values of β and thus α_{eq} presented here are specific to individual atomic positions within a molecule, rather than to the whole molecule. When equilibrium has been established with respect to non-equivalent groups in the same molecule, the molecular β factor can be estimated based on the individual β factors for each group, using the method derived by Galimov (1971). It takes on the form of the arithmetic mean of individual β factors weighted by the number of equivalent atoms in each group. In the text and figures, fractionation factors are often presented in terms of the isotopic enrichment factor ε_{eq} :

$$\varepsilon_{\text{eq}} = (\alpha_{\text{eq}} - 1)$$

which is reported in permil ($\%$) units for easier comparison with the standard $\delta^2\text{H}$ ($\%$) notation.

Finally, we remind the reader that we have followed the convention (Wang et al., 2009) of using Greek letters in subscripts to denote molecular positions of specific H atoms, i.e. H_α is the H atom on the first carbon (C_α) that attaches to a functional group, H_β is on the second carbon (C_β), etc. In addition, a saturated C atom is classified as pri-

mary, secondary or tertiary depending on how many other C atoms are attached to it, a descriptor which is also used to denote the H atoms attached to this C atom.

3. RESULTS AND DISCUSSION

3.1. Calculated fractionation factors

A complete list of α_{eq} values for all organic H positions calculated in this study is provided in Table 1 in the form of temperature-dependent functions over the range of 0–100 °C. We first note two general features of the results: (i) The value of α_{eq} for C-bound H is primarily determined by the atoms or functional groups attached to the same carbon center, i.e. the “cutoff effect” that has been observed in many studies (Stern and Wolfsberg, 1966a,b; Hartshorn and Shiner, 1972; Wang et al., 2009). We therefore define each H position by specifying all surrounding groups within two bonds, or further when necessary. (ii) H atoms attached to the same C atom are often sterically symmetric and thus have virtually identical α_{eq} values. However in some cases, e.g. the methylene H atoms on the C next to a double bond can show α_{eq} offsets up to 50‰ depending on their orientations relative to the double bond. Considering the rotation around C–C bonds, equivalent H atoms on the same C atom should be indistinguishable in nature. We therefore report α_{eq} as the average value of all H atoms on that C atom. Below, the results are summarized by compound class, accompanied by brief discussions of the underlying chemistry.

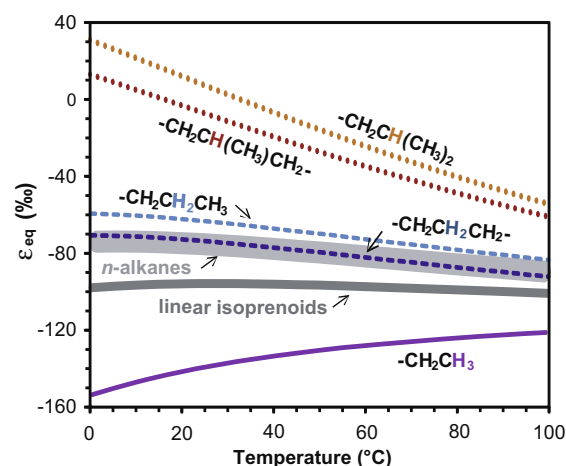


Fig. 1. Equilibrium $^2\text{H}/^1\text{H}$ isotopic enrichment factors (ϵ_{eq}) between organic H and water for five distinct H positions in linear alkanes (curves). Also shown (gray areas) are the ranges of ϵ_{eq} values for C_{14} – C_{33} *n*-alkanes and for phythane and pristane.

3.1.1. H in alkanes

We calculated ϵ_{eq} values for C_5 , C_6 , C_7 , C_9 , and C_{11} *n*-alkanes, and for 2-methyl, 3-methyl, and 4-methyl heptanes. These molecules contain no functional groups. The primary, secondary and tertiary H's are each characterized by distinct ϵ_{eq} values and temperature dependences (Fig. 1). At room temperature the values of ϵ_{eq} are near -140 ‰, -70 ‰ and 0 ‰ for primary, secondary and tertiary H, respectively. Results from the calculations by Knyazev

Table 1

Equilibrium $^2\text{H}/^1\text{H}$ fractionation factors (α_{eq} , between organic H and water) from 0 to 100 °C in the form of $1000 \ln \alpha_{\text{eq}} = A + 10^3 B/T + 10^6 C/T^2$ (T is temperature in Kelvins; standard deviations for α_{eq} are between 0.010 and 0.020). Also listed is the value of ϵ_{eq} at 25 °C.

