Sustainable thermogenic CH4 and H2 generation in the Nankai Trough subduction zone

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Abstract

Mud volcanoes, gas plumes, and gas hydrates comprising thermogenic and biogenic CH\(_4\) are widely distributed in the Nankai Trough subduction zone, showing ongoing significant CH\(_4\) activity. However, the source rocks of the thermogenic CH\(_4\) and the geological source of H\(_2\) for microbial CH\(_4\) production remain uncertain. Here, we reveal the timing and amount of the thermogenic CH\(_4\) and H\(_2\) generation in shales and metapelites during diagenesis to metamorphism and estimate their current generation in the Nankai Trough from the movements of the oceanic plate and the accretionary prisms. The results show that the thermogenic CH\(_4\) and H\(_2\) are generated mainly in the underthrust sediments below the décollement. The sustainable H\(_2\) supply from the underthrust sediments can be another potential H\(_2\) contributing to microbial CH\(_4\) production. The findings enhance our understanding of the active CH\(_4\) emission, large-scale gas hydrate formation, and subseafloor biosphere in the oceanic plate subduction zone.

Introduction

Methane (CH\(_4\)) is an energy resource and a greenhouse gas. Its accumulation in the subsurface and emission on the seafloor have long drawn research attention. On the other hand, the source and supply of hydrogen (H\(_2\)) in the geosphere have also attracted growing interest because H\(_2\) supply is a critical factor for sustaining the deep biosphere and the production of microbial CH\(_4\). In the geosphere, the molecular H\(_2\) is produced via the degradation of sedimentary organic matter biologically by H-producing bacteria (Parks et al., 2014) and inorganically by hydrothermal alteration such as serpentinization (Seewald, 2003; Mayhew et al., 2013) and interactions between water and the fractured surface of silicate minerals (Kameda et al., 2003; Saruwatari et al., 2004). H\(_2\) is also generated thermally with aromatization, condensation, and graphitization of sedimentary organic matter (Li et al., 2015, 2017; Suzuki et al., 2017). In an arc-trench system, marine sediments on the oceanic plate are transported deep into the crust and undergo metamorphic processes. The underthrust sediments below the detachment thrust (décollement) of an oceanic plate may serve as unknown CH\(_4\) and H\(_2\) source rocks and play a significant role in the accumulation and emission of CH\(_4\) in the plate subduction zone. However, few studies have been conducted on the potential of underthrust sediments as CH\(_4\) and H\(_2\) suppliers within an arc-trench system.

The arc-trench system comprising the Japanese island arcs, the Japan Trench, and the Nankai Trough is a typical example of such a system. The CH\(_4\) accumulations and emissions, such as mud volcanoes, methane plumes, and gas hydrates or bottom simulating reflectors (BSRs), are occurring widely in the forearc basins and accretionary prisms distributed along the Nankai Trough (Ashi et al., 2002; Hayashi et al., 2010; Kida et al., 2015; Asada, 2020) (Fig. 1). The total amount of CH\(_4\) in gas hydrate-bearing sediments in the eastern Nankai Trough has been estimated to be about 40 trillion cubic feet (1.1x10\(^{12}\)m\(^3\)), probably one of the world’s largest marine gas hydrates (Fujii et al., 2008). Dissolved-in-
water type gas deposits (dissolved gas deposits), mainly composed of CH₄, are distributed in the coastal land of the Tokai and southwestern Kyushu near the Nankai Trough, and CH₄ seeps also occur in these areas (Igari and Sakata, 1989; Kato et al., 2009, 2011; Sakata et al., 2012; Matsushita et al., 2016). These CH₄ accumulations and emissions are composed of thermogenic and/or microbial CH₄ (Igari and Sakata, 1989; Tsunogai et al., 1998; Waseda and Uchida, 2004; Kato et al., 2009, 2011; Sakata et al., 2012; Pape et al., 2014; Kida et al., 2015; Matsushita et al., 2016; Ijiri et al., 2018). It is, however, unclear where and how much thermogenic CH₄ is generated in the Nankai Trough subduction zone. In addition, although the significant CH₄ production by methanogens in the organic-poor environment requires geological H₂, the origin and source of H₂ remain uncertain (Parks, 2014). Understanding the spatial location and the rate of CH₄ and H₂ generation in the subduction zone will clarify the geological context of active CH₄ accumulations and emissions in an arc-trench system. In this regard, we focused on the underthrust sediments below the décollement of the subducting oceanic plate.

In contrast to the long time required for forming conventional oil and gas deposits, gas hydrates and mud volcanoes are formed within a geologically short time, indicating the availability of a sufficient supply of CH₄ relatively quickly. Hence, a great CH₄ flux (or a fast generation rate of CH₄) plays a critical role in forming gas hydrates and mud volcanoes. The convergence rates of the Philippine Sea Plates concerning the Japan Arc are estimated to be about 50 to 60 mm/yr (year) (DeMets et al., 2010; Loveless and Meade, 2010; Argus et al., 2011; Kimura et al., 2018), showing a much faster rate than the subsidence rates of the sedimentary basin. The subsidence rate is related to the heating rate, which can affect the thermal decomposition rate of sedimentary organic matter. The maturity level of the thermogenic CH₄ and H₂ generation in the subduction zone can be estimated based on the compositional change of residual gas in shales and metapelites from accretionary prisms exposed on land. From the heating and subsidence rates of the accretionary prisms and the underthrust sediments, we have predicted the spatial distributions and rates of thermogenic CH₄ and H₂ generation in the Nankai Trough subduction zone. The expulsion and migration of thermogenic CH₄ and H₂ have been discussed, considering the active seismogenesis and their solubility in the deep fluids. The present study shows that the generation rate of thermogenic CH₄ in the underthrust sediments is much higher than in the accretionary prisms, and the thermogenic CH₄ in the Nankai Trough subduction zone is mainly derived from the underthrust sediments. Following the thermogenic CH₄ generation, the thermogenic H₂ is generated significantly in the underthrust sediments during the metagenesis to metamorphism in the deep subduction zone. The thermogenic H₂ derived from the underthrust sediments can be another potential geological source of H₂ for microbial CH₄ production in the Nankai Trough. The sustainable supply of thermogenic CH₄ and H₂ from the underthrust sediments associated with the oceanic plate subduction can contribute significantly to the accumulation and emission of CH₄ represented by the formation of large-scale gas hydrates in the Nankai Trough.

