

R. Chaler · C. Dorronsoro · J. O. Grimalt ·  
L. M. Agirrezabala · P. A. Fernández-Mendiola ·  
J. García-Mondejar · I. Gómez-Pérez ·  
M. López-Horgue

## Distributions of C<sub>22</sub>–C<sub>30</sub> even-carbon-number *n*-alkanes in Ocean Anoxic Event 1 samples from the Basque-Cantabrian Basin

Received: 9 November 2004 / Accepted: 31 January 2005 / Published online: 18 March 2005  
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**Abstract** The Ocean Anoxic Event 1 (OAE-1) in central sites of the Basque-Cantabrian Basin exhibits very reducing depositional conditions of sedimentation. These sedimentation events have left a distinct mixture of hydrocarbons that are represented by C<sub>22</sub>–C<sub>30</sub> *n*-alkanes with a predominance of the even-carbon-number homologues, high relative proportions of squalane and C<sub>16</sub>–C<sub>24</sub> *n*-alkylcyclopentanes predominated by *n*-undecyl-, *n*-tridecyl- and *n*-pentadecylcyclopentane. Other minor compounds encompass a series of C<sub>18</sub>–C<sub>21</sub> *n*-alkylcyclohexanes and C<sub>18</sub>–C<sub>24</sub> dimethyl *n*-alkylcyclohexanes maximized by the even-carbon-number homologues as well as *iso*- and *anteiso*-alkanes. This unusual distribution of *n*-alkanes in this environment provides a new case for comparison with previously reported hy-

persaline and phosphorite sedimentary deposits where the occurrence of similar *n*-alkane distributions was reported. In the present case, these major *n*-alkanes and squalane are indicative of transformation under strong reducing conditions. In contrast, the occurrence of the alkylcyclopentanes, irrespective of the presence of even-carbon-number *n*-alkanes or squalane, suggests that reductive cyclization of fatty acids is less dependent on strong reducing conditions.

### Introduction

Sedimentary hydrocarbons currently exhibit mixtures with a predominance of odd-carbon-number *n*-alkanes or no carbon-number preference, the latter being more characteristic of mature organic matter. However, in some cases even-carbon-number *n*-alkanes predominate. These less common distributions were already identified at the beginning of the implementation of chromatographic methods in organic geochemistry (e.g. Welte and Waples 1973; Tissot et al. 1977), but surprisingly the understanding of their origin and geochemical significance still lags well behind the degree of knowledge achieved for other molecules.

The *n*-alkane distributions with even-carbon-number predominance reported so far can be grouped into two patterns, one involving distributions with a high predominance of even-carbon-number homologues in the C<sub>12</sub>–C<sub>20</sub> range (Nishimura and Baker 1986; Grimalt and Albaigés 1987; Kennicutt and Brooks 1990; Debyser et al. 1977; Grimalt et al. 1985, 1986) and the other encompassing C<sub>22</sub>–C<sub>30</sub> distributions with a moderate predominance of even-carbon-number *n*-alkanes (Welte and Waples 1973; Ogihara and Ishiwatari 1998; Tissot et al. 1977).

The former sometimes occurs together with distributions of even-carbon-number *n*-alk-1-enes (Grimalt and Albaigés 1987; Grimalt et al. 1985) and is found in relatively recent depositional settings. To the best of our knowledge the oldest reported occurrence for these distributions corresponds to Miocene samples (Grimalt et al. 1986). The latter has traditionally been attributed to reducing environments in hypersaline deposits (Tissot et al. 1977; ten Haven

R. Chaler · J. O. Grimalt (✉)  
Institute of Chemical and Environmental Research (CSIC),  
Jordi Girona 18,  
08034 Barcelona, Catalonia, Spain  
e-mail: jgoqam@cid.csic.es  
Tel.: +34-93-4006122  
Fax: +34-93-2045904

C. Dorronsoro  
Department of Geology, College of Chemistry, University of the  
Basque Country,  
P.O. Box 1072, 20080 Donostia-San Sebastian, The Basque  
Country, Spain

