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## Biodegraded oils in exhumed reservoirs in the Basque-Cantabrian Basin, northern Spain: a conventional approach

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### Abstract

A geochemical investigation has been undertaken on biodegraded hydrocarbons in reservoirs outcropping in the south-eastern margin of the Basque-Cantabrian Basin (Alava sector). The aim of the study was to characterize the geochemical features and biodegradation level of these hydrocarbons, and to determine their resemblance to oils from the Ayoluengo onshore oil field. Isotope analyses and Gas Chromatography-Mass Spectrometry were carried out. Most of the samples lack of *n*-alkanes, isoprenoids, PAHs, steranes, homohopanes, diasteranes and triaromatic steroids (PM scale=9). In one sample 25-norhopanes have been identified. Thermal maturity has been assessed with  $Ts/Ts+Tm$ ,  $MA(I)/[MA(I)+MA(II)]$  and  $TA/(TA+MA)$  and a  $Ro_{eq} \sim 0.8\%$  is estimated. High Gammacerane content,  $Dia/St$  and  $C_{35}/C_{34}$  homohopanes ratios suggest that the Alava hydrocarbons are derived from a carbonate rock deposited in a reducing, water-stratified and probably hypersaline environment. Isotopic signature ( $\delta^{13}C_{sat} = -28.06$ ;  $\delta^{13}C_{aro} = -25.77$ ) confirms that these hydrocarbons are not genetically related to the oils from Ayoluengo ( $\delta^{13}C_{sat} = -29.87$ ;  $\delta^{13}C_{aro} = -29.08$ ) and consequently, their origin has to be associated with a yet unknown source rock.

**Key words:** Basque-Cantabrian Basin, biodegradation, biomarkers, aromatic hydrocarbons, 25-norhopanes.

### Introduction

The Basque-Cantabrian Basin (northern Spain), is one of the regions of Spain where there has been more oil exploration. Oil shows occurrence in the western sector, known for more than a century, lead to exploration of the area and thus, in 1964 the Ayoluengo oil field was discovered.

The Ayoluengo oil field reservoir consists on non-connected Purbeck (Late Jurassic) sand levels. Geochemical studies carried out by Quesada et al. (1997) [1] and Beroiz and Permanyer (2011) [2] established that Ayoluengo oil source rocks are the Pliensbachian-Lower Toarcian shale levels. Outcropping tar sands in the western sector of the Basque-Cantabrian Basin have been isotopically correlated with the Ayoluengo oil [2].

However, oil shows are widely common throughout the Basque-Cantabrian Basin. In the eastern sector (Alava province), it is remarkable the occurrence of oil-impregnated Campanian and Maastrichtian carbonates and sands, outcropping beside diapiric structures.

This paper reports on hydrocarbons sampled in exhumed reservoirs nearby the Maestu, Peñacerrada and Santa Cruz de Campezo diapirs in order to: (i) characterize their biodegradation and maturity level, (ii) propose a type of source rock and (iii) establish a possible correlation with the hydrocarbons of the Ayoluengo oil field. For these purposes, a geochemical study including SARA quantification, carbon isotopic analyses and GCMS has been carried out.

### Geological overview

The Basque-Cantabrian Basin, in northern Spain, covers a wide area both onshore and offshore, and is located between

the Paleozoic Basque Massif in the East, the Paleozoic Asturian Massif in the West, the Tertiary Ebro and Duero Basins in the South, and the Bay of Biscay in the North (Figure 1). This Mesozoic-early Cenozoic basin was folded and thrust during the Pyrenean orogeny and its present structure consists of a north and south verging thrust belt [1].

The post-Hercynian geological history of the Basque-Cantabrian Basin is closely linked to the Permo-Triassic and Late Jurassic-Early Cretaceous rifting stages. The present day structure of the basin is also due to the Pyrenean compression (Late Eocene to Miocene), in which the Keuper evaporites played an important role, acting as a detachment level and promoting the formation of diapirs, characteristic of the basin [3].

### Methods and materials

A set of seven samples obtained from four outcrops have been studied. Loza samples (LOZ-1, LOZ-3), Atauri samples (ATA-3, ATA-4) and Maestu samples (MAE-1, MAE-7) come from exhumed reservoirs containing degraded oil. San Román de Campezo sample (SRC) consists of bitumen directly cut from the wall of an ancient asphalt mine. In order to compare, we also dispose of samples from the western part of the basin: two tar sand samples from Villanueva de

Rampalay (RAM-1, RAM-2), GCMS results of the saturated hydrocarbons of the Jurassic source rock from Cordovilla (COR-5) and carbon isotopic results of two Ayoluengo oils (AYO-37, AYO-38) (Figure 1).

