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Isotopically exchangeable organic hydrogen in coal relates to thermal maturity and maceral composition

M. Mastalerz[a,*], A. Schimmelmann[b]

[a]*Indiana Geological Survey, Indiana University, 611 North Walnut Grove, Bloomington, IN 47405-2208, USA*
[b]*Department of Geological Sciences, Indiana University, Bloomington, IN 47405-1405, USA*

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Abstract

Hydrogen isotopic exchangeability (H_{ex}) and δD_n values of non-exchangeable organic hydrogen were investigated in coal kerogens ranging in rank from lignite to graphite. The relative abundance of H_{ex} is highest in lignite with about 18% of total hydrogen being exchangeable, and decreases to around 2.5% in coals with R_o of 1.7 to ca. 5.7%. At still higher rank ($R_o > 6\%$), H_{ex} increases slightly, although the abundance of total hydrogen decreases. δD_n is influenced by original biochemical D/H ratios and by thermal maturation in contact with water. Therefore, δD_n does not show an overall consistent trend with maturity.

1. Introduction

Total organic hydrogen in coal encompasses hydrogen that is linked to carbon either directly or via bridging heteroatoms like O, S, and N. Some of this organic hydrogen can isotopically exchange with hydrogen from ambient water, with exchange half-lives ranging from seconds (in exposed hydroxyl, carboxyl, and amino groups) to millions of years (aliphatic carbon-linked hydrogen; Schimmelmann et al., 1999). The abundance of readily exchangeable organic hydrogen is expressed as "hydrogen exchangeability" (H_{ex}, in % of total organic hydrogen, measured after ca. 8 h of contact with deuterium-enriched water vapor at 115 °C; Schimmelmann et al., 1999). Exchangeable organic hydrogen is the most chemically reactive, polar hydrogen, and thus participates in oil and gas generation from coal. In contrast, non-exchangeable organic hydrogen may have preserved an isotopic paleoenvironmental signal, but deuterium/hydrogen (D/H, or $^2H/^1H$) stable isotope ratios in coals or coal kerogens are typically measured only for total hydrogen. The analytical isotopic noise from H_{ex} in total hydrogen is reduced in this study by equilibrating exchangeable organic hydrogen with isotopically characterized water vapors.

The amount of organic hydrogen in immature kerogen is insufficient to account for the total hydrogen in gas, oil, bitumen, and solid residue with increasing thermal maturity (Lewan, 1997; Schimmelmann et al., 1999). These and other studies point toward water-hydrogen as an additional source for organic hydrogen in thermally maturing organic matter, which implies that water-derived hydrogen may affect the D/H ratio of organic hydrogen in oil, gas, and coal. A better understanding of the isotopic composition and exchangeability of organic hydrogen in coal should help in evaluating the relevance of D/H ratios for paleoenvironmental reconstruction and in correlating between solid source material and the fluid products of maturation (gas, oil).

Limited data are available on the exchangeability of hydrogen in coals. Studies on the uptake of tritium (^3H) in bulk coal in contact with tritiated water at 50–400 °C in the laboratory (Ishihara et al., 1993; Qian et al., 1997)

* Corresponding author. Tel.: +1-604-228-2449; fax: +1-812-855-2862.
E-mail addresses: mmastale@Indiana.edu (M. Mastalerz), aschimme@indiana.edu (A. Schimmelmann).

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yielded (i) an initial trend of decreasing exchangeability with increasing temperature, and (ii) a reversed trend at higher temperature, but in the presence of inorganic hydrogen in mineral-containing bulk coal these results can only be suggestive with regard to the exchangeability of organic hydrogen in coal. Particle size has little effect on H_{ex} in coal, which suggests that water-derived hydrogen has easy access via micropores and fractures (Ishihara et al., 2000; Schimmelmann et al., 2001).

This study provides H_{ex} and D/H data for mineral-free kerogen from coals and their macerals with increasing rank, and demonstrates the influence of different maceral compositions.

2. Techniques

A suite of Pennsylvanian coals ranging in vitrinite reflectance (R_o) from 0.55 to 5.15% was initially selected for this study (Mastalerz and Schimmelmann, 2001). In addition, Triassic anthracite from Vietnam, Precambrian shungite from Karelia, natural graphite from British Columbia, and Miocene lignites from Poland were added to extend the range of thermal maturity. Vitrinite fractions from coals with reflectance below 1.25% were hand-picked and analyzed in addition to their respective bulk coals. A fusinite fraction from sample FGT-6 221 was hand-picked. 'Indiana paper coal' represents a coalified Pennsylvanian natural deciduous leaf assemblage (liptinite).

The ash content and elemental (ultimate) analyses of coals follow the ASTM method (1995). Vitrinite reflectance (random for coals with reflectance below 1.28%, and R_{max} for higher rank coals) and petrographic analyses were performed using a Leitz MPV-II microscope.

Prior to all isotopic analyses, mineral matter from coals and macerals was removed to yield kerogens. Our standardized kerogen preparation method employing mineral acids and heavy liquid separation, isotopic analytical procedures, and the reporting of H_{ex} in % and of δD_n values expressing D/H ratios of non-exchangeable organic hydrogen in customary δ-notation followed the description given in Schimmelmann et al. (1999). The precision is ±3‰ for δD, ±0.05‰ for $\delta^{13}C$, and ±0.5% for H_{ex} values.

Split aliquots of kerogens were analyzed using Fourier-transform infra-red spectroscopy (FTIR). Samples for FTIR analyses were prepared using the potassium bromide (KBr) pellet method. Pellets were analyzed on a Nicolet 20SXC spectrometer equipped with a DTGS detector collecting 1024 scans per sample at a resolution of 4 cm^{-1}. Bands were identified by comparison with published assignments (for example, Painter et al., 1981; Wang and Griffith, 1985; Sobkowiak and Painter, 1992).

