Origin and *in situ* concentrations of hydrocarbons in the Kumano forearc basin from drilling mud gas monitoring during IODP NanTroSEIZE Exp. 319

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ABSTRACT

NanTroSEIZE Exp. 319 of the Integrated Ocean Drilling Program (IODP) was the first cruise in the history of scientific ocean drilling with drilling mud circulation through a riser. Drilling mud was pumped through the drill string and returned to the drill ship through the riser pipe during drilling of hole C0009A from 703 to 1604 mbsf (meter below sea floor) and hole enlargement from 703 to 1569 mbsf. During riser drilling, gas from returning drilling mud was continuously extracted, sampled and analyzed in real time to reveal information on the gas composition and gas concentrations at depth.

Hydrocarbons were the only formation-derived gases identified in drilling mud and reached up to 14 vol.% of methane and 48 ppmv of ethane. The chemical and isotopic compositions of hydrocarbons exhibit a microbial origin. Hydrocarbons released from drilling mud and cuttings correlate with visible allochthonous material (wood, lignite) in drilling cuttings. At greater depth, addition of small but increasing amounts of hydrocarbons probably from low-temperature thermal degradation of organic matter is indicated. The methane content is also tightly correlated with several intervals of low Poisson's ratio from V_p/V_s observed in sonic velocity logs, suggesting that the gas is situated in the pore space of the rock as free gas. The gas concentrations in the formation, determined from drilling mud gas monitoring, reaching up to 24 $L_{gas}/L_{sediment}$ for methane in hole C0009A, in line with gas concentrations from *interpreted* downhole sonic logs.

1. Introduction

The Nankai Trough offshore Japan formed by northwestward subduction of the Philippine Sea plate beneath the Eurasian plate has a historical record of recurring great earthquakes that are typically tsunamigenic (Ando, 1975). IODP's Nankai Trough Seismogenic Zone Experiment (NanTroSEIZE) is a multiexpedition, multistage drilling program that aims to improve our understanding on the mechanics of stress accumulation and ruptures propagation along the Nankai accretionary prism (Kinoshita et al., 2006, 2009; Tobin and Kinoshita, 2006; Tobin et al., 2009). IODP NanTroSEIZE Exp. 319 conducted by D/V *Chikyu* was the first riser drilling cruise in the history of scientific ocean drilling (Saffer et al., 2010). Riser drilling of hole C0009A was carried out approx. 60 km SE of Shingu harbor from 703 to 1604 mbsf (meter below sea floor) and during hole enlargement from 703 to 1569 mbsf (Fig. 1).

Hole C0009A was drilled to retrieve cores and cuttings from the upper Kumano basin fill sediments in the hanging wall of the plate boundary fault, to conduct downhole tests (Doan et al., 2011), to measure *in situ* pore pressures and stress states (Lin et al., 2010), and for future installation of long-term borehole monitoring instrumentation. The hole intersects the cover sediments of the Kumano Basin and penetrates into the accretionary wedge below (Saffer et al., 2010; Hayman et al., 2012).

For the first time in the history of scientific ocean drilling, online mud gas monitoring was performed during Exp. 319 to reveal real time information on the composition of gases at depth and to estimate their *in-situ* concentration. Drilling mud as carrier of formation gases and fluids has been investigated during several continental drilling projects, e.g., during drilling the Silijan well (Sweden) (Hilton and Craig, 1989), during deepening of the

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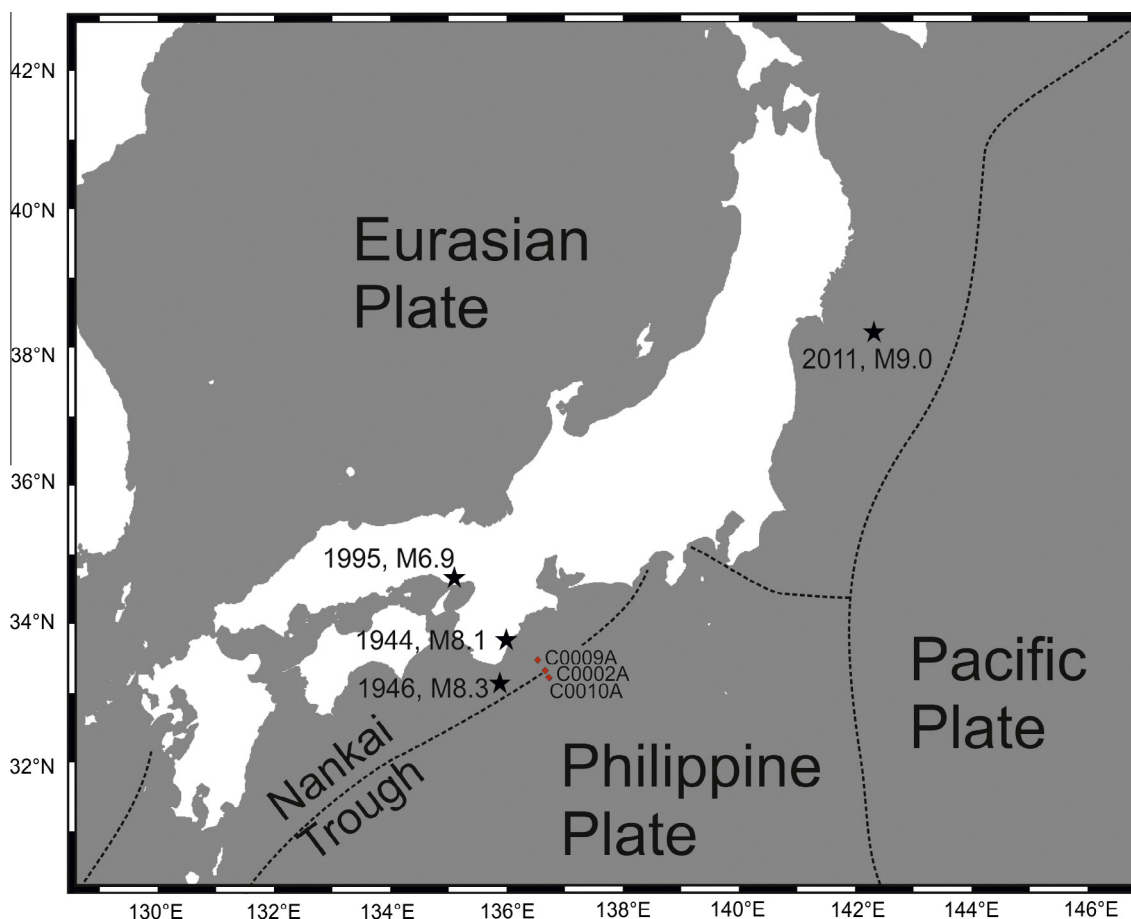 *E-mail address:* wiers@gfz-potsdam.de (T. Wiersberg).

Fig. 1. Map of the Expedition 319 study area offshore Japan, including locations of the Site C0009A (proposed Site NT2-11B) and C0010A (proposed Site NT2-01J). Indicated are the epicenters of the Tōnankai Earthquake from 1944, Nankaidō Earthquake from 1946, Kobe Earthquake from 1995 and the Tōhoku Earthquake from 2011.

