

Carbon and hydrogen isotopic compositions of *n*-alkanes as a tool in petroleum exploration

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Abstract: Compound-specific isotope analysis (CSIA) of individual organic compounds is a powerful but underutilized tool in petroleum exploration. When integrated with other organic geochemical methodologies it can provide evidence of fluid histories including source, maturity, charge history and reservoir processes that can support field development planning and exploration efforts. The purpose of this chapter is to provide a review of the methodologies used for generating carbon and hydrogen isotope data for mid- and high-molecular-weight *n*-alkanes.

We discuss the factors that control stable carbon and hydrogen isotope compositions of *n*-alkanes and related compounds in sedimentary and petroleum systems and review current and future applications of this methodology for petroleum exploration. We discuss basin-specific case studies that demonstrate the usefulness of CSIA either when addressing particular aspects of petroleum exploration (e.g. charge evaluation, source rock–oil correlation, and investigation of maturity and in-reservoir processes) or when this technique is used to corroborate interpretations from integrated petroleum systems analysis, providing unique insights which may not be revealed when using other methods. CSIA of *n*-alkanes and related *n*-alkyl structures can provide independent data to strengthen petroleum systems concepts from generation and expulsion of fluids from source rock, to charge history, connectivity, and in-reservoir processes.



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Petroleum geoscientists use organic geochemistry as an essential tool in oil and gas exploration and field development planning. Relatively low-cost, high-throughput bulk data are commonly used to screen for source rock quality (e.g. per cent total organic carbon (%TOC), hydrogen and oxygen indices) and thermal maturity (T_{max}, vitrinite reflectance equivalent). More in-depth geochemical analytical techniques are used in the context of full fluid and reservoir properties to correlate source rocks and reservoir oils, to determine fluid generation and migration history, including present-day reservoir connectivity, and to understand in-reservoir processes, such as biodegradation of in-reservoir oils. These tools are especially powerful when coupled with other measurements made during the exploration and development process, such as compositional analysis during drilling, downhole fluid analysis and other wireline measurements, and pressure, volume, temperature (PVT) and chemical analyses, integrated in the context of geological static and reservoir dynamic models.

Molecular biomarkers have been employed in petroleum exploration for several decades (Peters *et al.* 2005). The usefulness of bulk stable isotope

measurements of gases and oils was well demonstrated in the petroleum industry through the decades of the 1970s and 1980s (Stahl 1977; Schoell 1984; Sofer 1984). However, the use of compound-specific isotopic composition of light hydrocarbons, alkanes and biomarkers is less common. Nonetheless, these types of data can provide valuable additional information to distinguish oil families, perform oil–oil and oil–source rock correlation, and better understand in-reservoir processes that have had an impact upon fluid properties over time and that explain current emplacement. Compound-specific isotope analysis (CSIA) provides distinctive and substantive support to a fully integrated interpretation of fluid properties in petroleum exploration and development.

The purpose of this chapter is (a) to provide a review of mid- and high-molecular-weight alkane carbon (C) and hydrogen (H) isotope analytical methodologies and the factors that control stable C and H isotopes of *n*-alkane (C₆₊) compounds in sedimentary and petroleum systems, and (b) to review current and future applications of this methodology for petroleum exploration. CSIA of gas range (C₁–C₅) *n*-alkane and other molecular compositions is beyond the scope of this contribution.

CSIA of *n*-alkanes

We focus on compound-specific analysis of higher-molecular-weight *n*-alkanes and related compounds because: (a) they are the most abundant hydrocarbon groups present both in the source rock extracts and reservoir oils; (b) they are easy to extract, separate and analyse; (c) they can be analysed for both stable C and H isotope compositions using the same sample and using the same gas chromatograph isotope ratio mass spectrometer (GC-IRMS) instrument; (d) they provide a reasonable scope for in-depth review; and (e) they demonstrate the potential for growth of these underutilized techniques.

When integrated with the bulk isotope methodology, CSIA expands the usefulness of the stable isotope approach in petroleum exploration and adds several advantages. The methodology:

- (1) allows investigation of multiple organic matter sources and/or processes (e.g. by comparing the isotopic composition of organic compounds of different chain length) using a single sample;
- (2) enhances the ability to compare the chemical properties of individual organic compounds at different stages of their geochemical history (e.g. alkanes extracted from immature source rock are comparable to *n*-alkanes generated and expelled during thermal maturation of organic matter) so as to better understand the processes that have had an impact upon current and past reservoir fluid properties;
- (3) supports information to identify potential source origin and oil families, conduct oil–oil and oil–source rock correlations, and improve our understanding of the processes that have influenced fluid properties over time;
- (4) requires relatively small sample volumes.

The disadvantages are similar to other fluid evaluation techniques: the samples must be representative, and the interpretative strategy must include an integrated approach to enable the unravelling of the complex physical and chemical processes that occur over very long time periods.

Analytical methodology for compound-specific stable isotope analysis

Several previous reviews provide detailed information on analytical methods and on the use of compound-specific isotopic data on organic compounds in the natural and applied sciences (Meier-Augenstein 1999; Schmidt *et al.* 2004; Glaser 2005; Benson *et al.* 2006; Philp 2006; Sessions 2006; Evershed *et al.* 2007). The following section

briefly describes the general principles of acquiring C and H stable isotope data for individual organic compounds extracted from natural samples.

Sample preparation

The initial step of sample clean-up and fraction separation depends on the matrix, i.e. whether it is a source or reservoir rock or a liquid. For solid samples, the total extractable fraction can be collected using the Soxhlet apparatus, sonication, accelerated solvent, or microwave-assisted extraction systems (Lundanes & Greibrokk 1994; Rieley 1994; Letellier & Budzinski 1999; Smith 2003; Peters *et al.* 2005; Péres *et al.* 2006). The isolation and clean-up steps to obtain specific fractions will vary according to specific project needs. Alkanes subjected to CSIA can be isolated from either the whole oil or individual fractions (e.g. saturates, aromatics). Generally, especially for $\delta^2\text{H}$ measurements, an additional step to separate the branched from straight-chain compounds is recommended using urea adduction or molecular sieves (Grice *et al.* 2008).

Analytical procedures for compound-specific stable isotope measurements

The whole oil or the saturate fraction with *n*-alkyl compounds usually must first be analysed using a gas chromatograph flame ionization detector (GC-FID) or gas chromatograph mass spectrometer (GC-MS) to quantify the amount of sample needed to achieve reproducible results on the IRMS. To achieve the most precise $\delta^{13}\text{C}$ and $\delta^2\text{H}$ measurements, *n*-alkane peaks should have baseline resolution (if the sample contains other compounds in addition to *n*-alkanes) and a sufficient signal-to-background ratio (which is system specific); compound-specific measurements are made using the GC-IRMS coupled with combustion ($\delta^{13}\text{C}$) or high-temperature conversion ($\delta^2\text{H}$) reactors, respectively. Modern mass spectrometers equipped with a gas chromatograph and this type of ‘on-line’ set-up generally provide precision for $\delta^{13}\text{C}$ in the range ± 0.1 – 0.3‰ for compounds containing 0.1–5 nmol C, and for $\delta^2\text{H}$ in the range of ± 2 – 5‰ for compounds containing 10–50 nmol H (Sessions 2006). The user has to be aware of precision levels associated with C and H isotope measurements when designing a study and interpreting the results. Case studies discussed below demonstrate that this level of precision is sufficient for the use of the CSIA methodology in petroleum basin studies. We recommend that the end users carefully evaluate the IRMS chromatograms to ensure the separation of compounds is adequate, the baseline is clean, and the integration of individual peaks is consistent throughout the run and from sample to sample.

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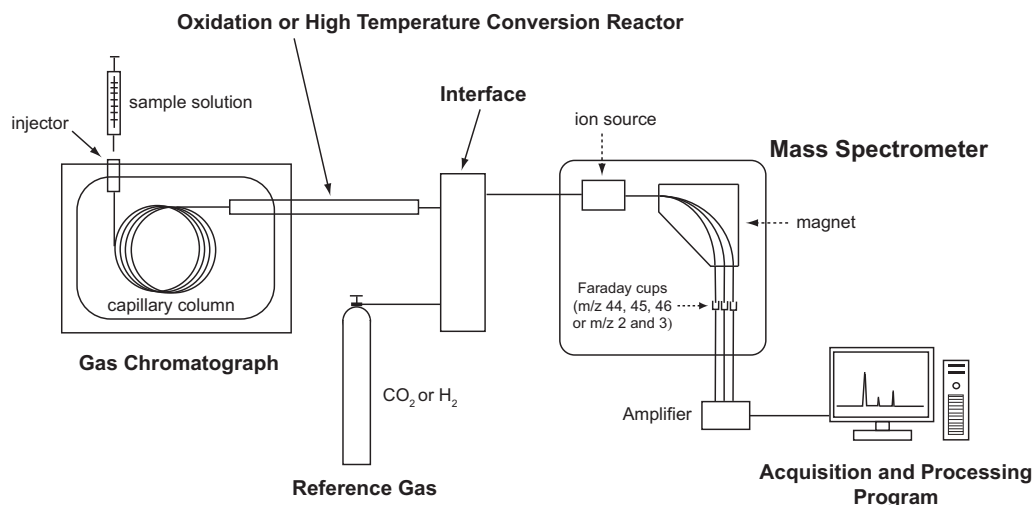


Fig. 1. A simplified schematic of a GC-IRMS system that can be configured for either $\delta^{13}\text{C}$ or $\delta^2\text{H}$ measurements.