3. Results

3.1. Coal characteristics

The majority of coals used in this study are Pennsylvanian in age and derive from the Illinois Basin (Indiana paper coal, FGT-6 221, and FGT-6 460.65, Table 1) and the Appalachian Basin (Elk Run, Herndon, Bolt, Ammonate, Baylor, and Anthracite P). Additional samples are from Vietnam (Triassic 'anthracite V'), Poland (Pennsylvanian 'anthracite LS', and Miocene lignites 2A and 14/96) and Russia (Pennsylvanian 'anthracite D'; Precambrian 'shungite B' and 'shungite D'). 'Graphite BC' is from British Columbia. These samples were selected to give a large range of coal rank, from lignite to graphite.

The ash yields of these bulk coals vary from below 1% (wt.%, dry basis) in anthracite V to more than 16% in FGT-6 221 (Table 1). H, C, N, S, and O contents from elemental (ultimate) analyses are listed in Table 1. The S content was below 1%, except for two Illinois Basin samples (FGT-6 221 and FGT-6 460.65). C and O contents in vitrinites are plotted against R_o in Fig. 1 and demonstrate well established trends of these elements with rank (Teichmüller and Teichmüller, 1979; Given, 1984; Van Krevelen, 1993). R_o ranges from around 0.2% in lignite to around 15% in graphite, thus covering coal ranks from high, medium, and low volatile bituminous, to anthracite, and meta-anthracite (Teichmüller, 1987). Reflectance of the graphite sample was not measured and is assumed to be around 15%, a value typical of well crystalline graphite (Kwiecinska, 1980).

3.2. Petrographic composition of coals

The petrographic composition of coals varies with rank. The two lignite samples consist almost exclusively of huminite (precursor of vitrinite), with traces of inertinite and mineral matter (Fig. 2). Although both lignites derive from vertical trunks of Miocene trees in the Bełchatów lignite deposit, Poland, they differ substantially with respect to humodetrinite and humocollinite maceral contribution (Drobniak, 2001). Coals with R_o of 0.55, 0.59, 0.88, and 0.92% show vitrinite contents between 70 and 80%, and variable amounts of liptinite and inertinite. Coals with R_o of 1.15% and higher do not contain liptinite macerals, and the amount of inertinite decreases relatively to coals with R_o of 0.55–0.92%.

3.3. Functional groups in coals

Lignite samples 14/19 and 2A stand out with respect to their abundances of chemical functional groups (Fig. 3). Sample 14/19 represents a very low gelification level and shows a much higher contribution of hydroxyl

groups (3488 cm^{-1}) than the more gelified sample 2A. Sample 14/19 also shows more pronounced aliphatic stretching bands (2800–3000 cm^{-1} region) and numerous bands likely representing cellulose-derived material (e.g., at 1512 cm^{-1}) that disappear during gelification towards 2A. In fact, the FTIR spectrum of the highly gelified lignite 2A shows more similarity to the spectrum of the high volatile bituminous coal FGT-6221 with R_o 0.55% (Fig. 4) than to lignite 14/96 (Fig. 3).

FTIR spectra of kerogens from vitrinite fractions of coals with R_o of 0.55 and 0.59% show minimal aromatic stretching modes (3000–3100 cm^{-1}) and low intensity out-of-plane aromatic bands (700–900 cm^{-1}) (Fig. 4). These aromatic bands intensify with increasing rank in coals with R_o of 1.15–3.04% (Figs. 4 and 5). The aliphatic stretching region (2800–3000 cm^{-1}) is well developed in all coals up to R_o 1.56%. Aliphatic and aromatic stretching bands are less developed in anthracites (Fig. 5) and thus are unreliable proxies for aromaticity at high maturity.

The relationship between R_o and a ratio of integrated areas of aromatic stretching bands (3000–3100 cm^{-1}) and aliphatic stretching bands (2800–3000 cm^{-1}) for coals of high volatile bituminous rank is shown in Fig. 6. Anthracites are excluded from this graph because their respective FTIR signals are weak. The aromatic/aliphatic signal ratio is useful as a proxy for aromaticity, and the relationship in Fig. 6 shows its direct correlation ($R^2 = 0.96$) with R_o. A comparison of these two plotted parameters from whole coal samples and their respective vitrinite fractions demonstrates that vitrinite fractions within R_o of 0.5% to about 0.9% feature slightly lower aromaticity than the bulk coal samples. For coal with R_o of 1.15 and 1.28%, the Ar/Al ratios for vitrinites and whole coal are either identical (for sample of R_o 1.15%) or very close (for sample of R_o 1.28%).

Table 1
Vitrinite reflectance (R_o), hydrogen exchangeability (H_{ex}), and H and C stable isotope ratios of kerogens from coals