Saturated and aromatic hydrocarbons, resins and asphaltenes have been isolated according to the procedures described by Bennett and Larter (2000) [4]. Bitumen was extracted using a soxhlet extractor and dichloromethane as solvent.

Saturated and aromatic hydrocarbons have been studied by GCMS. Analyses were performed on a Thermo Scientific Trace CG Ultra gas chromatograph with a DB-5 (Agilent Technologies) column (60 m x 0.25 mm d.i. x 0.10  $\mu\text{m}$  d.f.) coupled to a ITQ900 mass spectrometer. Data has been acquired in SIM mode.

Carbon isotopic analyses of whole oil and SARA fractions were performed on a Thermo Finnigan Series 1112 elemental analyser coupled to a Finnigan Mat Delta C mass spectrometer.

## Results and discussion

**SARA content.** Samples are mainly composed by NSO compounds. Aromatic hydrocarbons are comprised between 16.48% and 41.12% and saturated hydrocarbons are up to 15%, thus consisting of "heavy or degraded oils" [5]. Being resin contents small, asphaltenes tend to be the main component of these oils.

**GCMS. Biodegradation.** Biodegradation has been assessed with Peters and Moldowan (PM) scale [6]. As a general rule, samples from the eastern part of the basin lack of *n*-alkanes, isoprenoids, PAHs and dibenzotiofenenes. Steranes are only partially conserved in a few samples and pentacyclic hopanes tend to be highly altered. In most samples diasteranes and triaromatic steroids are degraded. As 25-norhopanes are absent, steranes were altered before hopanes [7, 8, 9].

The samples from Loza (LOZ-1 and LOZ-3) show a degree of biodegradation ranked 7 (PM scale).  $C_{27}$  and  $C_{28}$  steranes are highly degraded whereas  $C_{29}$  steranes are only partially removed. No preference for any isomer or stereoisomer is observed and  $C_{30}$  steranes and  $C_{21}$ - $C_{22}$  short chain steranes are unaltered. Both S and R  $C_{31}$ - $C_{35}$  homohopanes isomers are almost completely degraded and  $C_{29}$  y  $C_{30}$  17 $\alpha$ -hopanes are substantially depleted. Tricyclic terpanes are preserved except for the  $C_{29}$  and  $C_{30}$  pairs, which has been interpreted as they being already absent in the source rock [8]. Diasteranes, triaromatic and monoaromatic steroids are preserved. Samples lack of 25-norhopanes.

The samples from Atauri (ATA-4, ATA-3) and Maestu (MAE-1, MAE-7) are very similar and have a biodegradation degree ranging 9 (MAE-7) to 10 (ATA-3, MAE-1). Steranes, with the exception of  $C_{30}\alpha\alpha\alpha\text{R}$  (see discussion in next page), pregnanes, diasteranes and

triaromatic steroids are completely removed. Regarding hopanes and tricyclic terpanes, ATA-4 is slightly different from the rest of the samples, showing a low altered pattern with only the  $C_{31}$ - $C_{35}$  homohopanes slightly degraded. In the other samples homohopanes are almost (MAE-7) to completely removed (MAE-1, ATA-3), as well as  $C_{29}$  17 $\alpha$ -norhopane and  $C_{30}$  17 $\alpha$ -hopane. MAE-1 and ATA-3 lack of Ts, Tm and some tricyclic terpanes. Besides, monoaromatic steroids are altered and only monoaromatic diasteroids are preserved. 25-norhopanes have not been detected in any of the Atauri and Maestu samples.

The sample from San Román de Campezo (SRC) has a lesser biodegradation degree (PM=2), with partial loss of *n*-alkanes and isoprenoids, and preservation of PAHs. 25-norhopanes compounds have been identified (see discussion below).

Tar sands from the western part of the Basque-Cantabrian Basin (RAM-1, RAM-2) show a biodegradation degree PM 5-6. *N*-alkanes and isoprenoids are completely removed. In RAM-2 some naphthalene isomers are preserved, but both samples lack of phenantrenes and dibenzotiofenenes. Steranes, hopanes and more bioresistent compounds are unaltered. 25-norhopanes are absent.