Figure 1 shows a simplified schematic of a GC-IRMS system equipped with a combustion reactor for $\delta^{13}\text{C}$ measurements. The *n*-alkane-containing fraction is injected into the GC, where compounds are separated on a capillary column and then converted to CO_2 in the reactor, using a source of O_2 and a catalyst. The CO_2 gas is then transferred into the mass spectrometer, where it is ionized. Faraday cups for m/z 44, 45 and 46 are then used to collect ions corresponding to $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{18}\text{O}^{16}\text{O}$ isotopomers, respectively. (Other isotopomers potentially adding to m/z 45 and 46 are quantitatively insignificant.) The $\delta^{13}\text{C}$ values of individual compounds are calculated relative to either a

reference gas or a co-injected compound with a known isotopic $\delta^{13}\text{C}$ value. Figure 2 shows a typical GC-IRMS chromatogram. (The trace represents m/z 44 corresponding to CO_2 gas generated from the combustion of individual organic compounds.) The chromatogram shows six peaks of reference gas and a homologous series of *n*-alkanes from the saturate fraction of a Nigerian oil sample. The chromatograph displays a relatively low background and, for the majority of the *n*-alkane peaks, an absence of co-elution, which is the key to precise $\delta^{13}\text{C}$ measurements.

The $\delta^2\text{H}$ measurements require a pyrolysis reactor to generate H_2 gas; organic compounds are

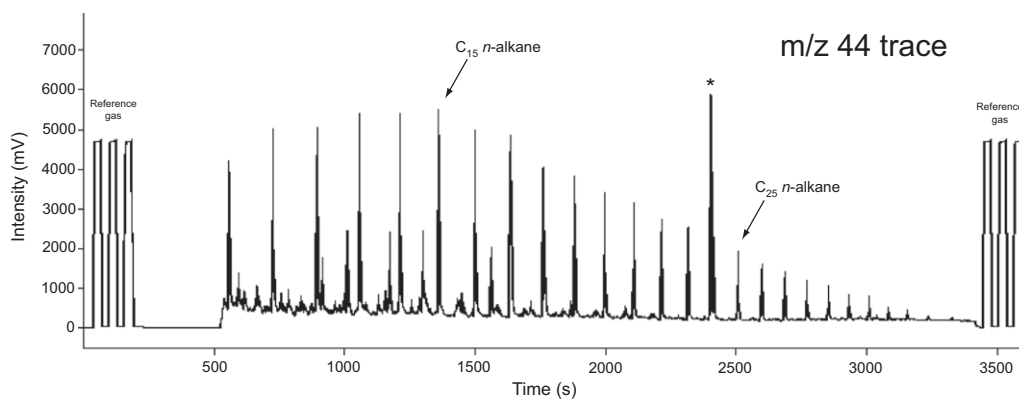


Fig. 2. A chromatogram showing an m/z 44 trace corresponding to CO_2 produced from the combustion of individual compounds (mainly a homologous series of *n*-alkanes) in the saturate fraction of a Nigerian oil. The symbol * designates a contaminant peak co-eluting with *n*- C_{24} alkane. The $\delta^{13}\text{C}$ values can be obtained for each individual peak in a single run.

carried from the GC column through a high-temperature conversion reactor typically set at 1450°C. Reduced H gas is then transferred to the mass spectrometer, with Faraday cups for m/z 2 and 3 corresponding to $^1\text{H}_2$ and $^1\text{H}^2\text{H}$, respectively. Hydrogen isotope measurements require careful monitoring of the effect of protonation reactions (taking place in the ion source) on the $\delta^2\text{H}$ values (Sessions *et al.* 2001a, b). The 'H₃-factor' needs to be determined daily, using a series of reference gas pulses of different magnitudes. Ideally, peaks corresponding to the compounds of interest should have $\delta^2\text{H}$ values similar to that of the reference gas for a reliable H₃-factor correction. Because of the complications when applying H₃-factor correction and peak integration by the acquisition software, $\delta^2\text{H}$ measurements are particularly sensitive to chromatography issues, such as high background and peak co-elution. Therefore, a urea or other adduction step is almost always required.

Modern GC-IRMS systems are typically configured for both $\delta^{13}\text{C}$ and $\delta^2\text{H}$ measurements, with both combustion and high-temperature reactors interfaced to a mass spectrometer with a multi-collector set-up for recording multiple m/z . Therefore, the amount of time for switching between $\delta^{13}\text{C}$ and $\delta^2\text{H}$ measurements is minimized. A single GC-IRMS set-up can be used to generate $\delta^{13}\text{C}$ and/or $\delta^2\text{H}$ compound-specific data on organic compounds of interest, depending on the needs of the organic geochemist. The user has to be aware, however, that even though $\delta^{13}\text{C}$ and/or $\delta^2\text{H}$ compound-specific data can be obtained using the same instrument, C and H isotope measurements require different acquisition modes. Therefore, separate injections are needed for these measurements.

Controls on $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values of *n*-alkanes

Isotope data interpretation relies on understanding the context of the fluid samples, petroleum system and reservoir characteristics. In this review, we highlight the main controls that need to be considered when interpreting compound-specific $\delta^{13}\text{C}$ and $\delta^2\text{H}$ data. Figure 3 provides an overview of the main factors and mechanisms that affect C and H isotopes of sedimentary organic matter (OM) and petroleum fluids.

OM formation

C isotopes. The C isotope composition of extant biomass contributing to sedimentary OM is controlled by the isotopic composition of the C source and several isotope effects associated with C uptake during biosynthesis. Early reviews by Fogel & Cifuentes (1993), Hayes (1993), Farquhar *et al.* (1989) and

Hayes (2001) have identified the most significant factors that control C isotope composition of biosynthates: (a) the isotopic composition of the primary C source; (b) the isotope effect associated with C uptake; (c) the isotope effect due to organism-specific biosynthetic and metabolic pathways; and (d) cellular C budgets. The reviews by Freeman (2001) and Pancost & Pagani (2006) further refined the knowledge of these controls and discussed potential applications of the compound-specific methodology in biogeochemistry and palaeoclimate studies.

One of the most striking features of C isotope composition of *n*-alkanes is the difference between terrestrial- and marine-derived OM. The review by de Leeuw *et al.* (1995) provides a summary of C isotope fractionations characteristic of aquatic and terrestrial plants, and we briefly describe the main observations here.

The $\delta^{13}\text{C}$ values of terrestrial higher plants are controlled by C isotope composition of atmospheric CO₂ and depend significantly on the biosynthetic pathway, i.e. C₃, C₄ or Crassulacean acid metabolism (CAM) pathways (Deines 1980). C₄ terrestrial plants are typically more enriched in ^{13}C (bulk $\delta^{13}\text{C} = -6$ to -23‰ , Schidlowski 1988) in comparison with other terrestrial plants. The diversity of C₃ plants and their diverse ecological zones lead to a large range in $\delta^{13}\text{C}$ values. The C isotope fractionation associated with terrestrial biosynthesis has remained relatively conservative (Arthur *et al.* 1985; Popp *et al.* 1989) over geological time.

In contrast, the $\delta^{13}\text{C}$ values of aquatic plants are controlled mainly by $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC). Aquatic plants are almost exclusively C₃ plants, and their $\delta^{13}\text{C}$ values vary significantly depending on the life form: cyanobacteria (-8 to -24‰); mat communities (-8 to -30‰); photosynthetic bacteria (-8 to -30‰); *Chlorobium* mat community (-23 to -25‰); sulphur-oxidizing bacteria (-30 to -32‰); and methanogenic archaeans (-18 to -38‰) (Schopf 2000). Marine algae are characterized by the following $\delta^{13}\text{C}$ values: green (-9 to -20‰); brown (-11 to -21‰); CO₂-using red algae (-30 to -35‰); and HCO₃-using red algae (-10 to -23‰) (Maberly *et al.* 1992). The $\delta^{13}\text{C}$ values of freshwater macrophytes are between -23 and -31‰ (Keeley & Sandquist 1992). Additionally, the $\delta^{13}\text{C}$ values of aquatic plants are strongly influenced by the level of biological productivity. During the production of marine OM over geological time, there have been major changes in C isotope fractionation (up to 10‰ , Hayes *et al.* 1999).

