VALIDATING THE ISOTOPIC FRACTIONATION OF GENERAL BIOMARKERS AS A pCO_2 PROXY USING MODERN NATURAL CO_2 VENTS IN JAPAN

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Introduction

Understanding the atmospheric concentration of carbon dioxide (pCO_2) is key to many earth system dynamics, yet reconstructing past pCO_2 remains a prevalent challenge. One promising proxy, the stable carbon isotopic fractionation associated with photosynthesis (ε_p), has been explored with mixed successes over the past several decades. The most explored biomarkers for calculating ε_p are alkenones, i.e. long-chain unsaturated methyl and ethyl *n*-ketones produced by select Haptophytes, but are limited in occurrence due to their evolutionary history.

Potentially offering a solution to ε_p as a pCO_2 proxy, general biomarkers offer a more defined source than bulk organic matter and a longer, more ubiquitous record than species-specific biomarkers, e.g. alkenones, over the Phanerozoic. One such general biomarker, the diagenetic product phytane derived from chlorophyll-a, has been used as a pCO_2 proxy for specific sites (Bice et al., 2006; Sinninghe Damsté et al., 2008; Naafs et al., 2016) but has not been methodically tested. To validate ε_p of general phototrophic biomarkers for reconstructing past pCO_2, seawater filters, phytoplankton net filters, and sediments were sampled from transects of naturally occurring CO_2 vents in Shikine Island (Japan) where concentrations range from 300 to 2000 ppm. CO_2 vents have been neglected in the literature partly due to their high sulfide concentrations which prevents microbial growth, a feature of CO_2 vents that Shikine Island lacks, allowing us to explore ε_p of phytoplankton in an otherwise uncommon field site.

Methods

Samples were extracted, saponified using base hydrolysis, eluted into polar fractions, analysed using gas chromatography with a flame ionization detector (GC-FID) and gas chromatography-mass spectrometry, and finally measured with isotope-ratio mass spectrometry. Figure 1 shows a GC-FID chromatogram with a high relative abundance of phytol, the chlorophyll sidechain from which phytane occurring in more ancient sediments is derived, as well as other potential pCO_2 biomarkers such as sterols. To calculate ε_p from the isotopic composition of the biomarkers, DIC will also be measured with isotope-ratio mass spectrometry.

Results and Discussion

The acquisition of data is currently on-going. The results are expected to offer insights into the potential of these biomarkers as paleo-pCO_2 proxies. These shallow CO_2 vents offer a unique approach for our pCO_2 proxy validation, minimizing the drawbacks of established approaches such as laboratory cultures and free-ocean CO_2 enrichment field experiments. Unlike their counterparts, CO_2 vents more accurately reflect the natural environment and lack difficult and time-consuming experimental set-up and maintenance. Furthermore, the CO_2 vents offer nearly limitless sample collection, which is vital for compound-specific isotope analysis which requires relatively high amounts of analyte.

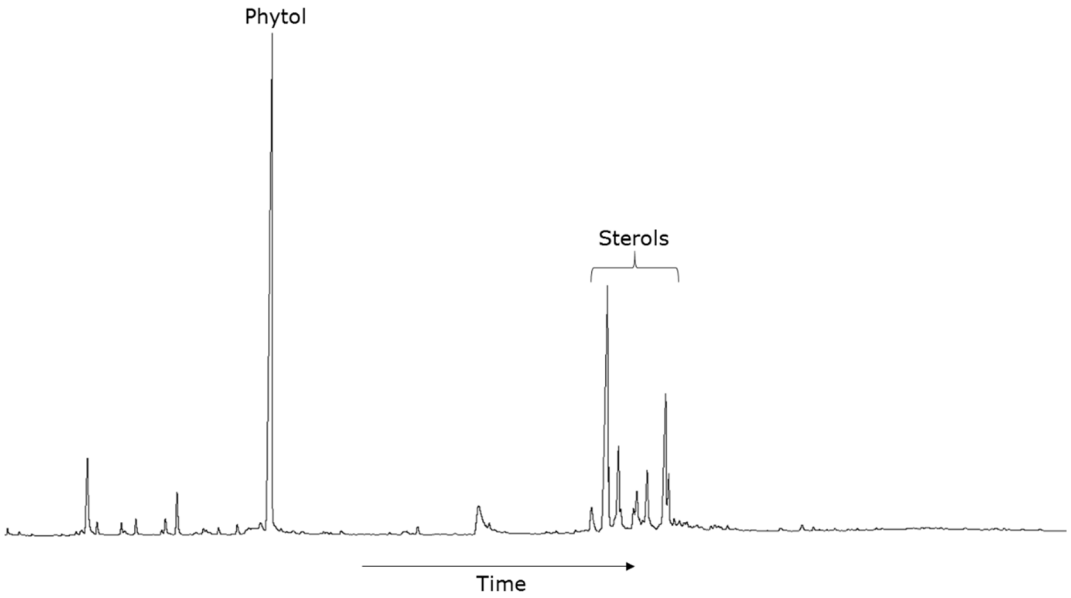

Figure 1. Chromatogram of the tetramethylsilane derivative of the particulate matter polar fraction collected at Shikine Island near a natural CO_2 vent.

References

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