

D/H ratios in terrestrially sourced petroleum systems

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Abstract

D/H ratios of terrestrially-sourced whole oils and their respective saturated, aromatic, and polar fractions, individual *n*-alkanes, formation waters and non-exchangeable hydrogen in kerogen were measured in potential source rocks from seven Australian petroleum basins. Data for 75 oils and condensates, their sub-fractions and 52 kerogens indicate that oil sub-fractions have δD values comparable to δD_{oil} , with a $\Delta\delta D$ offset ($\delta D_{kerogen} - \delta D_{oil}$) averaging ca. 23‰. The weighted-average δD of individual *n*-alkanes is usually identical to δD_{oil} and $\delta D_{saturate}$. A trend of increasing δD with *n*-alkane chain length in most oils causes individual *n*-alkanes from an oil to vary in δD by 30‰ or more. A modest correlation between δD for aromatic sub-fractions and formation waters indicates that about 50% of aromatic C-bound H has exchanged with water. In contrast, δD_{oil} and $\delta D_{saturated}$ show no evidence for H-exchange with formation water under reservoir conditions at temperatures up to 150 °C. Acyclic isoprenoids and *n*-alkanes show essentially indistinguishable δD , indicating that primary isotopic differences from biosynthesis have been erased. Overall, extensive exchange of C-bound H in petroleum with other hydrogen is apparent, but seems to have affected most hydrocarbons only during their chemical genesis from precursor molecules. Our isotopic findings from terrestrially-sourced oils should be qualitatively relevant for marine oils as well.

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1. Introduction

Hydrogen isotope (D/H) ratios of bulk organic hydrogen are a useful diagnostic tool in fossil fuel research (e.g., Peters et al., 1986; Schoell, 1983, 1984; Santos Neto et al., 1998; Santos Neto and Hayes, 1999; Li et al., 2001; Smith et al., 1982, 1983; Whiticar, 1996, 1999). Recent technological advances, especially the ability to measure D/H in individual compounds and improvements in instrument automation, have made such analyses simultaneously more accessible, economical and powerful for use in petroleum exploration and

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production (e.g., Li et al., 2001). However, there are still many questions about how best to utilize and interpret hydrogen isotopic data in exploration and paleoclimatology (Xie et al., 2000; Dawson et al., 2004).

In this study, D/H ratios were examined as a tool for correlating terrestrially-sourced oils with potential source rocks and for recognizing related oils in complex basins. In particular, we focused on oils derived from terrestrial source rocks, because these have not previously been examined at this level of detail. We analyzed multiple components (75 whole oils, oil sub-fractions, individual *n*-alkanes, 52 kerogens and formation waters that were co-produced with petroleum) from Australian petroleum systems that have previously been characterized by extensive biomarker analyses (AGSO and GeoMark Research, 1996; Blevin et al., 1998; Boreham and Summons, 1999; Edwards et al., 1999; Preston and Edwards, 2000; Geoscience Australia and GeoMark Research, 2002). We also examined evidence for the preservation of primary biosynthetic D/H ratios in petroleum hydrocarbons and kerogens, by studying the correlation between δD values of co-produced oil/water pairs, the correlation between δD values of kerogens and oils and by comparing δD values between isoprenoid and *n*-alkyl compounds within individual oils.

In Australia, where oils are largely sourced from multiple and heterogeneous terrestrial sequences, geochemical classification of oils into regional families is at the core of oil-to-source correlations. Isotopic anomalies can help diagnose 'vagrant' or anomalous oils, and thus may suggest the presence of previously unrecognized petroleum systems (Summons et al., 1998). The use of carbon isotope ratios ($^{13}C/^{12}C$) and biomarker composition has been successfully used within Australian petroleum provinces to determine oil families (AGSO and GeoMark Research, 1996; Boreham and Summons, 1999). However, the common occurrence of mixed oils creates difficulties in assessing relative source contributions when only one such parameter is used (Boreham and Summons, 1999). In marine source rocks, D/H ratios of the original organic matter were primarily controlled by the D/H ratio of the oceans, which has changed very little through most of Earth's history (Lécuyer et al., 1998), and so the variability preserved in petroleum D/H ratios from marine sources is limited (Li et al., 2001). However, in terrestrial environments large variations in D/H ratios of environmental water are common (Dansgaard, 1964). Consequently, organic matter in terrestrial environments records a much wider range of D/H ratios (Sternberg, 1988; Sauer et al., 2001), and oils sourced from terrestrial organic matter are expected to show a larger variability in δD values than those sourced from marine sediments. We thus hypothesized that D/H variability in terrestrially-sourced oils should be useful as an additional geochemical parameter for oil-to-source correlations.

The current study provides continent-wide coverage of Australia using mainly terrestrially-sourced oils. A few marine-sourced oils are included for comparison; oils show an increasing marine input in the order Carnarvon Basin, Bonaparte Basin, and Browse Basin, the latter being an almost 'pure' marine end-member (Blevin et al., 1998). Oils reported here range from Permian to Tertiary in age, and include members of Cretaceous petroleum systems in the economically important Gippsland, Otway and Eromanga basins.

2. Materials and methods

2.1. Selection and preparation of oil fractions and kerogens

Australian oils and their associated formation waters and source rocks were collected from wells, cores, cuttings, and mines located within seven basins with ages ranging from Early Permian to Late Eocene (Fig. 1; Tables 1 and 2). Potential source rock samples were screened by Rock-Eval and TOC analyses prior to selection. Based on previous biomarker analyses, oils derived from predominantly terrestrially derived organic matter were chosen. For comparison purposes, two marine-sourced oils were included in the study: Challis-7 oil from the Late Jurassic Vulcan Formation in the Bonaparte Basin, and the Early Cretaceous, mostly marine-sourced oil from Caswell-2 in the Browse Basin (Blevin et al., 1998). The oils were separated into sub-fractions (saturated, aromatic and polars) by Geoscience Australia. In brief, a 200 mg oil sample was 'topped' by leaving open at room temperature for 24 h to provide a uniform and reproducible lower molecular weight threshold for all samples. Asphaltenes were precipitated with *n*-pentane. The maltene fraction was separated into saturated (aliphatic) hydrocarbon, aromatic hydrocarbon and polar (or NSO) fractions using petroleum ether (60–80 °C), petroleum ether/ CH_2Cl_2 (1:1) and CH_2Cl_2 /MeOH (1:1), respectively, on a deactivated (2% water) silica gel column (maltene:silica gel, 1:100).

Kerogens, derived mainly from coals and carbonaceous shales, were prepared at Indiana University by powdering of rock in a ball mill, extraction of entrained bitumen with dichloromethane (DCM), demineralization with HF/ BF_3 (Robl and Davis, 1993), heavy liquid separation to remove pyrite and neo-formed fluorides and final extraction with DCM. The Robl and Davis method avoids strongly acidic pH and elevated temperatures during demineralization and is safer than the traditional use of hydrochloric and hydrofluoric acids. A few kerogens (marked in Table 2) were prepared at Geoscience Australia using demineralization with HCl/HF. Previous experiments have shown that both of these methods produce kerogens with comparable isotopic

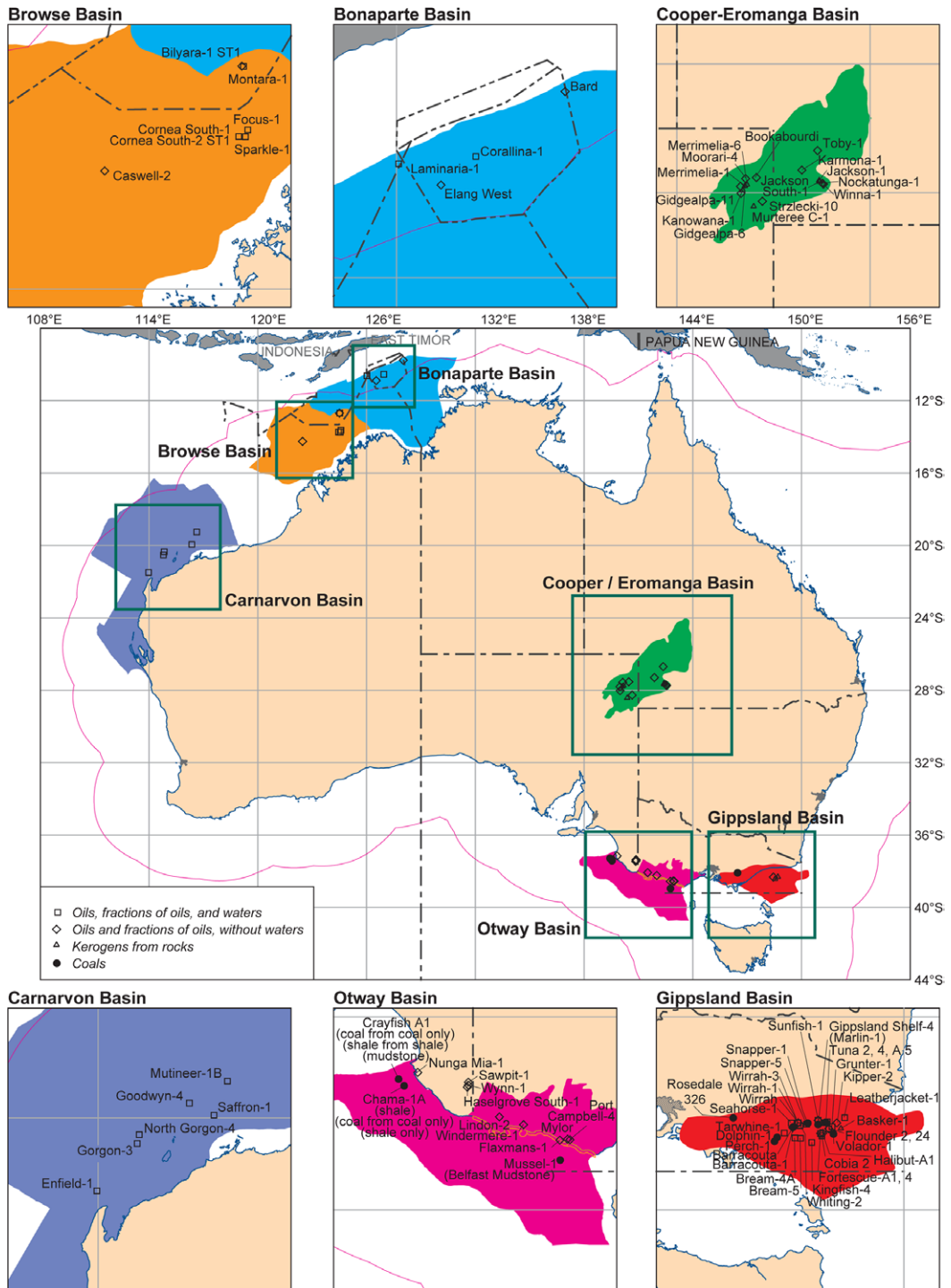


Fig. 1. Australian petroleum basins and sampling locations used in this study.

compositions (Schimmelmann et al., 2001). Most kerogen samples had a black to brown appearance, whereas a few source rocks yielded grey kerogens with lower

carbon content. Grey kerogens were analyzed at Geoscience Australia via X-ray diffraction (XRD) and found to contain residual rutile (TiO₂), anatase (TiO₂), pyrite

Table 1
Characterization of whole oils, oil fractions, and formation waters

Well name	Basin name	Depth (m)	Reservoir formation or group	Reservoir temperature (°C)	Reservoir age	Source age	Whole oil		Polar fraction		Aromatic fraction		Saturated fraction		Water δD (‰)	Biodegradation
							δD (‰)	$\delta^{13}C$ (‰)	δD (‰)	$\delta^{13}C$ (‰)	δD (‰)	$\delta^{13}C$ (‰)	δD (‰)	$\delta^{13}C$ (‰)		
Corallina-1	Bona-partie	3186.0	Elang Fm	120	Middle-Late Jurassic	Jurassic	-104	-26.1	-129	-26.4	-104	-25.5	-104	-26.0	-14	No
Laminaria-1	Bona-partie	3213.0	Elang Fm	107	Middle-Late Jurassic	Jurassic	-104	-25.9	-123	-26.2	-99	-25.3	-106	-25.7	0	No
Montara-1	Bona-partie	2628.0	Lower Vulcan Fm	108	Late Jurassic	Jurassic	-94	-26.9	-92	-26.7	-85	-24.5	-92	-26.3	7	No
Challis-7	Bona-partie	1373.4	Challis Fm	67	Late Triassic	Late Jurassic	-116	-27.2	-122	-27.5	-106	-26.4	-122	-27.5	1	No
Bilyara-1 ST1	Bona-partie	2718.0	Montara Fm	110	Late Jurassic	Jurassic	-99	-25.2	-108	-25.6	-94	-23.8	-93	-25.5	n.a.	No
Elang West-1	Bona-partie	2822.0	Darwin Fm	130	Early Cretaceous	Early Cretaceous	-120	-29.5	-120	n.d.	-107	-28.7	-132	-30.1	n.a.	No
Cornea South-1	Browse	798.4	Upper Heywood Fm	60	Early Cretaceous	Early Cretaceous	-65	-32.0	-123	-30.5	-102	-26.0	-62	-32.0	-17	Yes
Cornea South-2 ST1	Browse	817.0	Upper Heywood Fm	60	Early Cretaceous	Early Cretaceous	-99	-28.9	-130	-28.3	-110	-27.7	-97	-29.4	-5	Yes
Focus-1	Browse	718.0	Upper Heywood Fm	60	Early Cretaceous	Early Cretaceous	-109	-28.1	-113	-27.9	-105	-27.6	-115	-28.2	-8	Yes
Focus-1	Browse	770.9	Upper Heywood Fm	60	Early Cretaceous	Early Cretaceous	-111	-28.1	-115	-28.3	-106	-27.6	-115	-28.3	-5	Yes
Sparkle-1	Browse	625.1	Upper Heywood Fm	60	Early Cretaceous	Early Cretaceous	-107	-28.2	-116	-28.1	-109	-27.9	-115	-28.3	-9	Yes
Sparkle-1	Browse	625.1	Upper Heywood Fm	60	Early Cretaceous	Early Cretaceous	-111	-28.3	-114	-27.9	-107	-27.9	-116	-28.4	-7	Yes
Caswell-2	Browse	3265.5	Early Campanian	118	Late Cretaceous	Early Cretaceous	-111	-28.7	-114	n.d.	-100	-27.5	-114	-29.6	n.a.	No
Enfield-1	Carnarvon	2230.0	Depuy Fm	70	Late Jurassic	Jurassic	-119	-25.9	-127	-25.9	-115	-25.8	-126	-25.9	-27	Yes