**Results and Discussion**
Organic matter in the underthrust sediments

The oceanic lithosphere ages of the subducting Philippine Sea Plate slab in southwest Japan are estimated to be 15–30 Myr (Hua et al., 2018). Underthrust sediments comprise pelagic sediments that have been transported by the movement of the oceanic plate and marine and terrestrial sediments deposited in the trench. The pelagic sediments of the Philippine Sea Plate are composed of claystone, radiolarian and diatomaceous siliceous mudstones, and nannofossil calcareous mudstones (Moore et al., 2015; Raimbourg et al., 2017). Rock-Eval® analyses for Ocean Drilling Program (ODP)/Deep-Sea Drilling Project (DSDP)/Integrated Ocean Drilling Program (IODP) sediment samples equivalent to the subducting section in the Nankai Trough showed that the Cretaceous to Quaternary sediments deposited far from the continents were richer in marine organic matter (Type II kerogen) (Raimbourg et al., 2017). Conversely, those deposited in the ocean-continent subduction zone showed a significant terrestrial organic matter content (Type III kerogen). Frequent earthquakes in the subduction zone trigger the remobilization of surficial sediments along the landward slope to the trough, resulting in marine and terrestrial sediment accumulation in a trough (Ashi et al., 2014; Ikehara et al., 2020). In the Nankai Trough, the sediment sections on the Philippine Sea Plate are relatively thick (more than 1000 m), and the upper and younger parts of sedimentary layers were accreted to the landward plate to form accretionary prisms with plate subduction (Moore et al., 2015; Kimura et al., 2018). The underthrust sediments subducted beneath the accretionary prisms comprise the lower and older sedimentary sections. However, information about the lower sedimentary layers on the Philippine Sea Plate is lacking since few drilling operations have penetrated all the sedimentary layers above the basaltic basement.

Thus, the lithologies and organic types of underthrust sediments are diverse and unclear, and the abundance of organic matter varies. The TOC concentrations of Neogene sediments from IODP Expedition 333 drill sites (C0011 and C0012), close to the Nankai Trough, are low, ranging from 0.2 to 0.5 wt% (Henry et al., 2012). Raimbourg et al. (2017) have estimated the average TOC concentration of the underthrust sediments of the Philippine Sea Plate as about 0.5 wt%, considering the results of ocean drilling programs (ODP, DSDP, and IODP) in the Pacific Oceans. Although this TOC concentration seems somewhat higher than the average TOC concentrations of shale (0.44%, n = 28) and metapelites (0.33%, n = 41) from the old accretionary prisms in the Shikoku region (Table S1), the difference is reasonable considering the thermal decomposition during diagenesis to metamorphism. In the present study, the thermogenic CH$_4$ and H$_2$ generation in accretionary prisms and underthrust sediments of the Nankai Trough is estimated, assuming the initial TOC concentration as 0.5%.

Heating rate of accretionary prisms and underthrust sediments

Since the difference in the heating rate of accretionary prisms and underthrust sediments directly affects the generation rate of thermogenic CH$_4$ and H$_2$, the difference in their heating rates in the subduction zone was first examined. The heating rate of sediments in the Nankai Trough subduction zone can be estimated based on the thermal structures, movement of accretionary prisms, and the convergence rate of the Philippine Sea Plate. The Kumano-nada region, offshore of the Kii Peninsula, is one of the sections
in the Nankai Trough where the subduction history of the Philippine Sea Plate, the formation of accretionary prisms, and thermal structure, respectively, have been well investigated (Moore et al., 2015; Kimura et al., 2018) (Fig. 2). In the subduction zone ranging from 25–100 km landward from the trough axis, the heat flow is nearly constant and ranges from 50–65 mWm\(^{-2}\) (Kinoshita et al., 2011; Harris et al., 2013). The depth-temperature relationship below 200°C in the Kumano-nada basin (Fig. 2) is according to the long-term borehole monitoring system installed at Site C0002 during the IODP Expedition 332 (Sugihara et al., 2014) and that extrapolated to the subsurface temperature distribution in the Kumano-nada region (Fig. S2). Temperature distributions over 200°C (Fig. 2) were from the modeling results of the thermal structure around the Philippine Sea Plate (Figs. S3 and S4) (Ji et al., 2016; Suenaga et al., 2019).

The subduction resurgence of the Philippine Sea Plate with formations of the forearc basin and new accretionary prisms began about 6.0 myr ago (Moore et al., 2015; Kimura et al., 2018). The subduction zone with nearly the same geological structure as the present was formed about 2.2 myr ago (Screaton et al., 2009; Strasser et al., 2009). According to the sediment accretion models in the Nankai Trough (Saffer et al., 2008; Miyakawa et al., 2019), we estimated the lateral velocity of the accretionary prism. The thickness of the accretionary prism in the Kumano-nada region gradually increases landward. Considering the total volume of the outer prism and its initiation 2.2 myr ago, the average annual volume of sediment accretion along the 1 km trough is estimated to be approximately 53.2 \(\times 10^3\) m\(^3\)/yr (53.2 km\(^3\)/myr) (Figs. S5 and S6). The lateral velocity of the accretionary prism gradually decreases with an increased thickness and distance from the trough. The current lateral velocity of the thickest prism was estimated to be approximately 6.0 mm/yr (Fig. S6). The vertical subsidence rate of the accretionary prism was from the burial rate of the Kumano forearc basin (about 1.0 mm/yr) and the taper angle (7.5°) of the subducting plate (Moore et al., 2015). The average subduction rate of the Philippine Sea Plate along the Nankai Trough was set to 50 mm/yr (DeMets et al., 2010; Argus et al., 2011; Kimura et al., 2022). As a result, the movement velocities of the deepest part of the inner prism and the underthrust sediments were estimated as approximately 6.3 mm/yr and 50.2 mm/yr, respectively (Figs. 2 and S6). The heating rates of sedimentary rocks are mainly related to the vertical velocity of movement and the temperature gradient. Considering the subsurface temperature distribution in the Kumano-nada region, the heating rates of the accretionary prisms and the underthrust sediments were estimated to be about 30°C/yr and 125°C/yr, respectively (Fig. 2).

