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Pauline Roubira, Delphine Bosch, Ilham Bentaleb. Pb isotopic compositions of fin whale baleen plates - A clue to unravel individual migrations between the Atlantic Ocean and the Mediterranean Sea?. *Procedia Earth and Planetary Science*, 2015, 13, pp.173-176. 10.1016/j.proeps.2015.07.040 . hal-01690857

**HAL Id: hal-01690857**

**<https://hal.science/hal-01690857>**

Submitted on 23 Jan 2018

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11th Applied Isotope Geochemistry Conference, AIG-11 BRGM

## Pb isotopic compositions of fin whale baleen plates – A clue to unravel individual migrations between the Atlantic Ocean and the Mediterranean Sea?

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### Abstract

To assess Mediterranean fin whale ecology and impacts of environmental changes, Pb content and isotopic composition were measured on baleen plates of fin whales stranded on Mediterranean and Bay of Biscay coasts. Pb contents of fin whale baleen plate reflect that of their diet and thus of the dissolved Pb content of the upper 200 meters of the surface ocean. Using Pb isotopes, baleen plates allow reconstituting the evolution of anthropogenic Pb pollution and showing that stranded Mediterranean fin whales constitute a specific population that is resident of the Mediterranean Sea with occasional migrations to the Atlantic Ocean.

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Peer-review under responsibility of the scientific committee of AIG-11

**Keywords:** Balaenoptera physalus; Migration; Habitat; Mediterranean Sea; Atlantic Ocean; Baleen plates; Geochemistry; Pb isotopes

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### 1. Introduction

The fin whale, *Balaenoptera physalus*, is mainly threatened in the Mediterranean Sea by ship collisions, which can cause until 16% of standings<sup>1</sup>. These collisions are mainly provoked in the spring-summer period, in the Corsico-Ligurian-Provencal basin, when the number of ships is the most abundant<sup>2</sup> and fin whales regroup to feed its main prey, the krill *Meganyctiphanes norvegica*<sup>3</sup>. However, knowledge about fin whales distribution in the Mediterranean Sea in winter is scarce even if scientists tend to agree that individuals belong to a Mediterranean

resident population<sup>4,5,6</sup> which stays in the Mediterranean Sea in a more diffuse way during winter<sup>5,7</sup> although migrations in the Atlantic Ocean can occasionally occur through the year<sup>5,6,7</sup>. Thus, assessing the annual distribution of Mediterranean fin whales appears to be an emergency in order to better protect the population from human disturbances.

Baleen plates proved to be good life recorders and thus this tissue can be used to delineate the distribution of whales<sup>6,8</sup>. Previous measures of carbon and nitrogen isotopes in baleen plates of fin whales stranded in the Mediterranean Sea<sup>6</sup> revealed that these individuals mostly fed on krill and were, for most of them, resident of the Mediterranean Sea. However, the isotopic composition of some individuals tended to show a different feeding behavior and their distribution remained to be evaluated.

Lead isotopes were then used as a complementary and independent proxy for the distribution of fin whales as it has been done in recent studies on minke whales<sup>9</sup>. Pb isotopic composition of water is a mixing of atmospheric composition and of sediment composition<sup>10</sup> giving to each marine area its own Pb isotopic composition. As marine mammals absorb heavy metals mainly by food consumption<sup>11</sup>, Pb isotopic composition in baleen plates should thus correspond to the composition of whales feeding area and should allow assessing the distribution of each individual.

## 2. Material and method

A total of 10 baleen plates (BP) of *Balaenoptera physalus* were collected over the last 35 years (1975-2012): 9 along the Mediterranean coasts (BP1, 2, 3, 6, 7, 8, 10, 11, 15) and 2 (BC and BD) along the southern part of the French Atlantic Ocean coast (Bay of Biscay). For each sample, between 200 and 600 mg of baleen plate were extracted and when it was possible, between 2 and 4 samples have been collected at approximately constant spacing. Pb was extracted following a chemical procedure described by Bosch et al.<sup>12</sup> and the isotopic compositions were measured on a Nu 1700 ICP mass spectrometer. Pb blanks determined the accuracy of the method and NBS981 Pb standards ensured its reproducibility. An ANCOVA test was performed to calculate linear regressions between  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in order to test the potential of Pb isotopes to discriminate the stranding areas (i.e. Atlantic Ocean and Mediterranean Sea). The significance levels for statistical analyses was set at  $\alpha = 0.05$ .