Because of these known variations, CSIA investigations can be used to compare and contrast short *n*-C₁₇ and *n*-C₁₉ alkanes typically associated with algae, and *n*-C₂₉ and *n*-C₃₁ alkanes derived from higher plants, present in the same sample. C isotope

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CONTROLS ON ISOTOPIC COMPOSITION

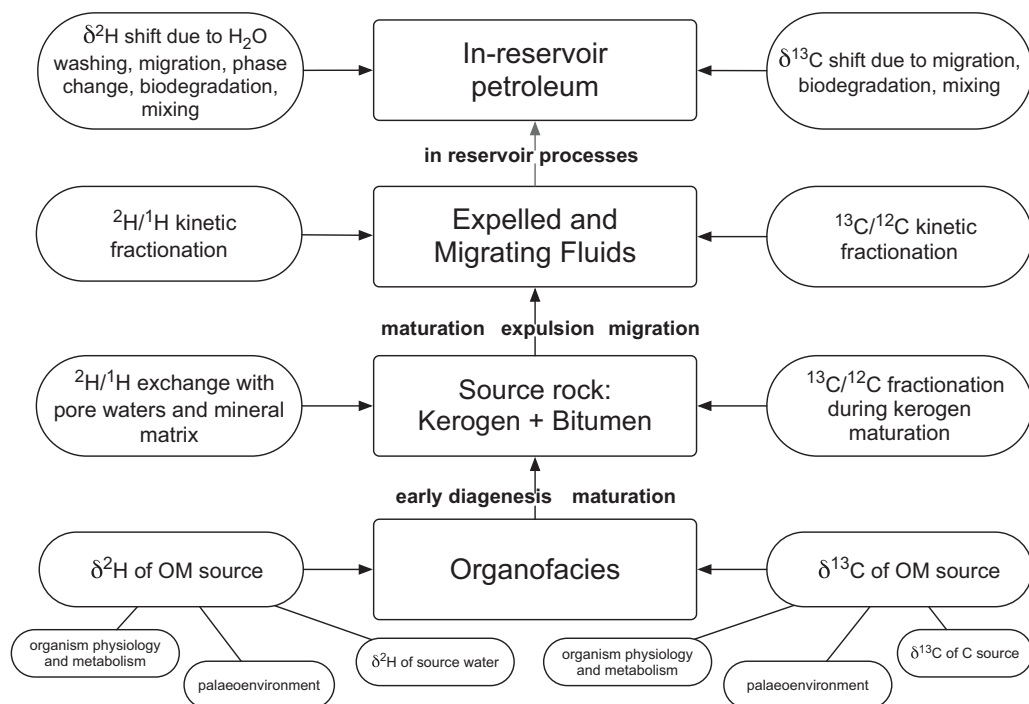


Fig. 3. The main factors that control C and H isotope compositions of *n*-alkyl lipids in the source rock and petroleum reservoir.

composition of individual organic compounds from a single sample can therefore provide information about multiple OM sources that contribute to the total sedimentary OM pool. This approach becomes particularly powerful when different groups of organisms, having specific HMW biomarkers (e.g. terpanes, steranes), contribute to the OM. The pioneering papers by Freeman *et al.* (1990), Hayes *et al.* (1990) and Rieley *et al.* (1991), and subsequent work by Summons *et al.* (1994), Grice *et al.* (1998) and Thiel *et al.* (1999), clearly demonstrated the advantage of CSIA for identifying different sources (e.g. primary producers v. bacterially mediated OM; algal v. higher plant input) of organic compounds within a single OM extract. Applying this approach in petroleum exploration can provide unique insights into different sources of hydrocarbons.

H isotopes. Two recent reviews provide comprehensive coverage of the state of knowledge on the use of compound-specific H isotope composition of organic compounds in biogeochemistry. Sachse *et al.* (2012) provide a detailed discussion of H

isotope systematics as applied to palaeohydrology, and Sessions (2016) evaluates factors that control H isotope composition of hydrocarbons in sedimentary settings. Here we focus on the main controls that have particular relevance to determining H isotope composition of organic compounds in source rock organofacies during OM synthesis. Two key factors play a role at this stage, with regard to both aquatic- and terrestrial-derived organic compounds, including *n*-alkanes: (a) the $^2\text{H}/^1\text{H}$ composition of source water for the organism, and (b) the physiological and biochemical processes involved in fixing water-derived H into organic compounds.

The $\delta^2\text{H}$ values of source water for plants are initially determined by the $^2\text{H}/^1\text{H}$ composition of meteoric precipitation. Additionally, terrestrial plants are subjected to a broad range of physiological and environmental factors that significantly influence H isotope composition of soil and leaf water used by the plant during photosynthesis. While the environmental controls on isotopic composition of precipitation and lacustrine/evaporative settings are generally well understood (Craig & Gordon 1965; Gonfiantini 1986; Rozanski *et al.* 1993), the mechanisms

responsible for controlling the isotopic composition of soil and leaf water, particularly to what extent the signal is incorporated into leaf waxes, are still unclear (Sessions 2016 and references therein). The importance of the latter was also recently highlighted by Tipple *et al.* (2014), Gamarra *et al.* (2016), Oakes & Hren (2016) and the Yale University group (Dirghangi & Pagani 2013; Tipple & Pagani 2013).

Significantly, in spite of the multiple steps and processes involved in the transfer of H from environmental water to plant biochemicals to organofacies to petroleum fluids, the original meteoric water H isotope signal can still have a strong influence on the $\delta^2\text{H}$ values of oils. The broad range of the $\delta^2\text{H}$ values of terrestrially derived oils (Schimmelmann *et al.* 2004), in comparison with those from marine systems, stems from the significantly greater variability of H isotope composition of precipitation over continents than in marine basins. There is also a considerable difference between the $\delta^2\text{H}$ values of environmental water from hypersaline v. marine settings, which could be used to distinguish these depositional environments in petroleum basin studies (Santos Neto & Hayes 1999).

Fractionation of H isotopes during biosynthesis is another major factor controlling the $\delta^2\text{H}$ values of organic compounds. Early studies that demonstrated large ^2H -depletion (at the bulk level) of OM relative to that of environmental water (Schiegl & Vogel 1970; Smith & Epstein 1970; Estep & Hoering 1980) were subsequently confirmed and expanded to include compound-specific H isotope investigations of various classes of lipids (e.g. isoprenoids v. *n*-alkyl lipids) as well as different ecological (marine and lacustrine algae v. terrestrial plants) and trophic (e.g. autotrophs v. heterotrophs) groups (Sessions 2016). Compound-specific H isotope studies have revealed that biosynthetic $^2\text{H}/^1\text{H}$ fractionation can lead to ^2H -depletion relative to source water by 100–250‰, though in rare cases fractionation can lead to values from +200‰ to –450‰ (Sessions 2016). The processes and mechanisms resulting in H isotope fractionation during biosynthesis are multiple and complex. The biochemistry and stable isotope systematics of H fractionation are described in detail by Hayes (2001), Schmidt *et al.* (2003) and Sachse *et al.* (2012). A number of laboratory and field-based studies (e.g. Sessions *et al.* (1999), Chikaraishi *et al.* (2009) and Zhang *et al.* (2009)) have demonstrated the complexity of the processes responsible for H isotope fractionation in lipids and highlighted the need for further research in this rapidly developing area of stable isotope biogeochemistry. We highlight the importance of understanding the complex interplay among the environmental and organism-specific physiological and biochemical processes that control $\delta^2\text{H}$ values of organic compounds synthesized by extant biota.

As indicated above, the reader is referred to Figure 3 for a summary of those processes that control and subsequently influence H (and C) isotope composition of individual organic compounds in a petroleum system. Depending on the geological context and history, highly specific information about the source (e.g. isotopic composition of precipitation, palaeoenvironment and plant physiology) may or may not be preserved in the sedimentary record. The ‘primary’ isotopic signature that would characterize a specific organofacies can be subsequently ‘averaged’, altered or totally erased by a number of diagenetic and post-diagenetic processes in the source rock and reservoir. The reader needs to keep this in perspective and interpret CSIA data with caution.

OM during diagenesis and early maturation

Three types of processes affect OM during diagenesis: (a) selective degradation of biomolecules; (b) preservation, alteration, condensation and vulcanization of sedimentary organic compounds; and (c) generation and incorporation of new organic compounds synthesized by soil/sediment biota. The first two processes have the potential to affect *n*-alkane concentrations and their $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values by either destroying or fractionating C and H isotopes during proto-kerogen formation. The third group of processes, however, results in an addition of isotopically different organic compounds, which, if synthesized in sufficient amounts, could lead to a significant alteration of the original isotope signal.

C isotopes. Lipids are among the most resistant biomolecules and are recalcitrant during diagenesis and early stages of OM maturation. Several early studies have indicated minimal to no diagenetic effects on C isotope composition of this group of biomolecules. Hayes *et al.* (1990) used theoretical considerations and compound-specific $\delta^{13}\text{C}$ data on porphyrins and isoprenoids to argue for a lack of diagenetic effect on these compounds in Cretaceous sediments. Huang *et al.* (1997) reported no significant alteration of the C isotope signature of higher-plant-derived *n*-C₂₃ to *n*-C₃₅ alkanes in a litter-bag experiment. Furthermore, Freeman *et al.* (1994) showed only minor (1.2‰ on average) ^{13}C -depletion of diagenetic polycyclic aromatic hydrocarbons (PAHs) extracted from Eocene sediments.

More recent work, however, has shown that the assumption about the conservative nature of lipid isotopic composition might not necessarily be correct, particularly when considering terrestrial OM sources. Terrestrially derived lipids could potentially undergo significant alteration in the soil and during transport before being deposited in lacustrine or marine depositional settings. On the basis of data

from a litter-bag experiment, Nguyen Tu *et al.* (2004) reported a *c.* 3‰ ^{13}C -enrichment of *n*-alkanes in comparison with those from fresh leaves. An intriguing aspect of this observation is that diagenetic alteration of the primary C isotope signal observed in *n*-alkyl lipids can result from the generation of new biomass by soil microbes, which could also explain a *c.* 4‰ ^{13}C -enrichment of soil *n*-alkanes and other *n*-alkyl compounds reported by Chikaraishi & Naraoka (2006). Clearly, there is a need for further investigation of the potential effect of diagenesis on $\delta^{13}\text{C}$ values of sedimentary *n*-alkyl compounds under different depositional conditions.