L. M. Agirrezabala · P. A. Fernández-Mendiola ·  
J. García-Mondejar · M. López-Horgue  
Department of Stratigraphy and Paleontology, College of  
Sciences, University of the Basque Country,  
P.O. Box 644, 48080 Bilbao, The Basque Country, Spain

I. Gómez-Pérez  
CASP, Earth Sciences Department, University of Cambridge,  
West Building, 181 Huntingdon Road,  
Cambridge, CB3 0DH, UK

M. López-Horgue  
Department of Mines Engineering, University of the Basque  
Country, School of Mines and Public Works Engineering,  
Colina de Beurko,  
48902 Barakaldo, The Basque Country, Spain

et al. 1988), but one recent study reported the occurrence of these distributions in phosphorite deposits related to hydrothermal activity (Ogihara and Ishiwatari 1998).

One of the aspects holding up the understanding of the geochemical significance of these distributions is the relatively small number of cases in which they have been reported. In the present study, these unusual distributions are described in Ocean Anoxic Event 1 (OAE-1) in the Basque-Cantabrian Basin which constitutes a margin-sag basin formed on thinned continental crust during the Mesozoic and early Tertiary periods (Einsele 1992). The basin lies to the western side of the Pyrenees in central north Spain. After a period of extension during the Triassic to the Santonian times, the reversal of the plate movement led to compression from the Campanian to the Oligocene, resulting in the formation of the Pyrenees and the basin conversion. The Aptian-Albian depositional history is controlled by synsedimentary fault activity in the framework of the Bay of Biscay opening and the southeastward drift of the Iberian plate (García-Mondéjar 1996).

The samples selected for study belong to three different areas (Fig. 1a). Those studied in Mutriku (Fig. 1b; Upper Albian) encompass calcareous, black sandy lutites (sample 1), which may host diagenetic carbonate concretions filled with asphalt (samples 2 and 3). These deep-water deposits were accumulated by hemipelagic settling of suspended fine-grained siliciclastic and calcareous particles and very diluted turbidity currents. Samples from Gorbea (samples 6 and 7; Fig. 1d) belong to the Axularpe

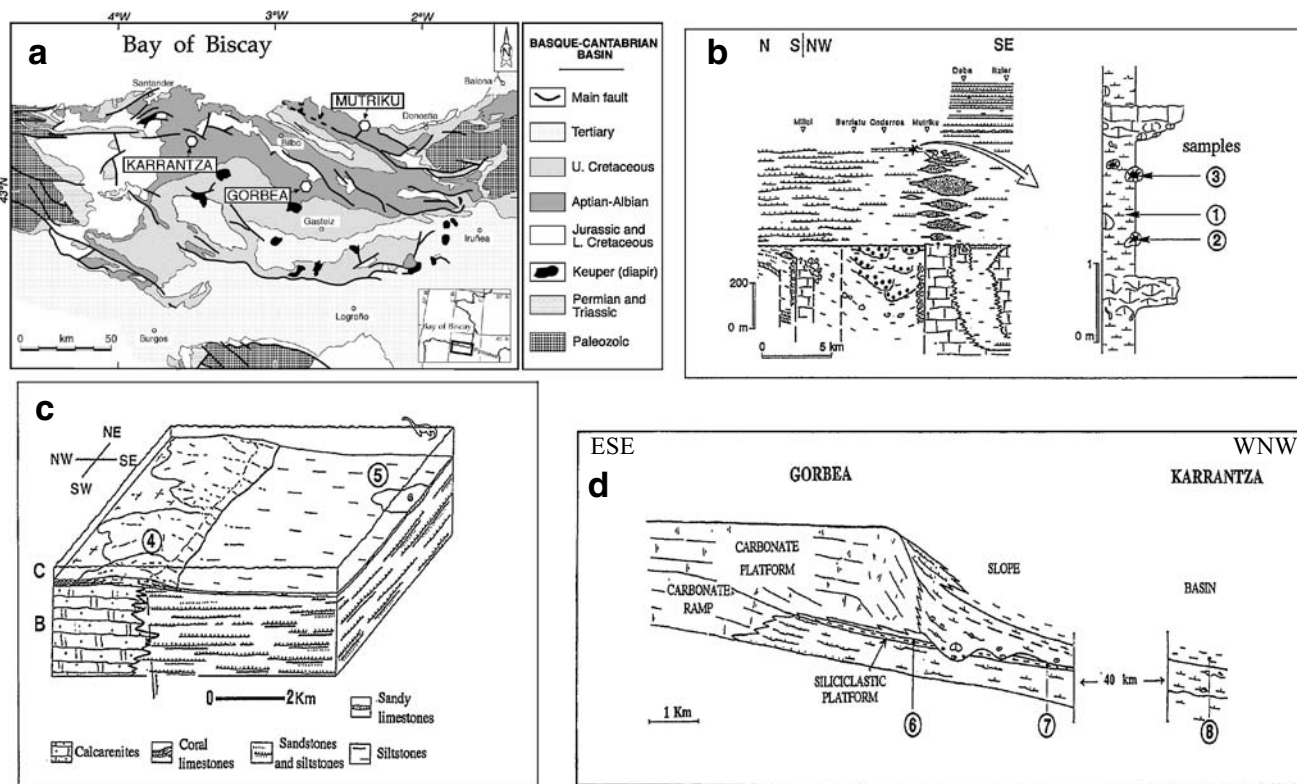
lutites. They encompass a siliciclastic platform system of early Albian age overlying a carbonate ramp. The black lutites are interpreted as deposits of a global anoxic event related to OAE-1 (Jenkyns 1980).