GPK-1 borehole in Soulz-sous-Forêts, France (Aquilina and Brach, 1995), during drilling of the Balazuc borehole in France (Aquilina et al., 1998) and the Western Canada Sedimentary Basin (Rowe and Muehlenbachs, 1999a, 1999b and Tilley and Muehlenbachs, 2006). These studies investigated samples from commercial mud logging, conducted for safety purpose, which does not necessarily aim to follow scientific targets. An assembly only for scientific purpose has been developed during drilling of the KTB in Germany (Zimmer and Erzinger, 1995) and has been deployed on several scientific drilling projects of the International Continental Scientific Drilling Program ICDP. Gas was continuously extracted from returning drilling mud, analyzed in real time and sampled for off-line studies during e.g. fault zone drilling, drilling for gas hydrates, and volcanoes (Erzinger et al., 2006; Tang et al., 2013; Tretner et al., 2008; Wiersberg and Erzinger, 2007, 2008, 2011).

For deep continental drilling, drilling mud is pumped through the drill string and flows back through the annulus between the drill pipe and the bore hole in order to stabilize the bore hole, to cool the drill bit, to extract drill cuttings and to insert e.g. core barrel or geophysical logging probes (Fig. 2). During riser drilling, drilling mud returns back from the seafloor to the vessel through the riser pipe that encloses the drill string. Conventional scientific ocean drilling uses sea water as drilling fluid, which does not return to the drilling vessel.

In this paper, we introduce a method for analyzing and sampling of gases that can be applied for core and cuttings riser drilling. Drilling mud gas monitoring yields a much higher data density than conventional IODP headspace or void gas analysis, which enables identification of changes in the gas composition even on small spatial depth scale. For the first time the drilling mud gas monitoring technique was used to gain information on in situ gas concentrations by combining data from drilling mud gas monitoring with data from drilling cuttings gas extraction. We compare our data with data from geophysical logging and cuttings analysis and discuss the results in the context of gas genesis, origin, and absolute gas concentrations in the forearc basin and the accretionary prism of the Nankai plate to quantify the input of volatiles from different provenances (in situ, sedimentary slab, mantle wedge) and to characterize possible mechanisms of fluid flow and migration from depth.

The role of fluids to reduce apparent shear stress along plate bonding fault zones is controversially debated (see e.g. Hickman et al., 1995). Processes that generate volatiles in subduction zones in situ are porosity reduction, diagnetic sediment dehydration and mineral dehydration of the subducting oceanic lithosphere (Kastner et al., 1991; Spandler et al., 2011). It is suggested by some authors (Peacock, 1990, Hacker et al., 2003) that the occurrence of shallow earthquakes (<50 km) in the Nankai plate boundary system and many other subduction zones is linked with slab dehydration. Volatiles from subduction zones may also contain atmospheric noble gases (Kita et al., 1993), sedimentary N_2, and hydrocarbons from thermal or microbial breakdown of organic matter (Whiticar, 1994). Volatiles could migrate from the slab or the mantle wedge into the overlying accretionary prism through permeable faults or other migration pathways (Hilton et al., 2002) or migrate from continental sources (Aquilina et al., 1997).
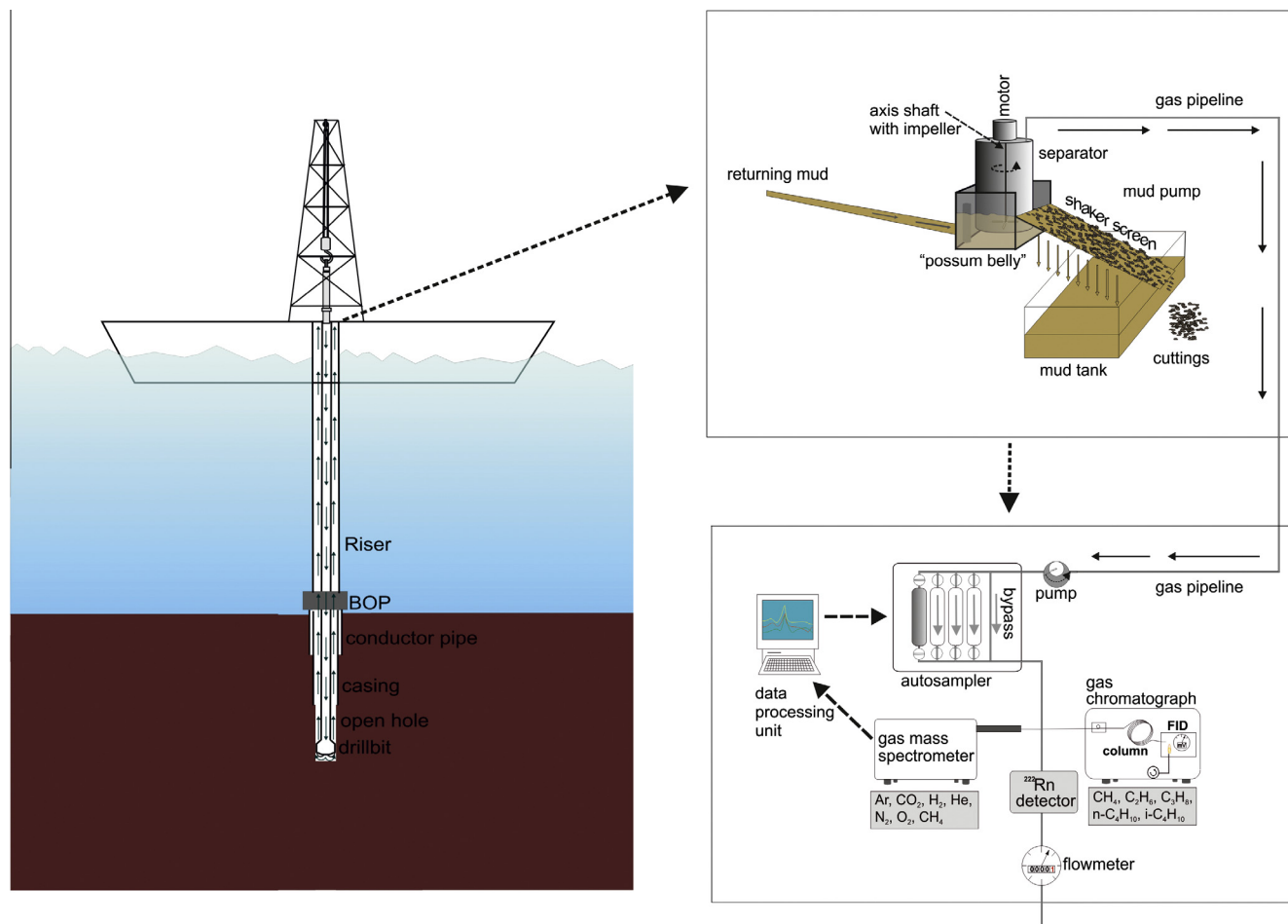
Fig. 2. Schematic drawing of the drilling mud gas monitoring experiment onboard R/V Chikyu during Exp 319 C0009A riser drilling and hole opening. Left side modified from www.jamstec.go.jp/chikyu/eng/science/drilling.html.

Hydrocarbons from mud volcanoes in the Kumano basin are thermogenic and most likely originate from the old accretionary prism deeper than 2300 m (Pape et al., 2014).

