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Chemical and isotope compositions of drilling mud gas from the San Andreas Fault Observatory at Depth (SAFOD) boreholes: Implications on gas migration and the permeability structure of the San Andreas Fault

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1. Abstract

In this contribution we present results from two individual gas monitoring experiments which were conducted during the drilling of the SAFOD (San Andreas Fault Observatory at Depth) boreholes. Gas from circulating drilling mud was monitored during the drilling the SAFOD III side tracks and was later analysed for $\delta^{13}\text{C}$ (CH_4 , C_2H_6 and C_3H_8), H/D (CH_4) and noble gas isotopes. Furthermore, gas accumulations induced by drill pipe retrieval (“trip gas”) from the SAFOD MH and the SAFOD III boreholes were also investigated. The data are interpreted in the context of gas migration processes and the permeability structure of the San Andreas Fault (SAF) around two actively deforming zones at 3194m and 3301m borehole depth.

Helium isotope ratios of $0.86 R_a$ at 3203m and between 0.51 and $0.88 R_a$ at 3262m (R_a is the atmospheric $^3\text{He}/^4\text{He}$ ratio) indicate an improved flow of mantle volatiles between both fault strands. Much lower values were observed at 3147m ($0.26 R_a$) and 3312m ($0.22 R_a$). Hydrocarbon concentrations coincide with the occurrence of shale at ~3150-3200m and below ~3310m depth. The molecular and isotope composition of hydrocarbons and their spatial distributions imply hydrocarbon generation by thermal degradation of organic matter followed by extensive diffusion loss. Carbon isotope data furthermore suggest a thermal maturity of the source rock of approx. $1.4 \%R_0$.

The concentration of trip gas is generally low in the interval 3100m-3450m but exhibits high spatial variability. At 3128m and 3223m depth, the trip gas concentrations are as low as in the granite section of the SAFOD Main Hole.

Considerable variations of R_a values, trip gas concentrations, and the molecular composition of hydrocarbons when penetrating the active fault strands let us conclude that the permeability of the fault transverse to the fault direction is limited and that the active fault has not been breached over many earthquake cycles such that little or no fluid exchange took place. Diffusion is the dominant mechanism controlling hydrocarbon migration through the fault strands. The elevated R_a values between both fault strands may reflect either episodic or continuous flow of mantle-derived fluids, suggestive of some limited permeability parallel to the fault direction.

Keywords: SAFOD, helium isotopes, drilling mud gas, shale gas, pipe tripping

2. Introduction

Investigations of fault veins and fracture mineralization from exhumed faults and laboratory studies on the permeability and porosity of fault rocks highlight an anisotropic behaviour of fault zone permeability in both space and time. Parallel to the fault, in fracture zones adjacent to the fault gouge enhanced fluid flow is commonly indicated. Fluid flow transverse to the fault is restricted by less permeable gouge rock (e.g., Wibberley et al. (2008), Boutareaud et al. (2008)). Models of the temporal evolution of internal structures of a fault zone involve areas with variable permeability in time, which are the dominant control of fluid migration within a fault (Byerlee (1990, 1993), Rice (1992), Sibson (1992), Caine et al., 1996). It is still under discussion how fluids with more than hydrostatic pressure may trigger processes occurring at seismogenic depths of active faults, and how elevated pore pressure within the fault core is generated, maintained, and linked with weakening the strength of a fault zone ((Rice (1992), Faulkner and Rutter, (2001), Imber et al., (2008)).

At the San Andreas Fault Zone (SAFZ) soil gas measurements and studies of surface gas discharges (hot springs and water wells) have been carried out in order to characterize sources and origins of fluids (Kennedy et al., 1997; Kharaka et al., 1999, Lewicki et al., 2003) and to identify temporal variation in the gas composition that could be linked to seismic processes at depth (Shapiro et al., 1982; King, 1986). Unfortunately, such surface data are often biased and limited in scope. The SAFOD project provided direct access to fluids from seismogenic depths of the SAF. Such fluids can be directly sampled by pore fluid extraction from drill core (Ali et al., 2009), by downhole fluid sampling (Thordsen et al., 2005) or by extraction of gas from circulating drilling mud (Erzinger et al., 2004; Wiersberg and Erzinger, 2007, 2008). While investigations of drill core and downhole fluid samples reveal information from only a

small number of sampling locations, investigations of drill mud gas provide data over the entire length of a drill hole with a depth resolution on the meter scale.

Based on chemical distinct compositions of formation-derived gases on the Pacific Plate and the North American Plates, Wiersberg and Erzinger (2008) considered that fluid flow transverse to the SAF is limited by the low permeability of the fault rock. These authors conclude that the SAF acts as a fluid barrier that separates distinct fluid regimes on the Pacific Plate vis-à-vis the North American Plate.

The Pacific and the North American Plates are also distinguished by having different contributions of mantle volatiles. Mantle-derived helium is low on the Pacific Plate, but increases away from the SAF (Wiersberg and Erzinger, 2007) when penetrating the North American Plate. The authors interpret that permeable country rock on the North American Plate is the principal conduit for mantle-derived fluids at the SAFZ. The higher amount of mantle-derived fluids rising up through the North American Plate, compared with the Pacific Plate, within the San Andreas Fault Zone system is in agreement with results from surface studies reported by Kennedy et al. (1997) and Kharaka et al. (1999).

In this contribution, we describe the chemical and isotope compositions of gases from returning drilling mud during drilling of the SAFOD III in 2007. The principle aim of the 2007 sidetrack drilling was to retrieve drill core samples from two active fault strands at 3194m (Southwest Deforming Zone, SDZ) and 3301m (Central Deforming Zone, CDZ), which have been identified by casing deformation of the SAFOD Main Hole.

Furthermore, we have determined the concentration of formation gases returning to the surface after pipe tripping ("tripgas") from the SAFOD MH and SAFOD III. These results are interpreted in the context of the permeability structure of the SAF at seismogenic depths, with the main focus of the area surrounding the active deforming zones at 3194m and 3301m borehole depth, corresponding to approx. 2630m and 2684m true vertical depth.

The San Andreas Fault Observatory at Depth (SAFOD), a component of the U.S. research initiative EarthScope and supported by the ICDP (International Continental Scientific Drilling Program) was drilled in multiple phases from 2002 to 2007. The drill site is located on the Coast Range of central California, 1.8km southwest of the surface trace of the San Andreas Fault on the Pacific Plate in close vicinity of the town Parkfield. The location was chosen due to the simultaneous occurrence of creep and repetitive seismicity at drillable depths, several historical M6 earthquakes, and an expected change in lithology from granite on the Pacific Plate to serpentinite on the North American Plate when intersecting the SAF at depth (Hickman et al., 2004).

In 2002, the straight SAFOD PH was drilled to 2168m depth, whereas the deviated SAFOD MH was drilled in two phases. In 2004, the SAFOD MH was drilled to a depth of 3051m (MH-I). After a downtime of about nine months, the well was deepened to a final depth of 3987m (MH-II). Between both drilling phases, a M6.0 earthquake shook Parkfield on September 28, 2004. At ~1445m depth, the MH is deviated to the northeast to intersect the SAF and penetrate into the North American Plate at seismogenic depth.

The SAFOD boreholes traverse 768m of Tertiary and Quaternary sediments on the Pacific Plate, which lie on Mesozoic granites of the Salinian Block. In contrast to the Pilot Hole, which retrieved only crystalline rocks below 768m down to the well bottom at 2168m, the MH encounters sedimentary strata at 1920m that persist to the bottom of the hole. Arkosic and lithic sandstones, interbedded by siltstone sequences, extend from 1920m to 3150m depth. Siltstones, mudstones, and shales are the prominent strata from 3150m down to the bottom (Bradbury et al., 2007). The first occurrence of serpentinite in drill cuttings is reported from ~3320m depth (Evans et al., 2005). Serpentinite is known from outcrops on the North American Plate as part of the Franciscan Complex, but only traces of serpentine have been found in drilling cuttings from the SAFOD MH. Hence, it was believed that the SAFOD MH probably did not penetrate into the Franciscan Complex, but into the Great Valley sequence.