H position	A	B	C	ϵ_{eq} (‰)	H position	A	B	C	ϵ_{eq} (‰)
<i>H in alkanes</i>					<i>H in carboxylic acids and esters</i>				
–CH ₃	–216.7	85.19	–19.66	–141	–CH ₂ CH ₂ COOH	–435.4	222.7	–22.84	56
–CH ₂ CH ₂ CH ₂ –	–242.3	75.23	–7.822	–75	–CH ₂ CH ₂ COOR ^a	–205.5	59.62	–9.613	–107
–CH ₂ CH ₂ CH ₃	–255.7	83.03	–8.085	–66	–CH ₂ CH ₂ CH ₂ COOR ^a	–275.4	93.53	–7.900	–49
–CH ₂ CH(CH ₃)CH ₂ –	–291.0	85.13	–0.239	–8	–CH ₂ COOCH ₃	–323.6	140.1	–18.16	–56
–CH ₂ CH(CH ₃) ₂	–310.3	96.26	–0.640	5	–CH ₂ COOCH ₂ CH ₃	–369.3	145.0	–8.419	22
<i>H in alkenes</i>					–CH ₂ COOCH ₂ CH ₂ –	–358.9	138.6	–8.074	15
CH ₂ =	–122.4	37.41	–20.46	–203	–CH ₂ COOCH ₂ CH ₂ CH ₂ –	–260.0	84.96	–7.771	–61
CH ₂ =CH– and (E)–CH=CH–	–158.2	42.44	–13.63	–156	<i>H in alcohols</i>				
(Z)–CH=CH–	–155.2	32.63	–8.973	–136	–CH ₂ OH	–477.8	270.3	–35.20	33
=CH(CH ₂)CH ₂ –	–238.2	73.33	–7.897	–78	–CH ₂ CHOHCH ₃	–469.3	257.0	–30.69	49
=CHCH(CH ₃)CH ₂ –	–273.8	111.8	–8.042	11	–CH ₂ CHOHCH ₂ –	–468.8	258.8	–31.77	43
=CHCH ₂ CH=	–232.5	84.70	–10.76	–67	–CH ₂ OH	–330.8	122.4	–8.060	–11
–CH=CHCH=CH–	–158.3	36.83	–10.53	–142	–CH ₂ CHOHCH ₂ –	–432.4	165.3	–2.670	96
–CH=CHC–(CH ₃)=CH–	–162.0	34.80	–8.284	–129	–CH ₂ CH ₂ OH	–248.2	78.43	–7.669	–69
<i>H in ketones</i>					–CH ₂ CH ₂ CHOH–	–228.0	67.36	–7.603	–84
–COCH ₃	–189.3	74.67	–21.81	–168	–CH ₂ CH ₂ CH ₂ CHOH–	–269.3	89.85	–7.717	–53
–COCH ₂ CH ₂ –	–188.0	51.18	–10.31	–124	<i>H in ethers</i>				
–COCH(CH ₃) ₂	–336.9	111.5	–0.8047	28	–CH ₂ OCH ₃	–283.2	116.8	–17.89	–89
–COCH(CH ₃)CH ₂ –	–309.6	95.75	–0.2783	8	–CH ₂ OCH ₂ CH ₃	–315.3	112.6	–7.324	–20
–COCH ₂ CH ₂ CH ₂ –	–268.4	90.03	–7.998	–55	–CH ₂ OCH ₂ CH ₂ –	–307.9	108.9	–7.591	–28
					–CH ₂ OCH ₂ CH ₂ CH ₂ –	–253.1	81.41	–7.847	–66

^a R represents either H (in carboxylic acids) or an alkyl moiety (in esters).

et al. (1992) and Sessions et al. (2004), $-163 \pm 78\%$ for primary H and $-56 \pm 102\%$ for secondary H at 27 °C, are consistent with these new estimates. Replacing an ethyl or longer alkyl branch with a methyl group increases the value of ϵ_{eq} for H located on the branching carbon. For example, in *n*-alkane molecules, ϵ_{eq} for the secondary H atoms on the C next to the methyl groups is $\sim 10\%$ higher than for the other secondary H atoms. Similarly, ϵ_{eq} for the tertiary H in 2-methylheptane is $\sim 10\%$ higher than the tertiary H in 3-methylheptane.

Consequently, five H positions with distinct ϵ_{eq} values can be used to summarize all relevant structures in natural linear (straight and branched) alkanes, specifically (target H position in bold), $-\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$, and $-\text{CH}_2\text{CH}(\text{CH}_3)_2$. The average values of ϵ_{eq} for each analogous position in all modeled alkane molecules are plotted against temperature in Fig. 1. To check for potential effects on ϵ_{eq} from distant functional groups, we also calculated ϵ_{eq} for the same five analogous H positions in 10 linear ketones. The effects of the carbonyl group on ϵ_{eq} are found to reach as far as H_β , but no farther. Thus when H_α and H_β in the ketone are excluded, then ϵ_{eq} values for equivalent H positions in linear alkanes and ketones are virtually identical (data not shown). We conclude that our results for linear alkanes are also suitable for estimating fractionations in the aliphatic chains of functionalized molecules.

The increase of ϵ_{eq} for H bonded to C with increasing alkyl substitution is likely related to the inductive electron-donating effect (+I) of alkyl groups, with the methyl group being the strongest donor. It acts to increase the electron density of the neighboring C—H bond, which gives rise to a stiffer bond and thus higher ϵ_{eq} values (Bigeleisen and Mayer, 1947; Hartshorn and Shiner, 1972). This effect is superimposed on the influence of functional groups, for example as seen in the similar patterns of ϵ_{eq} for primary, secondary and tertiary H in alkanes and adjacent to carbonyl groups in ketones (Wang et al., 2009). Therefore, in the following sections, ϵ_{eq} values for H near functional groups are compared to alkane H at analogous positions (i.e. primary, secondary or tertiary H) to highlight the effect of that functional group.

Values of ϵ_{eq} for linear aliphatic hydrocarbon molecules can be calculated as the weighted average of ϵ_{eq} for all individual hydrogen positions (Galimov, 1971). Results are between -70% and -90% for *n*-alkanes (C_{14} – C_{33}) and around -100% for pristane and phytane (Fig. 1). They agree well with the predicted range of -80% to -110% based on field data (Schimmelmann et al., 2006). The value of ϵ_{eq} for C_{14} – C_{34} *n*-alkanes increases with chain-length by 7–11‰ between 0 and 100 °C, due to the slightly higher