Goodwyn-4	Carnarvon	2856.0	Mungaroo Fm	100	Late Triassic	Jurassic	-129	-25.6	-117	-26.1	-120	-25.0	-135	-26.0	-27	No
Gorgon-3	Carnarvon	4032.0	Mungaroo Fm	150	Late Triassic	Jurassic	-100	-26.5	-131	-27.3	-110	-25.1	-96	-27.4	-24	No
Gorgon-3	Carnarvon	3765.0	Mungaroo Fm	140	Late Triassic	Jurassic	-104	-26.2	-129	-26.7	-112	-25.3	-99	-26.6	-24	No
Mutineer-1B	Carnarvon	3133.0	Angel Fm	116	Late Triassic	Jurassic	-105	-25.4	-126	-26.5	-97	-24.4	-108	-26.4	-32	No
North Gorgon-4	Carnarvon	3881.0	Mungaroo Fm	150	Late Triassic	Jurassic	-106	-26.3	-129	-26.9	-115	-25.6	-101	-26.6	-24	No
Saffron-1	Carnarvon	2104.0	Angel Fm	105	Late Jurassic	Jurassic	-110	-26.1	-120	-25.5	-105	-24.9	-122	-26.4	-18	No
Kanowana-1	Cooper	2834.6	Patchawarra Fm	123	Early Permian	Permian	-131	-24.8	-107	n.d.	-118	-24.5	-120	-25.6	n.a.	No
Gidgealpa-17	Cooper	2164.1	Patchawarra Fm	110	Early Permian	Permian	-138	-26.2	-126	n.d.	-122	-25.5	-133	-26.8	n.a.	No
Karmona-1	Cooper	2164.1	Toolachee Fm	116	Late Permian	Permian	-125	-25.2	-136	n.d.	-122	-25.0	-131	-25.4	n.a.	No
Strzlecki-10	Cooper	1936.7	Toolachee Fm	112	Late Permian	Permian	-135	-25.7	-136	n.d.	-128	-25.0	-141	-26.2	n.a.	No
Moorari-4	Eromanga	2150.4	Birkhead Fm	113	Middle Jurassic	Middle Jurassic	-164	-25.6	-126	n.d.	-156	-25.1	-179	-26.4	n.a.	No
Bookabourdi-8	Eromanga	2139.1	Birkhead Fm	115	Middle Jurassic	Middle Jurassic	-173	-25.7	-144	n.d.	-146	-25.0	-182	-26.4	n.a.	No
Nockatunga-1	Eromanga	1005.2	Murta Mbr	80	Early Cretaceous	Middle Jurassic	-154	-24.7	-162	n.d.	-155	-24.9	-164	-25.3	n.a.	No
Winna-1	Eromanga	993.2	Murta Mbr	80	Early Cretaceous	Middle Jurassic	-151	-24.6	-157	n.d.	-153	-24.6	-152	-25.2	n.a.	No
Toby-1	Eromanga	1740.0	Poolawanna Fm	114	Early Jurassic	?Early Jurassic	-158	-27.2	-152	n.d.	-138	-24.7	-164	-27.5	n.a.	No
Bream-4 A	Gippsland	1949.5	Latrobe Gp	90	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-126	-26.2	-107	-27.4	-101	-25.2	-134	-26.6	-19	No
Bream-5	Gippsland	2692.0	Latrobe Gp	110	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-121	-26.8	-117	-26.5	-98	-25.4	-130	-27.4	-4	No
Cobia-2	Gippsland	2421.6	Latrobe Gp	85	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-117	-26.0	-113	-26.4	-103	-25.2	-111	-26.8	-12	No
Flounder-A 2	Gippsland	2736.0	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-111	-27.1	-101	-27.0	-99	-26.3	-112	-27.7	1	No
Fortescue-4 (Esso)	Gippsland	2432.5	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-113	-26.2	-111	-26.6	-105	-25.2	-114	-26.9	-5	No
Fortescue-4 (Esso)	Gippsland	2438.0	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-114	-26.0	-111	-26.5	-105	-25.3	-115	-26.9	-5	No
Fortescue-4 (Esso)	Gippsland	2443.0	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-113	-26.0	-112	n.d.	-107	-25.3	-114	-26.9	-3	No

Table 1 (continued)

Well name	Basin name	Depth (m)	Reservoir formation or group	Reservoir temperature (°C)	Reservoir age	Source age	Whole oil		Polar fraction		Aromatic fraction		Saturated fraction		Water δD (‰)	Biodegradation
							δD (‰)	$\delta^{13}C$ (‰)	δD (‰)	$\delta^{13}C$ (‰)	δD (‰)	$\delta^{13}C$ (‰)	δD (‰)	$\delta^{13}C$ (‰)		
Grunter-1	Gippsland	3044.7	Latrobe Gp	115	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-124	-26.5	-130	-31.4	-108	-29.4	-114	-26.9	3	No
Kingfish-4	Gippsland	2270.0	Latrobe Gp	80	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-112	-25.8	-113	-26.5	-107	-25.2	-117	-26.7	-17	No
Leatherjacket-1	Gippsland	812.3	Latrobe Gp	50	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-120	-26.5	-115	-26.3	-110	-25.6	-129	-27.3	-1	No
Seahorse-1	Gippsland	1520.0	Latrobe Gp	75	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-120	-26.4	-121	-27.0	-110	-25.3	-121	-27.2	-27	No
Snapper-5	Gippsland	1410.5	Latrobe Gp	70	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-126	-26.4	-139	-27.6	-119	-25.7	-129	-27.1	-28	No
Snapper-5	Gippsland	1837.0	Latrobe Gp	80	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-117	-26.6	-110	-26.5	-110	-25.0	-119	-27.1	1	No
Sunfish-1 (#1)	Gippsland	2234.6	Latrobe Gp	103	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-133	-26.3	-115	-26.6	-116	-25.1	-138	-27.0	-18	No
Tarwhine-1	Gippsland	1398.0	Latrobe Gp	70	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-117	-25.2	-121	-27.0	-110	-25.1	-136	-26.4	1	No
Tuna-4	Gippsland	2919.5	Latrobe Gp	125	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-125	-25.9	-131	n.d.	-112	-25.1	-123	-27.0	-8	No
Tuna-4	Gippsland	2948.5	Latrobe Gp	125	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-129	-26.6	-119	-26.1	-117	-25.1	-131	-27.4	-2	No
Tuna-A 5	Gippsland	1917.0	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-125	-26.1	-126	-27.0	-112	-25.2	-125	-27.1	0	No
Whiting-2	Gippsland	2615.5	Latrobe Gp	115	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-110	-26.9	-134	-30.3	-102	-30.5	-114	-27.2	9	No
Wirrah-1 (#1)	Gippsland	1584.0	Latrobe Gp	80	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-116	-26.4	-136	-25.7	-111	-25.2	-120	-27.2	-10	No
Wirrah-3	Gippsland	2622.0	Latrobe Gp	80	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-111	-26.3	-127	-27.0	-110	-25.7	-114	-27.3	2	No
Wirrah-3	Gippsland	2936.8	Latrobe Gp	80	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-132	-26.1	-119	-25.9	-132	-25.1	-134	-26.8	-1	No
Flounder-A 19A	Gippsland	n.a.	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-115	-26.7	-136	-27.1	-102	-25.6	-117	-27.4	4	No
Dolphin-A 3	Gippsland	n.a.	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-129	-25.4	-128	-26.6	-115	-25.3	-142	-26.5	-32	No
Kingfish-A 17A	Gippsland	n.a.	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-113	-26.1	-121	-26.7	-105	-25.2	-116	-26.7	3	No
Cobia-F 11A	Gippsland	n.a.	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-112	-26.2	-119	-26.5	-108	-25.3	-115	-26.8	2	No

Cobia-A 10A	Gipps-land	n.a.	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-110	-26.0	-118	-26.4	-106	-25.2	-114	-26.8	3	No
Wirrah-1 (#2)	Gipps-land	1595.0	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-118	-26.4	-126	-26.8	-111	-25.0	-118	-27.2	n.a.	No
Flounder-A 24	Gipps-land	3345.0	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-117	-26.6	-133	n.d.	-111	-25.7	-120	-27.3	n.a.	No
Kipper-2	Gipps-land	1123.0	Seaspray Gp	65	Late Ter- tiary	Late Cret./ Early Tert.	-127	-26.3	-109	n.d.	-116	-25.6	-129	-27.0	n.a.	No
Sunfish-1 (#2)	Gipps-land	2243.6	Latrobe Gp	103	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-134	-26.3	n.d.	n.d.	-115	-25.2	-141	-26.9	n.a.	No
Sunfish-1 (#3)	Gipps-land	1939.4	Latrobe Gp	95	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-133	-26.2	-104	n.d.	-110	-25.3	-134	-26.9	n.a.	No
Wirrah-1 (#3)	Gipps-land	1532.0	Latrobe Gp	80	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-116	-26.3	-135	n.d.	-109	-25.2	-122	-27.2	n.a.	No
Fortescue-A 1	Gipps-land	3955.6	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-112	-26.0	-131	n.d.	-110	-25.5	-104	-26.9	n.a.	No
Halibut-A 1	Gipps-land	2291.4	Latrobe Gp	n.a.	Late Cret./ Early Tert.	Late Cret./ Early Tert.	-114	-26.1	-120	n.d.	-103	-25.4	-119	-26.9	n.a.	No
Barracouta-4	Gipps-land	1412.0	Gippsland Limestone	70	Late Ter- tiary	Late Cret./ Early Tert.	-121	-26.0	-112	n.d.	-107	n.d.	-126	n.d.	n.a.	No
Windermere-1 (#1)	Otway	1791.0	Eumeralla Fm	85	Early Cretaceous	Early Cretaceous	-202	-25.2	-164	-25.6	-176	-24.9	-195	-25.6	-14	No
Wynn-1	Otway	2780.0	Sawpit Sandstone	114	Early Cretaceous	Early Cretaceous	-221	-26.3	-183	n.d.	-210	n.d.	-229	n.d.	n.a.	No
Nunga Mia-1	Otway	2404.2	Pretty Hill Sandstone	105	Early Cretaceous	Early Cretaceous	-214	-25.6	-171	n.d.	-183	n.d.	-240	n.d.	n.a.	No
Sawpit-1	Otway	2514.0	Basement	105	Palaeozoic	Early Cretaceous	-207	-29.6	-167	n.d.	-198	-29.0	-226	-30.1	n.a.	No
Flaxmans-1	Otway	3305.0	Eumeralla Fm	130	Early Cretaceous	Early Cretaceous	-123	-25.9	-134	n.d.	-124	-24.2	-135	-26.4	n.a.	No
Haselgrove South-1 ST 1	Otway	2880.0	Pretty Hill Sandstone	120	Early Cretaceous	Early Cretaceous	-214	-25.8	-188	n.d.	-210	n.d.	-245	n.d.	n.a.	No
Port Campbell- 4	Otway	1789.0	Eumeralla Fm	90	Early Cretaceous	Early Cretaceous	-132	-25.2	-142	n.d.	-117	-24.7	-156	-26.0	n.a.	No
Lindon-2	Otway	908.0	Pebble Point Fm	55	Tertiary	Early Cretaceous	-177	-24.4	-151	n.d.	-145	-23.7	-203	-25.1	n.a.	No
Windermere-1 (#2)	Otway	1791.0	Eumeralla Fm	85	Early Cretaceous	Early Cretaceous	-198	-25.2	-136	n.d.	-175	-25.1	-231	-25.7	n.a.	No
Mylor-1	Otway	1671.8	Waarre Sst	80	Late Cretaceous	Early Cretaceous	-118	-23.3	-164	n.d.	-116	n.d.	-118	n.d.	n.a.	No

n.a. = not available; n.d. = not determined.