Active fault strands were revealed by casing deformation of the SAFOD MH at 3301m (Zoback et al., 2007) and later at 3194m (Hickman et al., 2008). Observations on drilling cuttings and few core samples from the SAFOD MH reveal the presence of sheared rocks at approximately 3100m – 3450m depth (Solum et al., 2006).

Three side tracks were drilled out of the MH in 2007 (Fig. 1) to retrieve a suite of drill core samples from the active fault strands and to place long-term monitoring equipment into the borehole. The side tracks include the holes SAFOD III-D (3137m - 3262m), -E (2952m - 3182m) and -G (3125m - 3356m). These sidetracks and the MH are nearly orthogonal to the SAF. Drill core samples were obtained from Hole E (3141-3153m) and from Hole G (3182-3195m and 3299-3316m). Figure 1 shows a cross section of the SAFOD site from 3100m to 3350m borehole depth including a simplified lithology based on drilling cuttings description from the SAFOD MH (http://www.icdp-online.org/upload/pdf/safod/Phase2_Mud_Log_PDF.pdf) and from drill core analysis (http://www.icdp-online.org/upload/projects/safod/phase3/Core_Photo_Atlas_v4.pdf).

To correlate SAFOD MH downhole logs with SAFOD III-G core data, Zoback et al. (2010) suggest that 5.03m should be subtracted from the depths indicated for drill core from the SDZ (Southwest Deforming Zone at 3194m SAFOD MH borehole depth) and 3.96m should be

added to depths indicated for core from the CDZ (Central Deforming Zone at 3301m SAFOD MH borehole depth). All depths from SAFOD III-G discussed in the following have been corrected in this manner.

3. Methodology and data evaluation

3.1 Drilling mud gas analysis

Analyses of drilling mud gas have previously only been reported in a few studies. Hilton and Craig (1989) performed noble gas studies on drilling mud gas samples from the Silijan well, Sweden. Aquilina and Brach (1995) applied a geochemical monitoring system (WELCOM) during deepening the GPK-1 borehole in Soultz-sous-Forêts, France. Aquilina et al. (1998) compared data from drilling mud gas with gas released from drill core leaching experiments from the Balazuc borehole in France. Rowe and Muehlenbachs (1999) and later Tilley and Muehlenbachs (2006) investigated drilling mud gas samples to characterize migration and mixing processes of hydrocarbons from the Western Canada Sedimentary Basin.

All aforementioned studies are based on data and samples provided by mud logging services. Commercial mud logging is conducted for safety purpose and does not necessarily aim to follow scientific targets (see e.g., Hilton and Craig, 1989). Commercial gas water separators are optimized for standardized, repeatable results. In such separators, gas is liberated from the drilling mud by stripping with air. This method is only feasible for gases significantly enriched in formation fluids, relative to the atmosphere, but e.g. not useful for helium. The helium concentration in drilling mud seldom exceeds the atmospheric value of 5.24ppmv by more than factor two.

For all our SAFOD studies, gas was extracted mechanically in a variable size, modified oilfield gas separator. This mechanism can be adapted to the actual drill site conditions so as to ensure high gas extraction efficiency in combination with low air contamination. This set-up had been developed as part of the drilling of the KTB (Zimmer and Erzinger, 1995) and has subsequently been further optimized during several scientific drilling projects (Erzinger et al., 2004, 2006, Wiersberg and Erzinger, 2007, 2008). Gas analysis is performed with a quadrupole mass spectrometer for N₂, O₂, CH₄, CO₂, H₂, He and Ar, with a gas chromatograph equipped with a FID-detector for saturated and non-saturated hydrocarbons, and with a radon detector for ²²²Rn. Technical details on the drill-mud gas monitoring have been reported by Erzinger et al., 2006.

An atmospheric component is always present in drilling mud, as both mud pumps and mud tanks are open to air. The most abundant gases in air are N₂ (78.09 vol.-%), O₂ (20.95 vol.-%)

and Ar (0.93 vol.-%). The presence of these gases in drilling mud is generally attributed to the atmospheric input. Wiersberg and Erzinger (2007) could proof the potential of noble gas studies for distinguishing between different sources of atmospheric gases in drilling mud, that is, air and atmospheric gases dissolved in meteoric water.

Different types of reactions between drilling additives or water with the casing steel or the drill bit can generate so-called artificial gases which typically contain hydrogen and an assemblage of non-saturated hydrocarbons (Whiticar, 1994). Non-saturated hydrocarbons in drilling mud are interpreted to be solely artificial because they are not stable over geological times. Formation-derived gases are either in-situ produced and accumulated in the pore space of rock or enter the borehole when penetrating permeable strata (e.g. open fractures, faults). In sedimentary strata, these gases include hydrocarbons, radon, He, CO₂, H₂S, and H₂.

Aquilina and Brach (1995) and later Aquilina et al. (1998) have used radon and the helium-radon couple to distinguish between fluids trapped in pore space and fluids that were actively circulating through permeable strata which were penetrated during the deepening the GPK-1 well at Soultz-sous-Forêts (Alsace, France) and when drilling the Balazuc-1 borehole at the northeast edge of the SE Basin (France), respectively. Radon and helium derive from the uranium and uranium plus thorium radioactive decay chains, respectively; both are highly soluble in water. However, radon itself is radioactive with a half-life time of 3.8d for its most stable isotope (²²²Rn). This short half-life time hampers radon accumulation in pore space fluids of rocks. Due to its low diffusivity, elevated radon concentrations in drilling mud gas are generally attributed to active fluid flow through permeable strata. In contrast to radon, helium is very mobile and is accumulated in the pore space after diffusing from its source in the crystal lattice of U and Th bearing minerals. Helium migration is not only controlled by diffusion, but also by fluid flow in rocks with interconnected pore space. Enhanced concentration of helium with low radon activity in formation fluids is therefore more indicative for high porosity of rock, whereas abundant radon in formation fluids suggests active fluid flow through permeable strata.

Helium and radon data from the SAFOD MH indicate that permeability is generally lower when drilling through the SAFZ as compared to borehole sections above and below (Wiersberg and Erzinger, 2008). However, frequent drill stops during SAFOD III caused radon accumulation in the hole which makes radon data difficult to interpret. We therefore use gas accumulations during drilling breaks and isotope studies to gain more information on the permeability structure of the SAF at seismogenic depth. Noble gas as well as carbon isotopes have the potential to identify the origin of geofluids and consequently also possible migration

mechanisms. A deep origin of gases as would be indicated by raised $^3\text{He}/^4\text{He}$ ratios can only be explained by fluid migration from depth when other gas sources (e. g., degassing of a shallow magmatic body) can be ruled out.

3.2 Drilling mud gas analysis during pipe tripping

Drilling mud is generally adjusted to be in balance with the formation pressure while drilling. In case that drilling mud is static (i.e., no mud circulation), the hole bottom pressure is defined by the weight of the mud column only, which is generally lower than the formation fluid pressure. Lower bottom hole pressure, such as occur when mud circulation is suspended in order to make a new drill pipe connection, produce such “connection gas” (e.g., Johnson and Pile, 2006). However, during SAFOD the drilling mud was slightly overbalanced, and no significant amounts of connection gas were detected.