Samples from Karrantza (late Albian) correspond to three different units: Sopeña, La Escrita and Rio Calera. Sopeña limestone is made up of bioclastic calcarenites and coral mounds. Sample 4 (Fig. 1c) shows coral septa filled with marine organic carbon-rich material (asphalt). The La Escrita unit is composed of lutites, sandstone and silty limestones which originated in a broad, shallow, marine platform with an estuarine influence. Sample 5 (Fig. 1c) is a silty limestone with wig porosity filled with asphalt. The Rio Calera unit is made up of laminated black and calcareous lutites and scattered sandstone which originated in a deep marine setting adjacent to a carbonate platform. Sample 8 (Fig. 1d) is a laminated black lutite reflecting hypoxic bottom conditions.

The cases described in the present study extend the number of known sedimentary settings in which these long-chain even-carbon-number distributions occur and illustrate new reducing depositional environments that could lead to their formation.

## Materials and methods

The analytical methods have been described elsewhere (Grimalt and Albaigés 1987). Briefly, the sediment sam-



**Fig. 1** a Geological map of the Basque-Cantabrian Basin showing the locations of the three areas considered in this study. Stratigraphic location of the samples from the b Mutriku, c Karrantza, and d Gorbea areas

ples were extracted with (2:1) dichloromethane–methanol in a Soxhlet apparatus. After concentration, they were hydrolyzed and fractionated by silica–alumina column chromatography. The aliphatic hydrocarbons were separated by elution with *n*-hexane. The fractions were evaporated to near dryness and redissolved in *iso*-octane.

Gas chromatographic (GC) analyses were performed using a Carlo Erba Vega HRGC 6130 equipped with a flame ionization detector and a splitless injector. A DB-5 capillary column (J&W; 30 m × 0.25 mm i.d. × 0.2- $\mu$ m film thickness) was used. Helium was the carrier gas (50 cm/min). The oven temperature program was 70–320°C at 6°C/min. Injector and detector temperatures were 290 and 350°C, respectively.

GC-mass spectrometric (MS) analyses were performed using a Thermo Quest MD 800 equipped with a HP-5 MS fused silica capillary column (30 m × 0.25 mm i.d. × 0.25- $\mu$ m film thickness). The chromatographic conditions were very similar to those of the GC method. Ion source and

transfer-line temperatures were 200 and 280°C, respectively. Mass spectra were acquired in electron impact mode (70 eV).