2. Methods

Conventional IODP shipboard methods of gas investigations require drill core, including gas sampling from core voids and headspace gas sampling, followed by onboard analysis (Pimmel and Claypool, 2001). These two methods have become standard techniques at IODP. Generally, sampling of void gas is undertaken in a way that a hole is drilled in the plastic core liner where core voids are visible immediately after core retrieval and gas is extracted with a syringe. Analysis of void gas yield data on the gas composition but no gas concentration data. An attempt to quantify *in situ* gas by normalizing methane from gas voids to nitrogen and/or argon was made during ODP Leg 201 (Spivack et al., 2006). Void gas sampling was conducted during Exp. 319 for onshore noble gas analysis (Horiguchi et al., 2009).

For headspace gas sampling, a core sample with calibrated volume is taken immediately after core retrieval on deck and placed in a gas-tight container that is filled up with known quantities of water and sealed. The container is heated at 60 °C for 30 min to extract the gas from the core. The evolved headspace gas phase is then sampled with a syringe through a septum (Paull et al., 2000). Besides the gas composition, also gas concentrations per core sample volume can be determined by the headspace gas technique, usually reported as μL/L wet sediment.

Void gas and headspace gas analysis often underestimate the *in situ* gas concentration through core degassing during retrieval and core handling on deck. Paull et al. (2000) describe a Pressure Core Sampler (PCS) to recover core samples at *in situ* pressure conditions to overcome this problem. The PCS has been deployed successfully for the first time on ODP Leg 164 (Paull et al., 2000) and was later used on ODP Leg 201 (Dickens et al., 2003), Leg 204, and IODP Exp. 311. Methane concentration was one- to two-orders of magnitude higher in PCS samples from Leg 164 than in headspace gas samples from corresponding depths.

2.1. The drilling mud gas monitoring technique

In the following we provide a brief summary of the Exp. 319 gas analysis set-up which is described in greater detail by Saffer et al. (2010). A modified oilfield gas separator (degasser) was placed in the mud ditch immediately behind the shale shakers to ensure high gas extraction efficiency in combination with low air contamination. The gas was extracted mechanically in the degasser with a motor-driven stirrer. Gas extraction was furthermore stimulated by applying vacuum. After extraction, the gas phase was continuously pumped through a plastic tube into a laboratory for analysis. On-line gas analysis in real time was carried out with a quadrupole mass spectrometer (QMS, Balzers OmniStar) for N_2, O_2, CH_4, CO_2, H_2, He, Kr and Ar. Delay time between gas extraction and analysis was determined to be in a range of less than 5 min.

Samples for further investigation were taken from the mud gas line in regular intervals and when a given threshold concentration

level for methane was exceeded at the mass spectrometer. A gas chromatograph (SRI 8610C) equipped with a FID-detector was used for offline determination of saturated (C1–C4) and non-saturated hydrocarbons onboard.

After acquisition, gas data were corrected for artifacts (i.e., gas accumulations during downtime) and correlated to the lag depth that takes into account the travel time (lag time) of the drilling mud from the drill bit to the surface and the travel time of the gas from the gas–water separator to the analytical devices. Lag time data were provided by the drilling company and calculated from the effective borehole volume and the drilling mud pumping rate. The lag depth was calculated from lag time, gas travel time from the degasser to the QMS, borehole depth and rate of penetration. Two carbide tests were performed to ensure the accuracy of the lag time calculations.

2.2. Extension of the drilling mud gas monitoring technique for in situ gas concentration determination

Drilling mud gas monitoring provides information on the gas *composition* at depth. To determine *in situ* gas *concentrations*, i.e. the amount of gas in a given volume of rock, the mud gas monitoring experiment was calibrated with a gas of known concentration. Due to pressure reduction during ascent of the drilling mud column, most but not all formation gases migrate from the pore space of the ascending solid (core, cuttings) into the drilling mud. To ensure that the complete gas phase was analyzed, gas in drilling mud and in the solid phase was investigated.

For calibration of the drilling mud gas monitoring experiment, acetylene from two carbide tests was used. Generally, calcium carbide (CaC_2) is dropped in a well bore to verify the lag time. Calcium carbide reacts with water forming acetylene (C_2H_2) that returns back with the circulating drilling mud. From the time difference between the drop of calcium carbide and the return of acetylene, the lag time is calculated.

Two carbide tests were performed during drilling of hole C0009A. Both times 500 g calcium carbide was pumped down the drill string with the drilling mud, producing 175L C_2H_2 at standard temperature and pressure [STP]. Acetylene was extracted from the drilling mud and measured with the mass spectrometer. Integration of the acetylene peak yields a peak area that corresponds to its absolute concentration (175 L). Although both carbide tests were conducted with the same amount of carbide, the peak area during phase II (for C0009A drilling phases see Saffer et al. (2010)) is factor 5.4 higher than the area from phase VIII (hole enlargement), see Fig. 3.

The methane concentration in drilling mud extracted during phase II drilling of hole C0009A is roughly the same factor higher compared to the phase VIII (hole enlargement), but the volume of drilled rock is similar during both phase (phase II (drilling a $12^{1/4}$ in. hole): 76 L per meter, phase VIII (borehole enlargement from $12^{1/4}$ to 17 in.): 70 L per meter. We therefore consider different drilling mud composition (lost circulation material was added to the drilling mud during phase VIII) and a different position of the degasser as most likely explanation for the different gas concentrations observed during both drilling phases.

A similar concentration ratio of acetylene observed during two calibration experiments and methane during the two drilling phases also underpins that gas flow form the wall rock into the drilling mud is of little relevance. If significant inflow of gas from the formation in the drilling mud would have taken place, the methane concentration ratio would be much higher, because *more* gas would have been extracted during phase II drilling and *less* gas during phase VIII when drilling the now gas-depleted formation.
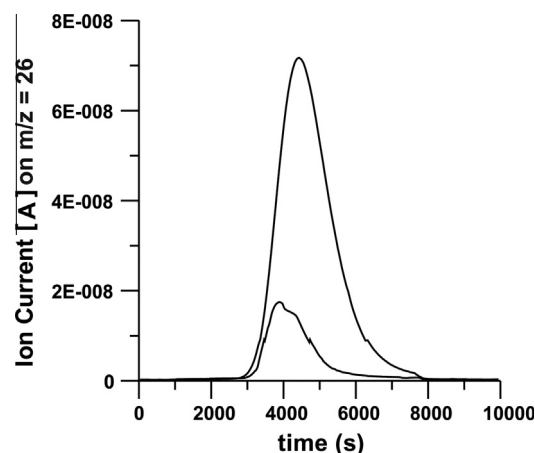

Fig. 3. Occurrence of C_2H_2, given as ion current [A] on m/z = 26, in drilling mud after dropping of 500 g CaC_2 during C0009A drilling (large peak) and hole opening (small peak). Peak reduction during hole opening probably derive from different drilling mud compositions (higher mud weight during hole opening).