An additional short-term reduction of the downhole pressure in the area ahead the drill bit is achieved when pulling the drill string. In this case, the drilling mud flow through the drill string and the borehole is not sufficient to keep the downhole pressure constant. A lowered bottom hole pressure induces fluids to flow from the adjacent wall rock in the borehole either through open fractures or from pore spaces. Pipe tripping may increase the pressure difference between the wall rock and the drilling mud column enough so as to induce fluids and gases hosted in pore space to flow into the well bore (also called “trip gas”). This would be the case in particular if the pore pressure is elevated (i.e., higher than hydrostatic). The presence of areas with elevated pore pressure in fault zones, be they either episodic or permanent in nature, is addressed by several models which explain fault zone weakening and failure. From other well bores in the vicinity of SAFOD it is known that in the Salinian block on the southwest side of the SAF pore pressures are slightly below hydrostatic whereas elevated pore pressure is observed on the north-east side of the fault in the Great Valley Formation (Kennedy et al., 1997). Observations during SAFOD drilling have found no evidence for anomalously high pore pressure within the fault zone (Zoback et al., 2007). Further evidence that trip gas data at SAFOD are indeed related to the permeability of the strata rather than to areas of variable pore pressure is provided from ^{222}Rn data (see below).

The amount of fluids and gases accumulating in the borehole during downtime generally increases with time; however the rate of change in pressure generally decreases with time due to pressure equilibration and progressive depletion of formation fluids in the surrounding wall rock. These gases accumulated during a round trip and will be brought to the surface when mud circulation resumes.

In the SAFOD MH, the most prominent formation-derived gases detected during drilling were CH₄, CO₂ and H₂ (Wiersberg and Erzinger, 2008). These gases also dominate the composition of gas accumulations induced by pipe tripping. These trip gases were analysed with the same analytical equipment as the drilling mud gas analyses. Data evaluation involved summing up the measured relative concentrations of the formation gases (CH₄, CO₂ and H₂) and trip gas peak integration. The concentration of gas is proportional to the area of the trip gas peak. To calibrate for absolute gas concentrations, the drilling mud needs to be spiked with a known volume of a test gas which was not performed in this study. We therefore discuss trip gas concentrations in arbitrary units (a. u.) from peak integration in the following. Because the drilling mud column may contain background gas (e. g. when drilling mud was not fully circulated out), a baseline subtraction is performed prior to peak integration.

The trip gas peaks generally have duration of about one hour, depending on the concentration of the formation gases, the gas pumping rate and the headspace volume of the degasser. Pumping rate and headspace volume were kept constant for all round trips. The trip gas amount from the SAFOD wells vary over three orders of magnitude, from 218 a. u. in the granite section up to about 163,000 a. u. in the sedimentary section at 3831m depth. The downtime before tripping back into the hole ranges from 7h to 468h.

In Table 3, we report gas amounts from peak integration as well gas amounts normalized to downtime. The distribution versus depth is similar when comparing integrated and downtime-normalized trip gas data, suggesting that the gas accumulation after pulling plays only a minor role. Therefore, we consider only gas amounts from trip gas peak integration in the following. As an example, the peaks of CO₂, CH₄ and H₂ versus time and the resulting trip gas peak when tripping back into the SAFOD III-D at 3197m are shown in Fig. 2A.

In order to distinguish between pore-space derived gas and gas related to permeability, Aquilina et al. (1998) made use of the helium-radon pair. However, the presence of both species in drilling mud could also be related to the uranium and thorium content in the surrounding strata. Drilling rocks significantly enriched in the He-Rn parent element(s) could misleadingly suggest high porous or permeable strata.

So as to circumvent this problem, in this study we compare trip gas concentrations from specific depths with ²²²Rn measured during drilling of the same interval. The radon data are taken from the SAFOD MH (Wiersberg and Erzinger, 2008). A cross-plot of gas amount from pipe tripping (trip gas) versus the ²²²Rn activity recorded during the drilling of the corresponding depth of the SAFOD MH is shown in Fig. 2B. These data show a linear correlation ($R^2 = 0.79$). The correlation between radon activity and trip gas concentration

emphasises that the trip gas content at SAFOD is related to fault zone permeability rather than elevated pore pressure in the fault.

4. Results

In the following, we present drilling mud gas data from the SAFOD III, drilled in 2007, as well as noble gas and stable isotope data from off-line samples. The complete real time gas monitoring dataset, including all recorded gas data from the three sidetracks, is available from the authors upon request.

Results from 30 off-line gas samples, taken either during drilling (18 samples) or pipe tripping (12 samples), are shown in Tables 1 and Table 2. Data of five round-trips from the SAFOD III and of 22 round-trips from the SAFOD MH-I and –II are shown in Table 3.

4.1 Drilling mud gas monitoring during SAFOD III

The most abundant formation-derived gases in drilling mud from the SAFOD MH were CO₂, H₂ and CH₄ (Wiersberg and Erzinger, 2008). Consequently, we discuss their drill mud concentrations at SAFOD III in the following.

When the MH penetrates the SAF, the concentration of CO₂ reached up to 5 vol.-%. CO₂ was also analyzed from drill-mud gas during the SAFOD III, but its concentration was distinctly lower than in the MH due to the use of CaCl₂ to adjust the drilling mud weight during phase III. In order to test if gaseous CO₂ can be sequestered by forming CaCO₃, about 600g of dry ice, equivalent to approx. 0.3m³ of CO₂ [STP], were placed in the drill string when making a new pipe connection, which was subsequently pumped down hole. No CO₂ was detected in the returning drilling mud, which implies a total consumption of CO₂ by the drilling mud.

The amount of hydrogen in drilling mud was generally high during drilling within the sedimentary section of the SADOD MH in 2005 (up to 10 vol.-%) and was relatively low (<0.1vol.-%) in the SAF (Wiersberg and Erzinger, 2008). Drilling of the sidetracks SAFOD III-D, G and E also exhibit only low hydrogen content in the drilling mud.

Depth progress was mostly achieved at SAFOD III by using a mud motor; however, the drill pipe sometimes rotates slowly to avoid pipe sticking. During these phases, the hydrogen amount in drilling mud was significantly higher, suggesting that hydrogen was generated by mechanical interaction between the drill pipe and the casing steel. The amount of hydrogen in the drilling mud further increased when coring was conducted. Coring was performed with a diamond impregnated drill bit, and it is known that such drill bits can generate artificial hydrogen (Zimmer and Erzinger, 1995). As hydrogen was not unusually enriched in this

interval when drilling the SAFOD MH with a conventional drill bit, we assume that most hydrogen in the sidetracks was of artificial origin.

The SAFOD MH and all sidetracks show a very similar distribution of hydrocarbons at depth (Fig. 4), but hydrocarbon concentrations in drilling mud gas differ significantly in the MH and the different sidetracks. Maximum methane concentration in the segment 3150-3200m were found in the SAFOD MH (4 vol.-%), followed by the SAFOD III-D (1 vol.-%) and the SAFOD III-G and -E (approx. 0.3 vol.-%). The trip gas concentration from the SAFOD MH at 3196m exceeded that from 3197m of the SAFOD III-D (Table 3). Nevertheless, both are higher than the concentrations from 3128m (SAFOD III-D) and 3223m (SAFOD III-G). These trends could be explained with progressive near field gas depletion of the intersected strata due to ongoing perforation with new boreholes, and hence may indicate slightly enhanced permeability in this segment. Diffusion as the driving force for gas depletion within 20m distance between the SAFOD MH and the SAFOD III-E and -G wells seems unlikely. Between the actively creeping fault strands at 3194m (SDZ) and 3301m (CDZ), the content of methane is distinctly lower than in the borehole sections above and below. Methane again increases in the MH and borehole G below 3310m.

