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Biomarker Isotopic Signatures of Methanotrophy in Santonian Methane Seeps from the Panoche Formation

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Contemporary methane seeps support complex and diverse ecosystems fueled by chemosynthetic microbes that produce signature biomarkers characterized by highly negative $\delta^{13}C$ values that serve as a legacy of their activity. Suites of diagnostic compounds, notably acyclic isoprenoid alkanes, derived from anaerobic and aerobic methanotrophs have been reported in ancient seep deposits ranging from Pliocene to Oxfordian [1-11] with $\delta^{13}C$ values of -60 to -120 ‰. Prior research has documented Paleocene methane seep carbonates associated with the Moreno Formation in the Panoche Hills [12,13]. However, an older series of seep carbonates occur in this basin within the Upper Cretaceous (Santonian; 84 Ma) Panoche Formation characterized by their associated fauna [14]. Samples from this sequence of seep deposits were collected at six sites (A-F) and found to contain diverse fauna, including bivalves and gastropods or inoceramids, prompting evaluation of biomarker evidence for methanotrophy. The aliphatic hydrocarbon fractions recovered by extraction and separation of biomarkers were evaluated using gas chromatography-mass spectrometry (GC-MS). Nine samples collected from three of the six sites were found to contain varying distributions and abundances of compounds that are characteristic of anaerobic and aerobic methanotrophs. Determination of their $\delta^{13}C$ values by GC-isotope-ratio-MS confirmed this association (Figure 1) for phytane/crocetane (avg. -111 ‰), PMI (avg. pentamethylicosane; -107 ‰), squalane (avg. -86 ‰) and biphytane (avg. -95 ‰). In addition, the $\delta^{13}C$ composition of pristane (avg. -95 ‰) is consistent with their origin from anaerobic methanotrophs, as observed elsewhere [10,11]. $\delta^{13}C$ values for tricosane (n-C_{23}; avg. -64 ‰) and 4,14-dimethylcholestane (-66 ‰) are similar to prior reports [3,4,6,7,10,11], suggesting they derive from aerobic methanotrophs.

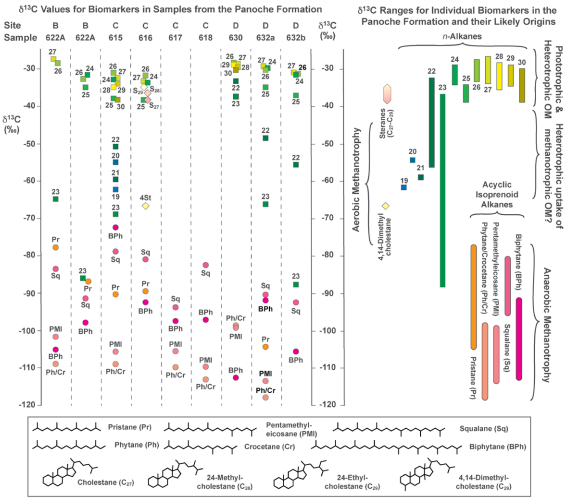


Figure 1: $\delta^{13}C$ Compositions of biomarkers in samples from three seep carbonate sites within the Panoche Formation that attest to the origins of specific compounds from anaerobic and aerobic methanotrophs.

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