**Timing of thermogenic CH\(_4\) and H\(_2\) generation in the subduction zone**

The thermogenic CH\(_4\) and H\(_2\) generation in the subduction zone was predicted based on the concentration changes of residual gases in shales and metapelites with increasing diagenetic and metamorphic temperatures. Although the residual gas concentration in pelitic rocks has an upper limit because of the limited capacity to retain gaseous components, it depends roughly on the total gas amount generated during diagenesis and metamorphism. Shales and metapelites were newly obtained from the same sampling route of the old accretionary prisms and analyzed for the residual gas by an improved analytical method. A small peak of O\(_2\) relative to the N\(_2\) peak in the chromatogram shows
negligible air contamination during analysis (Fig. S1). The CH$_4$, C$_2$H$_6$, CO$_2$, N$_2$, and H$_2$ were detected as residual gases in shales and metapelites from the old accretionary prisms (Fig. S1 and Table S1). The relationship between VR and the maximum heating temperature of the samples was determined using Easy%RoV (Burnham, 2019), considering the heating rate (30°C/myr) of the accretionary prisms in the Nankai Trough subduction zone (Fig. 2).

The concentration changes of residual C$_2$H$_6$, CH$_4$, and H$_2$ with increasing diagenetic and metamorphic temperatures are shown in Fig. 3, with some typical gas chromatograms of residual gas. The residual ethane (C$_2$H$_6$) concentration reaches its maximum concentration at around VR = 2.0% and almost disappears at the maturity level of VR = 2.5%. The residual CH$_4$ concentration rises at about 130 to 150°C (VR = 0.7%) and reaches a peak (1500–1700 µL/gTOC) at about 220 to 230°C (VR = 2.5%). Then, it decreases probably due to the formation of graphitic carbonaceous material (Galimov et al., 1973; Luque et al., 2012). The residual H$_2$ concentration rises at around 150 to 200°C (VR = 1.0 to 2.0%) and shows a higher concentration in the pelitic rocks at metagenesis to metamorphism (VR > 4.0%). In metapelites that experienced higher temperatures of more than 300°C, the volume concentration of H$_2$ exceeds that of CH$_4$ (Fig. 3). The residual CO$_2$ concentration decreases drastically from several hundred to less than 10 µL/gTOC in the maturation stage of VR < 2.0% (Table S1). The decrease in residual CO$_2$ is possibly due to the decarboxylation of sedimentary organic matter and the expulsion of CO$_2$ with porosity reduction.

Since some CO$_2$ is adsorbed on the mineral surface during pulverization, the residual CO$_2$ concentration measured is less than the total CO$_2$ retained in shale rocks (Suzuki et al., 2017). The concentration of residual N$_2$ ranges mostly from 100 to 1000 µL/gTOC and does not show any systematic change with increasing temperature (Table S1). The origin of residual N$_2$ is currently unknown. The residual C$_2$H$_6$, CH$_4$, and H$_2$ in the shales and metapelites are mainly derived from the thermal decomposition of sedimentary organic matter (Suzuki et al., 2017).

The thermogenic CH$_4$ is mainly generated by the thermal cracking of hydrocarbons and kerogen during the thermal condensation of macromolecular intermediates and kerogen. Therefore, the amount of thermogenic CH$_4$ generation is related to the expulsion of hydrocarbons. In the case of accretionary prisms and underthrust sediments, the average TOC concentration is estimated to be so low (0.5 wt%) compared to ordinary petroleum source rocks, suggesting minimal expulsion of hydrocarbons because of their poor saturation in the pore space. Hence, from the viewpoint of thermal decomposition, the thermogenic CH$_4$ generation is regarded as proceeding almost in a closed system. In closed-system pyrolysis experiments of sedimentary organic matter, the thermogenic CH$_4$ concentration gradually increases with increasing thermal maturation from VR = 0.7 to 4.0%, and C$_2$H$_6$ disappears at around VR = 2.5% (Behar et al., 1997; Xiong et al., 2016). These relationships between the concentration changes in thermogenic CH$_4$ and C$_2$H$_6$ and VR values are consistent with the maturation stages (VR values) of the residual CH$_4$ and C$_2$H$_6$ concentration changes in the old accretionary prisms (Fig. 3). The maturation level of the oil generation zone is generally variable due to the difference in kerogen type. However, the timing of wet and dry gas generations is not so dependent on the initial kerogen type because mature kerogens
are characterized by similar chemical structures dominated by C-C bonds (Waples, 2000). We assumed the endpoint of C₂H₆ generation and the CH₄ generation zone were at VR = 2.5% and VR = 1.5 to 4.0%, respectively, considering the closed-system pyrolysis experiments and the change of residual gas concentrations in the old accretionary prisms.

Hydrogen atoms and radicals produced during oil and wet gas generation are consumed immediately by secondary reactions, e.g., the hydrogenation of alkenes (Li et al., 2017). The formation of molecular H₂ proceeds significantly during the carbonization and graphitization of carbonaceous material in a metagenesis and metamorphic stage. The generation of thermogenic H₂ from kerogen at a high temperature, following CH₄ generation, has been confirmed in laboratory pyrolysis experiments (Li et al., 2015, 2017). We assumed that the thermogenic H₂ generation zone starts from VR = 2.5%, corresponding to the maturity level of the wet gas disappearance. The progress of the organic reaction under high pressure is generally retarded compared to that under low pressure (Dalla et al., 1997; Bayon et al., 2011). Since the metamorphism in the Nankai Trough proceeds under relatively higher pressures than other subduction zones (Peacock, 2009), the timing of thermogenic H₂ generation may be retarded compared to the old accretionary prisms. In the present study, the thermogenic CH₄ and H₂ generation zones have been estimated to range from VR = 1.5 to 4.5% and VR > 2.5%, respectively. Temperatures in the accretionary prisms and the underthrust sediments corresponding to these VR values are different because of their different heating rates. According to the Easy%RoV, the VR values of 1.5%, 2.5%, and 4.5% for the accretionary prisms with a lower heating rate of 30°C/myr correspond to 194, 222, and 268°C, respectively. On the other hand, the same VR values for the underthrust sediments with a higher heating rate of 125°C/myr are equivalent to 204, 233, and 279°C, respectively, which are about 10°C higher than the accretionary prisms. The thermogenic CH₄ and H₂ generation zones in the Nankai Trough subduction zone are shown in a schematic geologic section of the Kumano-nada region off the Kii Peninsula (Fig. 4).