H isotopes. As with C isotope systematics, there is uncertainty about the effect of diagenesis on the $\delta^2\text{H}$ values of *n*-alkyl lipids in soil and immature sediments. Yang & Huang (2003) argued for a lack of H isotope effect on *n*-alkyl lipids recovered from fossil leaves of Miocene lacustrine deposits. On the other hand, based on the results of a litter-bag experiment, Zech *et al.* (2011) argued for a significant effect of leaf degradation and seasonality on the $\delta^2\text{H}$ values of *n*-alkane biomarkers. The authors used the argument invoked by Nguyen Tu *et al.* (2011) – i.e. microbial contribution of *n*-alkanes with different H isotope composition. Further work is required to better constrain the effect of early diagenesis and accompanying soil microbiological processes on the H isotope record of sedimentary *n*-alkyl lipids.

The integrated environmental and biochemical H isotope signal acquired by organic compounds during OM formation can also be influenced by the exchange of C-bound H with H atoms in pore/formation H_2O and with H in clay minerals. Early H isotope studies by Yeh & Epstein (1981) and Schoell (1984) conducted on bulk oil have shown minimal exchange of C-bound H over geological timescales. More recent studies (Sessions *et al.* 2004; Wang *et al.* 2009*a, b*, 2013) involving H isotope investigation at the compound-specific level, however, do show that H exchange can take place. A broad range of $\delta^2\text{H}$ values typical of organic compounds from different compound classes (H in *n*-alkyl and aromatic structures, and H bound to and adjacent to heteroatoms), and thus a different degree of susceptibility of these compounds to H exchange reactions (both the extent and rates), provide ample opportunity for investigating the extent of H isotope exchange over geological timescales. Sessions *et al.* (2004), Schimmelmann *et al.* (2006) and Sessions (2016) gave detailed accounts of the processes involved in H exchange reactions in geological settings, for example, (a) mechanisms and rates of $^2\text{H}/^1\text{H}$ exchange, and (b) equilibrium $^2\text{H}/^1\text{H}$ fractionation.

Previous work clearly showed that the CSIA approach is well suited for investigating the

occurrence and the magnitude of H isotope exchange during OM sedimentation and diagenesis. Of particular interest are integrated $\delta^2\text{H}$ analyses of *n*-alkanes and isoprenoids, which can provide information about the extent of diagenetic alteration and the level of OM transformation at the early stages and more advanced stages of OM thermal maturation (Radke *et al.* 2005; Pedentchouk *et al.* 2006; Dawson *et al.* 2007; Kikuchi *et al.* 2010). These authors provided empirical data (supported by theory and experimental kinetic data) that suggest a more conservative nature of *n*-alkanes, in comparison with isoprenoids (pristane and phytane), with regard to H isotope exchange during early OM diagenesis.

OM maturation and petroleum generation

The primary environmental/biological C and H isotope signature of *n*-alkyl lipids is further modified by thermal maturation and hydrocarbon expulsion during petroleum generation. At least two outcomes are possible: first, the original environmental/source information can partially be preserved in petroleum hydrocarbons, and second, new additional information about the extent of stable C and H isotope overprinting can be acquired. Depending on the balance between the two, both types of information can be used in petroleum basin analysis, particularly in OM source and/or OM maturity investigations.

C isotopes. Carbon isotope composition of petroleum hydrocarbons is largely determined by the isotopic composition of the kerogen type (i.e. OM source material) and the depositional environment. Petroleum generation and maturation, however, affects the C isotope properties of kerogen and expelled products. These processes involve C—C bond cleavage, with kinetic effects resulting in the preferential breaking of ^{12}C — ^{12}C bonds relative to ^{13}C — ^{12}C bonds (Peters *et al.* 1981; Lewan 1983). Expelled gas and oil tend to be ^{13}C -depleted in comparison with the residual kerogen by *c.* 2‰. Even though the knowledge of these effects and of the extent of their control on bulk $\delta^{13}\text{C}$ values of petroleum has been used in petroleum exploration since the 1970s (Stahl 1977; Schoell 1984; Sofer 1991), the use of CSIA (Chung *et al.* 1994; Rooney *et al.* 1998; Whiticar & Snowdon 1999; Odden *et al.* 2002) would benefit from further knowledge of the effects of thermal maturation on individual hydrocarbons.

A number of laboratory and field-based studies have demonstrated the effect of thermal maturation on the C isotope composition of various petroleum hydrocarbons (Clayton 1991; Clayton & Bjørøy 1994; Cramer *et al.* 1998; Lorant *et al.* 1998). Theoretical, experimental and field information, however, are rarely integrated to derive a mechanistic

understanding of the processes that control C isotope composition of individual organic compounds. Tang *et al.* (2005) were among the first to not only link theoretical and empirical laboratory-based investigation of C isotope systematics but also integrate it with the CSIA of H (see the discussion below). On the basis of the quantitative kinetic model and controlled

closed-system pyrolysis experiment, Tang *et al.* (2005) identified a *c.* 4‰ increase in the $\delta^{13}\text{C}$ values from pyrolysate extracts of samples with $R_o = 1.5\%$ v. immature samples (Fig. 4). In contrast to the observations with regard to H isotopes (see the following *H isotopes* section), there was no clear link between ^{13}C -enrichment and *n*-alkane chain length.

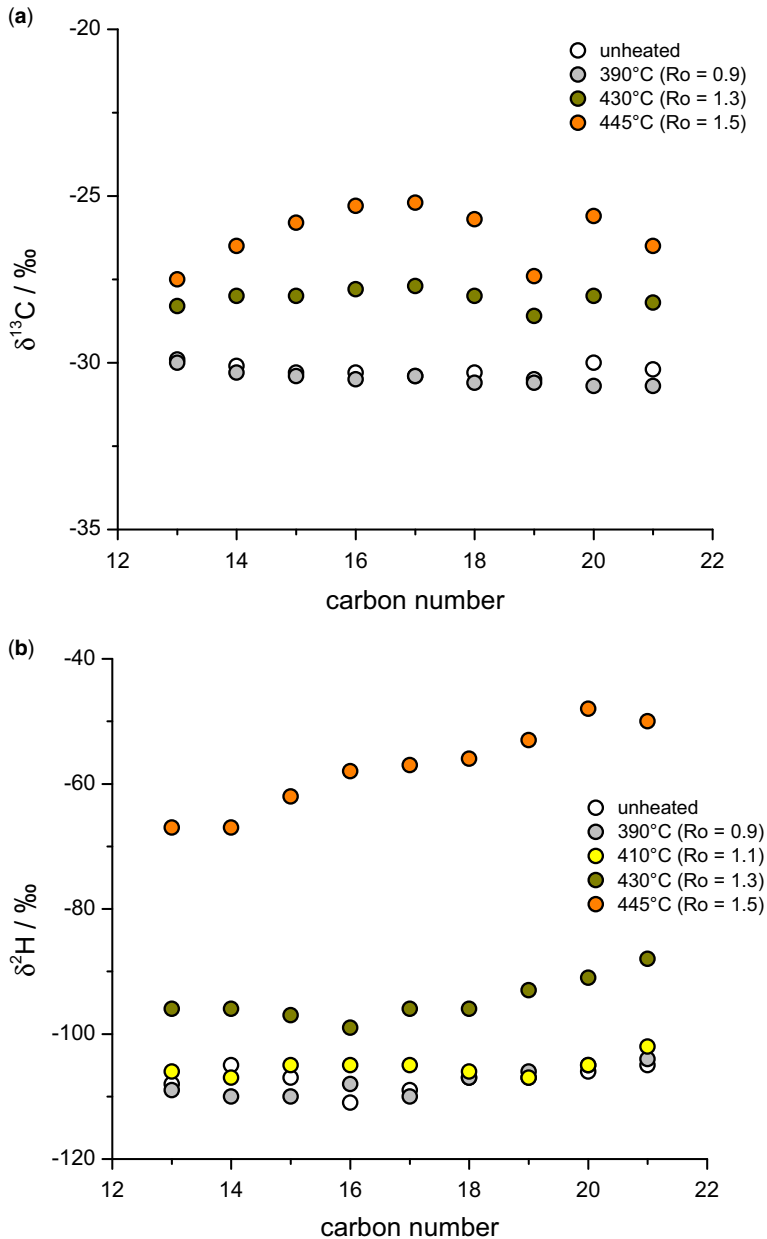


Fig. 4. (a) C and (b) H isotope compositions of *n*-C₁₃ to *n*-C₂₁ alkanes from North Sea oil used for pyrolysis experiment. Redrawn from Tang *et al.* (2005).

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Further studies are needed to fully understand these processes and effects.

H isotopes. Depending on the structure and the amount of time available for equilibrium $^2\text{H}/^1\text{H}$ fractionation during diagenesis, an organic molecule can provide an isotopic record of OM source/environment and the extent of diagenetic alteration during OM deposition. From a petroleum geochemist's perspective, however, the key processes and reactions start at the level of OM maturation when kerogen cracking, bitumen formation and petroleum fluid expulsion occur. During these processes, a C-bound H will undergo additional $^2\text{H}/^1\text{H}$ fractionation as a result of kinetic isotope effects.

Several field-based studies have shown that higher-maturity oils are typically characterized by higher $\delta^2\text{H}$ values (Li *et al.* 2001; Schimmelmann *et al.* 2004; Dawson *et al.* 2005). This observation would imply that processes leading to ^2H -enrichment of the residual fraction (kerogen, remaining oil) might be similar to those that lead to ^{13}C -enrichment of the remaining products during cracking. The effects of cracking on the $\delta^2\text{H}$ values of the products and remaining fraction, however, are difficult to separate from those that could result from equilibrium H exchange with formation H_2O . Therefore, tightly controlled laboratory investigations provide the best source of information with regard to the effect of cracking during oil generation. To our knowledge, the study by Tang *et al.* (2005) is unique in providing a thorough investigation of the kinetic isotope effects on CSIA $\delta^2\text{H}$ values, using the combined approach of theoretical calculations and heating experiments. The study used a simple kinetic model of oil cracking for qualitative prediction of ^2H -enrichment of *n*-alkanes of different chain lengths at different thermal maturities (Fig. 4). There was an increase in $\delta^2\text{H}$ values of up to 60‰ at 445°C. The effect was more noticeable for *n*-alkanes with longer chain lengths. The main outcome of this study is that the kinetic model can be used for qualitative prediction of $^2\text{H}/^1\text{H}$ fractionation during kerogen/oil cracking in natural settings. The kinetic isotope effects are likely to be significant at thermal maturities of $\text{Ro} > 1.5$.