Sample	Age System	Region	R_o (%)	Ash dry	H daf	C daf	N daf	S dry	O daf	H_{ex} (%)	δD_n (‰)	$\delta^{13}C$ (‰)
Graphite BC	J?	BC, Canada	15.00	nd	nd	nd	nd	nd	nd	13.1	−141.4	−14.09
Shungite B	MP	Russia	7.70	nd	0.6	97.5	0.8	0.3	0.8	5.7	−108.4	−37.25
Shungite D	MP	Russia	6.50	nd	0.5	97.3	0.7	0.4	1.1	3.8	−92.4	−29.75
Anthracite D	C	Russia	5.70	nd	nd	nd	nd	nd	nd	2.3	−88.2	−24.06
Anthracite LS	C	Poland	5.10	nd	nd	nd	nd	nd	nd	2.3	−89.0	−22.87
Anthracite P	C	Appallachian	5.15	2.6	2.01	94.65	0.91	0.41	1.30	3.0	−71.9	−23.49
Anthracite V	T	Vietnam	3.04	0.8	3.42	94.77	1.39	0.44	1.28	2.9	−94.3	−24.29
Baylor 13–1	C	Appallachian	1.70	5.6	3.10	92.35	1.50	0.45	2.60	2.2	−91.7	−23.33
Baylor 10–2	C	Appallachian	1.56	5.3	4.89	89.46	1.55	0.80	2.87	3.1	−97.0	−23.55
Ammonate	C	Appallachian	1.28									
Vitrain				1.9	5.24	91.36	1.67	0.60	1.13	2.9	−108.7	−23.86
Whole coal				11.6	5.24	89.85	1.53	0.72	2.66	2.6	−107.2	−23.9
Bolt	C	Appallachian	1.15									
Vitrain				1.3	5.05	90.97	1.47	0.54	1.98	2.8	−97.2	−24.24
Whole coal				2.5	5.28	90.92	1.73	0.53	1.53	4.4	−94.6	−24.01
Herndon	C	Appallachian	0.92									
Vitrain				5.9	5.80	86.77	1.74	0.84	4.85	8.3	−91.8	−23.16
Whole coal				3.7	5.70	87.29	1.75	0.75	4.51	5.3	−94.6	−23.63
Elk Run	C	Appallachian	0.88									
Vitrinite				1.2	5.54	86.82	1.83	0.68	5.13	6.3	−89.5	−23.92
Whole coal				2.4	5.45	86.90	1.65	0.65	5.36	5.3	−91.3	−23.64
FGT-6 460.65	C	Illinois Basin	0.59									
Vitrain				6.1	5.52	80.94	1.86	3.44	8.24	9.7	−83.5	−24.29
Whole coal				9.6	5.77	80.27	1.88	4.34	7.74	8.8	−87.8	−24.44
FGT-6 221	C	Illinois Basin	0.55									
Vitrain				9.2	5.60	80.98	1.69	4.88	6.85	8.7	−88.3	−24.01
Fusain				20.1	3.88	82.12	1.00	7.85	5.15	5.1	−72.6	−23.85
Whole coal				16.4	5.71	79.87	1.66	2.88	9.87	9.0	−90.1	−24.38
Indiana paper	C	Illinois Basin	0.54							6.3	−84.2	−24.4
Lignite 2A	N_1	Poland	0.23	2.4	5.56	67.70	0.42	0.70	25.50	18.6	−135.0	−23.1
Lignite 14/96	N_1	Poland	0.16	1.4	6.4	57.90	0.13	0.17	35.37	17.2	−87.0	−23.2

MP, Mesoproterozoic; C, Pennsylvanian; T, Triassic; J, Jurassic; N_1, Miocene; nd, not determined.
Elemental (ultimate) analyses utilized bulk coal, with reported values (wt.%) calculated on dry ash-free basis, with the exception of S.

3.4. Hydrogen in coals

The relative abundance of H_{ex} is highest in lignite with about 18% of total hydrogen and with rising maturity decreases to around 2.5% in coals with R_o of ca. 1.7 to ca. 5.7% (Table 1, Fig. 7A). The two data points in Fig. 7 with $R_o > 6\%$ suggest a late rise in H_{ex} with increasing maturity, in spite of the fact that the abundance of total organic hydrogen decreases (Table 1). The relationship between H_{ex} and total

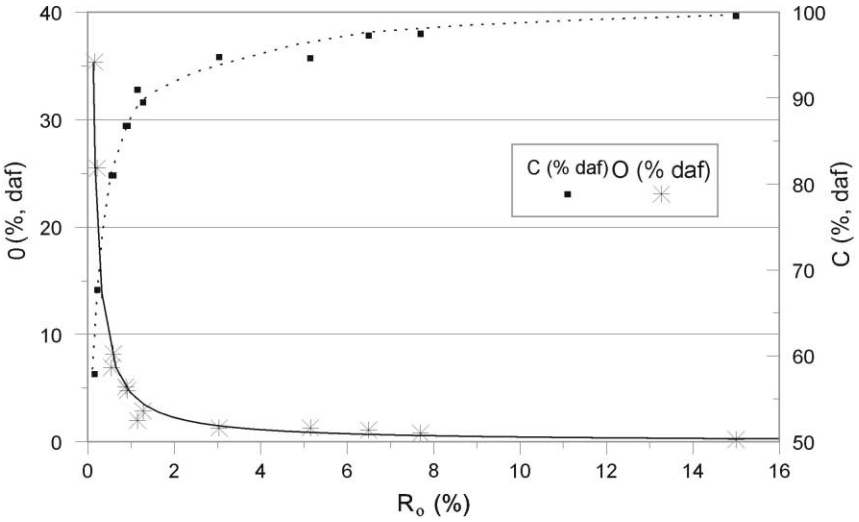

Fig. 1. Carbon and oxygen contents of coals, via elemental (ultimate) analysis, calculated for dry ash-free organic matter. Lines are drawn to indicate trends and to guide the eye.