Significant CH₄ and H₂ generation in the underthrust sediments

The low TOC concentration (0.5 wt%) estimated for the underthrust sediments is unfavorable for the oil expulsion since the oil expulsion from the sediments is promoted by an increase in oil saturation in the pore space. In addition, oil generation proceeds under lower permeable conditions due to the high compression pressure by the oceanic plate subduction. Accordingly, oil generated under low permeability does not expel sufficiently, resulting in more generations of CH₄ by thermal cracking of retained oil and wet gas. Another characteristic of underthrust sediments is a much faster subduction rate than the burial rate in the sedimentary basin. In the subduction zone, more sedimentary rocks are brought deep into the crust within a short time, and the thermal maturation of sedimentary organic matter proceeds rapidly. To clarify the respective contribution of the underthrust sediments and accretionary prisms to the thermogenic CH₄ generation in the subduction zone, their annual CH₄ generation rates were estimated and compared.
Although the sediments in the subduction zone comprise some terrestrial organic matter, we assumed the same Type II (marine) kerogen and TOC concentration (0.5 wt%) for comparison convenience. According to pyrolysis experiments of kerogen in a closed system, the ultimate yield of CH$_4$ from Type II kerogen was approximately 300 mgCH$_4$/gTOC (Behar et al., 1995; Xiong et al., 2016). Therefore, the annual generation rate of CH$_4$ can be estimated from the TOC concentration, the apparent sediment density (2.6), and the movement velocity of the underthrust sediments and the accretionary prisms. The underthrust sediments of about 1 km thick are moving through the CH$_4$ generation zone at a subduction rate of about 50.2 mm/yr in the Kumano-nada region (Fig. 2). Under these conditions, the annual generation rate of CH$_4$ in the underthrust sediments subducting along the 1 km Nankai Trough was estimated to be approximately $2.7 \times 10^5$ m$^3$/yr. In the case of accretionary prisms, only the sediments at the deepest part of the inner prism have reached the CH$_4$ generation zone (Fig. 4). The old accretionary prisms act as a static backstop and mainly comprise highly mature sediments, and metamorphic, volcanic, and plutonic rocks (Kimura et al., 2018; 2022), suggesting a significantly low current generation of thermogenic CH$_4$ and H$_2$.

In the accretionary prisms, it can be regarded that about a 2 km thick sediment layer above the décollement is moving landward through the CH$_4$ generation zone at a rate of 6.3 mm/yr (Fig. 4). Like the underthrust sediment, if the ultimate amount of thermogenic CH$_4$ was generated in the 2 km thick sediment layer moving at 6.3 mm/yr, the annual CH$_4$ generation rate in the accretionary prism along the 1 km Nankai Trough is estimated at approximately $6.9 \times 10^4$ m$^3$/yr. However, the highest temperature of the CH$_4$ generation zone in the inner prism is about 225°C (VR = 2.5%), and only a limited part has reached the CH$_4$ generation zone. Considering the thermogenic CH$_4$ generation zone (ca. 195–270°C) of the accretionary prisms, the generation level of thermogenic CH$_4$ in the inner prism is much less than 50% of the ultimate level. Therefore, the annual generation rate of CH$_4$ in the accretionary prism along the 1 km Nankai Trough is estimated to be much less than $3.5 \times 10^4$ m$^3$/yr, significantly lower than the underthrust sediments. The remarkably higher generation rate of thermogenic CH$_4$ in the underthrust sediments is attributed to sufficient thermal maturation with a faster subduction rate. The residual gas in highly mature shales and metapelites comprises the thermogenic H$_2$ at a volume concentration similar to CH$_4$, showing that the thermogenic H$_2$ generation rate is comparable to that of thermogenic CH$_4$ (Fig. 3).

Thermogenic CH$_4$ and H$_2$ generation in the underthrust sediments has continued for at least the past 2.2 myr, according to the evolutionary history of the subduction of the Philippine Sea Plate (Screaton et al., 2009; Strasser et al., 2009; Moore et al., 2015; Kimura et al., 2018; 2022). The total thermogenic CH$_4$ generation during the last 2.2 myr reaches approximately $5.9 \times 10^{11}$ m$^3$ per 1km width of the Nankai Trough. The movement velocity of the inner prism indicates that its lowest part arrived at the CH$_4$ generation zone about 2.0 myr ago. Since then, the thermogenic CH$_4$ generation in the accretionary prism has gradually continued increasing over time. However, the inner prisms of the Nankai Trough have not yet reached the thermogenic H$_2$ generation zone.
Spatial distribution of thermogenic CH$_4$ and H$_2$ generation zone