Table 2
Characterization of coals, shales, and kerogens

Well/location name	Basin name	Depth (m)	Formation or group	Source age	Kerogen		Rock TOC (wt%)	Rock T_{\max} (°C)	Rock-Eval parameters					
					δD (‰)	$\delta^{13}C$ (‰)			S1 mg HC/g	S2 mg HC/g	S3 mg CO ₂ /g	PI ^a	HI ^a mg HC/g TOC	OI ^a mg CO ₂ /g TOC
COALS ^b														
Gidgealpa-6	Cooper	2179.0	Patchawarra Fm	Early Permian	-118	-25.0	78.7	446	15.41	140.18	6.48	0.10	178	8
Gidgealpa-6	Cooper	2240.9	Patchawarra Fm	Early Permian	-127	-22.5	70.7	444	20.43	189.69	4.93	0.10	268	7
Gidgealpa-6 ^c	Cooper	2282.5	Patchawarra Fm	Early Permian	-123	-24.4	74.7	449	18.23	113.52	4.6	0.14	152	6
Merrimelia-1	Cooper	2428.3	Patchawarra Fm	Early Permian	-127	-24.0	81	447	11.7	95.03	3.29	0.11	117	4
Basker-1	Gippsland	3125.3	Latrobe Gp	Late Cret./ Early Tert.	-108	-26.5	64.8	435	17.45	216.18	7.45	0.07	334	11
Basker-1 ^c	Gippsland	3125.3	Latrobe Gp	Late Cret./ Early Tert.	-103	-26.5	64.8	435	17.45	216.18	7.45	0.07	334	11
Dolphin-1	Gippsland	1236.0	Latrobe Gp	Late Cret./ Early Tert.	-96	-25.5	61.60	408	15.32	180.71	19.02	0.08	293	31
Gippsland Shelf-1 (Barracouta-1)	Gippsland	1558.3	Latrobe Gp	Late Cret./ Early Tert.	-104	-27.1	69.57	426	7.025	97.73	17.95	0.07	140	26
Gippsland Shelf-1 (Barracouta-1)	Gippsland	1564.1	Latrobe Gp	Late Cret./ Early Tert.	-96	-27.1	67.56	425	4.17	93.77	41.66	0.04	139	62
Gippsland Shelf-1 (Barracouta-1)	Gippsland	2284.9	Latrobe Gp	Late Cret./ Early Tert.	-74	-26.8	69.05	435	2.54	108.2	26.72	0.02	157	39
Gippsland Shelf-4 (Marlin-1)	Gippsland	1448.1	Latrobe Gp	Late Cret./ Early Tert.	-110	-27.4	67.98	408	6.77	202.22	23.41	0.03	297	34
Gippsland-Shelf 4 (Marlin-1)	Gippsland	1455.1	Latrobe Gp	Late Cret./ Early Tert.	-90	-26.6	67.34	417	8.34	150.54	24.73	0.05	224	37
Gippsland Shelf-4 (Marlin-1)	Gippsland	1556.8	Latrobe Gp	Late Cret./ Early Tert.	-109	-28.1	61.34	424	5.18	97.78	34.74	0.05	159	57
Gippsland Shelf-4 (Marlin-1)	Gippsland	2210.1	Latrobe Gp	Late Cret./ Early Tert.	-98	-25.8	68.21	426	6.63	220.83	18.01	0.03	324	26
Perch-1	Gippsland	1165.9	Latrobe Gp	Late Cret./ Early Tert.	-88	-25.3	64.39	409	4.73	175.32	30.82	0.03	272	48
Rosedale-326	Gippsland	mine	Latrobe Gp	Late Cret./ Early Tert.	-113	-26.5	54.83	402	1.74	62.31	58.81	0.03	114	107
Snapper-1	Gippsland	1797.2	Latrobe Gp	Late Cret./ Early Tert.	-103	-24.5	73.67	431	34.42	244.08	10.34	0.12	331	14
Tuna-2	Gippsland	2030.1	Latrobe Gp	Late Cret./ Early Tert.	-92	-24.7	64.37	426	4.95	164.14	36.98	0.03	255	57

Tuna-2	Gippsland	2030.0	Latrobe Gp	Late Cret./ Early Tert.	-95	-25.2	45.7	426	9.38	164.08	17.95	0.05	359	39
Volador-1	Gippsland	4032.0	Latrobe Gp	Late Cret./ Early Tert.	-85	-26.1	76.73	442	10.02	173.37	10.49	0.05	226	14
Chama-1A ^d	Otway	2411.0	Eumeralla Fm	Early Cretaceous	-197	-25.3	72.83	439	11.82	163.76	7.47	0.07	225	10
SHALES/SHALEY COALS														
Gidgealpa-6 ^c	Cooper	2177.4	Patchawarra Fm	Early Permian	-121	-23.8	5.25	445	0.8	6.7	0.4	0.11	128	8
Gidgealpa-6 ^c	Cooper	2177.5	Patchawarra Fm	Early Permian	-122	-23.9	13.13	442	2.73	23.43	1.43	0.10	178	11
Gidgealpa-6 ^c	Cooper	2280.6	Patchawarra Fm	Early Permian	-111	-23.4	2.47	454	0.35	1.36	0.2	0.20	55	8
Gidgealpa-6	Cooper	2282.6	Patchawarra Fm	Early Permian	-119	-25.2	4.91	443	1.04	13.56	0.5	0.07	276	10
Jackson-1	Cooper	1508.8	Toolachee Fm	Late Permian	-132	-24.4	7.95	436	1.39	16.57	0.68	0.08	208	9
Jackson-1 ^c	Cooper	1508.8	Toolachee Fm	Late Permian	-128	-24.4	7.95	436	1.39	16.57	0.68	0.08	208	9
Jackson-1	Cooper	1600.2	Patchawarra Fm	Early Permian	-118	-23.5	27.3	444	6.48	56.52	0.87	0.10	207	3
Merrimelia-1	Cooper	1923.6	Birkhead Fm	late Middle Jurassic	-149	-22.3	2.64	434	0.89	12.55	0.52	0.07	475	20
Murteree-C 1	Cooper	1864.5	Roseneath Shale	Early Permian	-121	-23.5	16	435	2.45	36.22	0.99	0.06	226	6
Jackson-1 ^c	Eromanga	1143.0	Murta Fm	early Early Cretaceous	-125	-24.5	0.99	437	0.26	0.80	0.68	0.25	81	69
Jackson-1 ^c	Eromanga	1417.3	Birkhead Fm	late Middle Jurassic	-138	-24.6	1.83	437	0.81	2.17	0.7	0.27	119	38
Jackson South-1	Eromanga	1429.7	Birkhead Fm	late Middle Jurassic	-147	-24.0	5.85	432	3.87	26.03	0.35	0.13	445	6
Jackson South-1 ^c	Eromanga	1429.7	Birkhead Fm	late Middle Jurassic	-129	-24.0	5.85	432	3.87	26.03	0.35	0.13	445	6
Merrimelia-6	Eromanga	1591.3	Murta Fm	early Early Cretaceous	-135	-25.1	0.54	441	0.53	3.12	0.39	0.15	578	72
Winna-1	Eromanga	1016.3	Murta Fm	early Early Cretaceous	-147	-25.2	1.33	439	0.92	3.16	0.7	0.23	238	53
Basker-1	Gippsland	3078.0	Latrobe Gp	Late Cret./ Early Tert.	n.d.	-26.2	4.39	435	0.69	10.57	3.29	0.06	241	75
Basker-1	Gippsland	3118.2	Latrobe Gp	Late Cret./ Early Tert.	-109	-26.3	23	437	4	94.54	2.72	0.04	411	12
Basker-1	Gippsland	3174.0	Latrobe Gp	Late Cret./ Early Tert.	-99	-25.8	6.73	431	1.51	19.32	2.07	0.07	287	31
Basker-1	Gippsland	3120.0	Latrobe Gp	Late Cret./ Early Tert.	-101	-25.9	8.44	443	0.91	17.43	6.75	0.05	207	80

Table 2 (continued)

Well/location name	Basin name	Depth (m)	Formation or group	Source age	Kerogen		Rock TOC (wt%)	Rock T_{max} (°C)	Rock-Eval parameters					
					δD (‰)	$\delta^{13}C$ (‰)			S1 mg HC/g	S2 mg HC/g	S3 mg CO ₂ /g	PI ^a	HI ^a mg HC/g TOC	OI ^a mg CO ₂ /g TOC
Tuna-2 ^c	Gippsland	2011.5	Latrobe Gp	Late Cret./ Early Tert.	-88	-25.2	26.1	436	9.6	59.6	9.4	0.14	228	36
Tuna-2	Gippsland	2112.3	Latrobe Gp	Late Cret./ Early Tert.	-96	-25.6	36.5	432	7.73	140.94	12.45	0.05	386	34
Tuna-4	Gippsland	1980.0	Latrobe Gp	Late Cret./ Early Tert.	-85	-26.2	17.9	443	0.38	12.17	2.5	0.03	68	14
Volador-1	Gippsland	4536.0	Latrobe Gp	Late Cret./ Early Tert.	-94	-25.2	5.23	447	2.14	9.18	3.25	0.19	176	62
Chama-1A	Otway	1847.1	Eumeralla Fm	Early Cretaceous	-116	-24.5	0.32	442	0.02	0.08	0.73	0.21	24	228
Chama-1A	Otway	2301.2	Eumeralla Fm	Early Cretaceous	-163	-24.0	0.61	440	0.03	0.24	1.1	0.11	39	180
Crayfish-A1 ^d	Otway	1228.3	Eumeralla Fm	Early Cretaceous	-167	-24.8	39.89	428	4.29	105.86	15.13	0.04	265	38
Crayfish-A1 ^f	Otway	1533.1	Eumeralla Fm	Early Cretaceous	-144	-24.0	0.29	437	0.00	0.13	0.4	0.01	46	138
Crayfish-A1 ^d	Otway	1467.9	Eumeralla Fm	Early Cretaceous	-173	-23.5	28.05	428	2.19	69.2	12.43	0.03	247	44
Crayfish-A1	Otway	1860.0	Eumeralla Fm	Early Cretaceous	-187	-24.7	0.53	439	0.01	0.30	0.57	0.03	56	108
Crayfish-A1	Otway	2168.7	Pretty Hill Sandstone	Early Cretaceous	-162	-23.9	1.14	444	0.09	1.00	0.24	0.08	88	21
Mussel-1	Otway	1996.4	Belfast Mudstone	Late Cretaceous	-105	-25.4	1.04	429	0.00	0.36	1.16	0.01	34	112
Mussel-1	Otway	2237.1	Eumeralla Fm	Early Cretaceous	-113	-24.6	5.16	430	0.20	5.38	0.81	0.04	104	16

^a Rock-Eval parameters: PI production index = $S1/(S1 + S2)$; HI hydrogen index = $S2/TOC \times 100$; OI oxygen index = $S3/TOC$.

^b Coals defined here as having more than 40 wt.% TOC.

^c Kerogen from rock that was pre-extracted with organic solvent.

^d Density pre-treatment at Geoscience Australia; 'float' material from 2.0 g/cm³ density liquid.

^e Kerogen isolated at Geoscience Australia using HCl/HF method.

^f Density pre-treatment at Geoscience Australia; 'sink' material from 2.0 g/cm³ density liquid.

and occasional quartz. No hydrogen-containing minerals were observed by XRD.

2.2. Isotopic measurements of whole oils, sub-fractions, and kerogens

Crude oils were centrifuged and milligram amounts of the supernatant topped 'whole oil' were sealed in freshly drawn, z-shaped Pyrex® capillaries. These capillaries were then placed in 9 mm o.d. quartz combustion tubes, together with cupric oxide, copper metal, silver foil and a 6 mm o.d. inverted quartz cup riding on the top end of the sealed capillary (serving as a 'hammer' to break the capillary inside a sealed combustion tube). Combustion tubes were evacuated and flame-sealed, and z-shaped capillaries were broken by tapping (Schimmelmann et al., 1999). Oils were then combusted to water, reduced to H₂ over hot uranium (Bigeleisen et al., 1952), and analyzed by standard dual-inlet mass spectrometry (Schimmelmann et al., 1999, 2001). Low concentrations of dissolved water in natural petroleum do not significantly influence δD values of oils (Schimmelmann et al., 1999).

Aliquots of oil sub-fractions were sampled by partially filling open-ended quartz capillaries and sealing those capillaries into 9 mm combustion tubes as above (these sample capillaries were not sealed prior to evacuation of combustion tubes). Viscous samples were dissolved in a few drops of DCM from which aliquots were micro-pipetted into combustion tubes. Solvent was evaporated before sealing the combustion tubes under vacuum.

These analytical protocols result in the loss of the most volatile components from the whole oil and its sub-fractions (due to topping; sub-fractions were also briefly exposed to vacuum before sealing of combustion tubes). Evaporation is expected to shift the remaining liquid toward slightly more negative δD values as a result of vapor-pressure isotope effects (Hopfner, 1969; Wang and Huang, 2001). Competing with this effect, there is a trend of increasing δD with carbon number for *n*-alkanes in many oils (see below), whereby the loss of short-chain alkanes would increase the δD value of the bulk oil. The net effect on the oil sub-fractions is unknown but likely minimal.

Formation waters were sealed into Pyrex® capillaries that were broken by a falling magnet inside a vacuum line inlet. Water was converted to H₂ over hot uranium (Bigeleisen et al., 1952). Hydrogen gas was collected with a Toepler pump, manometrically quantified, and temporarily sealed in Pyrex glass tubes for isotopic analysis.