The molecular composition of hydrocarbons, denoted as gas dryness [$\text{CH}_4/(\text{C}_2\text{H}_6+\text{C}_3\text{H}_8)$], is very low from 3150m to 3200m (<10), then increases below 3200m to reach a maximum [$\text{CH}_4/(\text{C}_2\text{H}_6+\text{C}_3\text{H}_8)$] ratio of approx. 60 at 3260m, and finally drops to values <20 at 3310m, below which it remains constant down to the bottom of the SAFOD MH. Between 3190m and 3202m depth, the abundances of ethane, propane and butane relative to methane drop from 0.15 to 0.025 for $\text{C}_2\text{H}_6/\text{CH}_4$ (factor 6), from 0.07 to 0.0028 (factor 25) for $\text{C}_3\text{H}_8/\text{CH}_4$ and from 0.043 to 0.0007 (factor 61) for $\text{C}_4\text{H}_{10}/\text{CH}_4$.

In contrast to the variable concentration ratios between the various hydrocarbons, the isotope composition of hydrocarbons between 3147m and 3326m is more uniform and indicates a common source of hydrocarbons throughout the investigated segment. Ten samples from this interval have been analysed for $\delta^{13}\text{C}$ on methane, ethane and propane along with H/D determinations of the methane component (Table 2). The $\delta^{13}\text{C}$ values from methane range from -29.7‰ to -33.5‰, ethane values range between -23.6‰ and -27.1‰ and propane values range from -23.4‰ to -27.0‰ (PDB). H/D values of methane fall between -154‰ and -174‰ (SMOW). Such isotopic compositions imply a natural gas source from thermal degradation of organic matter.

Noble gas isotope studies have been performed on six samples from the SAFOD III. As the helium concentration in drill-mud gas samples is generally low at SAFOD, not exceed

concentrations of 6.7ppmv during phase III, five of the six noble gas isotope studies were performed on gas samples from pipe tripping. We discuss only the helium isotopic composition (given in R_a which is the determined value ratio against the atmospheric $^3\text{He}/^4\text{He}$ ratio of 1.39×10^{-6}). All R_a values are air-corrected according to the method described by Craig et al. (1978), assuming an air-like $^4\text{He}/^{20}\text{Ne}$ composition of the atmospheric component. The relative noble gas elemental abundances of all other noble gases, denoted as $F = [(X/^{20}\text{Ne})_{\text{measured}}/(X/^{20}\text{Ne})_{\text{air}}]$, are indistinguishable from air.

4.2 Data from pipe tripping in the SAFOD MH and the SAFOD III (“trip gas”)

For this study results from 27 round-trips (5 from SAFOD III boreholes, 22 from the SAFOD MH) have been evaluated (Table 2). We report both the integrated and the downtime-normalized concentration of trip gases. Depth profiles of trip gas concentration and ^{222}Rn from the entire length of SAFOD (0-3987m) are shown in Fig. 3. The profiles show good agreement.

The trip gas amount is low in the granite section (768-1930m) of the SAFOD MH at 826m depth, becoming somewhat elevated at 1325m and 1453m. At these depths, slightly enhanced formation gas was identified in drilling mud of the SAFOD PH (Erzinger et al., 2004) that coincides with the presence of shear zones. When running into sediments at depths below 1930m, the trip gas concentration starts to increase. The maximum trip gas concentration on the Pacific Plate is observed at 2986m (146,880 a. u.).

Within the San Andreas Fault zone (~3100m - 3425m), trip gas concentration varies by more than a factor of 20 over distances of as little as 20m. At 3128m, in an arkosic sandstone unit, the concentration (594 a. u.) is as low as in the granite section of the SAFOD MH (<1,332 a. u.). The trip gas concentration increases to 9,671 a. u. at 3144m and finally reaches a local maximum of 24,290 a. u. at 3197m. Below 3197m the trip gas concentration drops down to a minimum concentration of 458 a. u. at 3223m, then increases again to 19,797 a. u. at 3317m. The somewhat increased trip gas values around 3197m and 3317m may indicate an enhanced permeability parallel to the fault direction. From 3317m to 3652m, the trip gas concentration is much more homogeneous, varying only about a factor of 2 (18,022 – 40,435 a. u.). The trip gas concentration then increases again below 3652m to reach a maximal value of 162,759 a. u. on the North American Plate at 3831m.

5. Discussion and Conclusion

5.1 Hydrocarbon generation and migration

The abundance of hydrocarbons in drilling mud gas from the 3150-3350m segment of the SAFOD boreholes clearly correlates with the abundance of shale from drilling cuttings analysis (Fig. 4). Maturity studies on drill cuttings from 3150-3350m of the SAFOD MH also demonstrate that the shale is principally mature enough to generate hydrocarbons. Rock-Eval pyrolysis experiments on organic material from this interval reveal a thermal maturity within the window of hydrocarbon generation (D. Kirschner, personal communication). These observations lead to the conclusion that shale acts both as a source and reservoir rock for hydrocarbons at SAFOD.

The isotope composition of methane between 3147m and 3326m generally indicates a hydrocarbon source from thermal degradation of organic matter (Whiticar et al., 1994). Methane is somewhat enriched in ^{13}C at the contact shale/arkosic sandstone at 3147m ($\delta^{13}\text{C} = -30.8\text{‰}$) and shale/siltstone at 3202m ($\delta^{13}\text{C} = -29.7\text{‰}$) as compared with results from the shale unit at 3185m and 3193m ($\delta^{13}\text{C} = -32.1\text{‰}$ and -32.5‰ , respectively) and in the siltstone-dominated unit between both fault strands (-31.1‰ at 3225m and -32.2 at 3262m ‰). Despite the contact zones, the carbon and hydrogen isotope values from the entire section are quite uniform. In contrast, the molecular composition of hydrocarbons shows considerable variation. Gas dryness is very low from 3150m to 3200m (<10), then increases sharply with depth to 3200m, reaching a value of 60 at 3260m, below which it then again drops to values <20 at 3310m. $[\text{CH}_4/(\text{C}_2\text{H}_6+\text{C}_3\text{H}_8)] <10$ ratios, as observed in the shale unit, correspond to a thermal maturity of the organic source material much higher than indicated by Rock-Eval pyrolysis experiments (D. Kirschner, personal communication). This discrepancy can only be explained by fractionated gas loss via diffusion.

Hydrocarbon fractionation due to gas leakage has been the subject of several studies in the past (e.g., Leythaeuser et al., 1983; Prinzhofer and Pernaton, 1997; Zhang and Krooss, 2001; Schloemer and Krooss, 2004). Leythaeuser et al. (1983) describe drastically different concentration gradients of n-alkanes (ethane - n-pentane) at the contact between a mature siltstone and a sandstone interval. According to these authors, such a phenomenon can either result from different hydrocarbon generation due to differences in the hydrocarbon maturity of the source rocks, or from hydrocarbon redistribution after gas generation. The former can be ruled out for SAFOD, because such a scenario would require different post-burial thermal histories, that in turn would be displayed in more variable hydrocarbon isotope and rock maturity data, which is just the opposite of what is observed. Therefore it is unlikely that the distribution of hydrocarbon gas at SAFOD is controlled by the proximity of hydrocarbon source rock with no subsequent gas migration processes.

Laboratory studies on shale samples have revealed measurable carbon *isotope* fractionation of methane during gas diffusion. The degree of fractionation depends on several factors including temperature, stress and the total organic carbon content of the source rock (Zhang and Krooss, 2001). These authors report a significant depletion in ^{13}C in the diffusing gas phase. With increasing reservoir depletion, hydrocarbons in the reservoir become isotopically heavier (Schloemer and Krooss, 2004).