The spatial distribution of the thermogenic CH$_4$ and H$_2$ generation zones of the underthrust sediments and the accumulation and emission of CH$_4$ in the Nankai Trough is shown in Fig. 5. Gas hydrates and BSRs are located apart from the thermogenic CH$_4$ and H$_2$ generation zones, and distributed widely trough-ward. The mud volcanoes in the Kumano-nada region off the Kii Peninsula and the Hyuga-nada off Nichinan tend to be distributed landward compared to gas hydrates and BSRs and overlap with the CH$_4$ generation zones (Fig. 5). The $\delta^{13}$C values of CH$_4$ from mud volcanoes in the Kumano-nada region range from $-20$ to $-40\%$ (Pape et al., 2014; Ijiri et al., 2018), suggesting a significant contribution of thermogenic CH$_4$. The dissolved gas deposits are distributed in the coastal area from Miyazaki to Nichinan in the southeastern Kyushu region and Yaizu and Kawane in the Tokai region (Fig. 5). The $\delta^{13}$C value of CH$_4$ from dissolved gas deposits and gas seeps in the southeastern Kyushu and the Tokai region ranges from $-68\%$ to $-37\%$ and $-34\%$ to $-33\%$, respectively (Igari and Sakata, 1989; Kato et al., 2009, 2011; Sakata et al., 2012; Matsushita et al., 2016). Those from Nichinan and the Tokai region near the thermogenic CH$_4$ generation zone tend to have higher $\delta^{13}$C values (Kato et al., 2009; 2011; Sakata et al., 2012), suggesting a contribution of thermogenic CH$_4$. The mud volcanoes and dissolved gas deposits comprising thermogenic CH$_4$ are located above or near the thermogenic CH$_4$ generation zone in the underthrust sediments, suggesting their causal relationship. The $\delta^{13}$C value of CH$_4$ from gas hydrates in the subduction zone of the Nankai Trough varies within the range of $-70\%$ to $-40\%$, and, like water-dissolved gas deposits, those near the CH$_4$ generation zone tend to have higher $\delta^{13}$C values (Waseda and Uchida, 2004; Pape et al., 2014; Ijiri et al., 2018). The BSRs widely distributed in the Nankai Trough probably indicate the distribution of gas hydrates (Fujii et al., 2008; Hayashi et al., 2010). The gas hydrate samples, however, have recovered only from limited BSRs. Widely distributed gas hydrates possibly comprise mainly microbial CH$_4$, considering the lower $\delta^{13}$C values of CH$_4$ in available gas hydrates (Waseda and Uchida, 2004; Kida et al., 2015). Microbial CH$_4$ generation in an organic-poor environment like the Nankai Trough requires H$_2$ from geological sources (Parks, 2014). However, widely distributed gas hydrates comprising microbial CH$_4$ are set apart from the thermogenic H$_2$ generation zone.

Expulsion and migration of thermogenic CH$_4$ and H$_2$

The gaseous hydrocarbons generated in the underthrust sediments may cause overpressure in and around the décollement of the subducting plate, as suggested by Raimbourg et al. (2017). The present earthquake rupture area at a depth from 10–20 km along the plate interface (Hyndman, 2007; Kimura et al., 2018; Shi et al., 2020) almost corresponds to the thermogenic CH$_4$ and H$_2$ generation zone (200°C–350°C) in the underthrust sediments (Fig. 4). The expulsion of thermogenic gas presumably occurs intermittently due to the micro and macro fracturing of rocks and releases the overpressure associated with seismogenesis. The expulsion of thermogenic CH$_4$ and H$_2$ most likely occurs mainly in their generation zone corresponding to the earthquake rupture area. Many studies on fluids and fluid inclusions in the accretionary prisms and underthrust sediments have been conducted and shown active
uid migration in the Nankai Trough subduction zone (Saffer et al., 2008; Saffer and Tobin, 2011; Tsang et al., 2020). Slab-dehydrated fluid from the oceanic plate reaches the land surface, contributing to the formation of hot springs in the subduction zone (Kusuda et al., 2014; Kazahaya et al., 2014). Fluids from the deep slab also reach the Kumano forearc basin and Nankai Trough accretionary prisms (Katayama, 2014; Wiersberg et al., 2018; Tomonaga et al., 2020). In addition to slab-dehydrated fluids, those expelled from the underthrust sediments due to porosity reduction and clay/silica mineral dehydration migrate widely in the accretionary prisms through décollement megathrust and splay faults (Saffer et al., 2008; Kusuda et al., 2014). The active deep fluids may dissolve CH\textsubscript{4} and H\textsubscript{2} expelled from the source rocks to promote their secondary migration in the Nankai Trough subduction zone.

The solubility of CH\textsubscript{4} in water and salt water under high temperature and pressure has been studied over a wide temperature and pressure from 0 to 350°C and 1 to 260 MPa (e.g., Price, 1979; Krader and Franck, 1978; Duan et al., 1992). Based on these experimental results, Duan and Mao (2006) proposed a thermodynamic model for estimating CH\textsubscript{4} solubility in water and salt water from 0 to 300°C and 1 to 200 MPa. The experiments on the solubility of H\textsubscript{2} in water and salt water have been conducted under relatively low temperatures and pressures below 100°C and 50 MPa (e.g., Chabab et al., 2020; Scheuermann et al., 2020). Zhu et al. (2022) extrapolated the solubility of H\textsubscript{2} in water and salt water under higher temperatures and pressures up to 150°C and 110 MPa based on the particle interaction theory. This theoretical model considers the experimental results and can be applied to predict the solubility of H\textsubscript{2} to the deep fluids in the subduction zone. The solubility change of CH\textsubscript{4} and H\textsubscript{2} to pure water in the range from 0 to 150°C and 1 to 110 MPa predicted by Duan et al. (1992) and Zhu et al. (2022) are shown in Fig. 6. Solubility to the pure water of CH\textsubscript{4} and H\textsubscript{2} at high temperatures above 60°C generally increases with increasing temperature and pressure (Fig. 6). However, the increase in solubility of CH\textsubscript{4} with increasing temperature and pressure is not as high as that of H\textsubscript{2}. Since the thermogenic CH\textsubscript{4} generation from the source rocks (TOC = 0.5 wt%) has been assumed to be 300 mg/gTOC (1.9×10^{-2} mol/gTOC), the ultimate generation of thermogenic CH\textsubscript{4} is approximately 9.5×10^{-5} mol/gRock (9.5 mol/100kgRock). The solubility of CH\textsubscript{4} in water at 300°C and 200 MPa, roughly corresponding to the thermogenic CH\textsubscript{4} generation zone, is estimated to be about 2.8 mol/kgH\textsubscript{2}O (Duan and Mao 2006). Considering the limited amount of water in the deep subduction zone, much of the thermogenic CH\textsubscript{4} can behave as free gas in the deep subduction zone. Although the TOC concentration of sedimentary rocks in the Nankai Trough is assumed to be significantly lower than in the oil and gas fields, much of the thermogenic CH\textsubscript{4} can still behave as free gas in the deep subduction zone. In the oil and gas field, the main driving force for gas migration from the source rocks to the reservoir is thought to be buoyancy (Clayton, 1979). The thermogenic CH\textsubscript{4} in the subduction zone also possibly migrates upward by buoyancy. A comparable amount of thermogenic H\textsubscript{2} to the thermogenic CH\textsubscript{4} is suggested to be generated. Therefore, a part of the thermogenic H\textsubscript{2} may behave as a free gas like the thermogenic CH\textsubscript{4}. The free H\textsubscript{2} is more diffusive than free CH\textsubscript{4} because of the smaller molecular size, suggesting a wider dispersion of H\textsubscript{2} than CH\textsubscript{4}. Since the solubility of H\textsubscript{2} seems to be higher than CH\textsubscript{4} (Fig. 6), more H\textsubscript{2} than
CH_4 \text{ possibly migrates as dissolved in deep fluids. However, the solubility of H}_2 \text{ in deep fluids under high pressures and temperatures has not yet been fully clarified. Understanding the migration of the thermogenic H}_2 \text{ in the subduction zone is a future research topic.}