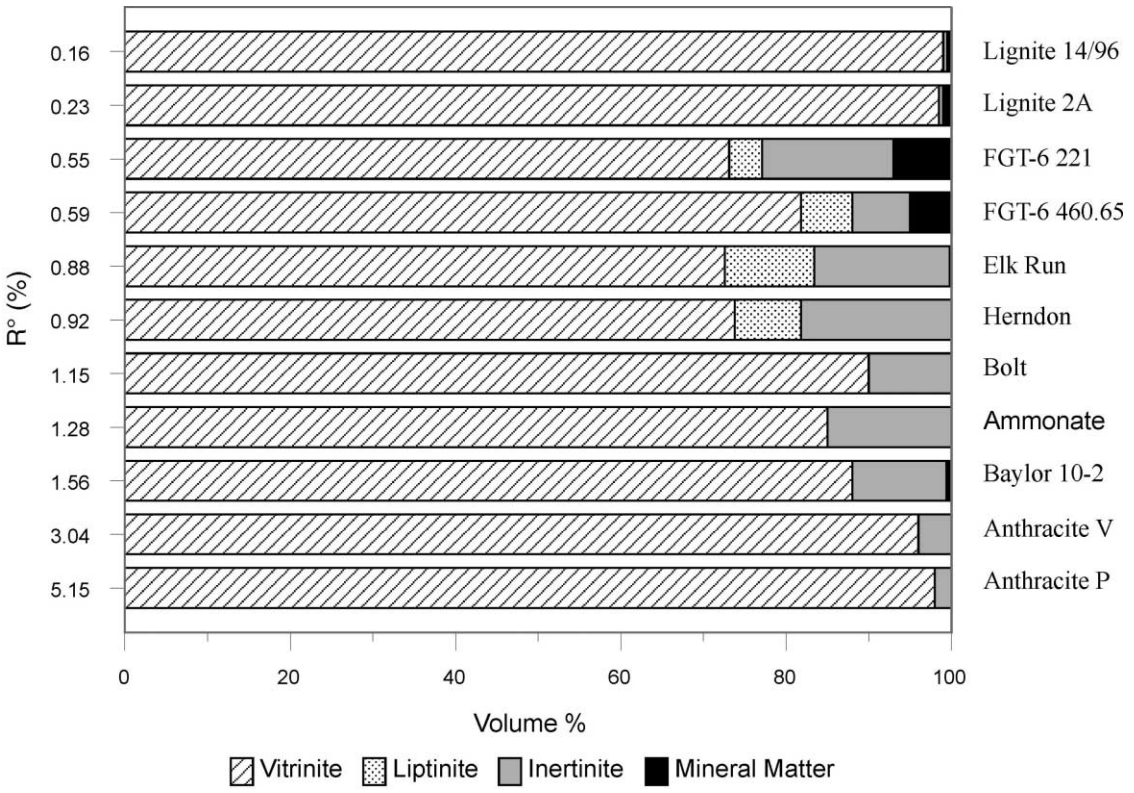

Fig. 2. Maceral composition of the coals. R_o—vitrinite reflectance.

organic hydrogen (dry wt.%) in kerogen is shown in Fig. 7B. The close similarity to Fig. 7A is based on the fact that the hydrogen content in coals is related to thermal rank. Thermally immature coals with much organic hydrogen also feature initially high H_{ex}. Both parameters decline with increasing rank, with H_{ex} quickly dropping at an accelerated pace and then staying level between R_o of 2–6%. At a more mature rank, H_{ex} shows an increase (up to 13.1% in graphite) while the hydrogen abundance continues its approach to a value of zero for ideal graphite.

Comparative data show that H_{ex} of kerogen from bulk coal tends to be smaller than H_{ex} of the vitrinite kerogen from the same coal (Fig. 8A), although the analytical precision of H_{ex} values of $\pm 0.5\%$ renders many comparisons uncertain. Fusinite from coal FGT-6 221 shows a reduced H_{ex} of 5.1% when compared with H_{ex} of 9.0% in kerogen from the parent bulk coal (Table 1, Fig. 8B). No liptinite fraction was available from this coal, but a comparison is possible with 'Indiana paper coal' that derives from a sequence with the same maturity and consists almost exclusively of cutinite (Crelling and Bensley, 1980). The H_{ex} value of 6.3% for 'Indiana paper coal' is intermediate between values for vitrinite and fusinite (Fig. 8B).

Hydrogen isotope ratios for the non-exchangeable organic hydrogen in kerogens do not show an overall consistent trend with maturity (Fig. 9). A trend is suggested toward negative δD_n values for Illinois Basin and Appalachian Basin coals within a R_o range of 0.55–1.4%. In most cases, δD_n values of non-exchangeable H in kerogens from whole coal samples are similar to those of the respective vitrinite fractions (Fig. 9). Fusinite, on the other hand, shows a significantly less negative δD_n value than the vitrinite and whole coal. Indiana paper coal features an intermediate value between vitrinite and fusinite.

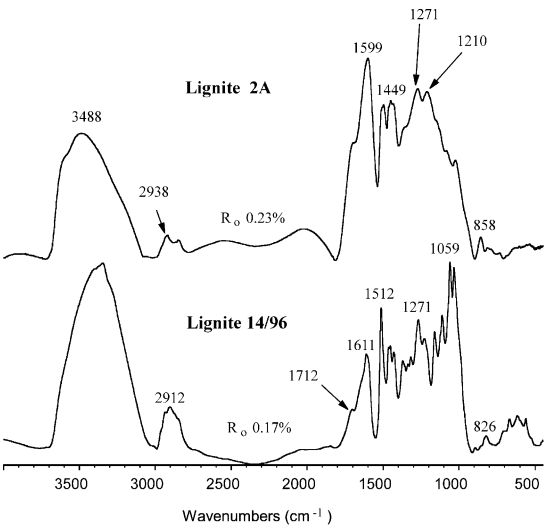

Fig. 3. FTIR spectra of lignite samples.

3.5. Carbon isotope ratios

With only three exceptions, all kerogen $\delta^{13}C$ values cluster narrowly between −22.87‰ and −24.44‰ (Table 1). The two Precambrian shungites are significantly more negative, a feature not uncommon for some Precambrian organic matter (Galimov, 1980; Schidlowski et al., 1983). In contrast, graphite is more ^{13}C-enriched which may in part reflect a history of thermal methanogenesis that eliminated ^{12}C in form of ^{13}C-depleted methane (Galimov, 1980).