Brooks and Sternhell (1957) demonstrated that oxygen in Australian brown coals and lignites is mostly in the form of -COOH and -OH groups. Thus a significant proportion of hydrogen in kerogen from such coals is

linked to oxygen. Most organic hydrogen linked to oxygen is exchangeable on timescales of seconds to hours. Together with hydrogen linked to nitrogen and some other labile organic hydrogen, the exchangeable hydrogen in kerogen amounts to several percent of total hydrogen and will be affected by the D/H of ambient water (Schimmelmann et al., 1999). Aliquots of kerogen were therefore equilibrated overnight in flow-through quartz ampoules at 115 °C in water vapor with known isotopic composition, in order to arrive at reproducible kerogen δD values (Schimmelmann et al., 1999). By equilibrating two aliquots of each kerogen with different water vapors ($\delta D_{\text{wat}} = -137\text{‰}$ or $+1169\text{‰}$), we determined via isotopic mass balance the δD value of non-exchangeable hydrogen in kerogen (hereafter denoted as δD_{ker}). Two small samples (Rosedale-326 from the Gippsland Basin, and Chama-1A 2301.2 m from the Otway Basin) could only be equilibrated once, making it necessary to assume typical hydrogen exchangeabilities of 8% and 4% of total H in kerogen, respectively. These estimates derived from comparable regional kerogens as necessary input for mass balance calculations. Carbon and hydrogen isotope ratios of kerogens were determined via offline combustion and reduction, as for the oils, oil sub-fractions and waters.

All bulk isotopic measurements were made at Indiana University using a Finnigan MAT 252 mass-spectrometer in dual-inlet mode. Isotopic data are reported in the standard δ -notation relative to VPDB (for $\delta^{13}\text{C}$), and for δD according to Coplen's (1996) guidelines relative to VSMOW (0‰) and normalized to SLAP (-428‰). Mass-spectrometric precision averaged $\pm 2\text{‰}$ for δD and $\pm 0.05\text{‰}$ for $\delta^{13}\text{C}$ values.

2.3. Isotopic measurements of individual compounds

Twenty-eight oils were selected for compound-specific isotope analysis (CSIA). Oils thought to derive from a single source were preferentially chosen. Pure *n*-alkane fractions were prepared by adduction with 5 Å molecular sieve, then recovery of the alkanes by dissolution of the sieve in HF and extraction of the alkanes into *n*-pentane (West et al., 1990). Measurements of branched hydrocarbons were conducted on the non-adducted fraction. D/H ratios of individual *n*-alkanes were measured using an Agilent 6890 gas chromatograph coupled to a ThermoFinnigan Delta +XL isotope-ratio mass spectrometer (GC/MS) via a 1440 °C pyrolysis interface. GC separation used a cool on-column injector, DB-1, 30 m length \times 0.25 mm ID capillary column with a 0.1 μm film thickness, 0.8 ml/min flow of He carrier gas, and a 5 °C/min oven ramp rate. Samples were analyzed separately by GC/MS for identification of individual compounds (Edwards et al., 1999). CSIA separations used a programmable-temperature vaporization (PTV) injector, a DB-5 ms, 60 m \times 0.32 mm

capillary column with 0.1 μm film thickness, 1.5 ml/min flow of He, and a 5 $^{\circ}\text{C}/\text{min}$ ramp rate.

Three standards were coinjected with every *n*-alkane analysis (all compound-specific isotope reference materials used in this study are distributed by Indiana University; a description is available at: <http://www.indiana.edu/~geosci/research/biogeochem/biogeochem.html>). C_{10} and C_{30} fatty acid methyl esters (FAMES) served as the isotopic reference peaks for the analysis ($\delta\text{D} = -214.3\text{‰}$ and -189.4‰ , respectively), while C_{20} FAME ($\delta\text{D} = -226.8\text{‰}$) was treated as an unknown to assess accuracy. No coinjected standards could be added to the branched-alkane fractions because of their complexity, hence external H_2 peaks were used as reference peaks. Corrections to raw ion currents for H_3^+ contributions were performed following the approach described by Sessions et al. (2001a), with the H_3 -factor determined by measuring reference gas peaks of varying heights. A standard mixture containing 15 *n*-alkanes, ranging in δD value from -43‰ to -256‰ , was used to construct a linear normalization to bring the measured δD values into agreement with the accepted VSMOW-SLAP calibration (Sessions et al., 2001b). This normalization was determined each morning, and typically produced a slope ('true' δD versus measured δD) of between 0.95 and 0.99.

Analytical precision, estimated as the pooled standard deviation of more than 2100 replicate δD values for unknown compounds, was 4.1 ‰ . Accuracy was estimated from 97 analyses of the C_{20} FAME internal standard, which give a root-mean-square (RMS) error

of 5.5 ‰ . For comparison, 44 analyses of the external *n*-alkane standard yielded a pooled standard deviation of 2.6 ‰ and an RMS error of 4.0 ‰ ($n = 616$).

3. Results and discussion

We begin by comparing isotope-based and biomarker-based oil family classifications for the Cooper/Eromanga, Otway, and Gippsland basins. We then move on to examine factors such as hydrogen exchange that may complicate isotope-based classifications and to discuss whether petroleum D/H ratios might also be used for paleoenvironmental reconstructions. Overall, values of δD for individual *n*-alkanes, oil sub-fractions and whole oils displayed remarkable variability (up to 150 ‰) between genetically different oils. At the same time, oils derived from a common source were generally homogeneous in their D/H composition. These data are consistent with our hypothesis that terrestrially-sourced oils contain a greater, and potentially more useful, D/H variability than do marine-sourced oils (Fig. 2).

3.1. Oil-source correlations

Many different geochemical parameters can be used for oil-source correlations. Here we focus on using combined δD and $\delta^{13}\text{C}$ values for individual *n*-alkanes, rather than those for whole oils or sub-fractions, because compound-specific data provide the most detailed

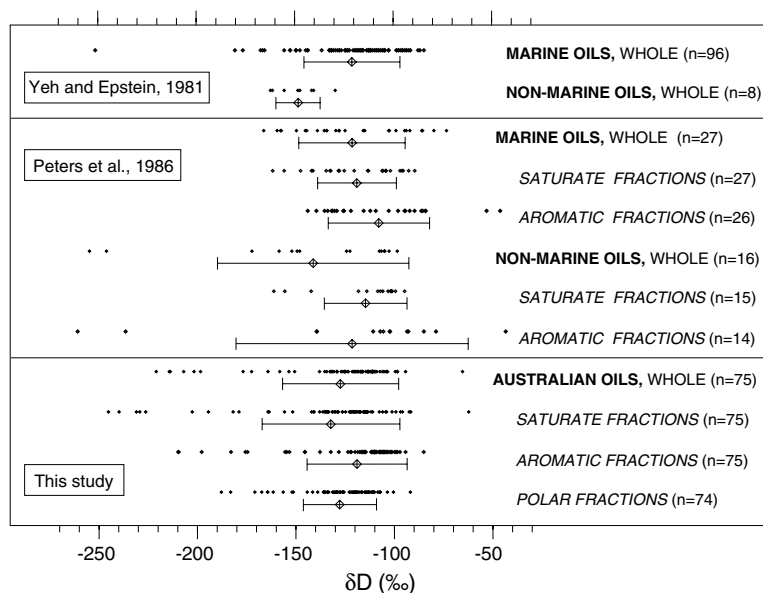


Fig. 2. Comparison of δD values for oils, condensates and their sub-fractions derived from marine versus terrestrial organic sources. Each data set is characterized by its mean value (diamond with inserted cross) and standard deviation (bars).

picture. Correlations based on bulk analyses are also useful (see discussion in Section 3.3), but, in general, offer less information than is available from compound-specific data, particularly in the case of mixing from multiple sources.

There is a significant advantage in using *n*-alkane isotopic compositions for source apportionment, namely that the *n*-alkanes, unlike biomarkers, represent a major fraction of the oil. Thus, they can serve as the basis for quantitative mass balance calculations, with numerous applications in both petroleum exploration and production settings. Moreover, the use of two isotope ratios (D/H and $^{13}\text{C}/^{12}\text{C}$) in multiple compounds can often provide enough information to resolve several sources for a single oil.

3.1.1. Cooper/Eromanga basins

The Cooper and Eromanga basins represent spatially juxtaposed strata of different ages (summarized by Boreham and Summons, 1999). The Cooper Basin contains Permian to Triassic rocks, including the important source rocks of the Patchawarra (Early Permian) and Toolachee (Late Permian) formations. The overlying Triassic Arabury Formation is an ineffective seal, allowing hydrocarbons generated from Permian rocks to migrate into younger strata. The Eromanga Basin lies structurally above the Cooper Basin and contains Jurassic to Early Cretaceous sandstones and shales. Although reservoirs in the Eromanga Basin produce four times more petroleum than those in the Cooper Basin (Heath et al., 1989), much of the oil in both basins is thought to derive from Permian source rocks. For example, Heath et al. (1989) proposed that all Jurassic oils were primarily from Permian coaly sediments, while Jenkins (1989) estimated a volumetric average of ~80% from Permian sources with only a minor local Jurassic source input to oils in the Jurassic and Cretaceous reservoirs. A major outstanding question in the Cooper/Eromanga petroleum system that could be addressed by examining the D/H ratios of the oils' *n*-alkanes is thus the quantitative apportionment of pooled oils to various sources.

Hydrogen- and carbon-isotopic data for nine representative oils from the Cooper/Eromanga petroleum system are shown in Figs. 3(a) and 4(a). Karmona-1 and Strzlecki-10, which are nearly 200 km apart, are both reservoired and presumably sourced in the Late Permian Toolachee Formation (Boreham and Summons, 1999). Values of δD for these oils range from -106 to -144‰ . The two oils have nearly identical carbon isotope and biomarker compositions, but show a slight separation (averaging $\sim 15\text{‰}$) in D/H ratios. The carbon isotopic composition of the Toolachee source rocks is quite homogeneous over long distances (Boreham and Summons, 1999), indicating a relatively uniform paleoenvironment. The δD offset between these oils may

thus reflect subtle hydrologic variations in the ancient environment. Strzlecki-10 *n*-alkanes also show an unusual concave-up pattern of δD versus carbon number (Fig. 3(a)), which we interpret as representing the addition of low molecular weight alkanes with more positive δD values. Oils derived from the Patchawarra Formation seem a likely candidate for this role, although the two representative Patchawarra oils we examined (below) both had equivalent, rather than more enriched, δD values. Alternatively, the concave-up pattern could represent input of low molecular weight liquids associated with more mature wet gas.

Kanowana-1 and Gidgealpa-17 are derived from the other major Permian source, the Patchawarra Formation. Values of δD again range from -107‰ to -149‰ (Fig. 3(a)) but, in this case, the two oils are clearly distinguished based on a combination of carbon and hydrogen isotopes (Fig. 4(a)). Boreham and Summons (1999) attributed the unusually heavy $\delta^{13}\text{C}$ values for Kanowana-1 *n*-alkanes to the very high maturity of that oil. Kanowana-1 *n*-alkanes are enriched in D relative to those from Gidgealpa-17 by roughly 10–30‰, consistent with the findings of Li et al. (2001) that increasing maturity leads to increases of 25–40‰ in δD of expelled oils. A careful evaluation of both source and maturity is needed to distinguish Toolachee and Patchawarra oils based on their isotopic signatures.

Moorari-4 and Bookabourdie-8 oils are both reservoired in the Jurassic Birkhead Formation of the Eromanga Basin. Based on aromatic biomarkers for conifer inputs there is a significant Jurassic contribution from the Birkhead Formation to the Permian oils (Alexander et al., 1988). Moorari-4 probably represents the best Birkhead endmember, although the addition of some oil from Permian sources is still likely. The two Birkhead oils are distinctive in having very negative δD values (down to -203‰), a relatively wide range of molecular weights and in their isotopic profiles which display flat patterns of $\delta^{13}\text{C}$ versus carbon number and strongly (positive) sloping δD profiles (Fig. 4(a)). The more positive δD values for the *n*-alkanes from Bookabourdie-8 compared to those from Moorari-4 may indicate a minor Permian input to the former oil. However, isotopic variations due to slight changes in organic facies within the Birkhead Formation cannot be excluded. Thus, carbon and hydrogen isotopic evidence both mark these oils as clearly distinct from Permian- and Cretaceous-sourced oils. Previous assessments of Birkhead sources have relied upon the presence of Jurassic biomarkers, or on the "steepness" of $\delta^{13}\text{C}$ versus carbon-number profiles, both of which are difficult to apply quantitatively. In contrast, apportionment using hydrogen isotopes in *n*-alkanes should be both simpler and more precise.