**Geological sources of H}_2 \text{ in the Nankai Trough**}

The generation, expulsion, and possible migration of CH_4 and H}_2 \text{ in the Nankai Trough subduction zone are summarized in Fig. 7. The accumulation and emission of thermogenic and microbial CH_4 \text{ are also shown in Fig. 7. The mud volcanoes and dissolved gas deposits are distributed nearly above the thermogenic CH_4 generation zone in the underthrust sediment and accretionary prisms (Fig. 5), suggesting the upward migration of free CH}_4 \text{ by buoyancy. The formation of mud volcanos occurs intermittently and quickly. It seems unlikely that the eruption of CH}_4 \text{ to form mud volcanoes occurs directly by the CH}_4 \text{ supply from the deep subduction zone. A type of CH}_4 \text{ chamber might have developed below the mud volcanoes and mediated the CH}_4 \text{ eruption (Fig. 7). The fracturing and deformation of the CH}_4 \text{ chamber due to earthquakes and tectonics can provoke CH}_4 \text{ outflow to form mud volcanoes and CH}_4 \text{ plumes. In the shallow subsurface below } 60^\circ \text{C, the solubility of CH}_4 \text{ in water does not change significantly even if the temperature and pressure decrease (Fig. 6). Therefore, if an aquifer unsaturated with CH}_4 \text{ is in the shallow subsurface, the free CH}_4 \text{ migrating upward can be dissolved and trapped by the aquifer to form dissolved gas deposits (Fig. 7).}

Some geological sources of H}_2 \text{ that might contribute to microbial CH}_4 \text{ production and sustain the subseafloor biosphere have been proposed. They are H}_2 \text{ generated by the thermal decomposition of organic matter under relatively low temperatures (< 120\degree \text{C}), H}_2 \text{ released during hydrothermal alterations and serpentinization of oceanic crust, and mechanochemical H}_2 \text{ formed with silicate rock fracturing due to earthquakes and tectonics (Parks et al., 2014). The open-system pyrolysis of kerogen shows that the molecular H}_2 \text{ is liberated from kerogen by thermal cracking of hetero-bonds, demethylation, aromatization, and condensation (Li et al., 2015). Since the heating rate of the underthrust sediments is higher, the generation rate of such low-temperature thermogenic H}_2 \text{ is expected to be higher than in the accretionary prisms (Fig. 7). However, hydrous pyrolysis of kerogen under the closed system shows that hydrogen radicals generated in the hydrocarbon generation zone are consumed quickly by hydrogen-requiring reactions such as hydrogenation of unsaturated compounds (Li et al., 2017). The hydrocarbon generation in the organic-poor sedimentary rocks can be regarded as proceeding in a nearly closed system. Hence, a sufficient amount of molecular H}_2 \text{ might not be generated in the hydrocarbon generation zone (< 120\degree \text{C}). Seismological analysis has detected slab dehydration and seismic velocity decrease near the surface of the oceanic crust beneath the Shikoku region, suggesting the slab serpentinization by released water (Shiomi et al., 2020). Low seismic velocity zones, possibly indicating serpentinization, have also been detected near the surface of the oceanic crust beneath the inner accretionary prisms off the Kii Peninsula (Kodaira et al., 2006). The serpentinization of oceanic crust beneath the inner accretionary prisms is thought to be due to the invasion of seawater through the fault
system extending to the mantle (Tsuji et al., 2013). The hydrothermal alteration and serpentinization, possibly ongoing in the subduction zone, can be the potential source of H₂ (Fig. 7). In the tectonically active subduction zones, the H₂ generated mechanochemically by the interaction of water and silicate rocks fracturing can also be expected as a potential H₂ source. The active fractures and faults in and around the décollement and earthquake rupture area are likely principal sites of mechanochemical H₂ generation (Kameda et al., 2003; Saruwatari et al., 2004) (Fig. 7). The thermogenic H₂ generated under relatively high temperatures (>220°C) discussed in the present study can be another potential geological source contributing to microbial CH₄ production in the subseafloor biosphere (Fig. 7). The expulsion of the thermogenic H₂ from the underthrust sediments is likely to occur associated with seismogenesis. Therefore, the mechanochemical H₂ generated in the earthquake rupture area would behave with the thermogenic H₂ generated in the underthrust sediments.