4. Discussion

4.1. Exchangeable organic hydrogen

Although all hydrogen in −OH, −COOH, $-NH_2$, −SH, and other H-containing functional groups is potentially exchangeable with ambient water hydrogen, the actual exchange reaction requires access of water molecules. Kerogen molecules are typically very large, chemically complex, and may have a sterically rigid 3D-structure that prevents or restricts access of water molecules to some functional groups, similar to large alphaltenes (Mujica et al., 2000). H_{ex} is therefore not an absolute measure for the abundance of hydrogen-containing functional groups in kerogen, but is operationally defined in this study to reflect isotopic exchangeability at 115 °C over 8 h. Nevertheless, H_{ex} is a proxy for the chemical accessability, and thus relates to the reactivity, of H-containing functional groups in kerogen macromolecules.

Exchangeable hydrogen accounts for 2.3–18.6% of total hydrogen in kerogens from coals (Table 1, Fig. 7A), with the highest values (18.6 and 17.2%) recorded for thermally immature Miocene lignite samples. Cellulose with H_{ex} above 20% (Schimmelmann et al., 1993) is a likely major contributor to the original precursor biomass of lignites.

H_{ex} shows some variability among coals of comparable thermal maturity, and even more between pure vitrinite fractions of these coals. The lignin-rich (phenolic) source material of vitrinite seems to be the reason that all vitrinite kerogens exhibit higher H_{ex} than kerogens from the respective bulk coals (except FGT221; Fig. 8A), with the largest difference for coals having reflectance values of R_o 0.92% (Herndon) and 1.15% (Bolt). No vitrinite fraction was available from coal with R_o 1.56% (Baylor). Homogenization of maceral properties in anthracites did not permit a separation of vitrinites. The H_{ex} of fusinite kerogen from coal FGT-6 221 is much lower than H_{ex} in kerogens from the

accompanying vitrinite or parent coal, suggesting that charring of wood during wildfires reduces H_{ex}. A significant contribution of fusinite or inertinite should thus decrease H_{ex} in bulk coal kerogen. The coal with the highest inertinite content (about 20% in Herndon coal with R_o 0.92%; Fig. 2) indeed shows relatively low H_{ex} regardless of the high H_{ex} of its vitrinite fraction. At a rank equivalent to R_o 1.28% and higher, differences in

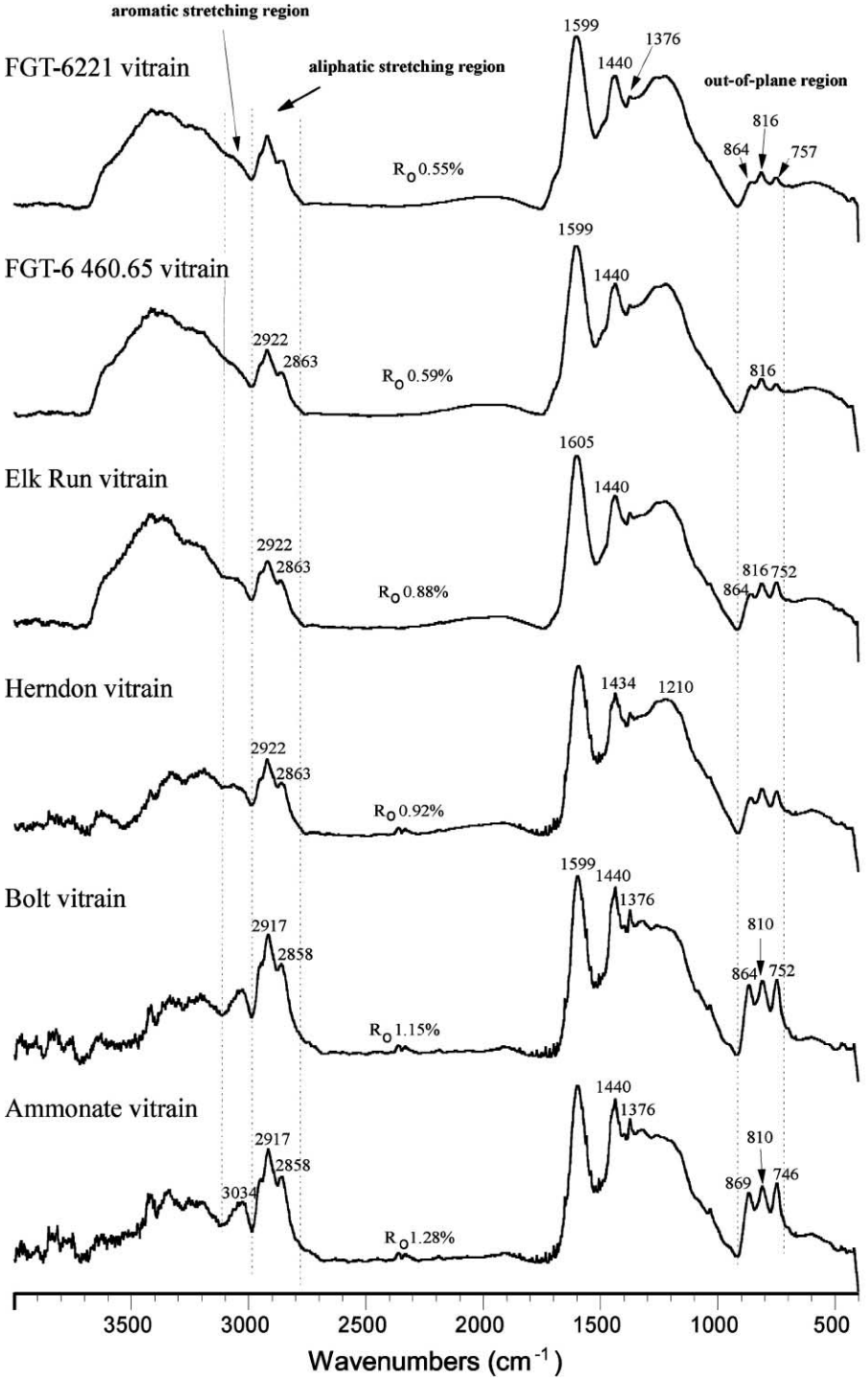

Fig. 4. FTIR spectra of bituminous coals.