To utilize acetylene as a calibration measure for the methane concentration in drilling mud, different mass spectrometer sensitivities of acetylene (detected on m/z = 26) and methane (detected on m/z = 15) have to be taken into consideration. To check for the different sensitivities, a measurement with a defined gas mixture containing methane and acetylene was carried out onshore after drilling. This measurement exhibits mass spectrometer sensitivity for acetylene 1.38 times higher than for methane. Furthermore, the different solubility of methane and acetylene in drilling mud needs to be taken into account. The overall solubility of both gas species in water is moderate to low with solubility of acetylene at 0 °C and 1 bar about 87 times higher than the solubility of methane (2.0 g/L and 23 mg/L, respectively).

With a degasser headspace volume of approximately 20 L and a gas pumping rate of ∼0.7 L/min, it takes about 30 min to produce the headspace gas volume. The headspace volume must be produced about three times (∼90 min) to fully replace a given gas component (see Fig. 3). The drilling mud gas monitoring method therefore delivers values averaged over the depth progress achieved in approximately 90 min.

The ICDP drilling through the San Andreas Fault (San Andreas Fault Observatory at Depth, SAFOD) had shown that formation-derived CO_2 does not achieve solubility equilibrium with water – based drilling mud during the time of drill mud ascent to the surface (Wiersberg and Erzinger, 2008). Lag-times at SAFOD and during Exp. 319 are similar. This and the fact that no second acetylene peak was observed after the first turnover of the drilling mud volume led us assume that acetylene release from the drill mud was complete and not significantly influenced by insufficient acetylene extraction.

2.3. Gas analysis from drilling cuttings

16 drilling cutting samples from different depths (812–1604 mbsf) have been collected to determine the gas fraction in drilling cuttings that was not liberated into the drilling mud during ascent (Table 1).

To minimize gas loss during surface handling, the cuttings were scraped from the shaker screen immediately after arrival at the surface, filled in gas bags and sealed, later weighted and spiked with a defined volume of krypton (10 ml or 15 ml). After approx. 100 h of extraction time, the accumulated gas phase was let into the QMS for total gas analysis (N_2, CH_4, CO_2, O_2, He, H_2, Ar, Kr). 1 cc of gas was taken with a syringe through a septum and injected

Table 1
Relative concentration and composition of hydrocarbons in drilling mud gas from C0009A C1, C2 and C3 concentrations given in ppmv, $\delta^{13}C$ in ‰ [PDB], H/D in ‰ [SMOW].

Sample #	Depth (mbsf)	Taken during	Sampling date (ddmmhhmm)	C1	C2	C3	C1/C2	C1/[C2 + C3]	$\delta^{13}C$ (CH$_4$)	H/D (CH$_4$)
1	723	r.d.	28060214	11,442	2	–[a]	5721	5721	–[a]	–[a]
2	726	r.d.	28060230	18,856	4	–[a]	4714	4714	−66.5	−127
3	772	r.d.	29060900	1867	1	–[a]	1867	1867	–[a]	–[a]
4	800	r.d.	29061100	7254	2	–[b]	3627	3627	–[a]	–[a]
5	840	r.d.	29061424	17,607	3	–[b]	5869	5869	−66.8	−123
6	898	r.d.	29061720	7375	1	–[b]	7375	7375	–[a]	–[a]
7	942	r.d.	29062026	35,829	9	1	3981	3583	–[a]	–[a]
8	976	r.d.	29062240	49,856	14	1	3561	3324	–[a]	–[a]
9	1018	r.d.	30061145	42,756	13	–[b]	3289	3289	−65.8	−130
10	1078	r.d.	30061530	73,166	24	2	3049	2814	–[a]	–[a]
11	1128	r.d.	30061835	104,420	48	2	2175	2088	−63.3	−145
12	1198	r.d.	01070007	77,990	28	2	2785	2600	–[a]	–[a]
13	1244	r.d.	01010353	52,138	18	–[b]	2897	2897	–[a]	–[a]
14	1268	r.d.	01070539	84,992	44	2	1932	1848	−66.3	−150
15	1328	r.d.	02070400	12,266	8	1	1533	1363	−68.1	−151
16	1438	r.d.	04072333	11,511	12	1	959	885	–[a]	–[a]
17	1537	r.d.	07070025	4759	5	–[b]	952	952	–[a]	–[a]
18	1537	r.c.	07071352	4932	5	–[b]	986	986	−67.4	−126
19	1547	r.c.	08070232	3966	4	–[b]	992	992	–[a]	–[a]
20	1556	r.c.	08070644	5562	6	–[b]	927	927	–[a]	–[a]
21	1585	r.c.	08072315	4130	4	1	1033	826	−65.6	−140

r.d. = riser drilling, r.c. = riser coring.
[a] Not detected.
[b] Below detection limit (1 ppmv).

into the GC for hydrocarbon analysis. To prove that gas release was completed, duplicated analyses were conducted on three samples from 896, 967 and 1060 mbsf after approx. 270 h. Methane concentration were similar at all times, suggesting that no gas was consumed or further liberated after 100 h. Apart from utilizing a gas spike and sample heating, the technique is similar to the regular IODP headspace gas method.

The gas concentration in drilling cuttings from C0009 was always much lower than in drilling mud from corresponding depths, suggesting that most gas hosted in pore space has been released into the drilling mud either during the drilling process or during ascent of the cuttings-loaded drilling mud.

2.4. Chemical composition and stable isotope studies

Drilling mud gas and cuttings gas was sampled in glass flasks and copper tubes for shorebased investigations. 16 gas samples from drill cuttings (Table 1) and 21 drilling mud gas samples (Table 2) and were analyzed with a gas chromatograph equipped with a FID-detector for saturated (C1–C4) and non-saturated hydrocarbons. Butane concentrations were always below detection limit (1 ppmv) and are therefore not reported here.

From eight drill mud gas samples, $\delta^{13}C$ and H/D was determined at GCA Isolab Sehnde (Geo Chemical Analyses) with a PDZ 2020 mass spectrometer (Europa Scientific Ltd.). Prior to gas inlet, hydrocarbons were separated with a gas chromatograph, combusted to CO_2, and carried by helium to the mass spectrometer. $\delta^{13}C$ isotope data are given relative to the $\delta^{13}C$ of the PDB carbonate standard, H/D isotope data are given relative to SMOW (Standard Mean Ocean Water). The repeatability of the isotope values is better than ±0.4‰ for $\delta^{13}C$ and ±3‰ for H/D.

3. Results and discussion

Real-time mud gas monitoring during drilling was performed in hole C0009A from 703 to 1594 mbsf (Phase II) and during hole enlargement from 703 to 1569 mbsf (Phase VIII). Although hole enlargement retrieved much lower gas concentrations, both datasets reveal similar gas distribution profiles. The entire dataset

(Saffer et al., 2010) is available at http://publications.iodp.org/proceedings/319/SUPP_MAT/GEOCHEM/.

Hole C0009A drilled four different lithological units (Unit I–IV, Fig. 4). Samples (cuttings, mud gas) were collected from Unit II–IV. Unit II is characterized by turbidites that are markedly thinner and finer grained than those in Unit I, and interpreted as a basin fill unit in the Kumano forearc basin. Unit III includes two subunits containing thinly bedded fine-grained turbidites that were deposited above the carbonate compensation depth and interpreted as basal Kumano forearc basin deposits. The lower subunit IIIB apparently had an increased supply of terrigenous organic matter (wood fragments), possibly because of a change in climate and/or topographic relief. Unit IV, on the other hand, is a mudstone also containing thin-bedded fine-grained turbidites, and could be interpreted as a weakly deformed package of accreted trench sediments, trench-slope deposits, or sediments deposited in the distal reaches of the early Kumano basin. At 1280 mbsf, an unconformity separates the gas-rich Unit III from Unit IV below, indicated from lithology, in seismic and paleobiostratigraphic data, and from physical property measurements (Saffer et al., 2010).