At SAFOD some ^{13}C enrichment of methane is observed at the contact between shale and arkosic sandstone at 3147m and at the contact between shale and siltstone at 3202m despite the observation that the carbon isotopic composition of the siltstone and the shale units are quite uniform in the segment 3147-3317m. A plot of $\delta^{13}\text{C}$ [CH_4] vs. $\delta^{13}\text{C}$ [C_2H_6] (Fig. 5) demonstrates that the variations in the isotopic composition of hydrocarbons from the SAF are related to extensive reservoir degassing (Schloemer and Krooss, 2004). This diagram exhibits that hydrocarbon reservoir rocks are more depleted in ^{13}C over the depth interval 3147-3317m. In contrast, hydrocarbons from the adjacent strata show an isotopically lighter signature.

The intersection between the straight lines that indicates the isotopic composition of an unaltered reservoir as a function of the rock maturity (Faber, 1987) and the reservoir depletion trend corresponds to the original isotopic composition of hydrocarbon gas prior to reservoir depletion (Fig. 5). By this we estimate an original isotopic composition ($\delta^{13}\text{C}$) of approximately -39‰ for methane and -29‰ for ethane, according to a rock maturity of approx. 1.4 % R_0 , corresponding to an isotope offset of 6 - 9‰ for methane and 2 - 5‰ for ethane relative to their measured values. Such large isotope offsets and the compositional variation of hydrocarbons suggest an extensive depletion of the reservoir (Schloemer and Krooss, 2004).

The extensive diffusive gas loss from the reservoir, in turn, requires huge amounts of hydrocarbons be present somewhere else. The drilling mud gas concentration profiles (Fig. 4, see also Wiersberg and Erzinger, 2008) confirm that the hydrocarbon content in the strata adjoining the shale units cannot fully accommodate the missing gas. The most likely explanation is that the missing hydrocarbons have simply migrated vertically from the reservoir toward the surface. Hydrocarbons have only partly migrated laterally from the shale into the adjacent strata intersected by the SAFOD wells.

The ^{13}C -enriched methane found at the lithological boundaries might represent residual gases after depletion of the reservoir at this zone; such an interpretation is consistent with the observed hydrocarbon concentration minima at these depths. Further investigations are

necessary to prove how this is related to, for example, the porosity of the fault gouge and/or local temperature anomalies from frictional heating.

5.2 Noble gases and trip gas

Because the Earth's mantle and the continental crust differ in their $^3\text{He}/^4\text{He}$ ratio by several orders of magnitude, helium isotopes can potentially distinguish between mantle-derived and crustal fluids. Samples from the upper mantle show uniform $^3\text{He}/^4\text{He}$ ratios of 8 R_a (Graham, 2002), whereas the $^3\text{He}/^4\text{He}$ ratios in the crust seldom exceed 0.02 R_a (Ballentine and Burnard, 2002). The higher $^3\text{He}/^4\text{He}$ ratio in the mantle is attributed to a mixture of mostly primordial helium with some radiogenic helium produced *in situ*. While ^3He in the mantle is predominantly primordial, the production of ^3He by the reaction $^6\text{Li} (n, \alpha) ^3\text{H} (\beta^-) ^3\text{He}$ (Mamyrin and Tolstikhin, 1984) and of ^4He from the U and Th decay chains govern the helium isotope composition of the continental crust, because the continental crust is highly depleted in primordial noble gases.

Helium, like all noble gases, is not affected by alteration through chemical reactions. Unlike the heavy noble gas species, helium is not accumulated in the atmosphere due to its steady loss to space. Hence the relative concentration of helium in the atmosphere is low. The heavier noble gases have accumulated in the atmosphere, which makes them more sensitive to atmospheric contamination. Furthermore, the heavy noble gas isotopic compositions in different reservoirs (mantle, atmosphere, crust) differ only to a small degree, are highly variable, or are otherwise just poorly constrained.

Studies on the helium isotopic composition of fluids from the San Andreas Fault zone as *the* major active plate-bounding fault zone have identified a wide range in mantle-derived helium (Kennedy et al., 1997; Kharaka et al., 1999; Wiersberg and Erzinger, 2007; Ali et al., 2009). However, at least 50% of the helium originated from a crustal source for all samples which have so far been described in the scientific literature. Mantle-derived helium has been attributed either to a continuous flow of mantle volatiles from the brittle-ductile transition zone (Kennedy et al., 1997; Kharaka et al., 1999) or from dehydrated serpentized mantle rocks from the Franciscan Complex (Fulton and Saffer, 2009).

Rocks of the Franciscan Complex are early Jurassic to Cretaceous in age (Kharaka et al., 1999). Fluids derived from such a source could have a $^3\text{He}/^4\text{He}$ ratio in the range of 1 R_a only if the uranium and thorium content of the source rocks were unusually low. This is, however, not the case: uranium and thorium concentrations from geophysical downhole logging of the SAFOD MH (Wiersberg and Erzinger (2008) and references therein) revealed ~1-2ppm for

uranium and 3-4ppm for thorium at depths where serpentinite was encountered in the SAFOD III-G borehole (3192m, see SAFOD Core Photo Atlas v.4). Assuming the minimum concentrations for the parent nuclides (U: 1ppm, Th: 3ppm), a minimum serpentinization age of 70Ma and a helium concentration of 5×10^{-7} ccSTP/g (Moreira and Kurz, 2001) for the subducted oceanic lithosphere, the current $^3\text{He}/^4\text{He}$ ratio for the Franciscan serpentinite can be modelled to be $0.27 R_a$, which is close to the lowest R_a values observed at SAFOD. It thus seems possible that serpentinite degassing might be responsible for the background of mantle helium observed at SAFOD.

Diffusion processes may explain the distribution of hydrocarbons near the shale units at SAFOD in the depth interval investigated here. Diffusion cannot readily account for the migration of mantle volatiles from greater depths. Assuming a maximum age of the SAF of 30Ma (Kennedy et al., 1997) and an estimated helium diffusion coefficient in a range of $\sim 10^{-5}$ cm^2/s at 400°C (Ozima and Podosek, 2002), a diffusion length of ~ 1.4 km can be calculated. At a lower temperature of 200°C , the maximum diffusion coefficient can be estimated with 10^{-6} cm^2 and the diffusion length would be 440m.

We therefore favour continuous flow of mantle volatiles along the brittle-ductile boundary into the seismogenic zone of the SAF that might be sufficient to generate lithostatic fluid pressures and therefore contributes to weakening of the SAF (Kharaka et al., 1999).

Wiersberg and Erzinger (2007) report that air-corrected $^3\text{He}/^4\text{He}$ ratios in drilling mud gas from the SAFOD MH increase away from the centre of the SAF on the North American Plate. On the Pacific Plate (down to $\sim 3100\text{m}$), the $^3\text{He}/^4\text{He}$ in drill-mud gas from the SAFOD MH is relatively constant ($\sim 0.4 R_a$). From 3433m borehole depth down to 3943 m (deepest sample of their study), R_a values steadily rise from $\sim 0.51 R_a$ to $\sim 0.95 R_a$. Evidence for an even higher contribution of mantle-derived helium on the North American Plate with greater distance from the centre of the SAF have been reported by Kennedy et al. (1997). These authors report $1.5 R_a$ in a borehole that is about 1500m away from the surface trace of the SAF (Phillips-Varian well).

Only one sample investigated by Wiersberg and Erzinger (2007) was derived from the interval between the two active deforming zones of the SAF and it produced a R_a value of 0.43 at 3196m depth. Based on these results, the authors have suggested that mantle-derived fluids mostly migrate through permeable country rock on the North American Plate.