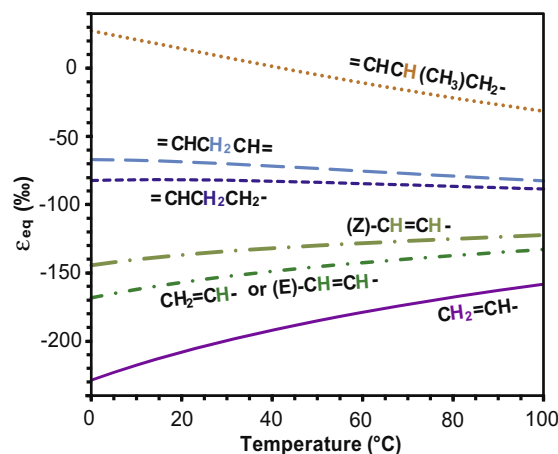


Fig. 2. Equilibrium $^2\text{H}/^1\text{H}$ isotopic enrichment factors (ϵ_{eq}) between various linear alkene positions and water.

proportion of secondary H in longer molecules. It has been shown that artificial thermal maturation of natural oils can produce ^2H enrichments with increasing chain-length by 4–17‰ due to kinetic fractionation (Tang et al., 2005). Therefore in some highly mature natural samples, the observed 10–30‰ increase with chain-length (Schimmelmann et al., 2004; Pedentchouk et al., 2006) could result at least partially from equilibrium isotope effects. Another noteworthy feature is that the value of ϵ_{eq} for these hydrocarbons varies only slightly with temperature over the range 0–100 °C. For *n*-alkanes, this reflects the fact that secondary H has little temperature dependence, whereas for isoprenoids the temperature dependences of primary and tertiary H are opposite and very nearly cancel.

3.1.2. H in alkenes

Values of ϵ_{eq} were first calculated for five monounsaturated alkene molecules, including 1-hexene, 3-methyl-1-hexene, 5-methyl-1-hexene, *trans*-5-decene and *cis*-5-decene. Results for specific H positions that are affected by the double bond are plotted in Fig. 2. At room temperature, ϵ_{eq} values for H atoms in $\text{CH}_2=$ are $\sim 60\%$ more negative than primary H in alkanes. A similar offset is observed between H in *cis* $-\text{CH}=\text{CH}-$ and secondary H in alkanes. H on a *trans* double bond is further depleted relative to the *cis* isomer by $\sim 20\%$. The decrease of ϵ_{eq} values with lower coordination number of the C atom in the C—H bond was also observed by Hartshorn and Shiner (1972) and Knyazev et al. (1992).

For H bonded to a C atom adjacent to a double bond (either *cis* or *trans*), one of the C—H bonds is lying in the plane containing the double bond, while the other two bonds are at $\sim 60^\circ$ angles to the plane. $\text{H}_\alpha^{\text{eq}}$ (equatorial)

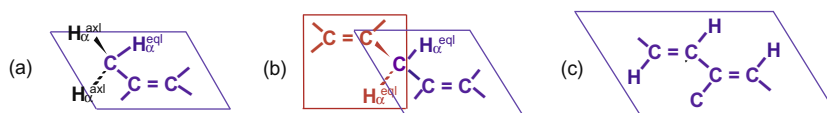


Fig. 3. (a) Configuration of H_α atoms next to a single double bond; (b) configuration of two “methylene interrupted” *cis* double bonds; (c) configuration of two conjugated double bonds with or without a methyl branch. Each box depicts a plane containing the bonds and atoms of the same color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

and H_z^{axl} (axial) are used to denote these two positions, respectively (Fig. 3a). Compared to analogous position in alkanes, ϵ_{eq} for H_z^{axl} is $\sim 30\text{‰}$ more negative, while ϵ_{eq} for H_z^{eq} is $\sim 15\text{‰}$ more positive. The average ϵ_{eq} for secondary H next to a double bond is thus slightly lower than that for secondary H in alkanes (Fig. 2). The depletion of ϵ_{eq} for H_z^{axl} is likely associated with the σ - π hyperconjugation effect, in which the σ -electron pair of the $C-H_z^{\text{axl}}$ bond interacts with the π -electrons on the double bond and reduces the electron density of the $C-H_z^{\text{axl}}$ bond because of its +I effect. At positions further away from the double bond, ϵ_{eq} values are indistinguishable from those for alkane H.

We also calculated ϵ_{eq} values for two types of doubly-unsaturated alkenes. The first has two *cis* double bonds separated by a $-CH_2-$ group, a structure often seen in multiply unsaturated fatty acids, i.e. ‘methylene interrupted’ unsaturations (Fig. 3b). The two double bonds are oriented in perpendicular planes, and the ϵ_{eq} value for H on either double bond is not appreciably affected by the other double bond. The secondary H atoms on the methylene group between the double bonds are each coplanar with one of the double bonds. They have ϵ_{eq} values that are slightly higher than secondary H in alkanes (Fig. 2). The other type of doubly-unsaturated alkenes contains two conjugated double bonds, either with or without a methyl group attached to the double bonds (Fig. 3c), a structure characterizing many carotenoid pigments. The conjugated double bonds are coplanar. At room temperature, the value of ϵ_{eq} is -160‰ for H on the two ends of the conjugated double bond and -140‰ for H in between, comparable to H on a single double bond. A methyl group attached to either double bond raises the ϵ_{eq} value of the neighboring H atoms on the double bonds by 10 – 15‰ , while H on that methyl group has the same ϵ_{eq} values as for primary H in alkanes.