Petroleum fluid migration

Isotope effects of fluid migration are different for (a) primary migration, i.e. the process of expulsion of generated petroleum from source rock, and (b) secondary migration, i.e. the process of fluid movement following expulsion. Partition coefficients govern the rate at which compound classes are released, but the expelled fluid composition will approach the composition of the generated petroleum (under steady-state conditions). However, it appears that

solution/dissolution processes do not discriminate isotopically for mid- and long-chain *n*-alkanes, and therefore the isotopic composition of expelled fluids should represent the generated fluid and source rock (Liao & Geng 2009).

There are many published accounts using petroleum geochemistry and stable isotope composition of gases to help assess migration issues (e.g. Seifert & Moldovan 1986; Curiale & Bromley 1996; Zhang *et al.* 2013) but few published contributions using CSIA of high-molecular-weight (HMW) alkanes to assess migration. Li *et al.* (2001) compared two oils from the same genetic source in Western Canada, with one proximal to the source rock (Pembina field) and one that had migrated 150 km updip (Joarcum field) (Creaney *et al.* 1994; Larter *et al.* 1996). Despite differences in migration, the $\delta^2\text{H}$ composition of the individual alkanes does not appear to have been affected, varying by only 4–8‰. The *n*-hexane/benzene ratio may have increased only about six-fold in the Joarcum field oils, which correlates to a relatively small volume of exchange with water along the migration route and may provide an explanation for the lack of $\delta^2\text{H}$ variation.

The use of gasoline-range hydrocarbons along with other markers of secondary migration, such as quinolines (Larter & Aplin 1995; Li *et al.* 2001), can create a more detailed picture of migration (e.g. distance and extent) and can help develop an understanding of the utility of the $\delta^2\text{H}$ of alkanes for correlations or as a sensitive tool for assessing the impact of migration. However, additional published case studies are needed.

Other in-reservoir processes

In-reservoir processes, such as evaporative fractionation (including gas washing), deasphalting, gravity separation, water washing, biodegradation and thermochemical sulphate reduction lead to secondary alteration of petroleum during and after emplacement (Wenger *et al.* 2002). To varying degrees, compound-specific C and H isotope composition of hydrocarbons, including straight and branched moieties in the C_5 – C_{30} range, may be influenced by, and therefore useful in understanding, in-reservoir processes.

Evaporative fractionation. Thompson (1987, 1988) originally defined evaporative fractionation as a multistep process, involving the addition of gas to an oil accumulation followed by a phase separation as the gas escapes, carrying additional components based on vapour-liquid partition coefficients (also referred to as gas washing – e.g. van Graas *et al.* 2000). The remaining liquid is enriched typically with higher-molecular-weight compounds. Evaporative fractionation may also occur from loss

of solution gas or gas cap (Masterson *et al.* 2001). Variations in the composition of *n*-alkanes and C_7 components are used to compare oils and determine and possibly quantify the impact of evaporative fractionation on fluid properties, which can also be used to determine the history of the petroleum system (Masterson *et al.* 2001; Losh *et al.* 2002*a, b*; Thompson 2010; Murillo *et al.* 2016). Experimental separation of liquid and gas phases shows the $\delta^{13}C$ of C_6 , C_7 and C_8 *n*-alkanes are identical in both the gas phase and the original oil. However, *n*- C_9 through *n*- C_{14} as well as 1-methylcyclopentane show a 1‰ ^{13}C -depletion in the gas phase, suggesting that the isotopic effect of in-reservoir phase partitioning is very minor (Carpentier *et al.* 1996). Therefore, in systems where evaporative fractionation has occurred, $\delta^{13}C$ values are conserved, and can therefore still be used in evaluating correlations, charge, etc.

Biodegradation. Subsurface biodegradation leads to a well-characterized sequence of compound class losses as microbial groups with anaerobic hydrocarbon-degrading enzymes (Head *et al.* 2003; Aitken *et al.* 2004; Bian *et al.* 2015) metabolize hydrocarbons, leading to generation of acidic compounds and loss of hydrocarbons in a characteristic sequence (*n*-alkanes > monocyclic alkanes > alkyl benzenes > isoprenoid alkanes > alkyl naphthalenes > bicyclic alkanes > steranes > hopanes) (Peters *et al.* 2005). Biodegradation preferentially removes ^{12}C and 1H , leaving ^{13}C - and 2H -enriched organic compounds (Stahl 1980; Clayton 1991; Odden *et al.* 2002; Jones *et al.* 2008). The impact of biodegradation on whole oil $\delta^{13}C$ values is minor, but, with increasing levels of biodegradation – as evidenced by the disappearance of *n*-alkanes (e.g. Marcano *et al.* 2013) – the $\delta^{13}C$ values of organic compounds in the saturate fraction will increase.

Analysis of a suite of seven Liaohe basin oils, from pristine to heavily biodegraded, showed that the $\delta^{13}C$ values are relatively conservative even at severe levels of biodegradation for HMW (C_{19+}) compounds (Sun *et al.* 2005). However, low-molecular-weight (LMW) compounds can show up to 4‰ ^{13}C -enrichment relative to unaltered oil from the same system. Only the LMW *n*-alkane compounds are significantly affected isotopically during progressive biodegradation. This also means that the HMW *n*-alkanes should still be well correlated with source rock $\delta^{13}C$ even in highly biodegraded reservoirs, assuming the compounds are still present and that no other significant processes have influenced the original values.

Experiments have also been conducted (Vieth & Wilkes 2006) on the CSIA of gasoline-range hydrocarbons in the Gullfaks field (North Sea) to assess how biodegradation changes the $\delta^{13}C$ composition

of LMW hydrocarbons. Butane through nonane from biodegraded oil were 3–7‰ ^{13}C -enriched, but toluene or cyclohexanes were not. (Surprisingly, toluene was not degraded at all in the Gullfaks oils, which led the authors to suggest that the microbial community in this particular field were not capable of degrading toluene.) The experimentally derived isotopic fractionation factor for *n*-hexane was used to apply the Rayleigh equation to data from the Gullfaks field to quantify hydrocarbons that had been lost to biodegradation (Vieth & Wilkes 2006; Wilkes *et al.* 2008).

Hydrogen isotope compositions appear to be less conservative as a function of biodegradation; variations of up to 35‰ have been observed (Sun *et al.* 2005), and therefore stable H isotopes are potentially useful in understanding and possibly quantifying the impact of biodegradation.

Thermochemical sulphate reduction. As thermochemical sulphate reduction (TSR) destroys organic compounds, the remaining organic compounds become ^{13}C -enriched (Rooney 1995; Whiticar & Snowdon 1999). There are also compositional changes as TSR oxidizes petroleum constituents to CO_2 through a range of polar, volatile and non-volatile intermediates (Walters *et al.* 2015). Therefore, the combination of compositional changes and the CSIA of gasoline-range hydrocarbons is a sensitive method to discriminate fluids influenced by TSR. Rooney (1995), as described in Peters & Fowler (2002), showed a 22‰ increase in the $\delta^{13}C$ of the *n*-alkane and branched hydrocarbons in TSR-affected oils, compared to a 2–3‰ increase in oils influenced only by increased thermal maturity. Other compounds, such as toluene, showed much smaller shifts in $\delta^{13}C$. Routine analysis of the C (and sulphur) isotope composition of the TSR-intermediates could potentially be used to create additional correlation and classification tools.

Applications of compound-specific stable isotopes of *n*-alkanes

The application of compound-specific stable isotopes of *n*-alkanes and related compounds can contribute to an understanding of the various aspects of fluid migration history, in-reservoir processes, and provide insights into oil–source and oil–oil correlations. Caveats to the applications are the same as for any reservoir fluid study. The user needs to (a) ensure that the samples are representative, (b) acknowledge any analytical uncertainties, and (c) understand that many complex processes – that have occurred over geological timescales – can change fluid properties.

Integrating CSIA with other geochemical methodologies for reservoir studies has several

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advantages. CSIA provides more resolution than bulk methods. It separates HMW and LMW compounds, which are influenced differently by different processes, and facilitates a direct comparison of individual compounds (*n*-alkanes and other biomarkers) from different sources (e.g. kerogen pyrolysates, oils, source rock extracts, etc.). CSIA may also give many additional components for resolving similarities and differences for correlation purposes. Ultimately, CSIA contributes to a more complete understanding of petroleum systems, within the context of other geological and fluid properties.

Case studies

Here we review a number of regionally organized case studies that show applications of the C and H isotopic compositions of *n*-alkanes in support of petroleum exploration and development activities. Figure 5 shows specific applications of CSIA as demonstrated by these case studies. A review of the full history of each basin is well beyond the scope of this contribution; our goal is to highlight cases in which the CSIA of *n*-alkanes have improved our understanding of fluid histories and properties.