H_{ex} between maceral types diminish greatly. Consequently, if the abundance of exchangeable hydrogen influences the gas potential of coals, the maceral composition will be a decisive factor up to high volatile bituminous rank, but will have lost much importance at higher ranks.

The influence of liptinite macerals on H_{ex} is unclear. Cutinite from Indiana paper coal shows a transitional value between fusinite and vitrinite of the same rank coal (Fig. 8B). However, the sample has been weathered and its H_{ex} value may be diagenetically lowered relative to unweathered cutinite. Liptinite macerals usually contain more hydrogen than associated vitrinite (Mastalerz and Bustin, 1993). If vitrinite and liptinite follow the same principle as vitrinite and fusinite (e.g., larger H_{ex} for more H within bituminous rank, Fig. 7B), larger H_{ex} would be expected from liptinite macerals. Additional data on fresh liptinite macerals are needed.

A dramatic reduction of H_{ex} occurs via thermal elimination of chemical functional groups (e.g., −OH, −COOH, etc.) and a relative increase in the abundance of aromatic ≡CH at the expense of aliphatic $=CH_2$ in coals during the transition from R_o 0.16 to 1.15% (Figs. 3, 4, 7A). Increased aromaticity of kerogens at higher maturity provides for increased relative abundances of aromatic carbon-bound H with low pK_a (proton acidity). This aromatic exchangeable hydrogen (Alexander et al., 1981; 1982; Long et al., 1981; Werstiuk and Ju, 1989) partially compensates for the loss of exchangeable hydrogen from thermally eliminated functional groups.

An isotopic implication of the presence of exchangeable hydrogen in coal for hydrocarbon generation is the transfer of ambient hydrogen (e.g., inorganic hydrogen from formation waters, or organic hydrogen in hydrocarbons, etc.) to organic exchangeable hydrogen in kerogen, providing a mechanism for the isotopic signature of formation waters (Polya et al., 2000) and other hydrogen pools to influence bulk δD values of kerogen and its maturation products. Chemical maturation reactions involving organic hydrogen are not restricted to isotopically exchangeable hydrogen. Based on hydrous pyrolysis experiments (Lewan, 1997; Schimmelmann et al., 1999), it has been argued that water plays an important role in hydrocarbon generation from source rocks, an idea also expressed earlier by numerous researchers (Jurg and Eisma, 1964; Hesp and Rigby, 1973; Lewan at al., 1979; Hoering, 1984; Stalker et al., 1998). According to Lewan (1997), utilization of inorganic H from formation waters promotes cracking and at the same time retards the thermal destruction of hydrocarbons by quenching free radical sites before they participate in organic cross-linking reactions. This, in turn, extends the thermal stability of hydrocarbons. The same considerations are likely important for natural gas generation from coal, where water is present in substantial quantities. Several thermolytic and catalytic pathways were suggested to operate in coal, depending on rank, chemical composition, and the availability of catalysts (Butala et al., 2000).

4.2. Non-exchangeable organic hydrogen

The isotopically non-exchangeable portion of organic H is chemically more stable than exchangeable H, and δD_n values of non-exchangeable H may therefore

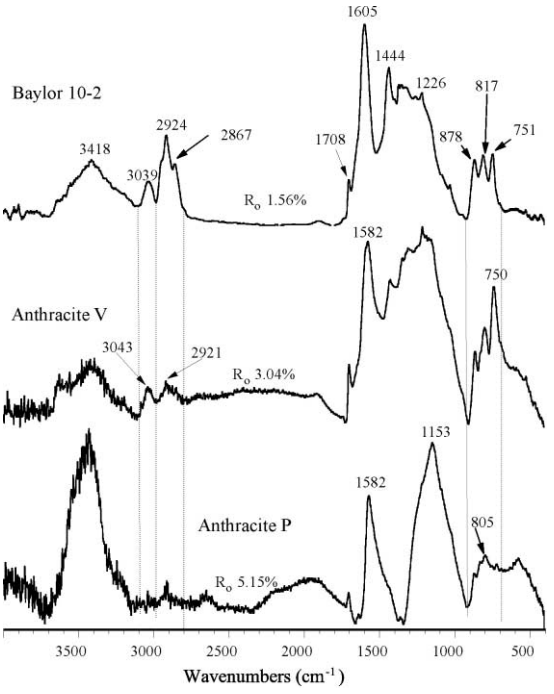

Fig. 5. FTIR spectra of Baylor coal and anthracites.

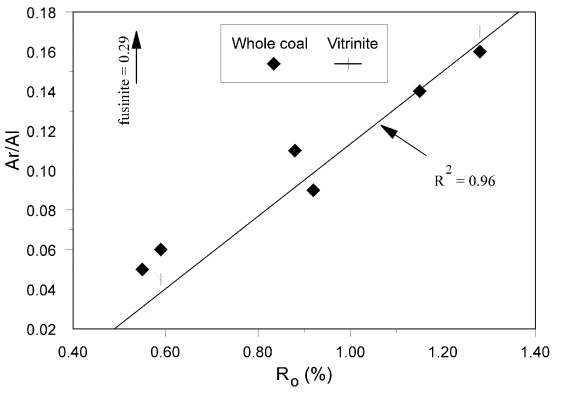

Fig. 6. Relationship between the ratio of integrated areas of the aromatic stretching bands (region 3000–3100 cm^{-1}) to aliphatic stretching bands (region 2800–3000 cm^{-1}) and vitrinite reflectance (R_o). A linear regression is fitted to the vitrinite data.

provide information about the depositional paleoenvironment (Smith et al., 1982, 1983; Krishnamurthy et al., 1995; Schimmelmann et al., 2000). Not only did the paleoenvironments of our samples differ greatly, but diagenetic changes in δD_n values of non-exchangeable organic hydrogen via thermal maturation reactions are likely (Schimmelmann et al., 1999, 2000), thus explaining the apparent lack of overall correlation between δD_n and reflectance values in this study (Fig. 9).