## 3. Result and discussion

The composition of the water column is clearly a mixture of atmospheric fall out (which is impacted by anthropogenic activities) and of rock/ore (natural composition)<sup>10</sup> (Fig. 1. a). Pb isotopic composition of samples is similar to the composition of the water column<sup>13, 14</sup> except for BP2 and BP15 whose composition is closer to that of the atmospheric Pb isotopes<sup>13, 15, 16, 17, 18</sup>. The Pb isotopic composition of baleen plate thus generally corresponds to the composition of the water column suggesting that Pb is mostly assimilated by food consumption as explained by Das et al.<sup>11</sup>. The composition is furthermore influenced by anthropogenic activities such as lead gasoline consumption<sup>19</sup>. A change in these activities could eventually explain BP2 and BP15 Pb isotopic compositions will be discussed later.

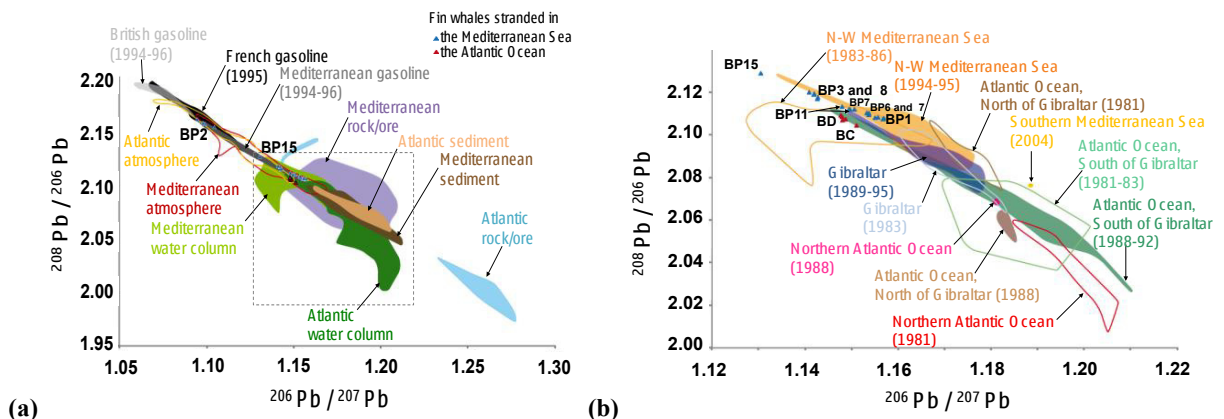


Fig. 1.  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  in baleen plates of fin whales stranded in the Mediterranean Sea (blue triangles) and in the Atlantic Ocean (red triangles) (a) Comparison with different Pb sources, the dashed square is the enlargement in b. (b) Comparison with data of water columns (year

of sampling in bracket).

Except for both BP2 and 15, individuals stranded in the Mediterranean Sea show the same composition as the North-Western Mediterranean Sea<sup>12</sup> (Fig. 1b). Individuals stranded in the Atlantic Ocean have the same Pb isotopic composition as the North-Eastern Atlantic area located South of Gibraltar latitude<sup>12, 13</sup>.

As Pb isotopic composition depends of each compartment (i.e. natural and anthropogenic), individuals of the same feeding area should be aligned on the same linear regression. Two linear regressions could thus be made for each stranding zone (Mediterranean Sea and Atlantic Ocean:  $y_{\text{Mediterranean}} = -0.977x + 3.234$ ;  $y_{\text{Atlantic}} = -0.977x + 3.229$ ;  $R^2 = 0.978$  with  $y = {}^{208}\text{Pb}/{}^{206}\text{Pb}$  and  $x = {}^{206}\text{Pb}/{}^{207}\text{Pb}$ ) and samples of each individual are plotted on its corresponding linear regression suggesting that they stranded in their feeding area.