3.1.3. H in ketones, carboxylic acids and esters

Values of ϵ_{eq} were calculated for differing H positions in 10 linear ketones. In addition to the six ketones described by Wang et al. (2009), we also included 2-octanone, 5-methyl-2-hexanone, 6-methyl-2-heptanone and 5-methyl-2-heptanone to obtain a larger dataset. Results for H positions affected by the carbonyl functional group are plotted in Fig. 4a. ϵ_{eq} values for primary and secondary H_α are lower by 30 – 55‰ compared to those in alkanes, consistent with the electron-withdrawing effect of the carbonyl group that acts to decrease the electron density of the $C_\alpha-H_\alpha$ bond. In contrast, ϵ_{eq} values for tertiary H_α in ketones are 15 – 20‰ higher than for alkane tertiary H, a result for which the mechanism is currently unclear. It is possibly associated with the stable conformation of the $O=C-C_\alpha-C_\beta$ dihedral, where one alkyl branch on the tertiary C_α is at 30 – 37° to the carbonyl group, compared to $\sim 0^\circ$ on the secondary C_α in straight-chain ketones (Wang et al., 2009). The effect of the carbonyl group is found to reach as far as H_β , where secondary H_β is 15 – 20‰ more enriched than secondary alkane H at equilibrium. The effect of a carbonyl group on H_β is in the opposite direction as that on H_α , which is also observed for esters and acids. It is possibly related to the field inductive effect from the functional group on H_β (see Section 3.2).

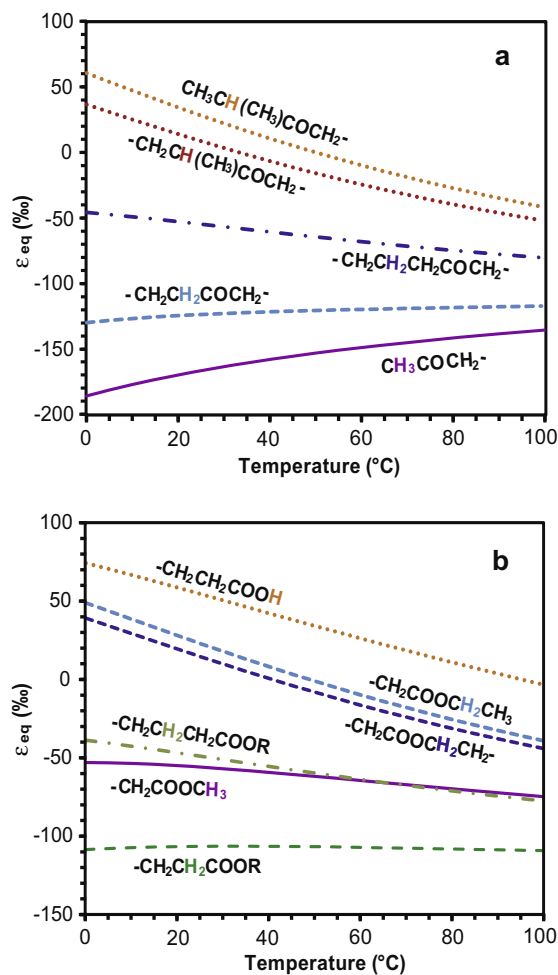


Fig. 4. Equilibrium $^2\text{H}/^1\text{H}$ isotopic enrichment factors (ϵ_{eq}) between organic H and water in (a) linear ketones and (b) linear carboxylic acids and esters. In (b), the R group can represent either H (acids) or an alkyl moiety (esters).

Values of ϵ_{eq} were calculated for pentanoic acid, hexanoic acid and methyl-, ethyl-, propyl-, and *n*-butyl-esters of pentanoic acid. Results for selected H positions are plotted in Fig. 4b. Just as in ketones, the $-(C=O)OR$ group ($R = \text{H}$ or alkyl moiety) is electron-withdrawing and leads to lower ϵ_{eq} values. Thus for secondary H_α next to the carbonyl group, ϵ_{eq} values are $\sim 30\text{‰}$ lower than for secondary H in alkanes. However, the electron lone pairs on the singly-bonded O in the acid/ester are donated towards the electron-deficient π -orbital of the carbonyl C (Amyes and Richard, 1996; Richard, 2002), which reduces the polarity of the $C=O$ bond and its subsequent effect on fractionation at H_α . Thus ϵ_{eq} values for H_α in acids/esters are $\sim 20\text{‰}$ higher (closer to that in alkanes) than for the same position in ketones. For esters, H on the C atom next to the singly-bonded O has ϵ_{eq} values $\sim 90\text{‰}$ higher than alkane H at room temperature, which could also be attributed to the strong electron-donating effect of the electron lone pairs on the singly-bonded O atom. The hydroxyl H in carboxylic acids is enriched in ^2H relative to water by $\sim 55\text{‰}$ at room temperature (see Section 3.1.4).

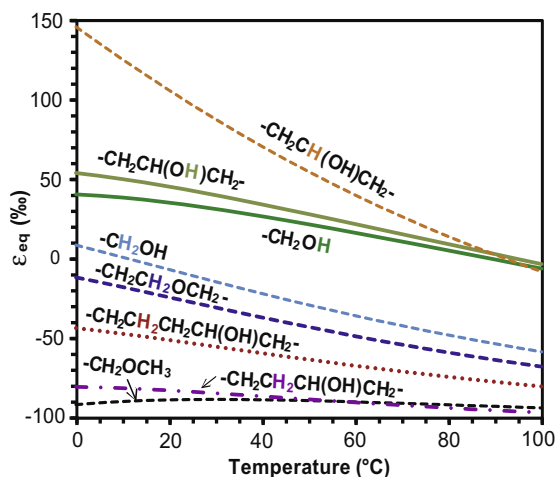


Fig. 5. Equilibrium $^2\text{H}/^1\text{H}$ isotopic enrichment factors (ϵ_{eq}) between organic H and water in linear alcohols and ethers.