## Results

C<sub>14</sub>–C<sub>18</sub> *n*-alkanes without odd/even-carbon-number preference are present in the GC traces of all samples (Fig. 2) being dominant in samples 2, 3, 5 and 8. This distribution is generally representative of algal and bacterial autochthonous contributions. Samples 1, 2 and 5–8 contain a second modal distribution of C<sub>22</sub>–C<sub>30</sub> *n*-alkanes with even-carbon-number preference maximized at the C<sub>24</sub> or C<sub>26</sub> homologues (odd/even *n*-alkane ratios between 0.69 and 0.80; Fig. 2).

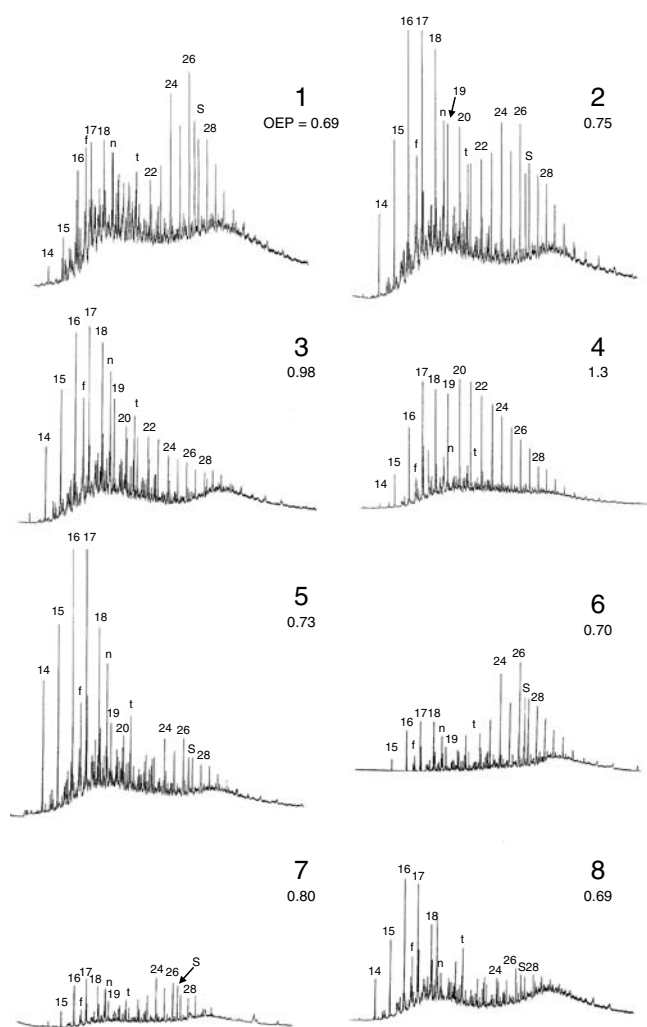
Squalane is found in a high relative proportion in the samples exhibiting dominance of even-carbon-number C<sub>22</sub>–C<sub>30</sub> *n*-alkanes (Fig. 2). This isoprenoid has been identified in methanogenic bacteria (Holzer et al. 1979). Samples 3 and 4 contain neither the above mentioned C<sub>22</sub>–C<sub>30</sub> *n*-alkane distribution nor squalane. The regular isoprenoids norpristane, pristane and phytane (e, g, l, respectively; Figs. 2 and 3) are found in all samples.

*N*-alkylcyclopentanes are also major constituents of these samples. They encompass a distribution of C<sub>16</sub>–C<sub>24</sub> homologues predominated by *n*-undecyl-, *n*-tridecyl- and *n*-pentadecylcyclopentane (f, n, t, respectively; Figs. 2 and 3). Two series of predominantly even-carbon-number cyclohexanes are also found in minor relative proportions, involving C<sub>18</sub>–C<sub>21</sub> *n*-alkylcyclohexanes (i; Fig. 3) and C<sub>18</sub>–C<sub>24</sub> dimethyl *n*-alkylcyclohexanes (n, r; Fig. 3). The structures of these compounds were assigned after GC-MS examination and comparison to other samples of known hydrocarbon composition. Mass spectra of some of these compounds have been reported elsewhere (Dong et al. 1993).