3.1. Origin of gaseous components

The principal formation gases found in drilling mud and in drilling cuttings from all investigated units were hydrocarbons, mainly methane (CH$_4$). He, Ar, Kr, and N$_2$ derive mainly from the unavoidable atmospheric input to the drilling mud, as indicated by relative proportions of these gases indistinguishable from air. The O$_2$ and CO$_2$ contents relative to other atmospheric compounds (Ar, N$_2$) are even lower, oxygen most likely due to consumption through oxidation reaction e.g. with the drill pipe steel, CO$_2$ due to its high solubility in the drill mud. Very low amounts of hydrogen have been detected which are probably artificially produced at the drill bit (Faber et al., 1988).

Up to 14 vol-% CH$_4$ was detected in the drilling mud during drilling of C0009A and up to 3 vol-% during enlargement. Down to 800 mbsf and below 1280 mbsf, the methane concentration in drilling mud is lower than in the interval between where methane peaks at several depths (Fig. 4).

Table 2
Hydrocarbon concentration and chemical composition from C0009A drilling cuttings.

Sample #	Depth (mbsf)	Cuttings-section	Extraction time (h)	CH_4(cc)	CH_4(cc)/rock (g)	C1	C2	C3	C1/C2	C1/[C2 + C3]
1	812	26	121	12.9	0.0144	41,277	48	2	860	826
2	896	44	116	0.9	0.0012	11,463	9	0	1274	1274
3	967	59	111	3.7	0.0047	41,314	31	3	1333	1215
4	1060	79	96	6.0	0.0069	14,896	26	4	573	497
5	1133	95	91	7.2	0.0110	79,487	95	7	837	779
6	1199	108	90	5.0	0.0081	19,330	35	3	552	509
7	1305	130	82	7.6	0.0123	4239	6	1	707	606
8	1329	136	63	10.4	0.0221	21,301	65	19	328	254
9	1405	151	59	1.4	0.0030	_[a]	_[a]	_[a]	_[a]	_[a]
10	1421	155	58	1.4	0.0027	4555	17	6	268	198
11	1475	166	54	1.1	0.0021	5980	30	10	199	150
12	1518	[b]	93	1.4	0.0043	1978	8	3	247	180
13	1538	[b]	82	0.6	0.0015	1459	8	3	182	133
14	1567	[b]	69	0.7	0.0020	2358	12	5	197	139
15	1585	[b]	59	0.7	0.0019	2731	18	8	152	105
16	1604	[b]	20	0.5	0.0012	6601	35	11	189	144
2-II	896	44	282	1.0	0.0013	19,157	19	1	1008	958
3-II	967	59	277	2.8	0.0035	37,404	35	4	1069	959
4-II	1060	79	264	6.5	0.0075	9029	18	2	502	451

[a] No data available.
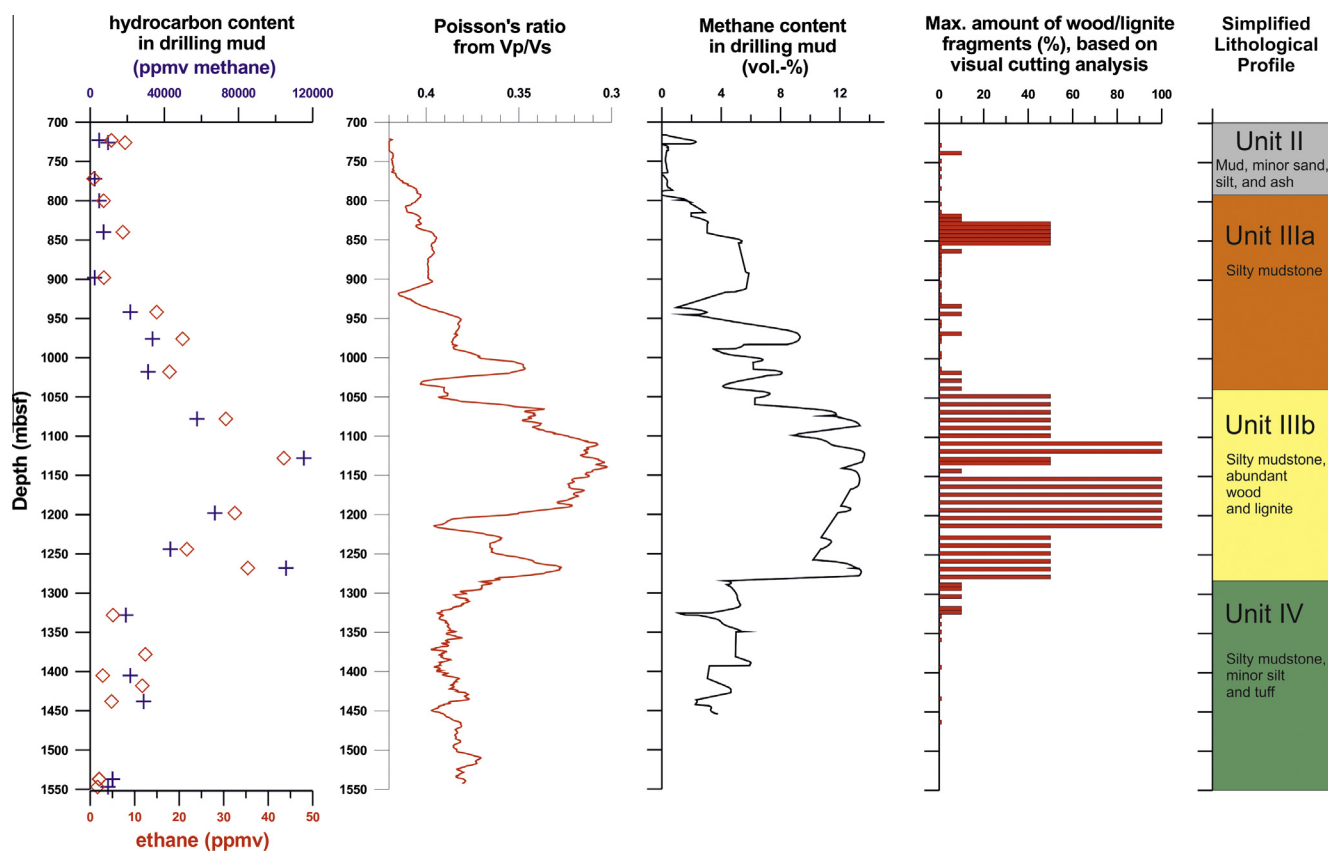[b] No cuttings number (cuttings from coring section).

Fig. 4. Left to right: depth profiles (Saffer et al., 2010) of (i) hydrocarbons in off-line drilling mud gas samples, (ii) Poisson's ratio, calculated from sonic velocity data, (iii) relative methane concentration in drilling mud from on-line gas monitoring, (iv) maximum wood and lignite content in drilling cuttings, and (v) a simplified lithological profile.

