

## $\delta^{13}\text{C}$ and $\delta\text{D}$ of Archaeal lipids in gas hydrate-bearing deep sediments

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Archaeal ecology associated with methanogenesis is poorly understood in deep marine sediments, although methane consuming process in aerobic/anaerobic conditions has been clarified at sub-surface sediments. Recently, we have found much archaeal isoprenoids in gas hydrate-bearing sediments at Cascadia margin (IODP exp 311). In this study, the archaeal lipid distributions with their carbon ( $\delta^{13}\text{C}$ ) and hydrogen ( $\delta\text{D}$ ) isotopic compositions are reported to evaluate the archaeal activities with their metabolisms.

A variety of archaeal biomarkers including crocetenes, 2,6,10,15,19-pentamethylcosane (PMI), and acyclic and tricyclic biphytane diols (BPD[0] and [3]) are abundant between 100 and 200 mbsf. Ether-bound cleavage of alcohol lipids gives isoprenoid hydrocarbons from membrane lipids. Concentrations of the resulting biphytanes (BP[0] to [3]) are about 100 times higher (e.g. BP[0]: 458  $\mu\text{g/gC}_{\text{org}}$  at 173 mbsf.) than those of crocetenes and PMI (up to  $\sim 5 \mu\text{g/gC}_{\text{org}}$ ). These biomarkers are isotopically divided into two distinctive groups (Fig 1). One group consists of BP[0], [2] and [3] with their isotopic compositions of  $\sim -20\text{‰}$  in  $\delta^{13}\text{C}$  and  $-280$  to  $-222\text{‰}$  in  $\delta\text{D}$ . As the  $\delta^{13}\text{C}$  value is comparable with that of bulk organic carbon, these biomarkers could be derived from heterotrophic archaea. Another group consists of phytane and BP[1] with  $\sim -40\text{‰}$  in  $\delta^{13}\text{C}$  and  $-204$  and  $-172\text{‰}$  in  $\delta\text{D}$ . The carbon isotopic composition indicates activity of chemoautotrophic archaea, probably methanogens.

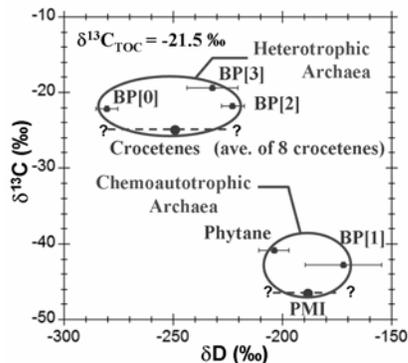


Figure 1:  $\delta\text{D}$ - $\delta^{13}\text{C}$  plot of ether-bound lipids at 142 mbsf.

## High $^3\text{He}/^4\text{He}$ reservoir – Highly depleted source?

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Many ocean island basalts (OIBs) show variable  $^3\text{He}/^4\text{He}$  ratios higher than those of MORBs (Mid-ocean ridge basalts) which are uniform of around 8Ra. OIB sources are generally regarded to be non- or less-degassed compared to those of MORBs. However, since high  $^3\text{He}/^4\text{He}$  ratios up to 50Ra have been found in Baffin island with MORB-like Sr and Nd isotope signatures [1], the high  $^3\text{He}/^4\text{He}$  reservoir has often been attributed to a highly depleted one [2] and a refractory phase such as olivine or dunite is raised as a candidate to retain such He due to its higher He/U ratio than the source material [3]. Since both He and U are highly incompatible elements with their partition coefficients of less than  $10^{-3}$  between crystal and a melt, He concentration in a refractory phase should be much lower than in the primary source.

Although OIBs from Hawaii and Iceland show high  $^3\text{He}/^4\text{He}$  of more than 20Ra and depleted characteristics for solid element isotopes (Sr, Nd, Pb, Hf), depleted characteristics can be explained by mixing with MORB-like asthenospheric components.  $^3\text{He}/^4\text{He}$  ratios higher than 20Ra can be also found in OIBs from Samoa, which are not highly depleted in solid element isotope signatures. To explain the observed isotope signatures,  $^3\text{He}$  concentration in the primary source should be  $> 10^{-10}\text{ccSTP/g}$ , which seems much higher than the expected value in a refractory phase ( $<< 10^{-12}\text{ccSTP/g}$ ).

Kimberlites also show high  $^3\text{He}/^4\text{He}$  ratios up to 26Ra [4] and their solid element isotope signatures tightly cluster close to BSE. Since such signatures are common for Group I kimberlites in quite different space and time, those characteristics would be attributed to that of the source. In the kimberlite source, the effect of ancient E-MORBs stored in the non-convective mantle for more than 2 b.y. has been suggested [5]. By taking account of such signatures,  $^3\text{He}$  concentration in the kimberlite source is estimated to be in the order of  $10^{-8}\sim 10^{-9}\text{ccSTP/g}$ . Thus, high  $^3\text{He}/^4\text{He}$  reservoir is not limited in a highly depleted source and at least should retain significant amount of  $^3\text{He}$ .

[1] Stuart *et al.* (2003) *Nature* **424**, 57-59. [2] Class & Goldstein (2005) *Nature* **436**, 1107-1112. [3] Albarède (2008) *Science* **319**, 943-945. [4] Tachibana *et al.* (2006) *Geology* **34**, 273-276. [5] Nowell *et al.* (2004) *J. Petrology* **45**, 1-29.