The H₂ from geological sources described above has the potential to contribute to sustaining the subseafloor biosphere and the CH₄ production by hydrogenotrophic methanogens. The low-temperature thermogenic H₂ generated in the shallow sedimentary rocks is comparatively close to the subseafloor biosphere. However, a sufficient amount of low-temperature H₂ generation seems unlikely compared to the thermogenic H₂ generation in the deep subduction zone. Other geological sources of H₂ are located deep in the subduction zone, and long-distance transportation of H₂ is required to support the subseafloor biosphere. The migration of slab-dehydrated fluids is active in the Nankai Trough subduction zone, and such deep fluids may play an essential role in the long-distance transportation of H₂. Compared to gas phase migration, migration of low-soluble gas by solution would be inefficient and require large volumes of fluids. The efficient transport of H₂ by gas phase migration might occur under a limited amount of fluid in the deep subduction zone. However, our knowledge of the solubility and the behavior of H₂ under high pressures and temperatures is currently limited. In addition, the generation rates of H₂ derived from the low-temperature thermal decomposition of organic matter, serpentinization of oceanic crust, and silicate rock fracturing are currently unknown. If the generation rates of H₂ from these geological sources are clarified, comparing them with that of the thermogenic H₂ from the underthrust sediments estimated this time, the degree of relative contribution of each H₂ for sustaining the subseafloor biosphere will be evident. Moreover, it will deepen our understanding of the geosphere-biosphere interaction leading to the significant microbial CH₄ production and the formation of large-scale gas hydrates in the oceanic plate subduction zone.

**Methods**

**Shales and metapelites from old accretionary prisms**

Shales and metapelites that experienced a paleo-temperature ranging from 100–600°C were collected from the Shimanto belt and the Sanbagawa metamorphic belt in the Kochi district. The rock samples used in the present study were collected from the same sampling route as our previous study (Suzuki et
The geologic background of the rock samples used in the present study has been described therein. The Sanbagawa metamorphic belt is divided into Ooboke Nappe and Besshi Nappe based on lithology and metamorphic age. The geologic age of the protoliths of the Sanbagawa metamorphic belt is Triassic to Jurassic, and the metamorphism of these rocks proceeded during the Late Cretaceous (Takasu and Dallmeyer, 1990). Metamorphic rocks of the chlorite, garnet, albite-biotite, and oligoclase-biotite zones are distributed along the sampling route of the Asemi-gawa River. The metamorphic temperature of metapelites increases gradually from the chlorite zone (300°C) to the oligoclase-biotite zone (610°C). The Shimanto belt of the Shikoku region is divided by the Aki Tectonic Line into a northern and a southern belt. The northern belt comprises the Lower Cretaceous Shinjogawa and the Upper Cretaceous Aki groups. The southern belt comprises the Eocene to the Lower Oligocene Muroto Peninsula Group and the Upper Oligocene to the Lower Miocene Nabae Groups. Shale samples were collected from outcrops of Aki and the Muroto Peninsula Groups distributed along the eastern coast of Tosa Bay. All the shale and metamorphic rocks were deposited in the marine environment with a variable contribution of terrestrial organic matter. There may be some differences in the organic type among the samples, but this would not have much influence on the geochemical characteristics of sedimentary organic matter at the highly mature stage (Waples, 2000). The paleo-maximum temperature of shales and metapelites was estimated by vitrinite reflectance (VR) and metamorphic mineral assemblages.

Pulverization and residual gas recovery

Gas released from shale fragments during pulverization was defined as residual gas. The pulverization of the shale fragments was conducted using a P-6 planetary ball mill and a tungsten carbide mill pot with needle valves for gas transfer lines (Fritsch GmbH, Idar-Oberstein, Germany). The inner volume of the mill pot is 69.6 mL. Shale and metapelite fragments of 5–7 mm were pulverized in the tungsten carbide mill pot under an ultra-high purity helium (He) atmosphere of 0.3 MPa. Cleaning of the mill pot by ultra-high purity He was repeated three times before the pulverization. Residual gas released in the mill pot was directly transferred to the gas sampling loop of the gas chromatograph through the stainless transfer line. The temperature of the tungsten carbide mill pot during pulverization was below 45°C. The grain size of the rock powder after the pulverization was measured by a laser diffraction-scattering method using a grain-size analyzer (LA-920: Horiba, Kyoto, Japan) and was generally from 3–7 µm.

Residual gas, elemental analysis, and vitrinite reflectance

The composition of the residual gas in the rock fragments was measured by gas chromatography (GC) using an instrument (7890A: Agilent, Santa Clara, CA, USA) equipped with a pulsed discharge helium ionization detector (PDHID) and a micropacked column containing ShinCarbon-ST 80/100 (2.0 m × 1.0 mm i.d.; Shinwa Co., Nagoya, Japan) (Fig. S1). The oven temperature of the GC was programmed to 40°C for 3 min, increased to 300°C at a rate of 15°C/min, and then held at 300°C for 15 min. Ultra-high purity He was used as the carrier gas. A constant amount of gas directly transferred from the tungsten carbide mill pot was introduced into the GC column using a 50 µL sampling loop. Compounds were identified and quantified by comparing the retention times with those of reference standards in a gas mixture.
containing CH$_4$ (495 ppmv), C$_2$H$_4$ (494 ppmv), C$_2$H$_6$ (495 ppmv), and CO$_2$ (480 ppmv) (Taiyo Nippon Sanso Group, Co., Kawasaki, Japan) and the ionization coefficients by Wentworth et al. (1994). The detailed analytical procedure is described in Saito et al. (2012). Total organic carbon (TOC) and total nitrogen (TN) contents were determined using an EA 3000 elemental analyzer (Euro Vector Co., Milan, Italy). The pulverized shale or metapelite was weighed and placed in a silver capsule with drops of 1 N HCl to remove carbonates. The carbonate-free sample was dried at 120°C for 2 hrs and analyzed by the elemental analyzer. The mean VR of randomly-oriented vitrinite grains was measured using a reflection microscope (Eclipse LV100ND; Nikon Corp., Japan) equipped with a stabilized halogen light source and photonic multichannel analyzer (PMA12; Hamamatsu Photonics K.K., Japan). The VR value was measured for a spot diameter of 20 µm at a wavelength of 542.8 nm by comparison with the standard values of polished glasses with VR values of 0.55, 0.79, 1.08, and 1.53%.