*25-norhopanes in SRC.*  $C_{27}$ - $C_{34}$  25-norhopanes have been identified in SRC (Figure 2). Therefore, this sample has been considered a mixture of a non-degraded and a severe degraded oil (PM>6). The presence of 25-norhopanes also suggests that in SRC the biodegradation processes may have been different.

**Correlation.** Due to the severe biodegradation and in order to infer information with biomarkers, a correlation between samples becomes necessary. Regular steranes and monoaromatic steroids ternary diagrams have been used. The steranes diagram suggests that RAM-1 and RAM-2 are genetically related to Ayoluengo source rock (COR-5), whereas the samples from the eastern part of the basin have a different origin. The monoaromatic steroids diagram confirms that tar sands from the western part of the basin are different from the eastern samples, and suggest that the sample from San Román de Campezo is slightly different from Loza, Atauri and Maestu samples, all located in the eastern part of the basin (Figure 3).

**Depositional environment and source rock type.** Several indexes have been calculated in order to infer characteristics of the sedimentary conditions and source rock type (Table 1). High *Dia/St* and  $C_{29}H/C_{30}H$  ratios suggest that the samples from the eastern part of the Basque-Cantabrian Basin were originated from a carbonate source rock, whereas oils and tars from the western part of the basin were originated from a shaly-siliciclastic type, as described in previous papers [2, 10]. Values higher than 1 of the  $C_{35}S/C_{34}S$  ratio suggest that the samples from the eastern part of the basin proceed from a source rock deposited in a reducing environment. Ts/Tm ratio, though conditioned by maturity, is higher than 1

in the samples from the western part of the basin and about 0.47 in the samples from the East, supporting the fact that the latter proceed from a carbonate source rock deposited in a reducing environment.

Samples from the eastern part of the basin are also characterized by a high Gammacerane content, which indicates water-stratified depositional environments [11], probably due to hypersalinity. Pregnane abundance in LOZ-1 and LOZ-3 or alternative high Preg/St values are also characteristic of hypersaline environments. Nevertheless, pregnane content may be slightly altered by maturity.

Samples from the western part of the basin proceed from marine organic matter [2, 10]. This is supported by COR-5 *n*-alkanes distribution and high steranes and steranes/hopanes (*St/Hop*) index. Regarding the eastern samples, *St/Hop* ratio has only been calculated in the least biodegraded sample (SRC) and a value of 0.28 was obtained. It suggests that organic matter may have a more terrestrial input. Nevertheless, a non-identified peak in *m/z* 217 may belong to C<sub>30</sub>αααR which, when present, is a clear marine origin indicator. GCMS-MS analysis would be needed to confirm its attribution.

**Maturity.** Several indexes have been calculated in order to determine thermal maturity (Table 2). Isomerization 22*S*/(22*S*+22*R*) in C<sub>31</sub>-C<sub>35</sub> homohopanes indicates that the main oil generation phase was reached. Apparently, samples from Aauri and Maestu are slightly more mature than Loza samples. By assuming a linear behaviour of the parameters *MA(I)*/*MA(I)+MA(II)* and *TA*/*TA+MA* with maturity, an equivalent %Ro of ~0.8 is estimated. Parameters obtained for SRC suggest that this sample is less mature than the others.

**Carbon isotopes (δ<sup>13</sup>C).** Isotopic signatures between samples from the eastern and western part of the Basque-Cantabrian Basin differ in about ~3‰ thus, a different origin has to be considered (Figure 4). SRC differs up to 1.42‰ from Loza, Maestu and Aauri samples. The isotopic signature shift could be explained by (i) SRC being a change of facies, (ii) SRC being a mixture with a lighter isotopic oil or (iii) SRC lesser degree of maturity.

## Conclusions

1. Hydrocarbons from the eastern part of the Basque-Cantabrian Basin were affected by severe biodegradation processes which removed *n*-alkanes, isoprenoids, PAHs, dibenzotiofenes and also steranes, homohopanes, diasteranes and triaromatic steroids.

2. Steranes were degraded before than hopanes.

3. The presence of 25-norhopanes in San Román de Campezo suggests that biodegradation processes were different in this sample.

4. Hydrocarbons from the eastern part of the basin reached a thermal maturity degree equivalent to a vitrinite reflectivity of ~0.8%, near to oil generation peak.