Two isotopic comparisons between specific samples are warranted. The two low-maturity lignite samples 2A and 14/96 were deposited ~18 Ma ago in a warm temperate climate at ~50 N (Burchart et al., 1988). They show surprisingly different δD_n values (Fig. 9), although both samples derive from the same Polish coal mine and represent the same Miocene tree species. Sample 2A is more gelified and likely contains less cellulose-derived organic matter than sample 14/96. It may be of importance that the horizons of the two fossil tree trunks are separated by a volcanic-derived tonstein layer that is a few centimeters thick. We speculate that geomorphological changes in the wake of the volcanic eruption

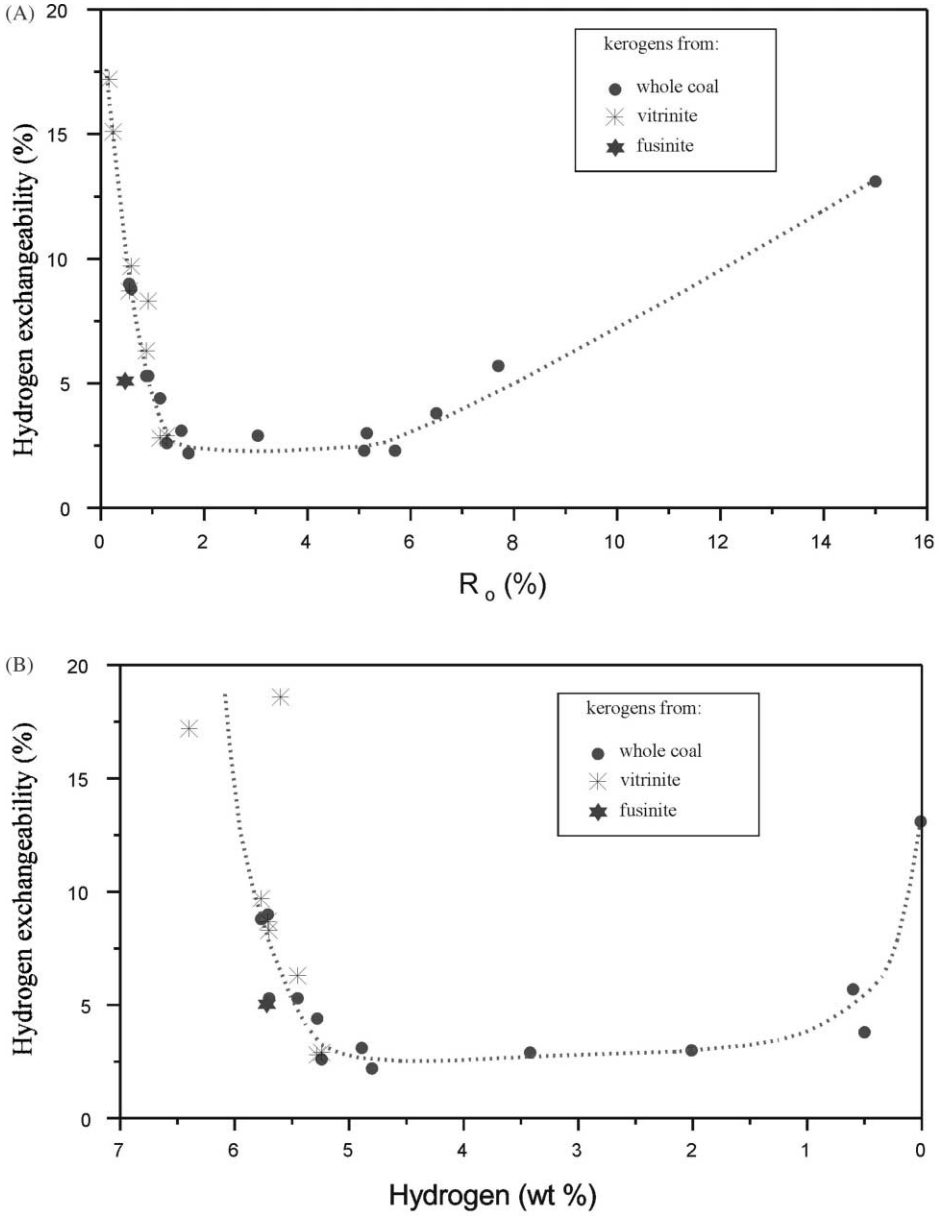

Fig. 7. (A) Relationship between hydrogen exchangeability (H_{ex}) and vitrinite reflectance (R_o). (B) Relationship between H_{ex} and total H content. Line is drawn to indicate trends and to guide the eye.

caused changes in the local hydrology and the isotopic signature of the water source available for tree growth.