*Iso*- and *anteiso*-alkanes are also found in minor proportions. They encompass distributions of C<sub>15</sub>–C<sub>20</sub> homologues and both series occur in similar relative concentration (a–d, j, k, p, q; Fig. 3).

## Discussion

None of the samples considered in this study exhibit even-carbon-number predominance in the C<sub>12</sub>–C<sub>20</sub> *n*-alkane range. These distributions have been described in a wide diversity of environments (Nishimura and Baker 1986; Grimalt and Albaigés 1987; Kennicutt and Brooks 1990), including oxic depositional settings (Grimalt et al. 1985), whereas those encompassing even-carbon-number C<sub>22</sub>–C<sub>30</sub> *n*-alkanes seem to be more restricted to anoxic sedimentary conditions. Nevertheless, it cannot be ruled out that the absence of even-carbon-number *n*-alkane predominance in the C<sub>12</sub>–C<sub>20</sub> range could be due to microbial diagenetic processes or early maturation transforming the shorter chain *n*-alkanes from these OAE-1 distributions.



**Fig. 2** Gas chromatograms of the aliphatic hydrocarbon fractions from the samples considered in this study (sample location is given in Fig. 1). Peak numbers indicate chain length of *n*-alkanes. Other peak labels refer to Fig. 3. OEP Ratio between odd- and even-carbon-number C<sub>22</sub>–C<sub>31</sub> *n*-alkanes

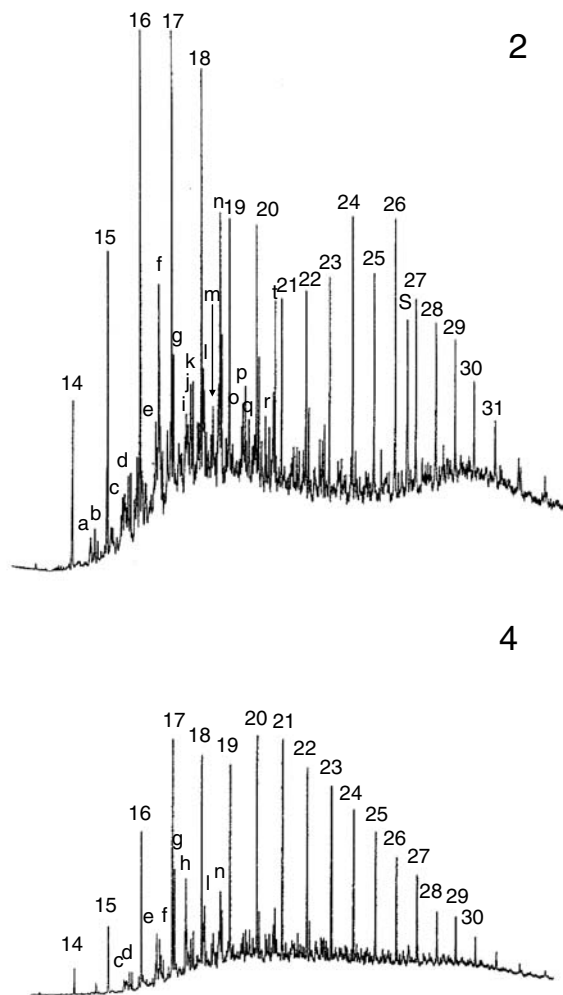
As mentioned above, C<sub>22</sub>–C<sub>30</sub> *n*-alkane mixtures with a predominance of the even-carbon-number homologues are currently associated with hypersaline deposition. However, the geological settings of the samples considered in the present study do not correspond to these conditions of sedimentation. Furthermore, other hydrocarbon marker features currently observed in samples deposited in hypersaline conditions such as pristane/phytane ratios lower than unit and hopane distributions maximized at the C<sub>34</sub>–C<sub>35</sub> homologues (ten Haven et al. 1988) are not observed.