Nockatunga-1 and Winna-1 represent oils sourced and reservoired in the early Cretaceous Murta Forma-

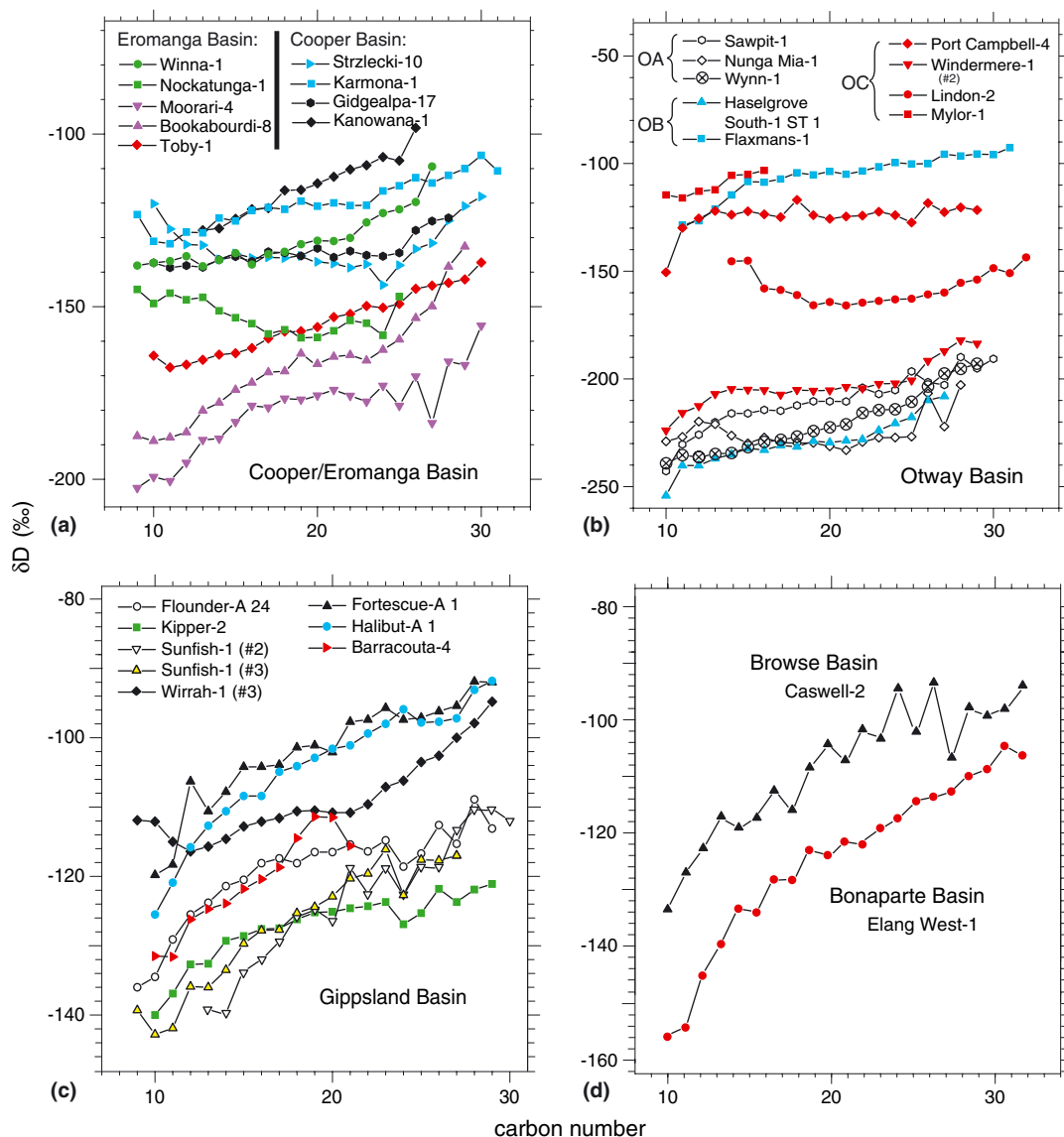


Fig. 3. Hydrogen isotopic composition of individual *n*-alkanes from individual basin wells. (a) Cooper/Eromanga Basin. Symbol color indicates the presumed source: green – Murta Fm., purple – Birkhead Fm., blue – Toolachee Fm., black – Patchawarra Fm., red – Poolawanna. (b) Otway Basin. Symbol coloring corresponds to the three genetic groups defined by biomarker analyses: white – family OA, blue – family OB, red – family OC. (c) Gippsland Basin. (d) Browse and Bonaparte Basin.

tion. They can be clearly distinguished from underlying Jurassic Birkhead oils on the basis of H isotopes, but are nearly indistinguishable from both Toolachee and Patchawarra Permian oils using both C and H isotopes (Fig. 4(a)). These oils contain Cretaceous-aged biomarkers (Powell et al., 1989, Alexander et al., 1988), but the quantitative contributions of Cretaceous versus Permian sources remains unclear. Nockatunga-1 is slightly depleted in D relative to Winna-1 and, like Strzlecki-10, displays an unusual concave-up δD versus carbon-

number pattern. Unlike Strzlecki-10, Nockatunga-1 is interpreted as having a sole Murta Formation source (Powell et al., 1989) so the D/H pattern is not likely due to mixing of different oils. On the other hand, the relative deuterium enrichment of the Winna-1 oil may indicate a dominant Permian contribution, much more prevalent than suggested from the biomarker data alone (Powell et al., 1989).

The Toby-1 oil, reservoir in the Late Jurassic Poolawanna Formation, has long been recognized as an

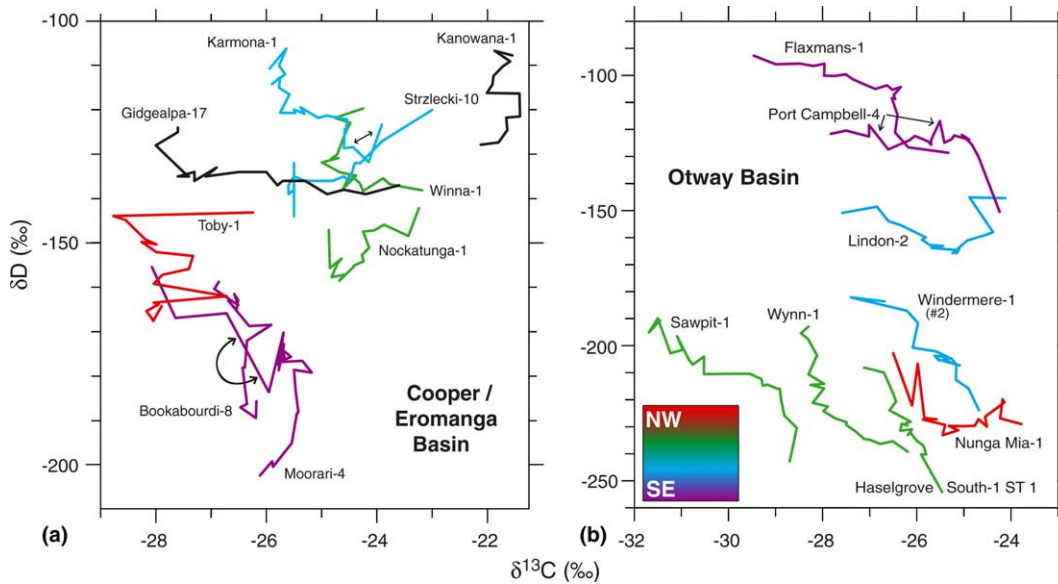


Fig. 4. Hydrogen and carbon isotopic compositions of individual *n*-alkanes. Each line represents the path in $\delta\text{D}-\delta^{13}\text{C}$ space traced by the homologous *n*-alkanes of a single oil/condensate. (a) Cooper/Eromanga Basin. Color corresponds to that in Fig. 3(a). (b) Otway Basin. Color corresponds qualitatively to the geographic location of wells from northwest (red) to southeast (dark blue).

anomalous sample, especially with respect to its negative bulk $\delta^{13}\text{C}$ value. Such a ^{13}C -depleted carbon isotopic ratio might indicate an early Paleozoic source, possibly from the marine Warburton Basin below the Cooper Basin. However the hydrogen isotopic data, combined with biomarker abundances, suggest the more likely scenario that this oil was sourced from the Basal Jurassic Poolawanna Formation. Moreover, the Toby-1 oil comes from a part of the Eromanga Basin where the Poolawanna is thicker and more mature than in most other areas. We note that bulk oil $\delta^{13}\text{C}$ values can be altered by secondary processes, for example varying abundances of aromatic versus saturate hydrocarbons, biodegradation, loss of volatiles and migration of bitumens. Compound-specific isotope data, both for carbon and hydrogen, provide more definite and higher-resolution evidence.

3.1.2. Otway Basin

Three main genetic groups (OA, OB and OC) can be distinguished on the basis of biomarkers in oils from the Otway Basin (Edwards et al., 1999; Geoscience Australia and GeoMark Research, 2002). Family OA, consisting of oils from the wells Sawpit-1, Nunga Mia-1, and the Wynn-1 condensate, have biomarker signatures indicating derivation from a predominantly lacustrine algal source with variable terrestrial contributions (Figs. 3 and 4). Such source rocks are present within the Early Cretaceous (Berriasian-Barremian) Crayfish Group whose distribution correlates with the location of Family

OA (Woollands and Wong, 2001). These source rocks are laterally variable within freshwater lake and fluvial systems and the Sawpit-1 oil probably represents a more algal end-member.

Family OB, consisting of Flaxmans-1 oil and a condensate from Haselgrove South-1, contains highly variable condensates with stronger land-plant source characteristics than family OA. These oils are probably sourced from terrestrial facies within the Crayfish Group, although Flaxmans-1 has some strong similarities to oils derived from the Early Cretaceous (Aptian-Albian) Eumeralla Formation. Family OC includes oils from Port Campbell-4, Lindon-2, Windermere-1 and condensate from Mylor-1. This family is derived predominantly from terrestrial organic matter in the Early Cretaceous Eumeralla Formation. This unit contains isolated, distinctive source pods, rich in coal and coaly shale, which lead to considerable variability in geochemical parameters within oils of this family.

Hydrogen and carbon isotope data for *n*-alkanes from representative Otway Basin oils and condensates are plotted in Figs. 3(b) and 4(b). With the exception of the Nunga Mia-1 oil, carbon isotope ratios are consistent with the biomarker-based classification. However, hydrogen isotope ratios show a very different trend. Family OA oils plot in a relatively narrow range of δD values while families OB and OC are highly variable (Fig. 3(b)). The overall range of δD values is -93‰ to -254‰ and that is a huge span considering that all oils are sourced from Early Cretaceous sediments.

While D/H ratios do not follow the genetic lines described by biomarkers, they do appear to follow a geographic trend. In Fig. 4(b), lines representing each oil are colored according to the geographic location of the well, stretching from the northwest part of the basin (Nunga Mia-1, red) to the southeast (Flaxmans-1 and Port Campbell-4, dark blue). Alkane δD values are consistently more depleted in D in the northwest compared to the far southeast. The exceptions to this pattern are Lindon-2 and Windermere-1, located in the central part of the western Otway Basin. The former oil has intermediate δD values whereas the δD values of the latter oil match those from further northwest. The geographic pattern is reflected in δD values of whole oils (Table 1), with the addition of an extremely D-enriched oil sample Mylor-1 (-118‰) at the southeastern fringe of the eastern Otway Basin.

A number of possible explanations for this geographic trend can be considered. Differences in oil maturity might produce such a trend and, in fact, different parts of the basin have different thermal histories (Woollands and Wong, 2001; Boulton and Hibbert, 2002). However, the northwest part of the basin – where the most D-depleted oils are found – has experienced the highest temperatures (House et al., 2002). Higher maturity leads to increasing δD values (Li et al., 2001) so this trend is in the opposite sense from the observed data. Similarly, hydrogen exchange between hydrocarbons and water should lead to increased δD values (Sessions et al., 2004) and should be most prevalent in the hottest parts of the basin. Biodegradation does not alter the δD values of the C_{12+} *n*-alkanes (Boreham, unpublished). The effects of water washing, migration and other processes are not yet understood. In any event, all of the oils we examined are broadly similar in their compositions with no indications of a basinwide trend in chemical processes.

The simplest explanation for the regional trend in oil δD values is that they reflect a similar trend in the δD of source rock organic matter. This, in turn, would be related directly to the isotopic composition of environmental water present at the time the organic matter was formed (Sauer et al., 2001; Huang et al., 2002). Oxygen isotope data obtained for calcite concretions from the southern margin – specifically in the Otway Supergroup, Otway Basin and Strzelecki Group, Gippsland Basin by Gregory et al. (1989) and by Ferguson et al. (1999) are quantitatively consistent with the proposed $\sim 100\text{‰}$ shift in δD . For example, Ferguson et al. measured $\delta^{18}O$ values for calcite of $\sim +7\text{‰}$ in the earliest Aptian (~ 125 Ma), reaching a minimum $\delta^{18}O$ value of $\sim +4\text{‰}$ in the mid-Aptian, then climbing to $+17\text{‰}$ by the end of the Albian (~ 100 Ma). Given a slope of ~ 8 for the meteoric water line (δD versus $\delta^{18}O$; Criss, 1999), a 13‰ increase in $\delta^{18}O$ of meteoric water would indicate an increase of 104‰ in δD of meteoric water, identical to the change

we observe for petroleum hydrocarbons. Our hypothesis for an isotopic shift of $\sim 100\text{‰}$ in δD of environmental water is also supported by δD_{ker} data from Chama-1A samples (Table 2); three kerogen samples, spanning a depth range of only ~ 600 m within the Eumeralla Fm., have δD_{ker} values of -196‰ , -163‰ , and -116‰ in ascending order. Thus, there appears to be a temporal as well as geographic component to the observed isotopic shift.

There are three possible contributing factors to account for a strong geographic/temporal D/H gradient in meteoric water. First, an isotopic decrease of $\sim 100\text{‰}$ in δD of environmental water, if related solely to temperature, is equivalent to a rise in air temperature of nearly 15 °C (Clark and Fritz, 1997). Such a strong regional warming seems unrealistic for the period of <40 million years during the Early Cretaceous. Although large climatic gradients are associated with the Australian Southern Rift System during the mid-Tertiary (Willcox and Stagg, 1990), the Early Cretaceous of the Otway Basin was a time of relative climatic stability (MacPhail, 2000). An isotopic temperature effect can also manifest itself in the form of the altitude-effect, whereby higher elevations with lower mean temperatures receive D-depleted precipitation that is then exported to lower elevations as runoff. For example, the Early Cretaceous could have featured regional mountains feeding rivers that reached the Otway Basin area. As the elevation of the mountains decreased over time and the source of runoff became less D-depleted, the organic matter synthesized at lower elevation recorded the temporal δD shift towards more D-enriched environmental waters.

