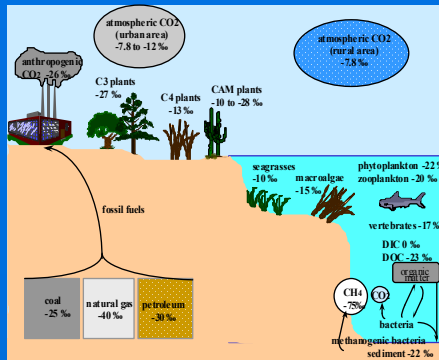


IN THE MARINE ENVIRONMENT; BIOMARKER SOURCES AND PALEOCLIMATE APPLICATIONS.

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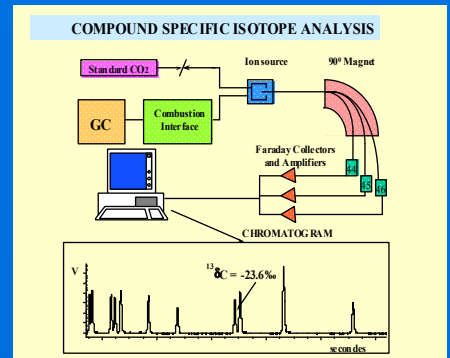
Introduction

In the natural environment, almost 99% of all carbon is <sup>12</sup>C, and only 1% is <sup>13</sup>C. The ratio of these two stable isotopes in natural materials varies as a result of isotopic fractionation during physical, chemical and biological processes.

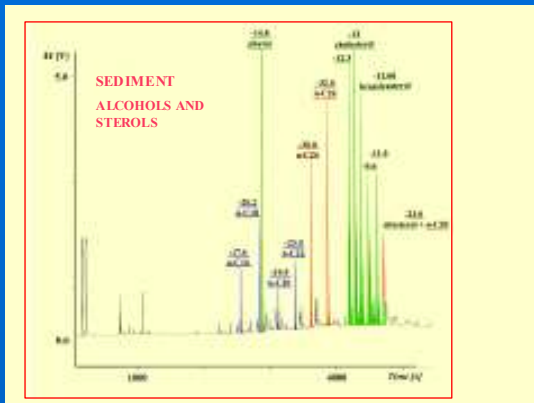
Such natural variations in <sup>13</sup>C can be used for the identification of sedimentary carbon sources and for the differentiation between marine and terrestrial sources.

<sup>δ13</sup>C values of bulk samples are sometimes controversial because <sup>13</sup>C is not uniformly distributed within the total organic matter. Therefore, compound specific isotopic analyses (CSIA) offers considerable advantages in determining the <sup>δ13</sup>C composition of individual compounds, avoiding the uncertainties of the pooled <sup>δ13</sup>C org sedimentary values. <sup>δ13</sup>C of specific biomarkers may also be useful for source identification, affording the origin of ubiquitous compounds with multiple potential sources and including the elucidation between terrigenous and/or marine organic matter.

Applications of the isotope techniques to palaeoenvironmental studies have been explored in recent years due to the observed trends between dissolved CO<sub>2</sub> in water and fractionation of carbon isotopes during photosynthetic fixation of CO<sub>2</sub>.