3.1.4. H in alcohols and ethers

We calculated ϵ_{eq} for four *n*-heptanol isomers with the hydroxyl group on C-1 through C-4, and for pentyl-methyl ether, pentyl-ethyl ether, and pentyl-propyl ether (Fig. 5). The hydroxyl H is ^2H -enriched relative to water by 35–50‰ at room temperature, similar to the hydroxyl H in carboxylic acids. The values of ϵ_{eq} for secondary H_α (H on the same C as the hydroxyl group) are found to be as high as 100‰ at room temperature and quickly decline with temperature to ~ 0 at 100 °C. In primary alcohols, positions beyond H_α are not appreciably affected by the hydroxyl group. In secondary alcohols, ϵ_{eq} for H_β is ~ 10 ‰ lower than analogous position in alkanes, while for H_γ (three carbon atoms away from the hydroxyl) ϵ_{eq} is higher by an average of ~ 25 ‰. For ethers, only H_α is significantly affected by the alkoxy group, with the ϵ_{eq} value ~ 50 ‰ higher than H at analogous positions in alkanes.

The effects of the hydroxyl group are characterized by the negative inductive ($-I$) effect of the O atom and the electron-donating effect of the electron lone pairs on the O atom. Hydroxyl H is primarily affected by the $-I$ effect that attracts electrons towards O along the σ -bond and by the electrostatic interaction with water molecules, particularly hydrogen bonding. The combined effects seem to consistently result in positive ϵ_{eq} values of 30–50‰ at room temperature for hydroxyl H in either alcohols or carboxylic acids. Note that since calculation errors due to omission of anharmonicity are systematically smaller for hydroxyl H than for C-bound H (Wang et al., 2009), applying the calibration curve based on ketones tends to overcorrect for hydroxyl H, i.e. underestimate the value of ϵ_{eq} for hydroxyl H by 6–10‰. Nevertheless, our estimates are still consistent with Bigeleisen (1965), who calculated the $^2\text{H}/^1\text{H}$ fractionation between hydroxyl H in small alcohol and carboxylic acid molecules (C_1 – C_4) and water to be 30–90‰.

The electron lone pairs on O are diffusive and can transmit their influence over relatively large distances via the field inductive effect (see Section 3.2). Consequently, the effect on nearby C–H bonds seems to depend heavily on the spatial orientation of the C–H bond relative to the hydro-

xyl group. For example, in secondary alcohols, where the hydroxyl group is on one side of the carbon chain, H_γ is more affected than H_β . This is probably because the C_γ – H_γ bonds are close and parallel to the hydroxyl group, which would facilitate σ -p hydroconjugation. In contrast, C_β – H_β bonds are pointing in the opposite direction due to the zig-zag structure of the aliphatic chain.

3.2. The effects of functional group on equilibrium fractionations of C-bound H

The presence of functional groups changes the fractionation of nearby C-bound H to various degrees depending on the chemistry, geometry and spatial orientation of the functional group. The influence is generally not further than H_β , but sometimes can reach as far as H_γ , e.g. in secondary alcohols. To compare the effects of various functional groups on the value of ϵ_{eq} for nearby C-bound H, we take the aliphatic fragment $-\text{CH}_2\text{CH}_2\text{CH}_2-$ (ideally in an infinitely long aliphatic chain) as the reference state, and calculate the equilibrium fractionation between secondary H in the vicinity of a certain functional group and secondary H in the reference aliphatic fragment. Results are plotted versus temperature in Fig. 6.

Fig. 6a demonstrates that H_α next to an electron-deficient atom in a π system, e.g. $-(\text{C}=\text{O})\text{R}$ and $-(\text{C}=\text{O})\text{OR}$, has a lower ϵ_{eq} value relative to alkane H, while H_α next to an atom with electron lone pairs, e.g. $-\text{OH}$, $-\text{OR}$ and $-\text{O}(\text{C}=\text{O})\text{R}$, has more positive ϵ_{eq} values. This pattern is analogous to the well-known substituent effects on an aromatic ring, which result from a combination of resonance and inductive effects of the functional group. In that system, the lone-pair electrons on the O atom that is singly-bonded to the benzene ring are strongly donating towards the arene system through p- π conjugation, even though oxygen is more electronegative than carbon. In contrast, the π - π conjugation between the $\text{C}=\text{O}$ double bond and the benzene ring results in electron-withdrawing from the arene system because of the high electronegativity of oxygen. Similarly, in the saturated system that we study the σ electrons in C–H bonds can interact with the π -electrons or lone pairs of the functional groups in an analogous way through σ - π or σ -p hyperconjugation, leading to enhanced or reduced electron density in the C–H bond and corresponding changes in the bond stiffness.

The effects of functional groups on H_β positions (Fig. 6b) or further are much smaller than those for H_α , but are nevertheless significant considering that $\delta^2\text{H}$ values can be measured with a precision of 2–5‰. Chemists have long recognized that there are two basic mechanisms by which a polar group conveys its influence on a remote probe in saturated systems, the σ - (through-bond) inductive effect and field (through-space) inductive effect (Robinson, 1932; Dewar and Gridale, 1962; Reynolds, 1980). Since Kirkwood and Westheimer (1938) highlighted the electrostatic field model, the importance of the field inductive effect has been gradually established via numerous experimental and theoretical studies (Adcock and Trout, 1999; Nolan and Linck, 2000; Otto and Zdeněk, 2007). In many cases it is difficult to accurately ascribe substituent effects to either mechanism. Nevertheless, a general consen-