5. Hydrocarbons from the eastern part of the basin were originated from a carbonate source rock deposited in a reducing and probably hypersaline environment.

6. Hydrocarbons from Rampalay tar sands are correlated to Ayoluengo oil, which originated from the shaly Jurassic source rock (Pliensbachian- lower Toarcian).

7. The origin of the hydrocarbons from the exhumed reservoirs in the eastern part of the Basque-Cantabrian is different from the one of the western oils and tars. A yet-undetermined source rock has to be postulated as the origin of hydrocarbons in the eastern sector of the basin.

## Acknowledgements

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Figures and tables

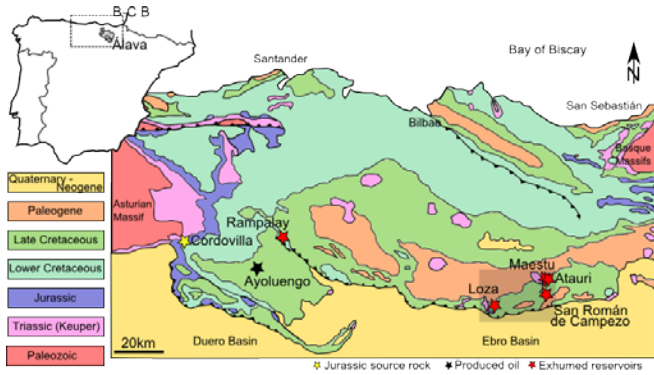


Figure 1. Geological map of the Basque-Cantabrian Basin. Main study area is shaded.

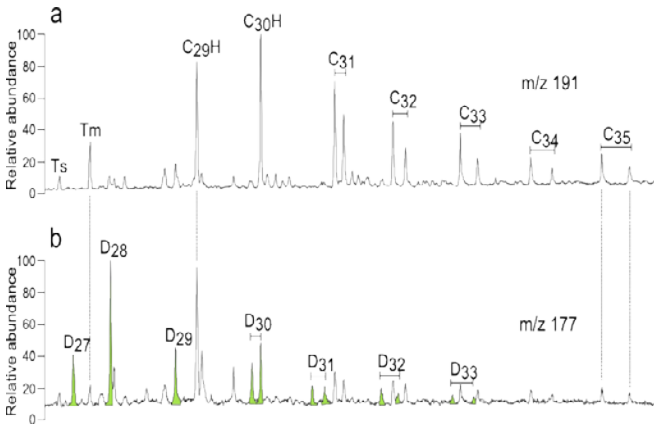


Figure 2. (a) Hopanes and (b) 25-norhopanes, labelled as 'D' and the number of carbons, in San Román de Campezo sample (SRC).

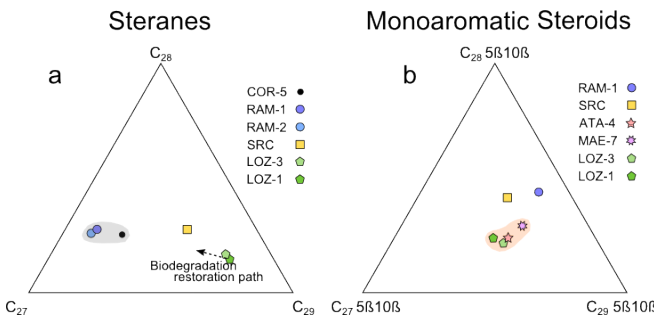


Figure 3. (a) Steranes and (b) monoaromatic steroids ternary diagrams. Samples from the western part of the basin (COR and RAM) are richer in C<sub>27</sub> steranes. The western sector (RAM and AYO). Within samples from the eastern sector, SRC is isotopically different.

Table 1. Depositional environment and source rock type parameters.

