4-3. Source of Methane: Thermogenic and/or Microbial

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Although there are some debatable questions for mixing ratio, mixing process, mass balance, etc., there is fairly general agreement that the origin of methane (C_1) in the Sea of Okhotsk is mixed-gas (thermogenic and microbial). Thermogenic C_1 is produced by thermal cracking process of organic matter in the deep layer of sediment. On the contrary, production of microbial C_1 is dominant in the surface layer (from sea bottom to several hundred meters in depth). Basic idea is that the thermogenic gas from the deep layer is ascending and mixing with the microbial gas in the shallow layer.

Fig. 4-3-1 shows the relation between $\delta^{13}C$ of C_1 and ethane (C_2), based on the classification of Milkov (2005). Though $\delta^{13}C$ of C_1 seems to be typical microbial in the Sea of Okhotsk (Fig. 4-3-1a), that of C_2 is rather thermogenic origin. $\delta^{13}C$ of C_2 at the seepage structures of CHAOS, VNIIOkeangeologia, and Giselle Flare is about -30 ‰, showed typical thermogenic C_2, and microbial C_2 is mixed at the other sites. This is one of the evidence of mixing between thermogenic and microbial gases. Because thermogenic gas contains a lot of C_2 and propane (C_3) in contrast to microbial gas, a mixing line between microbial and thermogenic gases are plotted like an "L-shaped distribution" between $\delta^{13}C$ of C_1 and C_2 (Fig.4-3-1b). Mixing ratio of thermogenic and microbial gases is a debatable point, but the result shown in Fig. 4-3-1a (the Sea of Okhotsk) suggests considerable contribution of microbial gas according to the deletion of C_1 ^{13}C.

The isotope data of Lake Baikal shows typical "L-shaped distribution" in Fig. 4-3-1b. The hydrate-bound C_1 and C_2 of Peschanka mud volcano show typical microbial gas, whereas those of Gorevoy Utes (oil seep site) show typical thermogenic gas. Those of other sites seem to be their mixture. Khlystov *et al.* (2007) showed an oil deposit in a schematic cross section at Gorevoy Utes. The existence of typical thermogenic gas is confirmed at Lake Baikal.

Matsumoto *et al.* (2009) reported that C_1 $\delta^{13}C$ is widely distributed in the hydrate-bound and dissolved gases retrieved off Joetsu basin, eastern margin of Japan Sea: C_1 $\delta^{13}C$ of hydrate-bound and seep gases are mostly from -50 to -30 ‰, corresponded to the range of thermogenic C_1, while dissolved C_1 in pore water in the peripheral areas of the seep sites is microbial ($\delta^{13}C$ is from -100 to -50 ‰). The typical thermogenic gas (^{13}C-rich C_1) is also encaged in the crystal lattice of gas hydrates at Lake Baikal (Gorevoy Utes, oil seep area).

$\delta^{13}C$ of microbial C_1 is widely distributed and ^{13}C seems to be rather depleted (from -110 ‰ to -70 ‰), while $\delta^{13}C$ of thermogenic C_1 is from -40 ‰ to -30 ‰ (Bernard *et al.*, 1976; Whiticar, 1999). Thermogenic C_1 is not yet found in the Sea of Okhotsk, though it is detected in the above study fields (Lake Baikal and Japan Sea). $\delta^{13}C$ of C_1 has been reported from -65 ‰ to -55 ‰ by researchers in the Sea of Okhotsk (Lein *et al.*, 1989; Ginsburg *et al.*, 1993; Hachikubo *et al.*, 2010a). The isotope data suggests microbial origin in the criteria of previous reports. Nevertheless, it is fair to say that the gas origin in the Sea of Okhotsk is a mixture between thermogenic and microbial gases.

Recently, isotopic fractionation during natural gas hydrate formation is discussed by Vaular *et al.* (2010). They raised a question that isotopic evidence classifies the hydrate-bound gas microbial while the composition and geological setting show tales of a thermogenic source. They speculated a fractionation of ^{13}C through hydrate formation, however, Hachikubo *et al.* (2007) has already reported that δD of hydrate-bound C_1 is several ‰ lower than that of residual C_1 in the formation processes while there was no difference in the case of $\delta^{13}C$. Therefore, isotopic fractionation is not the cause of depletion in C_1 ^{13}C. Somewhat filtering effect by the sediment particles (ex. diatom, clay, etc.) have to be checked in future.