Our new data show R_a values of ≥ 0.85 in samples from SAFOD III from 3203m, very close to the CDZ at 3194m, and from 3262m depth (Fig. 6). At 3262m, two samples were taken during downtime caused by pipe sticking. Both samples reveal elevated R_a values, but the #22

sample taken on July 15 shows a higher ratio ($R_a = 0.88 \pm 0.19$) than the sample taken three days later (#23, $R_a = 0.506 \pm 0.048$) and also contains more ^4He (12.3ppmv and 7.4ppmv, respectively). One can speculate that the extensive drill pipe retrieval operations conducted between samples #22 and #23 introduced crustal fluids from the pore space of the surrounding rocks due to significant lowering of the bottom hole pressure. In contrast to these high R_a ratios, the lowest R_a of all SAFOD drilling mud gas samples were observed in the SAFOD III-D at 3147m ($0.26 \pm 0.12 R_a$) and in the SAFOD III-G at 3312m ($0.22 \pm 0.12 R_a$).

Our results reveal striking variations in the helium isotope composition at seismogenic depths of the SAF at small spatial scales. By assuming a homogenous helium isotope composition of a deep volatile source, the observed variations must be due to varying degrees of mixing with *in situ* radiogenic helium during fluid upflow. The relative proportions of crustal and mantle helium in deep fluids depend on the concentration of uranium and thorium, the fluid volume and the fluid residence time in the crust.

The helium concentrations in our dataset vary by roughly a factor four, which might reflect biases between differing sampling techniques. Generally, trip gas contains more formation gases, relative to the atmospheric input, than drilling mud gas samples taken during drilling. The air-corrected $^3\text{He}/^4\text{He}$ ratios vary between $0.22 R_a$ and $0.88 R_a$ without any correlation between low $^3\text{He}/^4\text{He}$ ratios and elevated concentrations of ^4He . The low $^3\text{He}/^4\text{He}$ ratios found at 3144m and 3317m depths are therefore not simply caused by improved admixing of crustal helium to a fluid that flows with constant rate from greater depths. Variable production of ^4He in strata with differing uranium and thorium contents is therefore less likely to explain the observed variations in $^3\text{He}/^4\text{He}$ ratios; we believe that variations in fluid flow rates from depth is a more plausible explanation.

Variable fluid flow rates can result from differences in porosity and permeability. Assuming the fault gouge of the SDZ and the CDZ is less porous than the surrounding rocks; the residence time for fluids would be shorter in the gouge and the accumulation of radiogenic helium less significant. In such a case one would expect higher $^3\text{He}/^4\text{He}$ ratios within less porous strata, assuming constant permeability. This is opposite to the observations from the CDZ, where the lowest $^3\text{He}/^4\text{He}$ ratio appears close to the fault gouge.

Additional evidence that $^3\text{He}/^4\text{He}$ ratios are coupled with permeability can be extracted from trip gas data. The lowest $^3\text{He}/^4\text{He}$ ratios in all SAFOD boreholes were observed in the crystalline rocks and in the SAF at 3144m and 3313m. The granite section and the SAF are also the areas where the lowest trip gas concentrations were found. Both trip gas concentrations and the $^3\text{He}/^4\text{He}$ ratios increase on the North American Plate away from the

SAF. There are, however, discrepancies between helium isotope and trip gas concentration data, because pipe tripping samples are biased in favour of local formation fluids around the well bore, whereas $^3\text{He}/^4\text{He}$ ratios deliver information from greater depths. The sediments on the Pacific Plate between 1920m and ~3100m show constantly low $^3\text{He}/^4\text{He}$ ratios, but increasing trip gas concentrations with depth, because the granite section underlying these sediments restricts fluid flow from greater depths. Low trip gas concentrations appear between both fault strands, probably because only little gas has migrated laterally from surrounding reservoir rock through the fault branches that could be sampled by pipe tripping. The new data presented here suggest that the low permeability barriers that hamper fluid migration transverse to the fault (Wiersberg and Erzinger, 2007) are associated with fault strands at 3194m and 3301m depth. We conclude that variable $^3\text{He}/^4\text{He}$ ratios are more indicative of different permeability rather than porosity. The variations in R_a values and trip gas concentrations in the SAF appear at small spatial scales; which contrasts with the adjacent country rock where smoother trends were observed (Fig. 3; Fig. 6). An alternative explanation for the significant short range variability in the chemical and isotope composition of the SAF, namely the lack of any hydraulic gradient, seems less likely. In this case, fluid mixing would be restricted to diffusion processes only, independent of the permeability of the host rocks. However, pore pressures slightly below hydrostatic, but elevated on the north-east side of the fault in the Great Valley Formation (Kennedy et al, 1997), demonstrate a hydraulic gradient across the fault plane. Furthermore, drill pipe retrieval temporarily lowers the bottom hole pressure, generating a hydraulic gradient between the wall rock and the borehole. The trip gas concentrations data observed at the SAF are therefore most readily attributed to the rock permeability and not related to the hydraulic gradient.

6. Summary

Investigations conducted on returning drilling mud gas from the 3150-3350m segment of the SAFOD boreholes reveal considerable variations in R_a values and trip gas concentrations at small spatial scales. Wiersberg and Erzinger (2008) have shown that fluid flow transverse to the direction of the SAF is hampered at seismogenic depths. The new data suggest that these fluid flow barriers are associated with fault strands at 3194m (SDZ) and 3301m (CDZ) depths of the SAFOD wells. Significant variations in the chemical and isotope composition of gases at the active fault strands imply that the fault has not been open to fluid flow over many earthquake cycles.

Observed hydrocarbon concentrations correlate with the abundance of shale, identified by drilling cuttings analysis between ~3150m to 3200m and below ~3310m. The molecular and isotope compositions of hydrocarbons point to hydrocarbon generation in the shale units by thermal degradation of organic matter, followed by diffusion loss. Most hydrocarbons have already escaped from the reservoir rock and have migrated towards the surface. Progressive depletion of hydrocarbons with increasing molecular mass in the section between both active fault strands demonstrates that hydrocarbon migration transverse to the fault planes is restricted to diffusion mechanisms only.

Better quality $^3\text{He}/^4\text{He}$ data from between the two active fault planes at 3194m and 3301m lead us to conclude that the mantle-derived fluids pass the brittle-ductile barrier and are channelized at small spatial scales. Nevertheless, the principal path for mantle volatiles is permeable country rock at the North American Plate. It remains unclear whether improved flow of mantle volatiles between the SDZ and the CDZ might be episodic and e.g. triggered by earthquakes, or reflect continuous fluid migration.

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8. Appendix

8.1. Noble gas isotope analysis

The determination of noble gas concentrations and isotopic compositions from drilling mud gas involves gas intake into the system, purification, mass spectrometric analysis and data processing. Our analytical procedure is described in detail by Niedermann et al. (1997). The

preparation of drilling mud gas samples and the data processing follow protocols described in Wiersberg and Erzinger (2007). In the following we provide a condensed summary of the analytical procedure.

A split of the sample gas with a known volume and pressure is transferred into the purification line, where water vapour is condensed in a dry-ice-cooled cold trap. Nitrogen, oxygen and carbon dioxide are removed by two titanium sponge getters cycled from 750°C to 400°C; hydrogen, hydrocarbons and residual carbon dioxide are removed by two Zr-Al getters. The residual gas phase is let into one of two cryogenic cold heads. The first cold head, equipped with a stainless steel frit, is used for adsorption of argon, krypton and xenon at 50K. The inner surface of the second cold head is covered with charcoal, which induces helium and neon adsorption at 11K. For noble gas analysis, helium and neon are separately desorbed from the second cold head and admitted into the mass spectrometer. Desorption temperatures are 35K for helium and 120K for neon. During helium and neon measurements a stainless steel frit and an activated charcoal finger cooled with liquid nitrogen further reduce the argon and hydrocarbon background. The VG 5400 mass spectrometer is equipped with an off-axis Faraday cup and an axial electron multiplier. Values for blanks (in cm³ STP) are: ⁴He ~ 5 × 10⁻¹², ²⁰Ne ~ 0.5 × 10⁻¹² and ⁴⁰Ar ~ 5 × 10⁻¹⁰, which are all several orders of magnitude lower than those of the samples; therefore, a blank correction was not performed. Our method for overcoming the problem of the isobaric interferences of ²⁰Ne with double charged ⁴⁰Ar and ²²Ne with double charged ¹²C¹⁶O₂, based on the correlation between the mass spectrometer background and the efficiency of double charged ion production, has been described in detail by Niedermann et al. (1997).