Second, taking into account changes in humidity, the isotopic contrast in waters available for biota between a cold/moist and hot/dry environment would be much greater than that from changes in temperature alone. The effect of relative humidity on the hydrogen-isotopic composition of plants is variable but potentially quite large. For example, Terwilliger and DeNiro (1995) grew avocado seedlings in terraria with controlled humidity, and found that a drop in relative humidity from 95% to 85% resulted in an increase of leaf cellulose δD of more than 30‰ . Thus changes in relative humidity during the Cretaceous could account for much of the observed 100‰ isotopic shift in petroleum hydrocarbons.

Third, continentality describes decreasing δD values of rains as marine air masses lose moisture to precipitation while they move from the coast across a continent. Changes in geography and storm track patterns affecting meteoric waters in the Otway Basin during the Early Cretaceous could have contributed to the observed isotopic gradient, even if temperature and humidity stayed constant.

Any or all of the listed factors can contribute to the δD of environmental water, hence δD of organic matter, in any or all of the rocks we examined. They can con-

tribute either via locally derived meteoric water (i.e., changes in climate at the point of biosynthesis) or remotely as meteoric water from a geographically distant catchment flows to the point of biosynthesis via rivers and/or ground waters. Regardless of the mechanism for fractionation of meteoric and environmental waters, the Otway Basin oils support the notion that valuable climatic information can be preserved in oils and, by extension, in terrestrial kerogens.

3.1.3. Gippsland, Browse and Bonaparte basins

Compound-specific δD values for *n*-alkanes from the Gippsland, Browse, and Bonaparte basins cover similar ranges (Fig. 3(c) and (d)). Most Gippsland Basin oils

derive from a common Late Cretaceous-Tertiary Latrobe Group source rock and are saturate-rich, and waxy, with a low abundance of polar compounds (Shanmugam, 1985; Burns et al., 1987). Kerogens from 23 Tertiary to Late Cretaceous Gippsland Basin coals and shales represent near-coastal depositional environments (floodplain, freshwater peat swamp, fluvio-deltaic, coastal plain) while southern Australia remained at high latitude. Consequently the large number of analyzed Gippsland Basin kerogens and oils exhibit small isotopic variances relative to other basins that were examined in this study (Figs. 3(c) and 5).

The literature provides several H and C isotope ratios for Gippsland Basin oils that compare reassuringly with

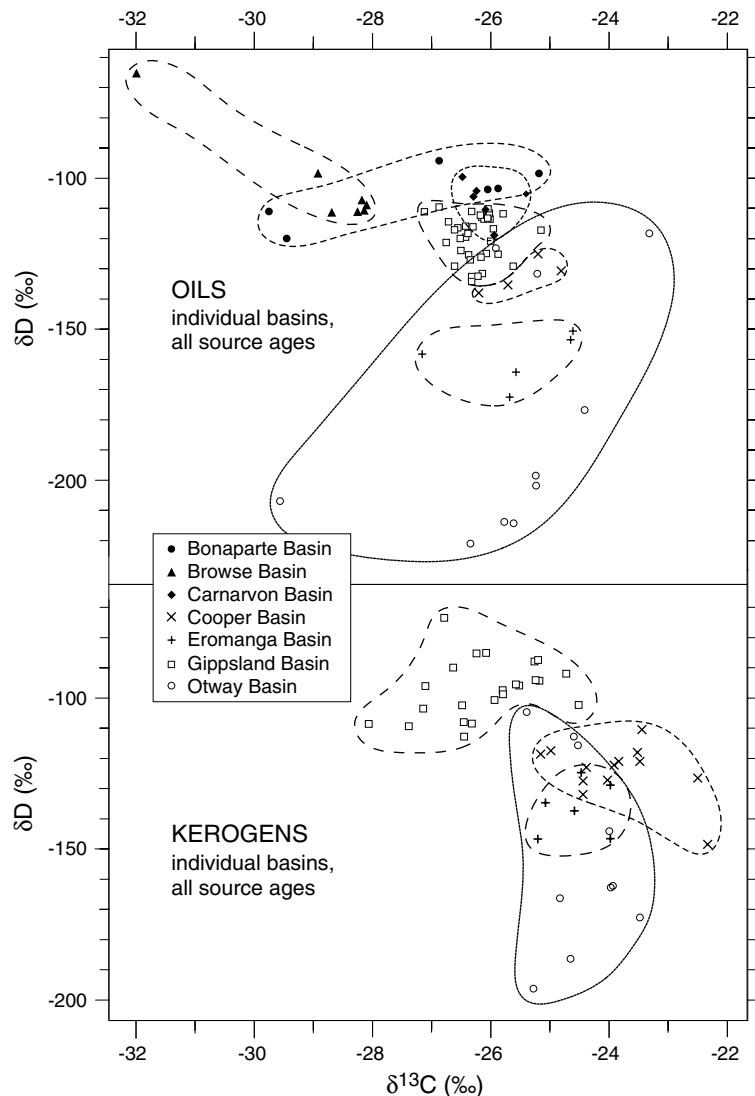


Fig. 5. δD and $\delta^{13}C$ values of kerogens and oils and condensates from seven basins, without distinguishing among different source ages that may be represented within a basin. Dashed contour lines help visualizing isotopic ranges for each basin.

data from this study. Rigby et al.'s (1981) study of 12 Gippsland Basin oils and their bulk alkane fractions provided mean values $\delta D_{oil} = -118\text{‰}$, $\delta^{13}C_{oil} = -25.8\text{‰}$, $\delta D_{alkane} = -113\text{‰}$, and $\delta^{13}C_{alkane} = -26.1\text{‰}$, whereas Yeh and Epstein (1981) reported values $\delta D_{oil} = -124\text{‰}$ and $\delta^{13}C_{oil} = -26.5\text{‰}$ for an upper Eocene oil from the Gippsland Basin. Our mean values for 35 Gippsland Basin oils and their saturated hydrocarbon fractions are $\delta D_{oil} = -119.5 \pm 7.4\text{‰}$ (range -134.4‰ to -109.7‰), $\delta^{13}C_{oil} = -26.24 \pm 0.38\text{‰}$ (range -27.12‰ to -25.15‰), $\delta D_{sat} = -122.6 \pm 9.5\text{‰}$ (range -142.0‰ to -104.4‰), and $\delta^{13}C_{sat} = -27.01 \pm 0.28\text{‰}$ (range -27.71‰ to -26.41‰ ; $n = 34$).

3.2. Hydrogen exchange with water

A significant question for understanding and using D/H ratios in petroleum systems is the extent to which those ratios might be altered by exchange with other reservoirs of hydrogen, including kerogen, formation water and at mineral surfaces (Sessions et al., 2004). In contrast to carbon, which generally does not exchange, carbon-bound hydrogen can potentially exchange with water even at low to moderate temperatures on time-

scales of 10^5 – 10^6 years. If such exchange is extensive within reservoirs or along migration pathways, then D/H ratios will not be conserved from source rock to reservoir oil and the potential for correlation is lost. As a first effort to quantify this effect, we analyzed 45 pairs of oil and formation water samples, each of which was obtained from a single well.

The rate of exchange between organic H and water varies widely with its chemical bonding environment. For example, hydrogen bound to organic nitrogen, sulfur, and oxygen (NSO-compounds containing $-OH$, $-COOH$, $-NH_2$, $-NHR$, $-SH$ groups) can exchange with water on a timescale of minutes, while C-bound hydrogen adjacent to carbonyl positions ($R-CH_2-CO-CR_3$) may exchange on timescales of days. Even for hydrocarbons there can be great variability, with aromatic hydrogen exchanging more rapidly than aliphatic hydrogen (Alexander et al., 1984). To account for this potentially large variability in exchange behavior, we measured δD in multiple sub-fractions of each oil, including saturated, aromatic, and polar compounds, as well as for the whole oils.

Values of δD for whole oils, saturated, aromatic, and polar fractions are plotted in Fig. 6 versus δD of coex-

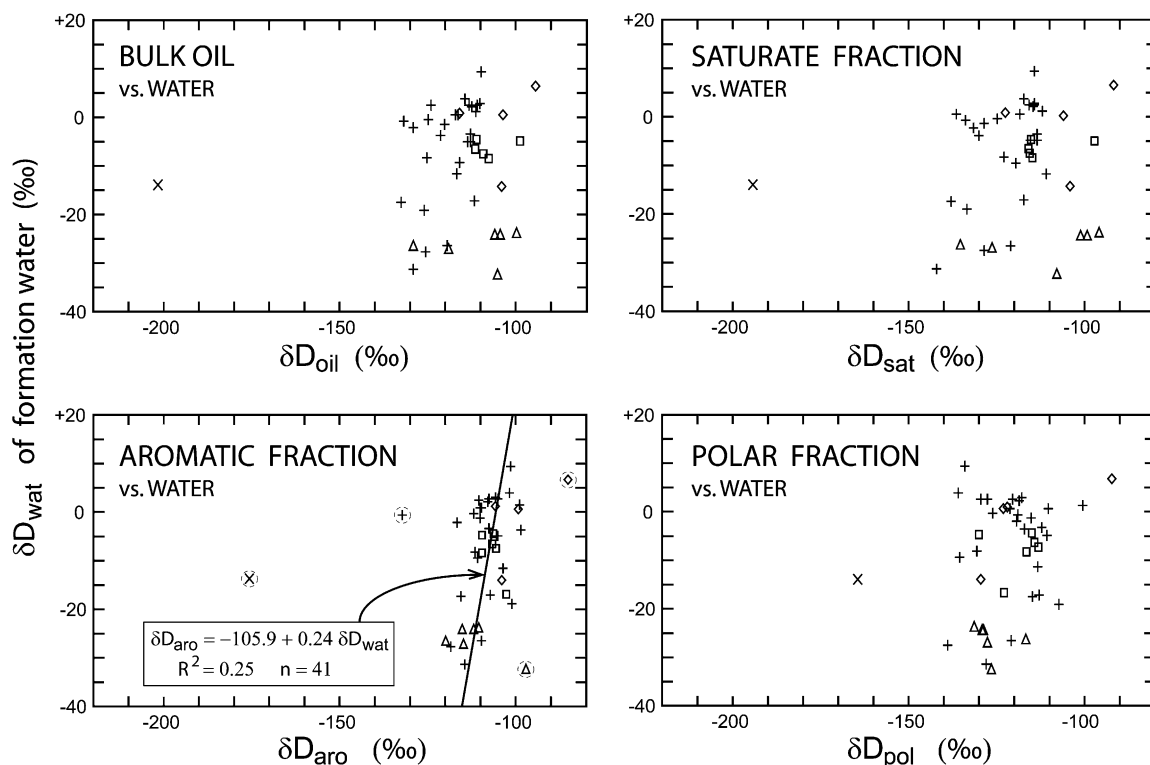


Fig. 6. Hydrogen isotopic composition of formation waters (δD_{wat}) versus those of associated bulk oils (δD_{oil}) and their saturated (δD_{sat}), aromatic (δD_{aro}), and polar (δD_{pol}) fractions from five basins: (\diamond) Bonaparte Basin, (\square) Browse Basin, (\triangle) Carnarvon Basin, (+) Gippsland Basin, and (\times) Otway Basin. Calculations and the significance of the functional regression for δD_{aro} are described in the text.

isting formation waters. For all fractions except the aromatic, there is no significant correlation, implying that there has been no isotopic exchange between organic H in these fractions and water. In contrast, there is a modest but significant correlation between the δD values of aromatic fractions and water. A two-tailed student's t statistic of all 45 data pairs indicates the correlation is significant within an 80% confidence interval ($t = 1.50$). If the single Otway Basin extreme value of $\delta D_{\text{aro}} = -176\text{‰}$ is eliminated, the confidence interval becomes 95% ($t = 2.0$).

We calculated a functional linear regression of δD_{aro} on δD_{wat} after eliminating three more extreme δD_{aro} outliers (eliminated data are in dashed circles in Fig. 6), yielding the relationship $\delta D_{\text{aro}} = 0.24\delta D_{\text{wat}} - 105.9$ ($n = 41$; $R^2 = 0.25$). The inclusion of multiple basins with varying thermal histories is a likely source of scatter in the relationship. Furthermore, exchange rate effects are also excluded since there is no correlation between D/H ratios and reservoir temperature (Table 1). Regardless, the slope of 0.24 allows the interpretation that, on average, about one in four hydrogen atoms in the aromatic fraction has equilibrated with water. Covariance alone cannot prove that such equilibration occurs via direct hydrogen exchange between hydrocarbons and water, though this is the simplest explanation.

The aromatic fraction also contains some non-exchangeable aliphatic hydrogen in side chains attached to aromatic structures, which will dilute the exchange signal from aromatic hydrogens. Using the H/C ratios of aromatic sub-fractions measured during isotopic analyses, we calculated the proportion of aromatic versus aliphatic hydrogen in those fractions. Icosane (H/C = 2.1) and anthracene (H/C = 0.71) were used as aliphatic and aromatic endmembers, and a linear correction of +0.16 was applied to all measured H/C ratios to account for the small amount of hydrogen lost during combustion of organic matter in sealed quartz ampules (Schimmelmann and DeNiro, 1993). This empirical correction factor is based on ca. 150 H₂O and CO₂ off-line, manometric yield determinations from individually combusted pure n -alkanes, other hydrocarbons, and FAMEs. Our calculations indicate that $58 \pm 6\%$ of the hydrogen in 'aromatic' sub-fractions is aromatic ($n = 46$, including data from all basins). That result in turn implies that about 50% of the aromatic hydrogen in oils may typically exchange with formation water.