The evolution of  ${}^{206}\text{Pb}/{}^{207}\text{Pb}$  ratio in baleen plates (Fig. 2) is similar to the evolution of this ratio in the atmosphere<sup>20</sup> showing a Pb isotopic composition strongly affected by leaded gasoline consumption until the 1990s regulation in European countries<sup>20</sup>. The difference of composition between BP1 and BP2 can be explained by a change of Pb source used in leaded gasoline: from 1980s, Australian Pb, with a lower  ${}^{206}\text{Pb}/{}^{207}\text{Pb}$  ratio, was the main Pb introduced in European gasoline<sup>20</sup>. After Pb banishment in gasoline, Pb isotopic composition of atmosphere reflected Pb emission by industrial activities and waste combustion whose  ${}^{206}\text{Pb}/{}^{207}\text{Pb}$  ratio is higher and closer to the natural ratio: this profile can be traced in baleen plates. However, BP15 shows a quite low  ${}^{206}\text{Pb}/{}^{207}\text{Pb}$  ratio suggesting that this individual could have been in a Mediterranean area close to countries where leaded gasoline was not entirely prohibited like in Algeria<sup>21</sup>.

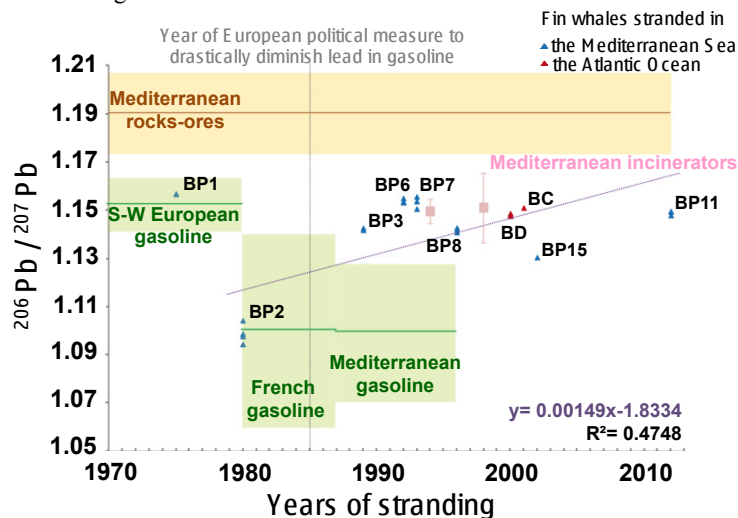


Fig. 2.  ${}^{206}\text{Pb}/{}^{207}\text{Pb}$  in relation with the year of baleen plate sampling.

The levels of Pb contents of all baleen plate samples were low ( $< 0.5$  ppm) except for the BP6 (1992) and BP8 (1996) animals, i.e. 3.55 and 1.46 ppm. These abnormally high values are likely due to the environmental pollution events. Indeed, some peculiar areas of Mediterranean are contaminated with metals such as, for example, the Eastern part of the Gulf of Lion where mussels could reach up to 6 ppm of Pb<sup>22</sup>.

#### 4. Conclusion

Pb isotopic compositions of baleen plate corroborate results obtained with C and N stable isotopes<sup>6</sup> suggesting that Mediterranean fin whales constitute a specific population which is year-round resident of the Mediterranean Sea. Its individuals may be distributed in the whole Mediterranean Sea in autumn-winter when their prey is scarcer. Therefore, individuals migrate very occasionally to the Atlantic Ocean through the strait of Gibraltar and the reason of such migrations remains to be understood. Thus, baleen plates record environmental events and can reconstitute the evolution of anthropogenic Pb pollution. This aspect has to be taken into consideration when Pb isotopes are used to study past distribution of whales.

## Acknowledgements

The authors are grateful to Béatrice Galland, Chantal Douchet, Laure Fernandez, D. Bechtel, L. Ducroix, M. Lapinski, C. Laforge and F. Witkowski for technical assistance and help during Pb extraction and analysis. Funding support provided to IB by the MISTRAL-BIODIVMEX CNRS program grant was used for funding the master project of Pauline Roubira and for analyzing lead isotopes. IB is very grateful to all members of BIODIVWHALE consortium and especially to Willie Dabin Franck Dhermain, Christophe Guinet, Thierry Legavre, Renaud de Stephanis, and the WWF, GIS3M, PELAGOS, GECEM and to Mr Fabre Jean-Louis, Bompard Jean-Michel and Maurer Jean. Eventually, we would like to thank Philippe Negrel for his constructive review.

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