The atmosphere is the principal reservoir for noble gases. Mud tanks and mud pumps are open to air; hence an atmospheric component is always present in drilling mud. This contribution of atmospheric noble gases often masks noble gases derive from a geologic source. Therefore, few noble gas studies on drill mud gas samples have been performed in the past. To our knowledge, three noble gas datasets from drilling mud have appeared in the scientific literature (Hilton and Craig, 1989; Aquilina et al., 1998; Wiersberg and Erzinger, 2007).

Helium is the only noble gas for which formation concentrations may exceed its atmospheric concentration (atmospheric concentration of He is 5.24ppmv). However, measured helium isotope ratios still must be corrected for the atmospheric input. This can be done by using either the ⁴He/²⁰Ne or the ⁴He/³⁶Ar ratio, assuming that all ²⁰Ne and ³⁶Ar are of atmospheric origin. In this study, the ⁴He/²⁰Ne ratios were used to correct the measured ³He/⁴He ratios according to the method described by Craig et al. (1978).

Wiersberg and Erzinger (2007) have measured noble gas elemental abundances in drill mud gas from the SAFOD MH, and have found it to clearly differ from air-saturated water, but not from air. These authors therefore assumed that the atmospheric component in drilling mud is more likely air, entering at the mud tank and piped down as bubbles rather than air equilibrated with the drilling mud (e.g., at the mud tanks). Within analytical uncertainties of 2σ , the fractionation factors $(X/^{20}\text{Ne})_{\text{measured}}/(X/^{20}\text{Ne})_{\text{air}}$ for all noble gases investigated in the present study, including Kr and Xe, which are the most sensitive for fractionation by equilibrium dissolution, are consistently indistinguishable from air. This clearly suggests that during drilling of the SAFOD III sidetracks the atmospheric component in drilling mud was also derives from air piped downstream. The correction of the measured $^3\text{He}/^4\text{He}$ ratios was therefore carried out assuming the $^4\text{He}/^{20}\text{Ne}$ ratio in air (0.319).

8.2 *Stable isotope analysis*

$\delta^{13}\text{C}$ and H/D determinations were carried out commercially at GCA Isolab Sehnde (Geo Chemical Analyses) with a PDZ 2020 mass spectrometer (Europa Scientific Ltd.). Prior to gas inlet, hydrocarbons were separated using a gas chromatograph, combusted to CO_2 , and carried by helium to the mass spectrometer. $\delta^{13}\text{C}$ isotope data are given relative to the $\delta^{13}\text{C}$ 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 $\pm 0.4\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 3\text{‰}$ for H/D.

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Figure captions

Fig. 1 Cross section of the SAFOD site from 3100m to 3350m borehole depth including a simplified lithology based on drilling cuttings description from SAFOD MH (http://www.icdp-online.org/upload/pdf/safod/Phase2_Mud_Log_PDF.pdf). The lithology from SAFOD III drill core analysis (http://www.icdp-online.org/upload/projects/safod/phase3/Core_Photo_Atlas_v4.pdf) is shown for comparison. To synchronize SAFOD III-G core data with SAFOD MH downhole logs, 5.03m is subtracted from the depths indicated for drill core from the SDZ (Southwest Deforming Zone at 3194m SAFOD MH borehole depth) and 3.96m is added to depths indicated for core from the CDZ (Central Deforming Zone at 3301m SAFOD MH borehole depth), see Zoback et al., 2010.

Fig. 2A Trip gas peaks of H₂ and CH₄ from tripping into the SAFOD III-E at 3197m borehole depth, together with the total trip gas peak. CO₂ was below detection limit. Data are shown before baseline subtraction. (B) Cross-plot of downtime-normalized trip gas concentration (arbitrary units) versus ²²²Rn activity (Bq/m³) from 20 different depths of the SAFOD MH. From the 22 trip runs in the SAFOD MH evaluated in this study, 20 are shown here. With the exception of a single outlier, the data show a linear correlation ($R^2 = 0.79$).

Fig. 3 Downtime-normalized trip gas concentration (arbitrary units) and ²²²Rn activity (Bq/m³) versus borehole depth. Radon data from Wiersberg and Erzinger (2008).

Fig. 4 Relative methane concentration (A) and the molecular composition of hydrocarbons CH₄/[C₂H₆+C₃H₈] (B) from SAFOD III and the SAFOD MH between 3100m and 3350m borehole depth. Gas data clearly correlate with the shale content (C). SAFOD MH gas data from Wiersberg and Erzinger (2008).

Fig 5 Cross-plot $\delta^{13}\text{C}$ [CH₄] vs. $\delta^{13}\text{C}$ [C₂H₆]. The variations in the isotopic composition of hydrocarbons from the SAF indicate that hydrocarbons were derive from a more depleted reservoir in the depth interval 3147-3317m, whereas hydrocarbons from the adjacent strata show a less depleted pattern. The maturity correlation of marine kerogen (Type I/II kerogen) is taken from Faber (1987).

Fig. 6 Helium isotope composition (air-corrected R_a values) vs. borehole depth. Data from the SAFOD MH are from Wiersberg and Erzinger (2007). Enhanced $^3\text{He}/^4\text{He}$ ratios are seen between both active fault branches of the SAF.

Fig. 1

Fig. 2A

2B

Fig. 3

Fig. 4 A

Fig. 5

Fig. 6

R/R_a (air-corrected)

Table 1 Chemical composition of drilling mud gas samples from SAFOD III boreholes