Europe

Austria (application in OM source, OM maturity and charge/migration investigations). In the Alpine foreland basin, a variety of Oligocene source rocks in

the Schöneck, Dynow and Eggerding formations, with shaly to marly lithologies, varying laterally and vertically from west to east, generated and expelled petroleum to two main reservoirs – sandstones from the Cretaceous and Eocene. In a study of the C and H isotopic compositions of the *n*-alkanes from both source rock and reservoir fluids, Bechtel *et al.* (2013) found ^{13}C -depletion varied from west to east by *c.* 2–3‰ for $\delta^{13}\text{C}$ and *c.* 30‰ for $\delta^2\text{H}$. The differences in fluid CSIA reflect the changing contribution of source rocks, with greater contribution from the ^{13}C -depleted unit ‘C’ of the Schöneck Formation towards the east, where that formation also thickens (Gratzer *et al.* 2011; Bechtel *et al.* 2012). The pattern of $\delta^{13}\text{C}$ values in the *n*-alkanes is also consistent with changing source rock properties, with $\delta^{13}\text{C}$ values decreasing to *n*-C₂₁ and then increasing from *n*-C₂₁ to *n*-C₃₁, which we illustrate in a cross plot of the C₁₉ and C₂₆ average $\delta^{13}\text{C}$ values for fluids and source rock (Fig. 6). The variations in $\delta^2\text{H}$ of *n*-alkanes also reflect source variations and are attributed to the ^2H -depletion in the more brackish, less marine depositional environment in unit ‘C’. The $\delta^2\text{H}$ values increase with *n*-alkane chain length and also increase with increasing maturity, providing additional evidence for maturity variations. The study also used benzocarbazole ratios as migration parameters, reflecting useful integration of additional molecular properties to further resolve charge history. This and related studies show that the Alpine foreland

SED. BASIN APPLICATION	Tarim	Niger	Barents	North Sea	WCSB	Sirte	West Sak	Austria	Potwar	Perth	Liaoh
OM Source											
OM Maturity											
Charge/Migration											
Oil-Oil Correlation											
Oil-Source Rock Correlation											
Biodegradation											

Fig. 5. Simplified table showing the specific applications of CSIA of *n*-alkanes from a number of case studies. Studies by Bjorøy *et al.* (1994) and Odden *et al.* (2002) in the North Sea were among the first to use CSIA data for correlation and then for additional follow-up investigations. Studies in other basins (Tarim, Niger, Barents and Western Canada Sedimentary) are further excellent examples of integrated geochemical basin analysis (Li *et al.* 2001, 2010; Samuel *et al.* 2009; Jia *et al.* 2010, 2013; He *et al.* 2012; Murillo *et al.* 2016). Other basin studies are examples of investigations that have focused on particular applications, such as charge evaluation (West Sak, Masterson *et al.* 2001), source rock correlation (Austria, Bechtel *et al.* 2012; Sirte Basin, Aboglia *et al.* 2010), and the interplay of maturity and in-reservoir processes (Perth Basin, Dawson *et al.* 2005; Potwar Basin, Asif *et al.* 2009; Liaoh Basin, Sun *et al.* 2005).

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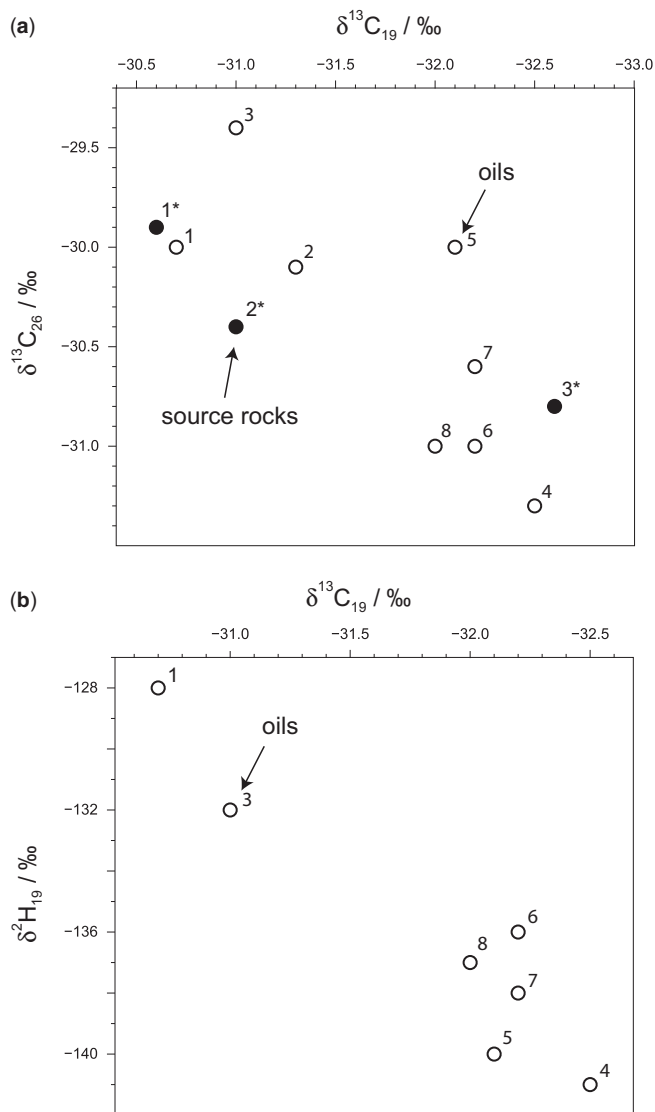


Fig. 6. Bechtel *et al.* (2013) provide average CSIA values from *n*-alkanes and isoprenoids in oils from the Molasse Basin, reflecting the west–east trend. We replotted these averages in cross plots of $\delta^{13}\text{C}$ of C_{19} alkane and (a) $\delta^{13}\text{C}$ of the C_{26} alkane, including three regional source rocks, and (b) $\delta^2\text{H}$ of C_{19} alkane. Labels on the graphs correspond to those used in Bechtel *et al.* (2013). Oil fields: 1 – K, Ktg, MS, R, St; 2 – Li, Sch, W, P; 3 – Trat; 4 – Gruenau (Alpine subthrust); 5 – Mdf, Sat, Eb, Ob, Ra, Sths, Wels; 6 – V. Hier; 7 – BH, Ke, En, Pi; 8 – Sier, Wir. Source rocks 1* – Obhf Schöneck Fm; 2* – Mlrt (Rupelian); 3 – Molln Schöneck Fm. This study illustrates the identification of patterns and correlations possible when comparing source rock and oils, and utilizing dual ($\delta^{13}\text{C}$ and $\delta^2\text{H}$) isotope systems.

basin provides an excellent natural laboratory to study the impact of source and maturity variations as well as migration on compound-specific isotope compositions and to further develop these tools in petroleum exploration. Applications of CSIA should also extend to other basins where lateral and vertical

variations in source rock are important (e.g. the Bakken, Eagle Ford).

Barents Sea (integrated basin analysis). Murillo *et al.* (2016) used a full suite of geochemical analyses on 16 fluid samples (from 15 wells) and ten source

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rock extracts to investigate questions on the Barents Sea Hammerfest Basin petroleum system, including source–oil correlation, oil–oil correlation, assessment of maturation and in-reservoir processes. In this case, $\delta^{13}\text{C}$ of *n*-alkanes ($>\text{C}_{15}$) were valuable for oil–source rock correlation and even quantification of the contribution from different source rocks. This proved especially useful for differentiating Triassic and Jurassic source contributions. For example, oil families III and IV are not distinguishable on the basis of $\delta^{13}\text{C}$ alone. However, Family II is obviously different from Families I, III and IV. Additionally, Family I oils have unique pristane and phytane $\delta^{13}\text{C}$ values, in comparison with *n*-alkane $\delta^{13}\text{C}$ values in the same oils. The oil families have the following characteristics:

Family I: $\text{C}_{10}\text{--}\text{C}_{14}$, -28 to -30% ; C_{15+} , -30 to -34% ; pristane and phytane, -31 to -32% ; branched alkanes, slight ^{12}C -enrichment with increasing molecular weight;

Family II: $\text{C}_{10}\text{--}\text{C}_{14}$, -31 to -33% ; C_{15+} , -33 to -36% ; pristane and phytane, -32.5 to -33.5% ;

Family III: $\text{C}_{10}\text{--}\text{C}_{14}$, -29 to -31% ; pristane and phytane, -30 to -31% ; branched alkanes, -28 to -29% ; cyclic alkanes, -25 to -29% ;

Family IV: $\text{C}_{10}\text{--}\text{C}_{14}$, -28 to -31% ; pristane and phytane, -32 to -33% ; branched alkanes, -28 to -30% .

The source rock extract $\delta^{13}\text{C}$ values are differentiating as well. The Triassic Kobbe Formation values range from -32 to -35% . The Upper Jurassic Hekkingen Formation ($>\text{C}_{20}$) *n*-alkanes have $\delta^{13}\text{C}$ values ranging from -28 to -31% – a 4–6% difference compared with the Triassic Kobbe Formation. These variations enable source assessment for the different oil families; the Triassic is the likely source for Families I, II and IV, while the Jurassic contribution is higher in Family III oils. A mixing model was applied to calculate more precisely the contributions of the different sources to the oils. This type of analysis forms a useful baseline to be used in future exploration, and also when assessing changes in production over time, depending on the field and reservoir properties.