These areas of low methane concentration correlate with Unit II (467–791 mbsf) and Unit IV (1287.7–1603.7 mbsf). The molecular composition of hydrocarbons (Fig. 5) and the isotope composition of methane (δ^{13}C from −63.3‰ to −67.4‰ PDB, Table 1) provide clear evidences for a microbial gas source with no indication for significant contribution of thermogenic or abiogenic methane.

Gas migration from the deeper part of the accretionary prism seems unlikely for hole C0009 but might have occurred at hole C0002, drilled 30 km southeast of C0009A. At C0002, δ^{13}C values $\geqslant$ −60‰ and CH_4/C_2H_6 ratios between 300 and 400 below 1700 mbsf from recent drilling mud gas monitoring (Moore et al., 2013) were interpreted with the presence of thermal
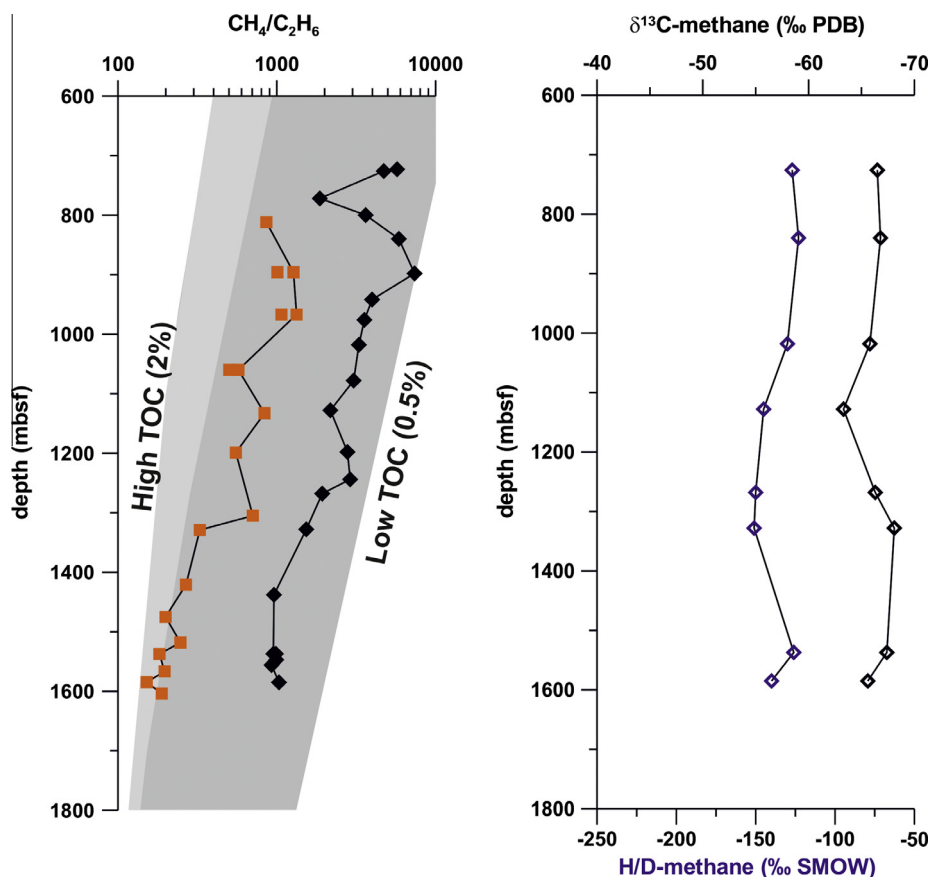
Fig. 5. Chemical composition (CH_4/C_2H_6) of mud gas (black diamonds) and cuttings samples (orange squares, left) and methane isotopic composition ($\delta^{13}C$, H/D) of mud gas samples versus depth (right). The isotopic composition of methane remains almost constant over the entire length of the investigated interval while CH_4/C_2H_6 decreases with increasing depth in drilling mud gas samples (black diamonds) and cuttings samples (red squares). The offset between drilling mud gas samples and cuttings samples is probably due to insufficient gas extraction of heavier hydrocarbons from drilling mud. The field for *in situ* hydrocarbon production between TOC = 0.5% and TOC = 2% is indicated in the diagram (Pimmel and Claypool, 2001), assuming a linear temperature gradient with T = 25 °C at 800 mbsf and 47 °C at 1600 mbsf for C0009A (Saffer et al., 2010). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

hydrocarbons. Studies on hydrocarbon from twelve submarine mud volcanoes in the Kumano forearc basin nearby hole C0009 indicate that these hydrocarbons originate from depths between 2300 and 4300 m of the old accretionary prism and derive from thermal cracking of organic matter (Pape et al., 2014) with $\delta^{13}C > -40‰$ PDB and $CH_4/C_2H_6 < 250$. These depths are greater than those penetrated by C0009 (1604 m).

The distribution of methane at C0009 correlates with the presence of visible lignite and wood fragments in drilling cuttings. This significant increase of wood/lignite fragments occurs at the lithologic boundary of Unit IIIA and Unit IIIB. Those subunits of Unit III contain thinly bedded fine-grained turbidites of basal Kumano forearc basin deposits. The lower subunit IIIB had an increased supply of terrigenous organic matter (wood/lignite fragments) possibly because of a change in climate and/or topographic relief (Saffer et al., 2010). The fragment abundance remains relatively high throughout subunit IIIB, with typical sizes of ~2 mm and some fragments as large as ~15 mm (Fig. 6).

In lithologic Unit IV, wood content decreases again. We can rule out any artificial origin of organic material (e.g. through drilling mud additives).

Drilling mud gas and cuttings gas samples were also analyzed for ethane and propane. With increasing depth, the ratio (CH_4/C_2H_6) decreases from 5721 (723 mbsf) to 1033 (1585 mbsf) in drilling mud gas and from 860 (812 mbsf) to 189 (1604 mbsf) in gas from drilling cuttings (Fig. 6). Our data plot in the field for *in situ* hydrocarbon production between TOC = 0.5% and TOC = 2%
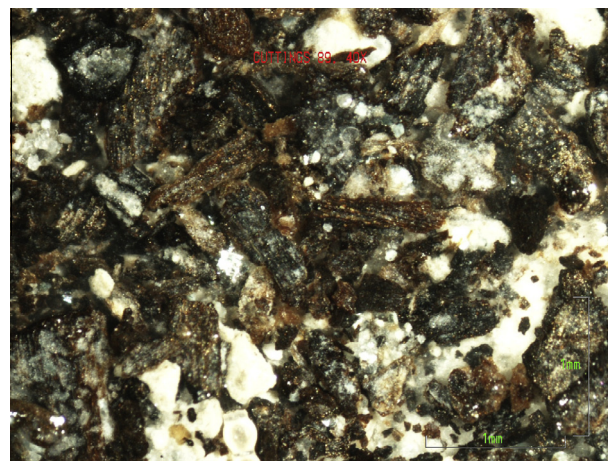

Fig. 6. Wood/lignite fragments in cuttings from subunit IIIB, with typical sizes of ~2 mm and some fragments as large as ~15 mm.