Fig. 6 also indicates that there is no exchange between polar oil fractions and formation water. This was unexpected, as the polar fraction should contain the most exchangeable hydrogen (Werstiuk and Ju, 1989), i.e. hydrogen bound to oxygen and nitrogen. In this case, we interpret the lack of correlation as due to rapid re-equilibration of the most labile hydrogen with water or water vapor during sample recovery, storage and

handling. In other words, the isotopic signature of rapidly exchanging organic hydrogen has been continuously adjusted in response to ambient moisture conditions since removal of oils from the reservoirs.

Water at neutral pH does not readily exchange with most carbon-bound hydrogen (Sessions et al., 2004) in the absence of catalysts. The exposure of hydrocarbons and oil fractions to heavy water (D₂O) in laboratory heating experiments (Köpp, 1978, 1979; Hoering, 1984), both with and without catalytic mineral surfaces, demonstrated that aromatic hydrogen is the most labile of the hydrocarbon fractions toward isotopic exchange. As an additional experimental test, we submerged aliquots of the saturated and aromatic fractions from Fortescue-4, Leatherjacket-1, and Snapper-5 in water with $\delta D = +1196\text{‰}$ at room temperature for 130 days. Samples were then freeze-dried under vacuum and analyzed for δD . Comparison with control aliquots of the same samples indicated no exchange for the saturated fractions ($\Delta\delta D_{\text{sat}} = -0.1 \pm 1.1\text{‰}$; $n = 3$) but minor exchange for the aromatic fractions ($\Delta\delta D_{\text{aro}} = +3.7 \pm 2.2\text{‰}$; $n = 3$). These results agree qualitatively with earlier observations of slow isotopic exchange of aromatic hydrogen (Alexander et al., 1982; Werstiuk and Ju, 1989) and the relationship indicated by Fig. 6. However, the data are insufficient to calculate accurate rate constants for the exchange.

Rates of isotopic exchange for petroleum hydrocarbons are still in question. Schoell (1984) demonstrated a lack of correlation between δD_{oil} values and the ages of more than 50 Cambrian to Tertiary oils, which was interpreted as evidence for a lack of hydrogen exchange. Sessions et al. (2004) recently reviewed evidence for hydrogen exchange in sedimentary organic matter and concluded that primary D/H ratios are likely conserved over timescales of millions of years, but are probably not conserved over hundreds of million years. An important distinction must be drawn, however, between exchange of sedimentary organic matter, consisting mainly of molecules adsorbed onto mineral surfaces, versus exchange in oils that form a separate, water-immiscible phase. We expect that exchange in pooled oil should be slower than in adsorbed organic matter as a result of restricted access to catalytic surfaces (Alexander et al., 1981, 1982). We conclude that exchange between saturated hydrocarbons and reservoir water is unlikely, even at moderately elevated temperatures (up to 150 °C, Table 1), over the long timescales (up to ~90 Ma for the Cooper Basin oils; Deighton et al., 2003) that oils typically inhabit a reservoir. The question of exchange within petroleum source rocks is addressed in Section 3.5.

3.3. D/H ratios of oil components

Hydrogen isotopic differences between whole oils and their sub-fractions are summarized in Table 3. The

Table 3
Summary of variations between δD values of oil fractions and the bulk oil ^a

Basin	Alkanes ^b	Saturated	Aromatic	Polar
Bonaparte	-7.7	-4.1 (6.6)	7.5 (4.6)	-7.3 (10.2)
Browse	-1.0	-2.9 (3.9)	-3.6 (16.3)	-15.7 (21.0)
Carnavon	n.d.	-2.0 (6.7)	-0.1 (8.7)	-15.1 (14.8)
Cooper-Eromanga	2.4 (10.2)	-4.1 (7.8)	10.2 (9.9)	9.2 (17.5)
Gippsland	2.7 (8.2)	-3.0 (5.1)	10.3 (6.1)	2.4 (25.9)
Otway	5.2 (15.5)	-17.1 (13.6)	15.4 (12.0)	20.6 (32.7)
All basins	2.9 (11.3)	-5.0 (8.4)	8.5 (10.1)	1.3 (25.4)

n.d. = not determined.

^a Tabulated values are $\delta D(\text{fraction}) - \delta D(\text{whole oil})$, in ‰ units, and were calculated individually for each oil before calculating the basin average. Standard deviation of values is given in parentheses.

^b The δD value of each *n*-alkane fraction was calculated as a weighted-mean value from compound-specific isotopic data using the mass-2 peak area as the weighting factor.

general pattern observed is that all sub-fractions have similar D/H ratios to their parent whole oils. Values of δD for the alkane and saturated fractions are generally within 5‰ of that for the whole oil, with individual oils deviating only slightly (<10‰) from this pattern. Aromatic fractions tend to be enriched in D by ~10‰, while the polar fractions are identical to the whole oils on average, but with a much larger ($\sigma = 25\%$) spread of values. The Otway Basin appears as an exception to this pattern, with the saturated fraction being depleted in D by 22‰ or more relative to all other fractions, including the average of *n*-alkanes.

Our observation of small differences in δD between whole oils and their fractions can be compared to several previously published data sets. Schoell (1984) noted lower D abundances with decreasing polarity in oils that were not altered by secondary processes. Waseda (1993) reported a similar systematic increase in δD values from the saturated fraction, to total oil, and to the aromatic fraction in 25 oils from Northeast Japan. Close isotopic similarity among different oil fractions was documented within two oils from Saskatchewan and Utah, with a variance of $\pm 1.5\%$ for hydrogen and $\pm 0.55\%$ for carbon (Yeh and Epstein, 1981). In contrast, an extensive data set from Peters et al. (1986) shows mean δD_{oil} values systematically more negative than mean δD values of all the oils' major fractions.

For the 28 oils that were analyzed by CSIA, the statistical correlation (R^2 value) between δD values derived from the weighted-mean of *n*-alkanes versus those from whole oil and saturated fractions, was 0.94 and 0.91, respectively. This tight isotopic mass balance is explained by the general observation that *n*-alkanes are a quantitatively important component of most unaltered oils, and lends strength to our earlier assertion that isotopic measurements of *n*-alkanes will be particularly valuable for quantitative apportionment of oil sources. We emphasize that these correlations were obtained for samples derived mainly from single sources. Where mixed oils are

found, such simple isotopic relationships will be unlikely and, therefore, compound-specific measurements may indicate the mixing relationships more clearly.

3.4. D/H ratios of individual *n*-alkanes

Fig. 3 indicates a persistent trend in the CSIA data, namely that δD values increase steadily with *n*-alkane carbon number. To investigate and quantify this phenomenon further we calculated a linear regression of δD values versus alkane carbon number (i.e., the slope for each oil in Fig. 3). The analysis includes data from three of the Australian petroleum systems as well as that reported by Li et al. (2001) for the western Canadian sedimentary basin. With only two exceptions, all oils exhibit positive slopes for δD versus carbon number (Fig. 7). Basin-wide averages ranged from 1.0 (‰ per carbon number) in the Cooper/Eromanga basins to 2.3 in the Williston Basin. The Canadian oils, which represent mainly marine source rocks, exhibited somewhat higher slopes on average. The mean value for the Williston Basin oils is significantly higher than for the three Australian basins at the 2 σ level, while that for the Alberta Province oils is significantly higher only at the 1 σ level. Values of R^2 for the regressions averaged 0.76, indicative of the fact that, for most oils, δD values increase linearly with carbon number.

The emerging picture is that systematic increases in δD with carbon number are a general feature of most petroleum systems, although exceptions do exist (K. Grice, personal communication). Moreover, there are subtle variations imposed on this general trend that may be related to some aspect of petroleum generation. A better understanding of the mechanisms responsible for this pattern may ultimately yield insights into the chemical processes of petroleum generation.

Five explanations for a positive "isotope slope" can be considered.

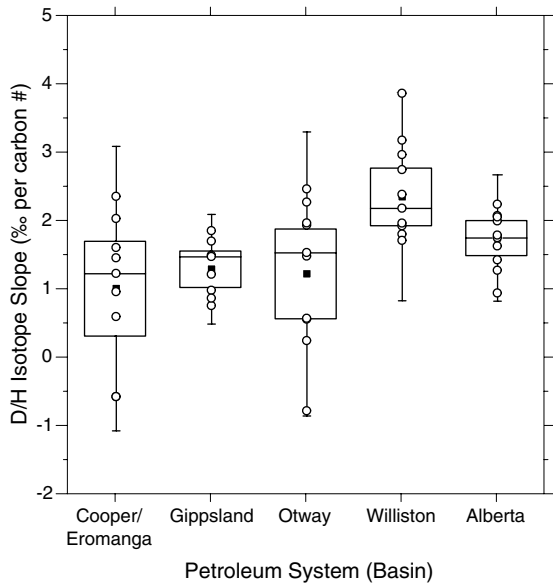


Fig. 7. Statistical analysis of the “isotope slope” for oils from 5 basins, with Cooper and Eromanga basins data combined. Open circles are individual data points, a solid square is the basin average, a horizontal line is the median. Boxes represent ± 2 standard errors of the mean value, and vertical lines describe $\pm 2\sigma$ of the population. Values for the Williston Basin and Alberta Province are calculated from data reported by Li et al. (2001). Calculations are described in the text.

(1) The isotopic trends might be attributed to analytical artifacts, such as nonlinearity or drift of the mass spectrometer. Several points argue against this. First, relative changes in δD are not correlated with abundance. Low-abundance, short-chain alkanes are depleted in D, while low-abundance, long-chain alkanes are enriched. Second, several oils with typical *n*-alkane abundance patterns do not exhibit increasing δD with carbon number, as would be expected if systematic errors were present. These results have been replicated several times on different dates. Finally, hydrocarbon reference material mixtures containing C_{16} to C_{30} *n*-alkanes, varying over a 5-fold range in concentration, show no indication of systematic analytical errors.

(2) The pattern might reflect the relative inputs of different source materials. For example, in a terrestrial petroleum system, long-chain *n*-alkanes derive primarily from plant leaf waxes (slightly enriched in D as a result of evapotranspiration; Chikaraishi and Naraoka, 2003; Yang and Huang, 2003), while shorter alkanes derive more from bacterial fatty acids. Although such a mechanism might well contribute to the observed pattern in some specific oils, it cannot plausibly be the sole mechanism for so many oils from such widely varying sources.

(3) Biochemical processes might produce a chain-length dependence of δD values in primary products, as

suggested by Li et al. (2001). No specific biochemical mechanism for such a pattern is currently known, nor has such a pattern been observed in higher plant *n*-alkanes (Sessions et al., 1999; Chikaraishi and Naraoka, 2003; Yang and Huang, 2003). However, we have observed a similar trend in C_{12} to C_{19} fatty acids from several species of sulfate-reducing bacteria grown in culture (Sessions, unpublished data) so the possibility must be considered.

(4) Physical processes cause isotopic fractionations that vary with molecular weight. For example, D-containing hydrocarbons are more volatile than those containing all H (an inverse isotope effect; Hopfner, 1969; Kiss et al., 1972) so, during evaporation the liquid, residue becomes depleted in D. During evaporation of an oil, more volatile (shorter-chain) compounds will become depleted in D relative to less volatile compounds. Similar effects also pertain to partitioning between organic and aqueous phases (Salem et al., 1994) and between liquid and adsorbed phases (di Corcia and Liberti, 1969). Again, this mechanism may contribute to the trend in some oils, but is probably inconsistent with such a narrow range of slopes in all oils derived from varied organic sources of differing ages.

(5) Oil-generating reactions are accompanied by kinetic isotope effects that favor reaction of D-depleted molecules. The substitution of D for H, for example in a methylene moiety, stabilizes not only that particular C–H bond (a primary isotope effect), but all of the other bonds to the C atom (a secondary isotope effect; Bigeleisen, 1965). Thus a C(HD)–C(H₂) bond is stronger, and reacts more slowly, than a C(H₂)–C(H₂) bond. The isotopic consequences of this effect have been well documented by bulk analyses that show released hydrocarbons are consistently depleted in ¹³C and D while the residual kerogen becomes enriched in ¹³C and D (Rigby et al., 1981; Schoell et al., 1983; see also Section 3.6, below).

Given that oil generation is largely the result of cleaving long-chain molecules into shorter ones, such isotope effects could cause the reaction products (smaller compounds) to become systematically depleted in D while the remaining reactants (larger compounds) become progressively enriched. This mechanism thus provides a simple explanation for both the direction and constancy of observed δD trends. It does not, however, explain why a small number of oils do not possess such an isotopic pattern.

3.5. DIH ratios of isoprenoid compounds

Because of differences in biosynthetic pathways, polyisoprenoid lipids (including sterols, hopanols, and phytol) are generally depleted in D relative to *n*-alkyl lipids (fatty acids and *n*-alkanes) by between 50‰ and 200‰ in living plants (Sessions et al., 1999; Sauer et al.,

Table 4
Values of δD for acyclic isoprenoid and *n*-alkane hydrocarbons from Otway Basin

Compound	Geoscience Australia (GA) number and well name					
	# 498 Flaxmans-1	# 10012 Windermere-1	# 10031 Sawpit-1	# 10369 Haselgrove-1 ST1	# 10374 Wynn-1	# 10376 Nunga Mia-1
<i>Acyclic isoprenoids</i>						
C ₁₆ isoprenoid	n.a.	–200	–230	n.a.	–245 ^a	–230 ^a
Norpristane	–102	–200	n.a.	–205	–233	–220
Pristane	–107	–210	–213	–238	–233	–214
Phytane	–95	–211	–220	n.a.	–216	–230
<i>n-alkanes</i>						
<i>n</i> -C ₁₂	–127	n.a.	–225	–234	–236	–231
<i>n</i> -C ₁₅	–108	–215	–218	–236	–232	–231
<i>n</i> -C ₁₈	–104	–208	–217	–233	–227	–228
<i>n</i> -C ₂₁	–105	–207	–212	–228	–221	–225
<i>n</i> -C ₂₄	–100	–204	–209	–218	–214	–222

n.a. = not available.