The presence of squalane in a high relative proportion is probably indicative of very reducing conditions of sedimentation and reflects methanogen inputs in marine sediments in which other Archaeobacteria are unlikely contributors (Brassell et al. 1981). In these depositional

settings, reduction of even-carbon-number distributions of functionalized lipids such as fatty acids (Kvenvolden 1970) and waxy alcohols (Welte and Waples 1973) is the likely mechanism for the formation of mixtures of even-carbon-number *n*-alkanes. Thus, the samples not showing the above-mentioned C<sub>22</sub>–C<sub>30</sub> *n*-alkane distribution or squalane (samples 3 and 4; odd/even *n*-alkane ratios 0.98–1.3; Fig. 2) are those corresponding to sites situated at lateral basin positions in which water column oxygen was probably less restricted.

The high relative abundance of *n*-undecyl-, *n*-tridecyl- and *n*-pentadecylcyclopentanes is also a distinct feature of these samples. The strong even-carbon-number predominance of the distributions suggests that they are generated by transformation of algal and bacterial fatty acids, since these compounds exhibit distributions predominated by C<sub>16</sub> and C<sub>18</sub> homologues (Volkman et al. 1980). Cyclization and decarboxylation of these compounds have been proposed for the occurrence of *n*-alkylcyclohexane distributions maximizing at C<sub>17</sub> (Rubinstein and Strausz 1979). The *n*-alkylcyclopentane distributions in the Basque-Cantabrian OAE-1 samples may be related to similar mechanisms, but not involving the decarboxylation step. The prevalence of fatty acid reduction over decarboxylation is again associated with reducing environments (e.g. Welte and Waples 1973). However, in the context of the present study these *n*-alkylcyclopentanes are found in all cases, not only concurrently with dominance of the even-carbon-number distributions. Therefore, reductive fatty acid cyclization does not seem to be so restricted to reducing environments such as those leading to high amounts of squalane and a predominance of even-carbon-number C<sub>22</sub>–C<sub>30</sub> *n*-alkanes.

A recent study on hydrothermally altered phosphorite nodules from the Kusu Basin (northern Kyushu, Japan; 0.2–0.5 million years old) has shown similar distributions to those observed in the Basque-Cantabrian OAE-1 samples, involving even-carbon-number preference among the C<sub>20</sub>–C<sub>28</sub> homologues, high relative proportions of C<sub>16</sub>, C<sub>18</sub> and C<sub>20</sub> *n*-alkylcyclopentanes and *iso*- and *anteiso*-alkanes (Ogihara and Ishiwatari 1998). In this case, even-carbon-number preference is also observed among the C<sub>14</sub>–C<sub>20</sub> *n*-alkanes which constitutes a difference with respect to the Basque-Cantabrian OAE-1 distributions. These phosphorite mixtures do not contain squalane in significant amounts, which represents another aspect of differentiation with respect to the present study. Obviously there are significant differences both in terms of geological settings and sample hydrocarbon composition between both studies. However, comparison of both cases gives further support to strong reducing environments for the formation of C<sub>20</sub>–C<sub>28</sub> *n*-alkane distributions with a predominance of even-carbon-number homologues.



**Fig. 3** Expanded gas chromatographic traces showing the composition of the major hydrocarbons in samples 2 and 4. Peak numbers indicate *n*-alkane chain length. a 2-Methyltetradecane, b 3-methyltetradecane, c 2-methylpentadecane, d 3-methylpentadecane, e norpristane, f *n*-undecylcyclopentane, g pristane, h *n*-dodecylcyclopentane; i *n*-undecylcyclohexane, j 2-methylheptadecane, k 3-methylheptadecane, l phytane, m dimethyl-*n*-decylcyclohexane, n *n*-tridecylcyclopentane, o *n*-tetradecylcyclopentane, p 2-methylnonadecane, q 3-methylnonadecane, r dimethyl-*n*-dodecylcyclohexane, s squalane, t *n*-pentadecylcyclopentane

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