The second comparison focuses on coals from the Illinois Basin and Appalachian Basin. This group shifts towards more negative δD_n values with increasing maturity (Fig. 9). The Pennsylvanian coals from both basins were deposited geographically close to one another (~5° S) in similar tropical climates (Scotese, 1994). The isotopic trend suggests that maturation either preferentially eliminated deuterium ^2H and/or preferentially added ^1H to kerogen. Organic H linked to oxygen and nitrogen tends to be more enriched in deuterium than carbon-linked organic hydrogen (Schimmelmann et al., 1999). Some of this ^2H in functional groups is sterically inaccessible to water during isotopic equilibration and thus contributes to the pool of non-exchangeable hydrogen. We hypothesize that thermal maturation eliminates some ^2H-enriched functional groups, thus accounting for the observed shift towards

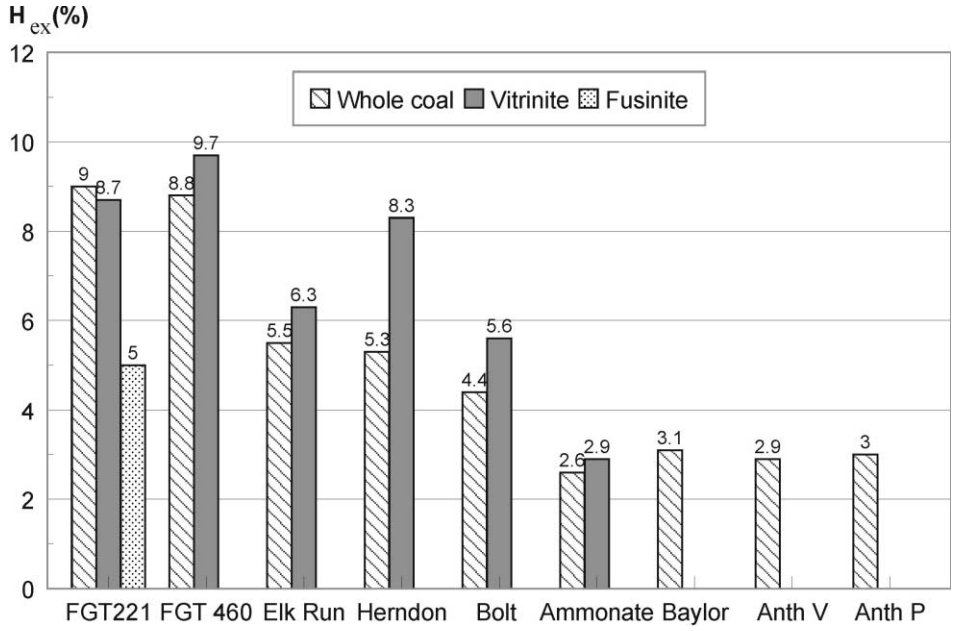

Fig. 8. (A) Hydrogen exchangeability H_{ex} in kerogens from whole coal and vitrinite fractions for individual coal samples. H_{ex} for fusinite was determined for sample FGT221.

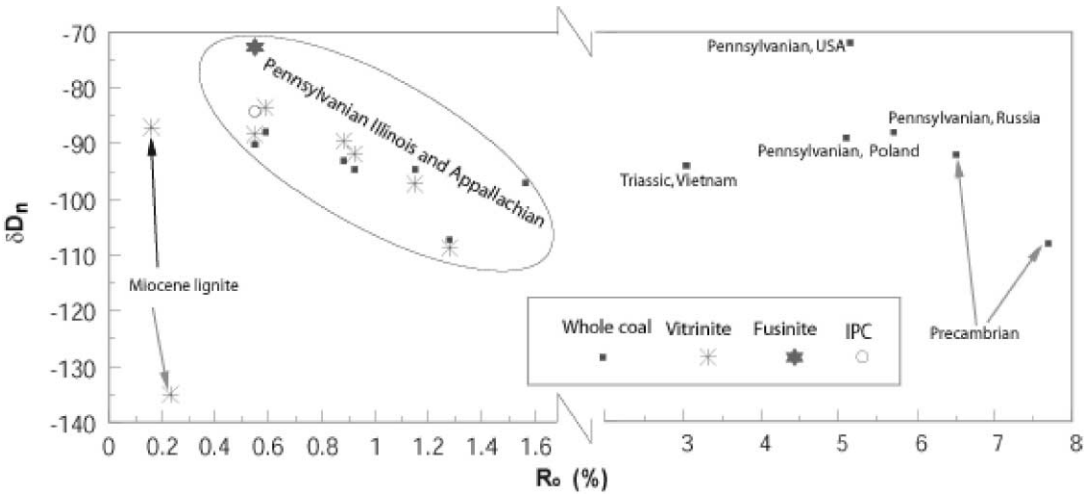

Fig. 9. δD_n values of non-exchangeable organic hydrogen in kerogens from the coals studied.

more negative δD_n. An alternative explanation, namely addition of water-derived ^1H to organic hydrogen, is possible when thermally maturing kerogen is in contact with ^2H-depleted formation waters that derive from mid- to high-latitude precipitation. Coals of tropical origin would need to have their pore waters exchanged before coalification. There is no paleogeographic evidence that the coals in question were ever in contact with strongly ^2H-depleted meteoric waters before they reached the present level of maturation.

For the higher rank kerogens with $R_o > 3$ (Fig. 9) we observe no statistically significant isotopic trend with maturation. The isotopic similarity of Carboniferous coals from Russia and Poland and the Triassic coal from Vietnam may reflect their common tropical origin, within a few degrees of the equator (Fig. 9).

5. Conclusions

- Exchangeable hydrogen accounts for 2.3–18.6% of total hydrogen in kerogens from coals (Table 1, Fig. 7A), with the highest values (18.6 and 17.2%) recorded for lignite. Its abundance depends primarily on coal rank. The maceral composition influences H_{ex} up to the rank of high volatile bituminous coal and becomes irrelevant at higher ranks.
- Quantification of hydrogen isotopic exchangeability in kerogen from bulk coal and in isolated macerals offers an analytically independent proxy for assessing organic-geochemical processes during thermal maturation.
- Directly measured hydrogen stable isotope ratios of bulk coal, even after careful demineralization, reflect (1) the maceral composition and original isotopic signals from biomass, (2) the history of coal-water isotopic interaction during thermal maturation of organic matter, and (3) the presence of isotopically exchangeable organic hydrogen. The latter complication can be mitigated by isotopic double-equilibration of exchangeable hydrogen, thus arriving at the isotopic composition of non-exchangeable organic hydrogen.

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