(Pimmel and Claypool, 2001), assuming a linear temperature gradient with T = 25 °C at 800 mbsf and 47 °C at 1600 mbsf for C0009A (Saffer et al., 2010). The TOC content in drilling cuttings from C0009 is always ⩾2%, suggesting that the ratios CH_4/C_2H_6 from drilling cuttings are more reliable. The offset between drilling mud gas samples and cuttings samples is best explained by higher

solubility (=lower extraction efficiency) of ethane and propane in drilling mud compared to methane. An alternative explanation, namely bacterial methane consumption during gas extraction from drilling cuttings is less likely, because no decrease in the methane concentration was observed between 100 h and 270 h in gas sampled from drilling cuttings.

The origin of ethane and propane in cold marine sediments has been a subject of controversial debates. Biological formation of ethane and propane in marine sediments from the Equatorial Pacific and Peru margin through reduction of acetate is proposed by Hinrichs et al. (2006). Rowe and Muehlenbachs (1999a, 1999b) suggest hydrocarbon generation (C1–C4) through low temperature degradation of marine shales to explain the isotopic and chemical composition of hydrocarbons from the Upper Cretaceous Colorado Group of the Western Canadian. Generation of ethane and propane at temperatures as low as 50 °C by pyrolysis experiments on Missisipian marine shales is reported by Mango and Jarvie (2009).

Ethane and propane concentration depth profiles from our study are very similar to those from methane, implying that *in situ* gas generation through decomposition of organic material is the most probable mechanism to create heavy hydrocarbons instead of ascent of thermogenic gases from greater depths. Decreasing CH_4/C_2H_6 ratios with increasing depth suggest that formation temperatures also play a role for ethane and propane generation. It is speculative wether decomposition of organics that leads to formation of heavy hydrocarbons is a thermal or microbial driven process at C0009A. Due to the low concentrations of ethane and propane in drilling mud gas and cuttings gas, no ^{13}C measurements could be performed on these species to provided additional information on hydrocarbon generation. C_2H_6/C_3H_8 ratios between 3 and 24 calls for thermogenic gas generation, where ethane is generally enriched relative to propane (Tissot and Welte, 1984). In contrast, similar ethane and propane abundances (C_2H_6/C_3H_8 ~1) have been found in hydrocarbon gas from the Equatorial Pacific and Peru margin for which biological formation is proposed (Mango and Jarvie, 2009). We therefore suggest that low temperature degradation of organic material is the principle source of heavy hydrocarbons in the part of the Kumno basin drilled by

C0009. The Bernhard diagram (Fig. 7) demonstrates that if ethane and propane were of thermogenic origin, the maximum contribution of thermogenic gases, assuming $CH_4/[C_2H_6 + C_3H_8] = 10$ and $\delta^{13}C = -42‰$ [PDB] for the thermogenic endmember (Whiticar, 1994) would be in the lower percent range.

3.2. Estimation of in situ gas concentration

Our estimation on total gas concentrations relies on the assumption that gas, hosted in the pore space, is either released into the drilling mud or remains in the pore space of the drilled rock material during ascent and can later be extracted from cuttings or core. The linear depth trend of the ratio CH_4/C_2H_6, the lack of helium anomalies and the solely microbial origin of methane suggest that Hole C0009 is not connected to deep fluid reservoirs through permeable faults or fractures.

To determine the total concentration of gas from drill mud gas data, the concentration of gas in a given time interval and the drilled volume of rock in the same time interval must be calculated. The determination of the gas concentration in drilling mud as described above reveales methane concentrations between 0.6 and 585 l [STP] per minute. From the known rate of penetration (ROP) and the effective borehole area, the drilled volume of sediment per minute is calculated, which ranges between 9 and 35 liter per minute. Synthesizing both datasets reveal methane concentration reaching up to ~24 liter per liter of drilled sediment (Fig. 8).

Cuttings are characterized by a higher surface/volume ratio than core which promotes gas loss from cuttings during their ascent. Gas liberated during cuttings ascent does accumulate in the drill mud where it later becomes detected with the drilling mud gas. However, gas loss in the short time span between cuttings arrival at the surface and sampling cannot be ruled out.

The methane concentration extracted from cuttings falls in the range between 3.3 and 60 mL/L, assuming a sediment density of 2.7 kg/L. The contribution of cuttings gas to the total gas (=cuttings + drilling mud gas) is always ≪ 1% and was therefore not taken into consideration for the calculation of the total *in situ* gas content.
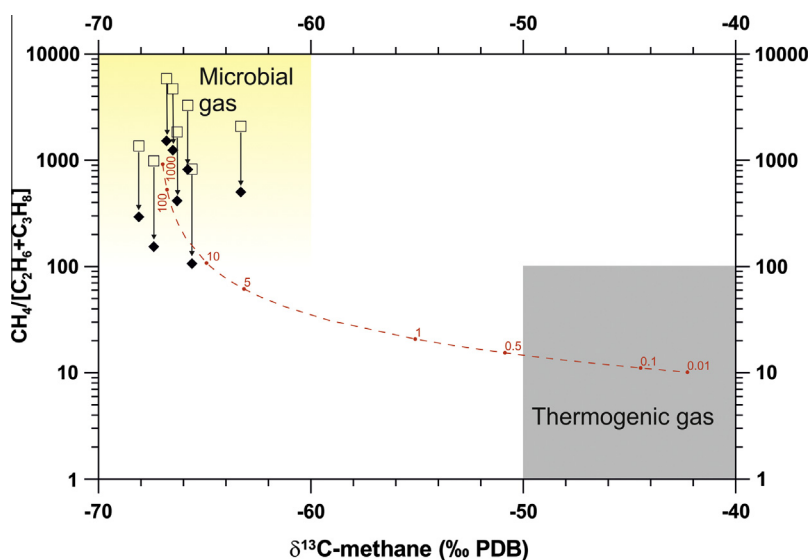