**Declarations**

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**References**


**Figures**
Figure 1

The distribution of mud volcanoes, gas hydrates (BSRs), dissolve gas deposits, and condensate/gas seeps in the study area of the Nankai Trough subduction zone (Igari and Sakata, 1989; Kato et al., 2011; Hayashi et al., 2010; Matsushita et al., 2016; Asada, 2020). The black line with triangles represents the trough axis of the Nankai Trough. The water-depth map is courtesy of the Hydrographic and Oceanographic Department of the Japan Coast Guard.
Figure 2

The subsurface temperature distribution, the movements of the inner accretionary prisms and the underthrust sediments, and their heating rates in the Nankai Trough subduction zone. A schematic geologic section of the Kumano-nada region off the Kii Peninsula is from Kimura et al. (2018). The boundary between the outer and the inner prisms is the Kumano basin edge fault zone (KBEFZ) (Martin et al., 2010). The average annual sediment accretion along the 1 km trough was estimated to be approximately $53.2 \times 10^3$ m$^3$/yr ($53.2$ km$^3$/myr) based on the total volume of the outer prism (about 117 km$^3$) and the initiation of its formation 2.2 myr ago (Figs. S2 and S3). The present-day lateral velocity of the accretionary prism decreases gradually with increasing thickness of the prisms and distance from the trough, estimated to be approximately 6.0 mm/yr at the thickest prism (about 8.9 km). The depth-temperature relationship in the Kumano-nada region is according to the long-term borehole monitoring system installed at Site C0002 during the IODP Expedition 332 (Sugihara et al., 2014) (Fig. S4). Temperature distributions of more than 200$^\circ$C are from the modeling results of the thermal structure of the Philippine Sea Plate (Ji et al., 2016; Suenaga et al., 2019) (Figs. S5 and S6).
Figure 3

The concentration and compositional change with increasing temperature of residual CH$_4$, C$_2$H$_6$, and H$_2$ in shales and metapelites from the old accretionary prisms in the Shikoku region. The relationship between the VR and the paleo-maximum temperature was computed by Easy%RoV (Burnham, 2019), assuming 30°C/myr as the heating rate of the samples. Maximum temperatures of metapelites were estimated from metamorphic mineral assemblages. Some typical gas chromatograms for the residual gases show the change of relative abundance of H$_2$, N$_2$, CH$_4$, and C$_2$H$_6$ with increasing the maximum temperature. A part of the dataset is from Suzuki et al. (2017).
Figure 4

The thermogenic CH$_4$ and H$_2$ generation zones of the accretionary prisms and the underthrust sediments in the Kumano-nada region off the Kii Peninsula. The CH$_4$ and H$_2$ generation zones in the accretionary prisms are in the temperature ranges from 195 to 270°C and >220°C, respectively, under the heating rate of 30°C/Myr. Those in the underthrust sediments are in the temperature ranges from 205 to 280°C and >235°C, respectively, under the heating rate of 125°C/Myr. The deepest part of the inner prism has not yet fully reached the CH$_4$ and H$_2$ generation zone. The subducting underthrust sediments pass through the CH$_4$ and H$_2$ generation zone and sustainably generate CH$_4$ and H$_2$. The thermogenic CH$_4$ and H$_2$ generation rate in the underthrust sediments is higher than in the accretionary prisms due to sufficient thermal maturation and a faster subduction rate.
Figure 5

The spatial distributions of the thermogenic CH$_4$ and H$_2$ generation zones and the accumulation and emission of CH$_4$ in the Nankai Trough. Although the heating rate of the underthrust sediments is different by location, it was assumed to be the same at 125°C/myr as the Kumano-nada region. Therefore, the CH$_4$ and H$_2$ generation zones were set to the temperature ranges from about 205 to 280°C and >235°C, respectively. The red contours show the temperatures of the upper surface of the subducting Philippine Sea Plate in the Kyushu, Shikoku, and Kii Peninsula regions (Ji et al., 2016) and the Tokai region (Suenaga et al., 2019), respectively. The blue contours show the depths of the upper boundary of the Philippine Sea Plate (Baba et al., 2002; Nakajima and Hasegawa, 2006; Hirose et al., 2008).
Figure 6

Solubilities of CH₄ and H₂ in pure water under high temperatures and pressures. The solubilities of CH₄ and H₂ are from laboratory experiments (Duan et al., 1992) and the particle interaction theory (Zhu et al., 2022), respectively. The 100 to 120 MPa nearly corresponds to the overburden pressures at a burial depth of 4 to 5 km (Peacock, 2009, Sugihara et al., 2014). The solubility of H₂ in the hydrous fluids changes linearly and increases more than that of CH₄ with increasing temperature and pressure.
Figure 7

The generation, expulsion, and possible migration of CH$_4$ and H$_2$ in the Nankai Trough subduction zone.

Thermogenic CH$_4$ and low-temperature H$_2$ generation zones in the accretionary prisms are not indicated. The thermogenic CH$_4$ and H$_2$ generation rate in the underthrust sediments below the décollement is significantly higher than in the accretionary prisms because of the sufficient thermal maturation and faster subduction rate. The thermogenic CH$_4$ and H$_2$ generation zones of underthrust sediments overlap with the earthquake rupture area, suggesting the expulsion of thermogenic CH$_4$ and H$_2$ associated with earthquakes. The mud volcanoes and dissolved-in-water type gas deposits comprising thermogenic CH$_4$ are distributed nearly above the thermogenic CH$_4$ generation zones of the underthrust sediments and the accretionary prisms. The thermogenic CH$_4$ expelled from the source rocks in the deep subduction zone migrates upward to form mud volcanoes and dissolved gas deposits. Gas hydrates comprising the biogenic CH$_4$ are also widely distributed in the Nankai Trough. In the organic–poor sedimentary environment, microbial CH$_4$ production requires H$_2$ from geological sources. The low-temperature H$_2$ generated by thermal decomposition of immature organic matter, H$_2$ released during serpentinization and thermal alteration, and mechanoochemical H$_2$ formed with rock fracturing have been proposed as the potential geological sources of H$_2$. The thermogenic H$_2$ generated from sedimentary organic matter during metagenesis to metamorphism can be another potential geological source contributing to microbial CH$_4$ production. The migration of the slab dehydrated fluids possibly plays an essential role in transporting H$_2$ from geological sources to the subseafloor biosphere.

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