^a Compound coelutes with a C₁₄ cyclohexylalkane and a C₁₅ isoalkane.

2001; Chikaraishi and Naraoka, 2003) and bacteria (Sessions et al., 2002). Conversion of these biolipids to hydrocarbons involves the net addition of only a few hydrogen atoms, so in the absence of exchange these compounds should preserve markedly different δD values in oil. Table 4 shows that this is clearly not the case for Otway Basin oils where isoprenoid and *n*-alkyl compounds have identical δD values within the limits of uncertainty.

Sessions et al. (2004) report similar data for a suite of bitumen samples ranging in age from 340 to 1640 Ma, in which *n*-alkyl and isoprenoid hydrocarbons have essentially identical δD values. Li et al. (2001) report systematic differences between pristane and *n*-alkanes that range from ~30‰ to more than 65‰ for oils from western Canada, larger than those seen in the Otway Basin but still considerably smaller than the primary biosynthetic fractionations. The similarity in δD values between isoprenoids and *n*-alkanes in a diverse range of oils provides strong evidence for the alteration of primary δD values in many oils (see also Sessions et al., 2004).

Several studies have documented the preservation of primary lipid δD values in cool and relatively young sediments (Andersen et al., 2001; Yang and Huang, 2003). Presumably, the convergence of δD values occurs slowly, with increasing thermal stress, although to our knowledge quantitative relationships between thermal maturity and isotopic composition have not yet been published. It is also unknown whether this alteration affects all hydrocarbons or simply a subset of molecules, such as the isoprenoids. The fact that isoprenoid δD values appear to change more rapidly than those of *n*-alkanes might simply reflect the fact that they are farther

from isotopic equilibrium with H₂O than are the *n*-alkanes (Sessions et al., 2004).

3.6. Isotopic shifts in the generation of oil from kerogen

The thermal breakdown of the kerogen macromolecular structure, generation of mobile hydrocarbon molecules, expulsion of oil from the source rock and migration of oil into a reservoir all result in a net isotopic fractionation between the original kerogen and the reservoir oil. The isotopic composition of kerogen may also change as it is transformed to bitumen, oil and gas. We selected data for parent kerogens and associated reservoir oils from four different basins in which the link between oil and source kerogen is relatively clear (Fig. 8). However, we note that the process of oil migration from a source kitchen into a reservoir makes it impossible to unambiguously match a specific source rock sample with an oil sample.

To assess this source of H-isotopic fractionation, we averaged available isotopic data from oils and kerogens from each petroleum system within a certain age group. Permian kerogens and oils from the Cooper Basin, Middle Jurassic and Cretaceous samples from the Eromanga Basin, and Late Cretaceous/Early Tertiary samples from the Gippsland Basin all plot in quite distinct isotopic ranges for each basin, with a uniform trend toward more negative δD and $\delta^{13}C$ values from kerogen to oil. The mean δ -values of Early Cretaceous kerogens and oils from the Otway Basin show a similar shift, although the individual data for kerogens and oils are spread over much larger ranges and thus indicate significant heterogeneity within Otway Basin source rocks. The overall weighted-average isotopic shifts from kero-

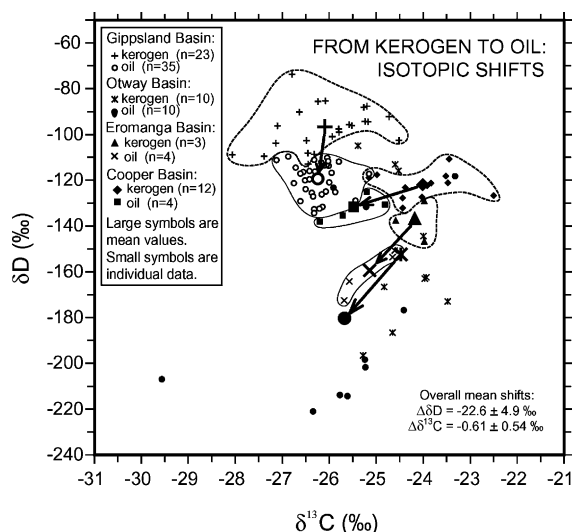


Fig. 8. Hydrogen and carbon isotopic compositions of kerogens and reservoir oils from four basins with distinct source rock ages: Cooper Basin (Permian), Eromanga Basin (Middle Jurassic), Otway Basin (Early Cretaceous), and Gippsland Basin (Late Cretaceous/Early Tertiary). Small symbols indicate individual isotopic results, whereas large symbols represent basin-specific mean δ -values. For the Cooper, Eromanga, and Gippsland basins, dashed contour lines indicate the isotopic ranges of kerogens, and solid lines help visualize the isotopic ranges for oils. Calculations are described in the text.

gen to oil for the four basins were calculated to $\Delta\delta D_{\text{oil-ker}} = -22.6 \pm 4.9\text{‰}$ and $\Delta\delta^{13}\text{C}_{\text{oil-ker}} = -0.61 \pm 0.54\text{‰}$ (Fig. 8), based on a weight distribution of samples from Gippsland 23 : Otway 10 : Eromanga 3 : Cooper 4.

The few published D/H and $^{13}\text{C}/^{12}\text{C}$ comparisons between source rocks and related oils or extracts did not report their δD -values in terms of non-exchangeable hydrogen in kerogen ($\delta\text{D}_{\text{ker}}$), but instead measured δD of bulk hydrogen in kerogen, or of bulk coal without demineralization (Rigby et al., 1981; Schoell, 1984; Schou et al., 1985). Nevertheless, the comparisons show similar trends, and $\delta\text{D}_{\text{bulk kerogen}}$ values may in fact approximate $\delta\text{D}_{\text{ker}}$ values near the oil window when exchangeable hydrogen is depleted (Mastalerz and Schimmelmann, 2002). Our observation of D- and ^{13}C -enrichment in source rock kerogen relative to oils is in qualitative agreement with data from Schoell et al. (1983) and Schoell (1984, p. 40) from a Mahakam Delta depth-sequence where Type III kerogens are predominantly enriched in the heavy isotopes relative to saturated fractions, aromatic fractions and polar-extract fractions. The ratio $\delta\text{D}_{\text{bulk kerogen}}/\text{D}_{\text{polar-extract}}$ was suggested to serve as a maturity parameter M_{D} that approaches unity at maturities within the conventional oil window.

Similar H- and C-isotopic patterns were observed between bulk coal, oil and alkane extracts in Australia's Gippsland and Bass basins, with extractables being typically more D- and ^{13}C -depleted than the parent bulk coal and with isotopic differences decreasing with increasing coal maturity (Rigby et al., 1981; Smith et al., 1985). More specifically, Yallourn brown coals from the Gippsland Basin were reported to have δD values of $< -165\text{‰}$ for aliphatic resins and between -80‰ to -120‰ for gellite, woody coal, leaf coal, pollen coal, etc. (Rigby et al., 1981; Smith et al., 1982). Oil and alkane extracts were always more depleted in deuterium than their parent coals by as much as 60‰ . We find broad agreement with our observed mean $\delta\text{D}_{\text{ker}}$ data from Gippsland Basin coals ($\delta\text{D}_{\text{ker}} = -97.0 \pm 10.2\text{‰}$; $n = 20$) and shales/mudstones ($\delta\text{D}_{\text{ker}} = -98.1 \pm 3.4\text{‰}$; $n = 3$) although the earlier coal δD data were based on mineral-containing coal and macerals rather than kerogen, and the isotopic influence of exchangeable hydrogen had been ignored.

It is easy to rationalise that oils should be depleted in D and ^{13}C relative to kerogen, for two reasons. Biolipids are typically depleted in deuterium relative to other biochemical fractions in biomass (Smith and Epstein, 1970; Estep and Hoering, 1980; Sternberg, 1988; Sessions et al., 2002). Maturation leads to preferential chemical liberation of the aliphatic and aromatic hydrocarbon moieties from kerogen resulting in a release of deuterium-depleted extract/oil/gas and a deuterium-enriched residue (Schoell, 1984). Secondly, the kinetic isotope effect in the breaking of bonds during thermal maturation should favor the liberation of smaller molecules with lower $\delta^{13}\text{C}$ and δD values (Criss, 1999, p. 59–60).

In comparison to other types of kerogen, the terrestrially derived Type III kerogens that are predominant in this study have a low oil potential which can be partially explained by the low aliphatic content of the ligno-cellulosic precursor material (Behar and Vandembroucke, 1987). A different mean $\Delta\delta\text{D}$ relationship between expelled oil and kerogen may be expected for more aliphatic kerogen Types I and II.

3.7. The nature of hydrogen exchange in petroleum systems

Several existing lines of evidence are relevant to the question of hydrogen isotope exchange in petroleum hydrocarbons: (1) water hydrogen is demonstrably incorporated into hydrocarbons released during hydrous pyrolysis of kerogens (e.g., Schimmelmann et al., 1999; Leif and Simoneit, 2000); (2) expected biochemical fractionations between isoprenoid and n -alkyl carbon skeletons are present in immature sediments (e.g. Andersen et al., 2001), but are either absent or greatly reduced in petroleum (e.g. Sessions et al., 2004); (3) no

correlation is observed between whole oil and formation water δD values; and (4) meteoric water D/H signals can apparently be preserved in oils, for example in the Otway Basin.

All of these apparently conflicting results can be reconciled if (i) extensive hydrogen exchange occurs largely during hydrocarbon generation by thermal decomposition of precursor macromolecules, and (ii) if the bulk isotopic composition of the hydrogen in source rocks reflects that of the original depositional environment. The first requirement focuses on energetic chemical reactions during thermal maturation. When a precursor organic molecule is excited to a transition state (e.g., ionic or radical), a brief ‘window of opportunity’ permits incorporation of water-, organic- and mineral-derived hydrogen into subsequently non-exchangeable organic hydrogen positions. This applies to hydrocarbon reaction products and remaining kerogen. The generation of an immiscible petroleum/bitumen phase probably contributes to the recalcitrance of hydrocarbons towards exchange.

The second requirement is quite plausible, given that source rocks frequently have both very low permeability, limiting subsequent fluid flow, and relatively high contents of organic matter and clay minerals, both of which will buffer changes in the δD of porewater. In contrast to porewater in the deeper source rock, the formation water in contact with oil in a reservoir is more prone to isotopic changes over time; deep basin formation waters are mainly related to meteoric water of various ages and marine connate water deposited with shales and siltstones in sedimentary basins (reviewed by Clauer and Chaudhuri, 1995). In particular, several studies reported that formation waters associated with petroleum are principally derived from younger local meteoric water (Kharaka and Carothers, 1986, p. 315).

In any event, the δD values of petroleum largely seem to reflect the hydrogen isotopic composition of the source rock environment, including organic matter, porewater and mineral hydrogen. To the extent that source rock and paleowater δD values are correlated, petroleum *n*-alkanes may serve as a proxy for paleoenvironmental water as suggested by Li et al. (2001). However, the relationship is far from simple and requires further study in its own right.

4. Conclusions

- Oils derived from terrestrial organic matter preserve a much larger range of δD values than do oils derived from marine organic matter. This presumably reflects the greater variability of δD in the terrestrial hydrologic cycle and provides a useful tool for oil-to-source correlations. The combination of H- and C-isotopic data can provide greatly enhanced resolution in com-

plex systems where a single isotopic system may be inadequate.

- Comparison of δD values for oils, oil fractions and associated formation waters demonstrates that isotopic exchange under reservoir conditions is limited to the aromatic (and probably polar) fractions, whereas aliphatic hydrocarbons remain isotopically conservative.
- In oils derived from a single source, the whole oil, individual oil fractions (saturated, aromatic, and polar compounds) and *n*-alkanes all have similar δD values. This reflects the fact that *n*-alkanes are a major component of oils and shows that isotopic measurements of *n*-alkanes can be used for quantitative apportionment of sources in mixed oils.
- Australian oils from four sedimentary basins are on average depleted in D by 23‰ and in ^{13}C by 0.6‰ relative to their respective source rock kerogens, which likely reflects fractionation during hydrocarbon generation.
- There is a consistent and significant pattern of increasing δD with carbon number in *n*-alkanes in all petroleum systems reported thus far. We hypothesize that this relationship reflects fractionations occurring during hydrocarbon generation.
- D/H ratios for isoprenoid and *n*-alkyl hydrocarbons from Otway Basin oils are virtually identical indicating that extensive exchange has occurred at some time following biosynthesis. At the same time, these oils preserve a range of δD values of more than 100‰, apparently reflecting climatic and depositional environmental signals from the Early Cretaceous. These results can be reconciled if we assume that the bulk hydrogen within Otway Basin source rocks – including porewater, organic H, and mineral H – is correlated with paleowater δD . The implication is that some paleoenvironmental information may be preserved in petroleum D/H ratios despite extensive isotopic scrambling between individual molecules.

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