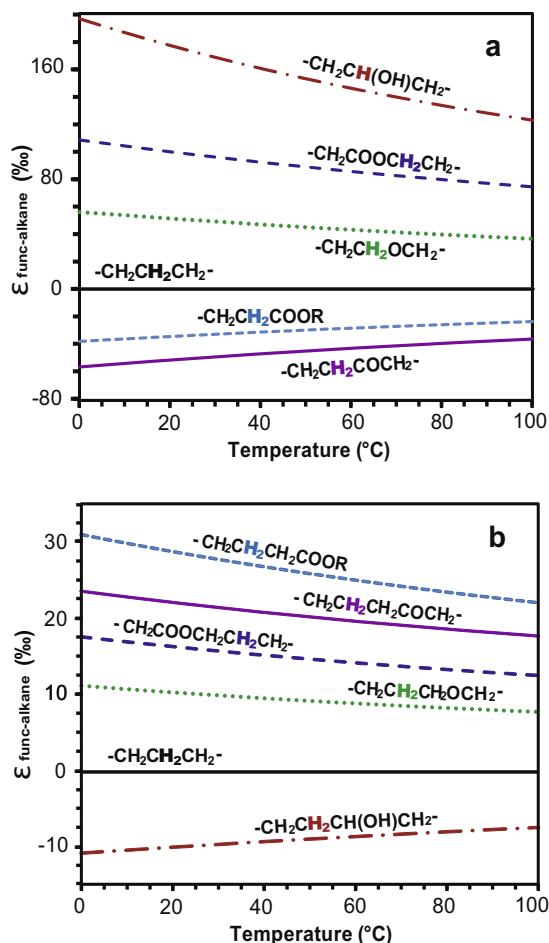


Fig. 6. $^2\text{H}/^1\text{H}$ fractionations ($\epsilon_{\text{func-alkane}}$) between secondary H near various functional groups and secondary H in the alkane fragment $-\text{CH}_2\text{CH}_2\text{CH}_2-$ (the reference state). Panel (a) compares H_α positions, while panel (b) compares H_β positions. To facilitate comparison between (a) and (b), the same line pattern and color are assigned to the same fragment in both panels. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

sis is that for probe groups beyond two bond-lengths the field effect is the dominant “inductive” mechanism (Bowden and Grubbs, 1996; Otto, 1999). We thus infer that functional group effects on fractionation at H_β and further are caused mainly by the through-space inductive effect.

The magnitude of field effects is a complex function of the geometry and dielectric properties of the molecule and the cavity it occupies in the solvent continuum (Ehrenson, 1977). In other words, there is no simple relationship between the electronic properties of a functional group and the shifts in ϵ_{eq} values that it induces either for H_β or H_γ . As a result, the effects of functional groups on fractionation at H_β are observed to be generally uncorrelated with those at H_α (Fig. 6).

3.3. Temperature dependence and the equilibrium vapor–aqueous fractionations

The temperature dependence of ϵ_{eq} for C-bound H is observed to be generally positive for H positions with

$\epsilon_{\text{eq}} < -100\text{‰}$ and negative for H positions with $\epsilon_{\text{eq}} > -100\text{‰}$. In other words, the ϵ_{eq} values for various C-bound H tend to converge from both sides towards a depletion of $\sim 100\text{‰}$ relative to water as temperature rises. Therefore the fractionations between various H positions will continuously decrease with increasing temperature. At higher temperatures, the calculated β factors for C-bound H display the expected linear decrease towards unity with increasing temperature squared (Bigeleisen and Mayer, 1947; data not shown). In addition, a cross-over effect (i.e. the sign of ϵ_{eq} changes) is observed between 0 and 100 °C for tertiary H in alkanes, tertiary H next to a double bond or carbonyl group, and secondary H next to oxygen in esters.

We also calculated the equilibrium vapor–aqueous fractionation for selected linear hydrocarbon molecules. The results are generally from 0‰ to 10‰ for various C-bound H positions over 0–100 °C, with the vapor phase being enriched in ^2H . Wang and Huang (2001) measured the vapor pressure isotope effect of low molecular weight *n*-alkanes (C_7 – C_9) during progressive vaporization and found results around 4‰, consistent with our calculation. This inverse vapor pressure isotope effect (VPIE), as well as the cross-over effect, has been theoretically predicted and experimentally observed for many small hydrocarbon molecules (Jancso and Vanhook, 1974). It results from the effects of dispersion forces on the internal vibrational motions and a lack of intermolecular bonding effects, e.g. hydrogen bonding, which give rise to the normal VPIE for water (Bigeleisen, 1961; Jancso and Vanhook, 1974). The agreement between calculated and experimental estimates of vapor pressure isotope effects lends further credence to the accuracy our calculations.

3.4. Application to organic geochemical studies

Here we review published $\delta^2\text{H}$ data for sedimentary organic matter (SOM) and oils with regard to the equilibrium $^2\text{H}/^1\text{H}$ fractionation factors that we have calculated. Discussion is focused on the potential mechanisms for $\delta^2\text{H}$ changes during maturation and on estimation of the extent of H exchange in natural systems.

3.4.1. $\delta^2\text{H}$ changes during maturation of organic matter in natural systems

Post-burial changes in the $\delta^2\text{H}$ values of organic matter have been documented by numerous field measurements and laboratory maturation experiments. Schimmelmann et al. (2006) recently reviewed the results of more than 20 field and 15 experimental studies. They paint a coherent picture in which $\delta^2\text{H}$ values increase both for bulk SOM and for individual molecular components during maturation and oil generation. At the same time, offsets in $\delta^2\text{H}$ between linear and isoprenoid lipids that are present in modern sediments steadily disappear.