Hydrogen and carbon CSIA of *n*-alkanes also provide information about the extent of thermal maturation and other physical processes. Oils show increasing $\delta^2\text{H}$ values with increasing C number, reflecting thermal maturation. Condensates also show the same trend, but with even higher $\delta^2\text{H}$ values, showing the impact of evaporative fractionation revealed as greater ^2H -enrichment with increasing C number (Murillo *et al.* 2016). As one of the most complete and comprehensive recently published studies utilizing *n*-alkane CSIA in the context of other fluid properties, Murillo *et al.* (2016) provide an excellent case study on how to use CSIA to

improve the understanding of the source origin of oil families, and how this methodology can contribute to long-term field exploration, development planning, and potentially production monitoring.

He *et al.* (2012) performed another regional study of the Barents region, focusing on the Timan–Pechora Basin. The study consisted of 32 oil samples from 25 fields and also included two surface samples from the island of Spitsbergen. The samples were allocated into six families (using a chemometric approach with 20 biomarker parameters and two isotopic parameters) and were inferred to correlate with the respective source rocks (Devonian marl, Devonian carbonate, Triassic/Devonian carbonate, Triassic, Lower/Middle Jurassic and Upper Jurassic). CSIA of *n*-alkanes was used on a subset of presumed end-member and mixed samples, to better identify source rocks for the mixed oil families. The Upper Jurassic family (V), the Triassic family (I) and the two Devonian families (marl, II and carbonate, III) tend to have values that bracket those of the mixed Triassic/Devonian carbonate (IV, *c.* -29 to -32%). The Upper Jurassic family (V) has the most ^{13}C -enriched values (*c.* -27 to -29%), and the Devonian families (II, III) are generally the most ^{13}C -depleted (-33 to -34%). Therefore, again the additional information provided uniquely by CSIA of *n*-alkanes supports and refines the oil–source rock correlations and strengthens the understanding of the regional petroleum system.

Asia and Australasia

Potwar Basin (applications in source rock depositional environment, source rock–oil relationships, oil–oil correlation, and biodegradation investigations). The Potwar Basin contains sedimentologically diverse Precambrian through Tertiary units and is structurally complex because of the intense tectonism associated with the Tertiary Himalayan Orogeny. There are multiple reservoir targets, including Cambrian, Jurassic and Eocene formations, with fluids ranging from 16° to 49° API gravity. Organic-rich potential source rocks include Precambrian evaporite/carbonate/clastic facies and Permian shale and carbonate units (Asif *et al.* 2011).

The petroleum geochemistry of the Potwar Basin was examined using 18 crude oil samples, biomarkers and $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of whole oil, saturates and aromatics. On the basis of OM source, Asif *et al.* (2011) identified three distinct oil groups: a terrigenous-origin oil family, and two marine oil families, differentiated by suboxic and oxic depositional conditions.

A more in-depth study, including the $\delta^2\text{H}$ CSIA on *n*-alkanes, pristane and phytane, was used to assess the level of biodegradation in eight crude oils that ranged in gravity from 16° to 41° API (Asif *et al.* 2009). The $\Delta\delta^2\text{H}$ ($\delta^2\text{H}$ isoprenoids $-\delta^2\text{H}$ *n*-alkanes) has a positive correlation with

API gravity ($\Delta\delta^2\text{H}$ decreasing with decreasing API gravity), showing preferential ^2H -enrichment in *n*-alkanes. The $\Delta\delta^2\text{H}$, therefore, provides a useful tool for classifying and differentiating oil families and also for possibly assessing low levels of biodegradation.

Taken together, these studies contribute to a deeper understanding of potential source rocks, oil classification and in-reservoir processes in the Potwar petroleum system.

Perth Basin (application in OM maturity investigation). This study used $^2\text{H}/^1\text{H}$ measurements: source rock and oil molecular properties were compared to show the relationship between thermal maturity $\delta^2\text{H}$ values of sedimentary hydrocarbons, and the $\delta^2\text{H}$ values of *n*-alkanes and acyclic isoprenoids. Dawson *et al.* (2005) studied nine samples, representing immature to mature OM, collected from the Triassic Hovea Formation, onshore in the northern Perth Basin. They compared the $\delta^2\text{H}$ of *n*-alkanes and isoprenoids with data from two crude oils, which are thought to be sourced from the organic-rich sapropels in the same formation. Generally, with increasing maturity, *n*-alkane $\delta^2\text{H}$ values remained consistent except in the highest maturity samples, where a 42% increase in $\delta^2\text{H}$ was observed. Pristane and phytane, however, became ^2H -enriched even at lower levels of maturity. The authors suggest that the H isotopic exchange mechanism (exchange at chiral C) is more rapid in isoprenoids (e.g. compounds containing tertiary C centres). Therefore, $\delta^2\text{H}$ values of pristane and phytane are well correlated with vitrinite reflectance equivalent values and maturity values derived from the terpane biomarker C_{27} 18 α (H)-22,29,30-trinorhopane to C_{27} 17 α (H)-22,29,30-trinorhopane (Ts/Tm) ratio. The magnitude of the offset between the $\delta^2\text{H}$ values of *n*-alkanes and the $\delta^2\text{H}$ values of isoprenoids suggests that the $^2\text{H}/^1\text{H}$ content of these compounds could be used in determining the thermal maturity of a source rock. Relatively simple targeted studies of $\delta^2\text{H}$ of pristane and phytane from a wide variety of basins would expand on the observations from this study and be a useful addition to standard molecular geochemistry studies.

Tarim Basin (integrated basin analysis). The Tarim Basin is one of the most important petroleum basins in China and has been extensively reported in the literature. A full review is well beyond the scope of this contribution, and we focus on a few examples in which CSIA has provided important insights and utility to petroleum exploration in the Tarim Basin, especially source correlation and charge history, connectivity and in-reservoir alterations.

Briefly, the Tarim Basin is large and geologically complex; fluid types range from light to heavy,

normal to waxy, early mature to secondarily cracked to gas. A range of in-reservoir processes related to multiple charge events and biodegradation also influence fluid properties. Large variations in stable C isotopic composition of *n*-alkanes in fluid compositions reflect mixing from many distinct source rocks (Jia *et al.* 2010; Li *et al.* 2010). More recently, using both C and H CSIA of *n*-alkanes, Jia *et al.* (2013) untangled complex source contributions in the Tabei and Tazhong uplift areas and ultimately distinguished oils from the same source rock at different maturity levels as well as contributions from different sources also at different maturity levels (Jia *et al.* 2013).

On the basis of biomarker and isotopic properties, the Tabei and Tazhong basin oils fall into two groups. Most oils fall into Group I, which have relatively low $\delta^{13}\text{C}$ values (–31.0 to –34.5‰) and *n*-alkane $\delta^2\text{H}$ values from –75 to –110‰. (Group II includes only two samples of heavy oil, with $\delta^{13}\text{C}$ values of –29 and –30‰, and $\delta^2\text{H}$ values of –142 to –145‰.) The $\delta^{13}\text{C}$ values of *n*-alkanes generally correlate with the biomarker maturity indices, and this positive correlation shows maturity is controlling, at least in part, the isotopic composition of the *n*-alkanes. Because the impact on $\delta^2\text{H}$ is stronger during thermal maturation (e.g. Tang *et al.* 2005), the relative ^2H -enrichment of *n*-alkanes is seen as the result of kinetic fractionation during oil maturation.

The fluids of the Tazhong Basin show much greater variation than those from Tabei, with light and waxy oils displaying a larger $\delta^{13}\text{C}$ range, from –31 to –36‰. In addition, there are greater variations with respect to molecular weight – the shorter-chain compounds (C_{10} – C_{16}) are ^{13}C -depleted, while the HMW compounds (C_{16+}) are slightly ^{13}C -enriched. These patterns, along with distinctive biomarker correlations, led the authors to propose several scenarios for source and charge history. One suite of oils also contains 25 nor-hopanes and features similar, relatively low $\delta^{13}\text{C}$ values (<–33.5‰) in the saturate fraction *n*-alkanes and in the asphaltene-released *n*-alkanes. Moreover, the asphaltenes do not contain biodegraded residues (Jia *et al.* 2008). This led to the conclusion that a biodegraded fluid was charged later by a non-biodegraded fluid. Thus $\delta^{13}\text{C}$ values of the *n*-alkanes helped reveal both charge history and in-reservoir biodegradation of the earlier charge.

Another suite of oils shows mixing of oil from one source but at different maturities. In this example, cross plots of maturity parameters and average $\delta^{13}\text{C}$ of *n*-alkanes were used to propose a likely mixing scenario in which fluids generated from a Middle Ordovician source filled reservoirs during Cretaceous through Tertiary times. To further explain the more complex fluid properties in the Tazhong Basin, the authors used both biomarkers and $\delta^2\text{H}/\delta^{13}\text{C}$ of *n*-alkanes to show possible

mixing of oils from different sources, namely the Cambro-Ordovician and the Middle–Upper Ordovician.

As Murillo *et al.* (2016) have demonstrated in the Barents area, the Tarim Basin studies also show that the CSIA of *n*-alkanes provides evidence of variable fluid histories in source, maturity, charge history and reservoir processes, which can be integrated in petroleum systems concepts and models to aid field development planning and future exploration efforts.