Fig. 7. Bernhard diagram ($CH_4/[C_2H_6 + C_3H_8]$ versus $\delta^{13}C$) showing eight drill mud gas samples from Site C0009A. Open squares: measured values; black diamonds: values corrected for incomplete extraction of higher hydrocarbons from drill mud. A mixing line has been added between a hypothetic microbial endmember ($\delta^{13}C = -67‰$ PDB, $CH_4/[C_2H_6 + C_3H_8] = 1000$) and a hypothetic thermogenic endmember (gas from mature Kerogen I/II with $\delta^{13}C = -42‰$ PDB and $CH_4/[C_2H_6 + C_3H_8] = 10$, see Whiticar, 1994). Along the mixing line, different ratios of microbial hydrocarbon gas versus thermogenic gas are indicated. The maximum contribution of thermogenic hydrocarbon at Site C0009A is in the lower percent range.
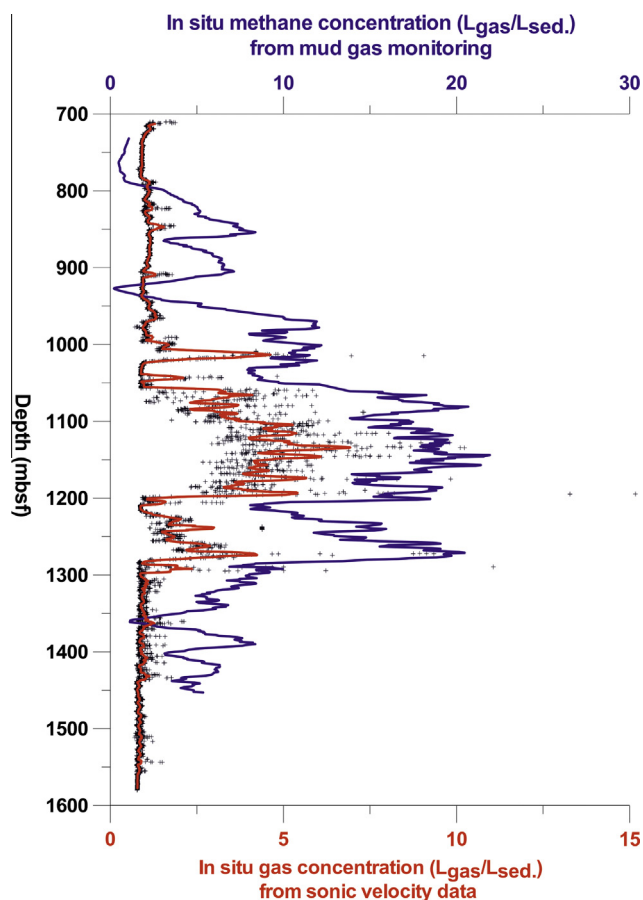
Fig. 8. *In situ* methane concentration per drilled rock volume calculated from drilling mud gas (blue line, running average over 19 data points) and sonic velocity data (black diamonds; red line = running average over 35 data points (~5 m)). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and a salinity of 1 mol/L (Saffer et al., 2010). At this conditions, the solubility of methane in water is in the range of approx. 3 L_{gas}/L_{water} (Duan et al., 1992). Given the water content stored in intergranular pores by Doan et al. (2011), maximum methane concentrations of ~15 $L_{gas}/L_{sediment}$ were calculated for C0009A.

Between 1000 and 1300 mbsf, the maximum *in situ* gas concentrations from drilling mud gas monitoring (~24 $L_{methane}/L_{sediment}$) and sonic velocity data (~15/$L_{sediment}$) are in good agreement (Fig. 8). Below 1300 mbsf, the gas load of the drilling mud was too high for complete gas extraction at the surface and gas-bearing drilling mud was recycled into the drill string. The observed positive correlation furthermore implies that formation gas is located in the pore space of the rock and does e.g. not penetrate into the borehole through fractures and faults.

Both methods have the advantage of providing a continuous gas concentration profile without using drill core. However, to convert the gas saturation from sonic velocity analysis into *in situ* gas concentration values, data on the downhole pressure, temperature, and gas composition from other measurements are necessary, and assumptions (ideal gas behaviour) need to be made.

The accuracy of absolute gas concentrations determined by the drilling mud gas method is limited by (i) the unknown difference in solubility of methane and acetylene in drilling mud at given drilling conditions, (ii) possible recycling of gas-loaded drilling mud (i.e. insufficient liberation of gas at the surface), (iii) unknown gas loss from the drilling mud and cuttings between arrival at the surface and sampling, (iv) possible gas flow from the wall rock into the drilling mud (which seems not relevant for borehole C0009). Methane in drilling mud and in drilling cuttings exhibits similar depth profiles, but gas concentrations are distinctly lower in drilling cuttings. It is furthermore important to point out that drilling mud gas monitoring has the potential to provide information on the *in situ* concentration of gas in real-time. A future comparison study between PCS, drilling mud gas monitoring and sonic velocity analysis would be helpful to check the reliability of all methods and to improve their application.

Our findings are in reasonable agreement with data from other ODP Legs. Kvenvolden and Lorenson (2000) report headspace gas concentrations from gas hydrate bearing sediments from Cape Fear (ODP Site 991, 992 and 993) and the Black Ridge (ODP Site 996) as less as 20 mL/L at depths below the Bottom Simulating Reflector, BSR. However, Paull et al. (2000) assume that conventional headspace gas analysis grossly underestimates the *in situ* gas concentration. PCS gas concentration data from ODP Leg 164 boreholes at Blake Ridge are in average 2–3 orders of magnitude higher than headspace gas concentration.

3.3. Comparison between drilling mud gas monitoring and sonic velocity analysis

A method to quantify free gas, namely the analysis of high quality sonic data from wireline logging to infer the porosity and estimate the water content stored in intergranular pores and the gas saturation, is reported by Doan et al. (2011). Given the temperature and pressure at depth of hole C0009A (Saffer et al., 2010), gas saturation data were converted into concentration data, assuming ideal gas behavior. This conversion results in concentration values of up to 14 $L_{gas}/L_{sediment}$ at STP in the gas phase. However, besides gas in the gas phase, also gas dissolved in pore water has to be taken into consideration to estimate the total *in situ* gas concentration. The content of gas dissolved in pore water was calculated assuming that the water is saturated with methane at the given conditions of pressure and temperature at the respective depth

4. Conclusion

For the first time in the history of scientific ocean drilling, drilling mud gas monitoring was conducted during D/V *Chikyu* IODP NanTroSEIZE Exp. 319 Hole C0009A riser drilling into the Kumano forearc basin and accretionary prism of the Nankai forearc between 703 to 1594 mbsf. Drilling mud gas monitoring provides an inexpensive way to reveal information on the composition and *in situ* concentration of gases that neither interferes with drilling operations nor requires drill core samples. Methane content in drilling mud of hole C0009A semi-quantitatively correlates with visible allochthonous material (wood, lignite) in drilling cuttings (Saffer et al., 2010). The chemical (C1–C3) and isotope (^{13}C, H/D) composition of hydrocarbons, the only formation-derived gases identified in drill mud, demonstrate microbial hydrocarbon gas mixing with small but increasing amounts of higher hydrocarbons (ethane, propane) most likely from low temperature thermal degradation of organic matter at greater depth. Our data bear no evidence for the presence of gases from the subducting slab or the mantle wedge. To calibrate the mud gas monitoring experiment for gas concentrations, a defined amount of C_2H_2 from a carbide test was used. An alternative method to quantify free gas was the analysis of high quality sonic data from wireline logging to infer the porosity and estimate the water content stored in intergranular pores and the gas saturation (Doan et al., 2011). Both methods reveal similar depth concentration profiles for hole C0009A and *in situ* gas concentrations of up to 15 $L_{gas}/L_{sediment}$ from sonic velocities and up to 24 $L_{gas}/L_{sediment}$ from drilling mud gas

monitoring, respectively, in good agreement with findings from other IODP Legs using the PCS.

Formation gas from hole C0009A is clearly dominated by *in situ* produced hydrocarbons with almost no evidence for the input of gases from greater depth. Pape et al. (2014) report on submarine mud volcanoes nearby hole C0009A. Submarine mud volcanoes are surface expression of fluid flow from depth. However, the molecular composition of hydrocarbons from these mud volcanoes and the geothermal gradient suggest a formation depth of hydrocarbons between 2300 and 4300 mbsf, deeper than the final depth of hole C0009A (1604 mbsf). Downhole logging and testing of hole C0009 does also not provide evidence for major fluid flow (Saffer et al., 2010). Based on these findings, we consider that deep-ranging permeable fractures and faults are not penetrated by C0009A and that fluid circulation around C0009, if any, is pervasive and not channelized.

Acknowledgements

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