Two potential mechanisms have been invoked to explain these changes. Peters et al. (1981) and Schoell (1983) attributed $\delta^2\text{H}$ increases in bulk SOM to a progressive loss of ^2H -depleted gaseous hydrocarbons, i.e. as a result of kinetic fractionations during hydrocarbon cracking. However, this

process should produce equivalent ^2H enrichments in kerogens of similar type and thermal maturity regardless of their original $\delta^2\text{H}$ value or the $\delta^2\text{H}$ value of the formation water. This prediction is inconsistent with empirical data. Moreover, loss of ^2H -depleted gases cannot easily explain the convergence of $\delta^2\text{H}$ values between isoprenoid and n -alkyl molecules (Dawson et al., 2005; Pedentchouk et al., 2006).

The alternative explanation, previously proposed by Schimmelmann et al. (1999, 2001), involves H exchange between water and organic H during maturation reactions, e.g. isomerization, cracking, rearrangement and dehydration. Several studies have lent further support to this mechanism (see Schimmelmann et al., 2006, for a recent review). Lis et al. (2006) compared two kerogen sequences of the same type with similar source rock and depositional environment. The primary difference between them was that the formation water associated with one kerogen had $\delta^2\text{H}$ values that were 40‰ higher than in the other. Within comparable ranges of maturity ($R_o \sim 0.3 - 1.4\%$), the $\delta^2\text{H}$ value of the first kerogen was observed to increase twice as much as for the second, indicating that water does play a role in altering the isotopic compositions of kerogen. dos Santos Neto and Hayes (1999) measured $\delta^2\text{H}$ values of oils from lacustrine, marine-evaporitic, and transitional paleoenvironments across a maturity gradient in the Potiguar Basin, Brazil. At low thermal maturity, the three paleoenvironments were distinguished by their $\delta^2\text{H}$ values (lacustrine $\delta^2\text{H} \sim -90\%$; transitional $\delta^2\text{H} \sim -110\%$; marine-evaporitic $\delta^2\text{H} \sim -120\%$ to -135%). But at higher maturity, oils from the three paleoenvironments converged from both sides toward $\delta^2\text{H}$ values of -110% . Several other studies have documented cases in which there was no measureable change in $\delta^2\text{H}$ values with increasing thermal maturity, both for bulk organic matter (reviewed by Schimmelmann et al. (2006)) or for individual n -alkanes (Pedentchouk et al., 2006). A common feature of these studies is that the organic compounds were depleted relative to water by 80–110‰.

Based on these data, Schimmelmann et al. (2006) predicted that the equilibrium fractionation between hydrocarbons and water must lie in the range of -80% to -110% . While we do not yet have appropriate data for cyclic and aromatic compounds, this prediction is now confirmed for linear alkanes by our experimental and theoretical estimates of ϵ_{eq} (Fig. 1). Moreover, the disappearance of biosynthetic offsets in $\delta^2\text{H}$ values between n -alkyl and linear isoprenoid lipids can be fully explained by their similar equilibrium fractionations: -90% to -70% for n -alkanes and near -100% for linear isoprenoids, both over the range of 0–100 °C. We are thus confident that the hypothesis of Schimmelmann et al (1999, 2001), attributing changes in SOM $\delta^2\text{H}$ values to hydrogen exchange, is generally correct.

Our data provide two other conclusions about the interpretation of $\delta^2\text{H}$ values in thermally mature SOM and oils. First, the molecular equilibrium fractionation factors change minimally with temperature. Once equilibrium is achieved, any further changes in $\delta^2\text{H}$ values are likely not attributable to exchange. Thus fractionations between hydrocarbons and water, or between different linear hydrocarbons, will not yield reliable geothermometers. Second,

$\delta^2\text{H}$ enrichments up to 11‰ are possible as the chain-length of n -alkanes increases. Similar patterns have been recognized in moderately to highly mature organic matter (Sessions et al., 2002; Schimmelmann et al., 2004; Pedentchouk et al., 2006), although to a larger extent (typically 10–30‰). These patterns likely reflect a combination of isotopic equilibrium and the effects of kinetic fractionations during hydrocarbon cracking (Tang et al., 2005).

3.4.2. Constraints on the use of organic $\delta^2\text{H}$ as a paleoenvironmental proxy

Many recent studies have sought to use the $\delta^2\text{H}$ values of sedimentary lipids as a proxy for paleoenvironmental conditions (Huang et al., 2002; Dawson et al., 2004; Sachs et al., 2006). Implicit in this approach are the assumptions that (i) biosynthetic fractionations between water and lipids are known, and (ii) the $\delta^2\text{H}$ values of lipids have not been significantly altered by isotopic exchange. Limitations to the former assumption have been discussed elsewhere (Sessions et al., 1999; Zhang and Sachs, 2007; Zhang et al., 2009). For the latter assumption, the ability to detect isotopic exchange in ancient lipids is obviously key.

A number of studies have attempted to rule out isotopic exchange in ancient lipids by showing that the $\delta^2\text{H}$ values of n -alkanes are very different from formation water, or that they do not change with increasing thermal maturity. For example, Yang and Huang (2003) studied leafwax lipids isolated from plant fossils in Miocene lacustrine deposits, and found $\delta^2\text{H}$ offsets between lipid H and sedimentary water of -103% to -108% for n -alkanes and -88% to -102% for n -acids. These offsets are similar to their modern relatives (-81% to -144%), and the authors concluded that no isotopic exchange had occurred over the 15–20 Ma history of the sediments. Pedentchouk et al (2006) studied a lacustrine sediment core from the Lower Cretaceous that spans ~ 20 Ma, and showed that there was no change in n -alkane $\delta^2\text{H}$ values over this range. They concluded that the n -alkanes had not been affected by isotopic exchange, and would thus make a suitable target for paleoenvironmental reconstruction. Our data now clearly shows that both approaches are problematic, because in many cases the $\delta^2\text{H}$ values of sedimentary n -alkanes lie close to isotopic equilibrium with environmental water. In these cases we should expect that n -alkane $\delta^2\text{H}$ values will change little, even with extensive H exchange. Nor does the situation improve with increasing temperature, because the fractionations are insensitive to temperature. These ‘tests’ for isotopic exchange are thus inconclusive, and do not have the ability to discern appreciable exchange in the n -alkyl lipids.