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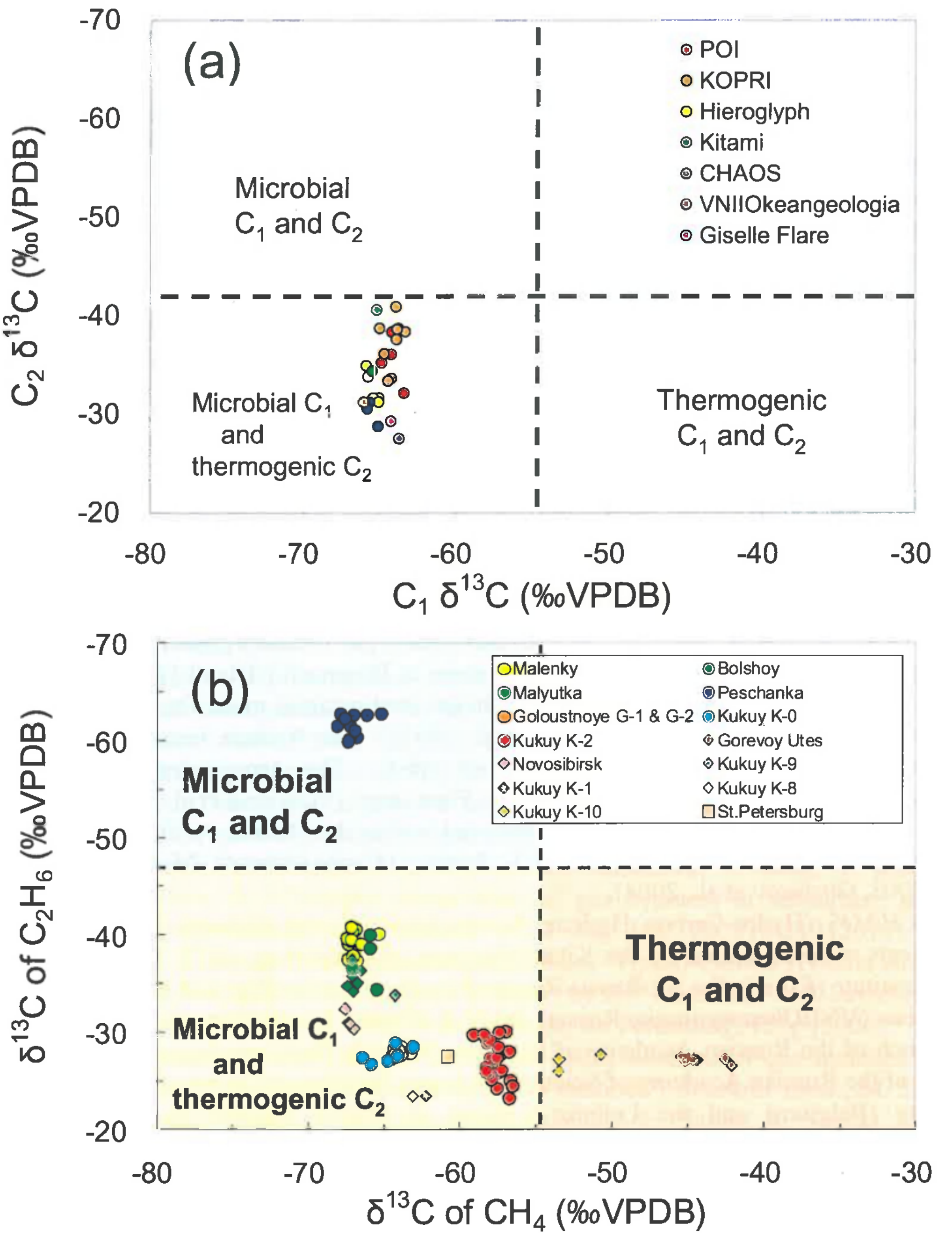

Fig. 4-3-1 Relationship between $\delta^{13}C$ of methane and ethane in the hydrate-bound gases (data: Hachikubo *et al.*, 2010a; 2010b; Shoji *et al.*, 2011). (a) The sea of Okhotsk. (b) Lake Baikal.