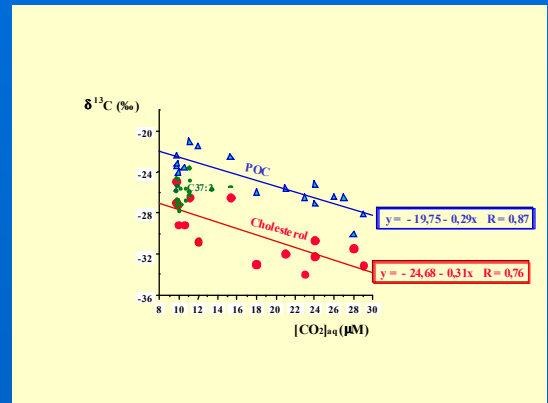


BIOMARKERS SOURCES



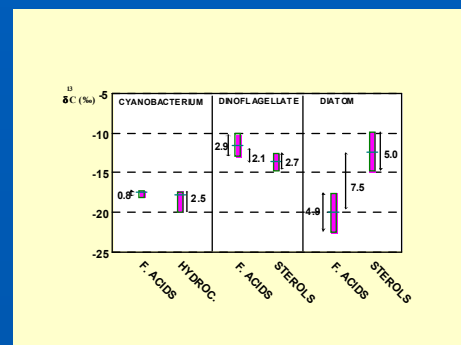
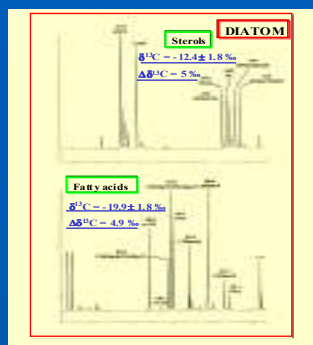
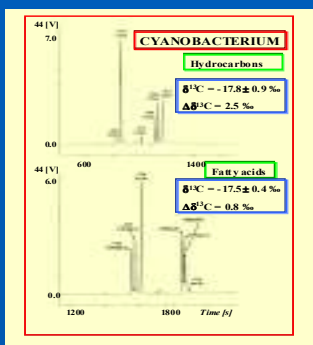
The long-chain *n*-alkanol (*n*-C<sub>24</sub>, *n*-C<sub>26</sub>), which are components of vascular plant waxes, exhibit <sup>δ13</sup>C depleted values (-30 to -32 ‰), typical of terrestrial plant biomarkers, whereas the more <sup>δ13</sup>C enriched values of -18 to -23 ‰ for the short-chain *n*-alkanol (*n*-C<sub>16</sub> to *n*-C<sub>22</sub>) indicates a marine source. Among the numerous possible terrigenous and marine biological sources of sterols, the enriched values found here let us infer a marine source. In particular, the C<sub>27</sub>Δ<sup>5</sup> sterol (24-ethylcholesterol-5-en-3β-ol) is composed of two epimers, β-sitosterol (24α) of higher plant origin and chionastrol (24β) of marine origin. Both epimeric sterols are not resolved in the commonly used apolar and semipolar GC columns, but our value of -23 ‰ for the composite peak (C<sub>27</sub>Δ<sup>5</sup> sterol and the *n*-C<sub>30</sub> alcohol of terrestrial origin) clearly indicates a predominance of the marine derived 24-ethylcholesterol-5-en-3β-ol. In the case of a terrestrial origin, values of -28 ‰ would be expected. These results point out that the combination of biomarker distributions and isotope measurements can enhance our ability to trace the inputs of organic material and help to clarify origins of terrigenous and/or marine organic matter.

PALEOCLIMATE APPLICATIONS



The distribution of <sup>δ13</sup>C of the particulate organic matter of phytoplankton vs the molecular CO<sub>2</sub> dissolved in surface waters has shown only good correlation for the autotrophic phytoplankton and not for those communities dominated by mixo/heterotrophic organisms. Investigations of the use of some marine biomarkers for the recovery of the CO<sub>2</sub> related signal, which would provide much better estimate of the palaeo-pCO<sub>2</sub> reconstruction for all sea-surface waters have been done. The long-chain C<sub>27</sub>-C<sub>30</sub> *n*-alkenes, derived exclusively from primary producers, are known to be particularly suitable as recorders of CO<sub>2</sub> levels. However, its low concentration in the particulate matter from low productivity regions has fostered the study of other more abundant biomarkers, such as cholesterol, which has a general planktonic origin with a large proportion derived from zooplankton inputs. A significant correlation between <sup>δ13</sup>C cholesterol of the suspended particulate fraction from the water column in the Indian Ocean and dissolved CO<sub>2</sub> concentrations was found. These results provide evidence that CSIA could offer important information on the CO<sub>2</sub> exchanges between oceans and atmosphere.

ISOTOPIIC COMPOSITION OF MOLECULAR COMPONENTS OF PHOTOSYNTHETIC ORGANISMS



CONCLUSIONS

Compound specific isotope analysis allows a more accurate assessment of the sources of organic carbon. The use of this technique in combination with biomarker studies is recommended for biogeochemical and paleoclimate studies.

Care must always be taken in the interpretation of the isotopic composition of individual biomarker compounds in terms of their source contributions since isotopic variations within and between compound classes metabolized by the same organism can be substantial.