More convincing tests for isotopic exchange in n -alkanes would involve the preservation of $\delta^2\text{H}$ values that are far out of equilibrium with porewaters, such as might be found for high-latitude terrestrial leafwaxes deposited in marine sediments, or the preservation of differing $\delta^2\text{H}$ values between homologous compounds. For example, Dawson et al (2004) studied n -alkanes from immature torbanites deposited over widely ranging paleolatitudes during Late Carboniferous to the Late Permian. They showed that n -alkanes in torbanites deposited under glacial conditions are

depleted in deuterium by up to 70‰ relative to *n*-alkanes deposited under a tropical climate regime, and that there is a “saw-toothed” profile of $\delta^2\text{H}$ values for the alkanes with offsets up to 40‰. These data indicate that the original isotope ratio in some cases can be preserved for hundreds of millions of years.

A second approach to evaluating isotopic exchange in ancient lipids is to compare $\delta^2\text{H}$ values between hydrocarbons with *n*-alkyl and linear isoprenoid carbon skeletons (Andersen et al., 2001; Sessions et al., 2004). Extensive field and culture data shows that these lipids classes are biosynthesized with very different $\delta^2\text{H}$ values (Sessions et al., 1999; Zhang and Sachs, 2007; Li et al., 2009), whereas their equilibrium fractionations versus water are quite similar (Fig. 1). Thus isotopic exchange leads to a convergence of $\delta^2\text{H}$ values in linear isoprenoids and *n*-alkanes over time. Examples of such a pattern have now been conclusively shown for Cretaceous lacustrine sediments (Pedentchouk et al., 2006) and for Triassic shales (Dawson et al., 2005). Andersen et al. (2001) documented $\sim 100\%$ offsets between $\delta^2\text{H}$ values of 5α -cholestane and *n*-docosane in a Messinian sapropel, similar to that seen in fresh biomass. Accurate estimates for equilibrium $^2\text{H}/^1\text{H}$ fractionation between polycyclic and linear hydrocarbons are not yet available, although they seem unlikely to be as large as 100‰.

A significant advantage of this second type of test for isotopic exchange is that the $\delta^2\text{H}$ value of exchanging porewaters does not need to be known. However, we caution that such measurements are only able to resolve isotopic exchange in the isoprenoid structures (which usually lie far from isotopic equilibrium), and not the *n*-alkanes. It has been observed that H exchange near a tertiary carbon center proceeds much faster than in *n*-alkanes when catalyzed by clay minerals, presumably due to a catalytic mechanism involving carbocation-like intermediates (Larcher et al., 1986). Nevertheless, a pattern of changing isoprenoid $\delta^2\text{H}$ values with constant *n*-alkane $\delta^2\text{H}$ values could still be consistent with significant isotopic exchange of the *n*-alkanes. In particular we note that isoprenoid $\delta^2\text{H}$ values are never (to our knowledge) observed to increase above those of coexisting *n*-alkanes, which might be expected in certain cases if only the isoprenoids were undergoing appreciable exchange. In summary, we believe that the existing body of evidence supports the conclusion that sedimentary *n*-alkanes are largely resistant to isotopic exchange during diagenesis, and thus are generally suitable targets for paleoenvironmental reconstruction. However, explicitly testing this conclusion for specific samples remains problematic, and is likely to hamper our ability to push the use of organic $\delta^2\text{H}$ measurements deeper into geologic time.

4. CONCLUSIONS

We report equilibrium $^2\text{H}/^1\text{H}$ isotopic enrichment factors (ϵ_{eq}) between 0 and 100 °C for various H positions in alkanes, alkenes, ketones, carboxylic acids, esters, alcohols, and ethers, with total uncertainties typically in the range of 10–20‰. The values are based on ab initio calculations of molecular vibrational frequencies and are calibrated to experimental ϵ_{eq} values for H_α in ketones. These data

should be useful for applications seeking to predict ^2H abundance in numerous geochemical, chemical, and biological reactions. The effects of functional groups are found to increase the value of ϵ_{eq} for H next to electron-donating groups, e.g. —OR, —OH or —O(C=O)R groups and to decrease the value of ϵ_{eq} for H next to electron-withdrawing groups, e.g. —(C=O)R or —(C=O)OR groups. Smaller but significant effects are also observed for H_β and sometimes H_γ positions, probably due to the field inductive effect of the functional group.

Estimated values of ϵ_{eq} for *n*-alkanes and linear isoprenoids agree well with the range predicted by field data from sediments and oils (–80‰ to –110‰), and support the conclusion that changes in the $\delta^2\text{H}$ value of sedimentary organic matter during maturation are likely caused by H exchange towards an equilibrium state. The progressive convergence of $\delta^2\text{H}$ values for linear isoprenoid and *n*-alkyl lipids are also consistent with isotopic equilibration. Since in many cases *n*-alkyl lipids are biosynthesized with $\delta^2\text{H}$ values close to equilibrium with water, a lack of down-core variation in $\delta^2\text{H}$ values for *n*-alkyl lipids cannot be construed as evidence for no exchange.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2009.08.018](https://doi.org/10.1016/j.gca.2009.08.018).

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