	COR-5	RAM-1	RAM-2	SRC	LOZ-1	LOZ-3	MAE-7	ATA-4
Dia/St <sup>1</sup>	0.57	0.67	0.69	0.08	0.07	0.11	NA	NA
Ts/Tm	1.07	2.14	2.14	0.29	0.36	0.4	0.6	0.72
GammIndex	0.06	0.09	0.09	0.12	0.82*	0.92*	0.86*	0.39
Su/H <sup>2</sup>	0.81	0.96	0.87	0.28	NA	NA	NA	NA
Preg/St <sup>3</sup>	0.14	0.22	0.23	0.12	0.36	0.43	NA	NA

<sup>1</sup>Dia/St = (C<sub>27</sub>βaS+C<sub>27</sub>βaR)/(C<sub>27</sub>βaS+C<sub>27</sub>βaR+C<sub>29</sub>αaaS+C<sub>29</sub>αββR+C<sub>29</sub>αββS+C<sub>29</sub>αaaR), in m/z 217.  
<sup>2</sup>Su/H = (C<sub>27</sub>+C<sub>28</sub>+C<sub>29</sub>)/(C<sub>29</sub>H+C<sub>30</sub>H+C<sub>31</sub>+C<sub>32</sub>+C<sub>33</sub>+C<sub>34</sub>+C<sub>35</sub>), in m/z 217 and m/z 191.  
<sup>3</sup>Preg/St = (C<sub>21</sub>+C<sub>22</sub>)/(C<sub>21</sub>+C<sub>22</sub>+C<sub>29</sub>αaaS+C<sub>29</sub>αββR+C<sub>29</sub>αββS+C<sub>29</sub>αaaR), in m/z 217.  
 \* Affected by biodegradation (partial loss).  
 NA: complete loss of biomarker(s).

Table 2. Maturity parameters

	SRC	LOZ-1	LOZ-3	MAE-7	ATA-4
C <sub>31</sub> 22S/C <sub>31</sub> 22(S+R) <sup>a</sup>	0.63	NA	NA	NA	0.62
Ts/(Ts+Tm)	0.23	0.27	0.29	0.38	0.42
MA(I)/(MA(I)+MA(II)) <sup>b</sup>	0.04	0.38	0.38	0.44	0.56
Ro <sub>eq</sub> (%) <sup>c</sup>	0.55	0.83	0.82	0.87	0.97
TA/(TA+MA) <sup>d</sup>	0.52	0.82	0.86	NA	NA
Ro <sub>eq</sub> (%) <sup>e</sup>	0.56	0.71	0.73	NA	NA
MP[2+3/1+9]	1.49	NA	NA	NA	NA
4-MDBT/1-MDBT	1.17	NA	NA	NA	NA

<sup>a</sup>Average homohopanes C31-C35 isomerization value  
<sup>b</sup>MA(I)/(MA(I)+MA(II)) = (C<sub>21</sub>+C<sub>22</sub>)/(C<sub>21</sub>+C<sub>22</sub>+C<sub>27</sub>+C<sub>28</sub>+C<sub>29</sub>); in m/z 253.  
<sup>c</sup>Ro<sub>eq</sub> = 0.8\*MA(I)+0.52 [6]  
<sup>d</sup>TA/(TA+MA) = (C<sub>20</sub>TA+C<sub>28</sub>RTA+C<sub>28</sub>STA)/(C<sub>20</sub>TA+C<sub>28</sub>RTA+C<sub>28</sub>STA+C<sub>29</sub>ββRMA+C<sub>29</sub>ββRDMMA+C<sub>29</sub>αβRMA), in m/z 231 and m/z 253.  
<sup>e</sup>Ro<sub>eq</sub> = 0.5\*TA/(TA+MA)+0.3 [6]  
 NA: complete loss of biomarker(s).

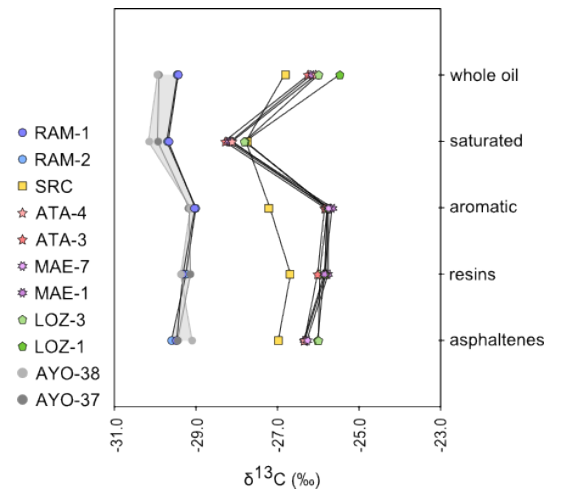


Figure 4. Carbon isotope values of whole oil and SARA fractions. Samples from the eastern part of the basin are isotopically heavier than samples from the western part of the basin (COR and RAM). The western sector (RAM and AYO).