Africa

North Africa (applications in OM source and oil–source rock correlation investigations). Source age and family correlations were also made in the Sirte Basin petroleum system using biomarkers and $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of *n*-alkanes. Aboglia *et al.* (2010) analysed 24 wellhead-sampled oils in seven areas of the Sirte Basin, across a roughly 120-km north–south transect, representing six different reservoir formations, from Precambrian to Eocene age. Two oil families were defined based on maturity, as derived from several parameters: Family A is of higher maturity, with source rock possibly showing a higher percentage of terrigenous component; Family B is less mature, with dominantly marine source markers. The authors found that the *n*-alkanes in Family A have higher $\delta^{13}\text{C}$ values, which is consistent with a terrigenous source rock origin and a higher level of thermal maturity. Additional evidence for the more extensive thermal maturity of Family A oils came from higher $\delta^2\text{H}$ values of pristane and phytane in these oils in comparison with those from Family B oils. In another study in North Africa, Peters & Creaney (2004) found substantial variations in the $\delta^{13}\text{C}$ in *n*-C₁₇, *n*-C₁₈, and pristane and phytane, that enabled them to distinguish between Silurian- and Devonian-sourced oils in Algeria. These observations are therefore age-diagnostic, and can also be useful markers for long-term production monitoring as well as in exploration.

Niger Delta (integrated basin analysis). A study by Samuel *et al.* (2009) reassessed the evidence for petroleum charge from multiple source rocks in the Niger Delta petroleum system. They studied 58 crude oil samples from both shallow and deepwater fields and core samples from the Late Cretaceous Araromi Formation in SW Nigeria. The CSIA of *n*-alkanes proved useful in distinguishing the influence of different source facies on present-day reservoir fluid distributions. From alkane and biomarker distributions, three oil families were deduced on the basis of source (terrigenous, mixed marine–terrigenous and dominant marine). Biomarker distributions including C₃₀ tetracyclic polyprenoids (TPPs) were used to calculate the TPP proxy (Holba *et al.* 2003), oleanane indices (Eneogwe & Ekundayo

2003; Matava *et al.* 2003), and the tricyclic terpane index (TTTI) to discriminate between the marine (mostly western deepwater oils) and terrigenous source rocks, and also to suggest mixing of lacustrine and terrestrial-derived oils.

Generally, however, the *n*-alkanes in the western deepwater and some western shallow-water oils show a nearly flat trend of *n*-alkane $\delta^{13}\text{C}$ values, ranging from -24‰ to -30‰ , with little variation with increasing C number. Other western shallow-water oils also have a relatively flat trend of $\delta^{13}\text{C}$ values with increasing C number but are also more ^{13}C -enriched than the western deepwater oils, especially in the *n*-C₁₂–C₁₆ range. Samuel *et al.* (2009) attributed these values to a marine source with uniform C isotopic composition during deposition (e.g. a well-mixed, buffered carbonate system). In contrast, the rest of the shallow-water samples (central, east and west) all demonstrate decreasing $\delta^{13}\text{C}$ values with increasing C number; values range from -23 to -28‰ at *n*-C₁₂, and decrease to values between -28 and -34‰ at *n*-C₃₀. (*n*-C₂₇ is also systematically ^{13}C -depleted by *c.* 0.5–1.5‰). ^{13}C -depletion with increasing C number is observed in many other basins around the world, notably the Tertiary systems of Australasia (Murray *et al.* 1994; Wilhelms *et al.* 1994) and south Texas (Bjørøy *et al.* 1991).

The authors found no clear correlation between maturity and the $\delta^{13}\text{C}$ values. Therefore, CSIA of *n*-alkanes appears to reflect mainly source kerogen isotopic properties. However, available source rock samples were limited in this study and only the Araromi formation samples from the Dahomey Basin were extracted and compared with the oils in this study. The Araromi formation is the youngest unit in the Late Cretaceous Abeokuta Group, with TOC ranging from *c.* 0.5% to 5% and hydrogen index (HI) values of 0 to *c.* 400 mg HC g⁻¹ TOC. The biomarker and *n*-alkane distributions, as well as the C isotopic composition of the *n*-alkanes, proved to be a poor match to the studied oils.

The geochemical complexities of the Niger Basin petroleum system are beyond the scope of this contribution and/or are also largely unpublished, but the inclusion of CSIA-alkane analysis provides an additional tool for comparing and separating oil families and excluding specific source rock contributions.

North America

West Sak–Kuparuk–Prudhoe (application in charge evaluation investigation). C isotopes of gasoline-range hydrocarbons were used to understand the source of primary and secondary charge, as well as in-reservoir processes and their impact on fluid properties, and ultimately they aided field development planning in the West Sak reservoirs

(Masterson *et al.* 2001). The similarity in biomarker ratios was used to show that West Sak reservoirs shared primary charge with the Prudhoe reservoirs to the east. However, the $\delta^{13}\text{C}$ values of an apparent secondary charge, rich in gasoline-range hydrocarbons, matched the underlying Kuparuk reservoirs. Faulting in the thick shale units separating Kuparuk and West Sak reservoirs is hypothesized to provide the conduit for this charge. The $\delta^{13}\text{C}$ values and distribution of the gasoline-range components in the upper West Sak fluids were shown to be further affected by biodegradation. The biodegradation results in more viscous fluid, and thus reduces producibility of the West Sak oils. Therefore, the light hydrocarbon secondary charge is the key to reducing viscosity of the reservoir fluid, and to the economic viability of West Sak production. Understanding the source of the secondary charge, using CSIA of gasoline-range hydrocarbons, provided a tool to identify the origin of the secondary charge and to therefore de-risk future development targets. The $\delta^{13}\text{C}$ values of organic compounds have provided an important piece of information for understanding charge history, basin development and economics.

Western Canada Sedimentary Basin (integrated basin analysis). Large variations in the difference between H isotopic compositions of *n*-alkanes and acyclic isoprenoids (pristane and phytane) was used effectively for source correlation in the Western Canada Sedimentary Basin (WCSB), including the Alberta and the Williston basins (Li *et al.* 2001). From Alberta, 13 oils from 12 fields were analysed, representing at least eight source units including Devonian, Triassic, Jurassic and Upper Cretaceous organofacies. From the Williston Basin, 13 oils from seven fields were studied, representing putative Cambrian, Ordovician, Devonian and Mississippian facies.

Within this rich dataset, there are examples that show how the H isotopic composition of the source material is preserved in the compound-specific H isotopic composition of the *n*-alkanes and acyclic isoprenoids, which then enables correlation of oils to source rocks. For example, the $\delta^2\text{H}$ of the *n*-alkanes from both the Cambrian and the Upper Cretaceous range from -160 to -190‰ , and are more ^2H -depleted than the Mississippian–Devonian source oils in both the Alberta and Williston basins (-80 to -160‰). Also, the $\delta^2\text{H}$ values of the *n*-alkanes from the Devonian–Mississippian oils of the Williston Basin are intermediate between a Lodgepole and a Bakken end-member signature – oils from different vertical depths in the same well – which gives a strong indication of mixing of these two sources. Furthermore, known lacustrine-, marine- and evaporite-derived oils show different

$\delta^2\text{H}$ values, which demonstrate preservation of source-water H isotope compositions, e.g. oils derived from evaporites show more ^2H -enriched values.

As also shown in the Perth Basin (Dawson *et al.* 2005), maturity too has an impact on $\delta^2\text{H}$, which potentially allows $\delta^2\text{H}$ values to be used as evidence of thermal maturity level, especially as other biomarker ratios of thermal maturity either reach equilibrium or disappear altogether in the highest maturity liquids. In this case, the ^2H -enrichment leads to a 40‰ increase in the weighted-average $\delta^2\text{H}$ values.

This study illustrates the interpretive power and resolution of H isotopic compositions on *n*-alkanes for oil–oil and oil–source rock correlation, as well as how they can provide evidence for mixing and thermal maturity. Although such studies may be undertaken internally within exploration and production groups in national and international petroleum companies, there are few examples in the literature or published datasets. Yet, such datasets can benefit both palaeoclimate and petroleum geochemists.

Summary

CSIA of *n*-alkanes provides evidence of fluid histories including source, maturity, charge history and reservoir processes that – when integrated in petroleum systems concepts and models – can support field development planning and exploration efforts. For source rock determination, the C and H isotope compositions of *n*-alkanes and related compounds can provide differentiation between marine, lacustrine and evaporitic palaeoenvironments. These observations can add confidence to correlation among oils, and between oils and source rocks.

In some cases, the use of CSIA is targeted to determine particular processes. Single-basin studies are examples of particular applications, such as charge evaluation (West Sak), source rock correlation (Austria, Sirte, Potwar), and interplay of maturity and in-reservoir processes (Perth, Potwar, Western Canada Sedimentary Basin).

In other cases, CSIA of *n*-alkanes is used to corroborate interpretations from integrated petroleum systems analysis, providing unique insights, which may not be revealed when using other methods. Studies in the Tarim, Niger, Barents and Western Canada Sedimentary basins are good examples of integrated geochemical basin analysis.

Overall, CSIA of *n*-alkanes and related *n*-alkyl structures can provide independent data to strengthen petroleum systems concepts from generation and expulsion of fluids from source rock, to charge history, connectivity and in-reservoir processes (Fig. 5). The studies should be fully integrated

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in basin analysis, with CSIA being used to reduce uncertainty and increase confidence in basin evaluation.

As highlighted by Curiale (2008), whether directly comparing organic geochemical data from putative source rocks and oils, or inferring possible source rock properties from oil data, correlation and in-reservoir process determination can be continually updated and improved as data are incorporated into conceptual, basin, geological and reservoir models. Likewise, the integration of the full range of fluid and rock properties, the creation and/or consolidation of large datasets, and the use of the next level of analytical tools such as compound-specific isotopic compositions, can significantly refine and improve basin and reservoir understanding, and reduce the risk of field development planning.

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