sample #	depth (m)	type	hole	CH ₄ (ppmv)	C ₂ H ₆ (ppmv)	C ₃ H ₈ (ppmv)	i-C ₄ H ₁₀ (ppmv)	n-C ₄ H ₁₀ (ppmv)	Ar (vol.%)	CO ₂ (ppmv)	H ₂ (vol.%)	He (ppmv)	N ₂ (vol.%)	O ₂ (vol.%)	C1/ (C2+C3)
1	3127.2	Trip	E	697	18	10	--	12	0.96	69	0.15	4.6	82.4	16.5	25
2	3141.3	Trip	E	532	58	21	--	7	1.09	4	1.80	6.0	88.0	9.1	7
3	3144.3	Trip	D	22 110	660	102	5	20	0.95	--	0.29	10.5	83.3	15.4	29
4	3146.8	Mud	D	16 465	372	39	--	5	0.92	--	0.20	6.0	81.2	17.7	40
5	3148.0	Trip	E	663	41	32	--	104	1.19	224	0.61	8.5	87.0	11.2	9
6	3151.6	Mud	G	609	24	14	--	--	0.92	27	0.084	4.7	80.0	19.0	16
7	3157.1	Mud	G	1 416	128	31	--	11	0.89	--	0.039	3.4	80.4	18.6	9
8	3157.4	Mud	E	640	81	27	5	57	0.91	151	0.089	4.7	79.7	19.3	6
9	3159.6	Mud	E	1 136	114	38	--	79	0.89	319	0.11	3.5	80.2	18.8	7
10	3160.2	Mud	G	1 526	226	62	8	28	0.90	9	0.085	4.1	80.4	18.6	5
11	3161.7	Mud	D	4 548	684	217	17	57	0.89	44	0.13	4.7	80.4	18.6	5
12	3165.0	Mud	E	1 250	180	67	6	20	0.88	117	0.33	3.3	79.9	18.9	5
13	3168.4	Mud	G	3 405	526	159	15	89	0.88	48	0.091	3.4	80.5	18.5	5
14	3182.1	Trip	E	2 827	472	192	21	95	0.93	188	6.92	4.8	80.5	11.6	4
15	3185.3*	Mud	G	2 640	395	184	22	91	0.90	24	0.21	3.7	80.4	18.5	5
16	3193.0*	Mud	G	1 590	129	48	6	81	0.90	140	0.20	3.6	80.8	18.1	9
17	3193.0*	Trip	G	2 972	243	77	8	40	0.91	46	0.83	5.1	79.7	18.5	9
18	3195.4*	Mud	G	4 134	293	89	11	82	0.93	93	0.39	5.5	80.8	17.9	11
19	3203.1	Trip	D	61 556	1 530	173	8	35	0.93	--	0.26	11.1	81.9	17.0	36
20	3214.1	Mud	G	641	17	8	--	15	0.91	144	0.036	4.3	80.2	18.8	26
21	3224.8	Mud	G	1 682	64	18	--	18	1.16	220	0.10	7.6	91.2	7.5	21
22	3262.0	Trip	D	20 368	400	52	--	54	0.87	247	1.23	7.4	79.0	18.9	45
23	3262.0	Trip	D	46 317	1 149	158	9	36	1.13	171	0.27	12.3	85.0	13.6	35
24	3267.2	Mud	G	748	31	12	--	--	0.92	41	0.33	4.9	79.6	19.1	17
25	3298.9*	Trip	G	1 459	49	13	--	20	0.89	100	1.30	4.9	79.7	18.1	24
26	3303.8*	Mud	G	641	20	9	--	--	0.92	114	0.21	5.3	80.0	18.9	22
27	3304.7*	Trip	G	14 207	497	103	11	36	0.94	63	1.12	7.0	80.4	17.5	24
28	3316.6*	Trip	G	10 646	488	109	10	35	0.96	162	1.42	9.2	80.5	17.1	18
29	3317.5*	Trip	G	15 026	630	126	12	53	0.95	71	0.69	7.1	81.1	17.3	20
30	3329.7*	Mud	G	32 306	1 620	336	35	119	0.93	51	0.65	6.7	80.1	18.4	17

* Depth is corrected according to Zoback et al., 2010

-- Below detection limit

Analytical errors (2σ) are ±2ppmv for hydrocarbons (absolute), ±5% for Ar, CO₂, H₂, N₂, O₂ and ±10% for He (relative)

Table 2 Isotope data and noble gas abundance of drilling mud gas from SAFOD III boreholes

sample #	depth (m)	type	hole	$\delta^{13}\text{C}$ CH ₄	$\delta^{13}\text{C}$ C ₂ H ₆	$\delta^{13}\text{C}$ C ₃ H ₈	H/D	Ra (air-corr.)	±	F (⁴ He)	±	F (⁴⁰ Ar)	±	F (⁸⁴ Kr)	±	F (¹³² Xe)	±
3	3144.3	Trip	D	-	-	-	-	0.26	0.12	1.508	0.013	1.005	0.058	1.036	0.063	1.09	0.37
4	3146.8	Mud	D	-30.8	-26.7	--	-168	-	-	-	-	-	-	-	-	-	-
15	3185.3*	Mud	G	-32.5	-27.0	-25.5	--	-	-	-	-	-	-	-	-	-	-
17	3193.0*	Trip	G	-32.1	-27.0	-25.0	-161	-	-	-	-	-	-	-	-	-	-
19	3203.1	Trip	D	-29.7	-25.8	-25.1	-165	0.857	0.095	1.760	0.035	1.035	0.074	1.024	0.063	1.12	0.39
21	3224.8	Mud	G	-32.2	-25.8	--	--	-	-	-	-	-	-	-	-	-	-
22	3262.0	Trip	D	-32.1	-23.6	-23.4	-170	0.88	0.19	1.493	0.013	1.009	0.058	1.062	0.064	-	-
23	3262.0	Trip	D	-31.1	-27.1	-27.0	-173	0.506	0.048	3.479	0.027	1.002	0.057	-	-	-	-
27	3304.7*	Trip	G	-32.7	-26.2	-25.2	-163	(0.84)	(0.56)	1.1149	0.0095	1.003	0.058	1.00	0.10	1.19	0.37
28	3316.6*	Trip	G	-33.5	-26.8	-26.2	-154	0.22	0.12	1.327	0.023	1.02	0.054	-	-	-	-
30	3329.7*	Mud	G	-32.4	-26.6	-25.6	-173	-	-	-	-	-	-	-	-	-	-

* Depth is corrected according to Zoback et al., 2010

- Not detected

-- Below detection limit

$\delta^{13}\text{C}$ values in ‰ (PDB), analytical errors are $\pm 0.4\text{‰}$

H/D values in ‰ (SMOW), analytical errors are $\pm 3\text{‰}$

$F = [(X/^{20}\text{Ne})_{\text{measured}}/(X/^{20}\text{Ne})_{\text{air}}]$, errors are 2σ

Table 3 Relative gas concentration accumulated in SAFOD boreholes during 27 round trips

well	depth (m)	POOH** (dd/mm/yyyy) (hh:mm)	downtime (h)	tripgas concentration (Σ [CH ₄ +CO ₂ +H ₂])	Downtime- normalized tripgas	²²² Rn (Bq/m ³)***
SAFOD MH-I	168	14/06/2004 18:30	53	11 529	219	-
SAFOD MH-I	313	20/06/2004 06:26	10	1 807	186	232
SAFOD MH-I	387	21/06/2004 20:13	7	954	134	112
SAFOD MH-I	826	05/07/2004 06:51	8	218	26	108
SAFOD MH-I	1325	27/07/2004 23:07	9	1 332	143	100
SAFOD MH-I	1453	05/08/2004 23:32	7	818	110	32
SAFOD MH-I	2081	23/08/2004 13:27	17	14 370	823	156
SAFOD MH-I	2403	30/08/2004 05:44	51	65 022	1 280	228
SAFOD MH-I	2586	03/09/2004 12:28	11	55 280	4 950	312
SAFOD MH-I	2665	05/09/2004 23:43	23	113 221	4 977	408
SAFOD MH-I	2875	11/09/2004 17:18	17	54 080	3 184	916
SAFOD MH-I	2986	15/09/2004 01:52	12	146 880	12 172	500
SAFOD III-E	3128	02/08/2007 04:08	59	594	10	-
SAFOD III-D	3144	05/07/2007 23:41	30	9 671	322	-
SAFOD MH-II	3196	15/06/2005 22:54	63	24 290	385	262
SAFOD III-D	3197	08/07/2007 06:00	53	13 135	248	-
SAFOD III-G	3223	01/09/2007 16:52	13	458	35	-
SAFOD III-G	3317*	06/09/2007 15:43	55	19 797	360	-
SAFOD MH-II	3322	20/06/2005 19:13	17	18 022	1 033	220
SAFOD MH-II	3433	23/06/2005 11:10	468	14 578	31	174
SAFOD MH-II	3492	14/07/2005 06:07	42	40 453	957	154
SAFOD MH-II	3564	17/07/2005 20:24	18	19 565	1 097	154
SAFOD MH-II	3652	20/07/2005 10:40	41	18 996	461	166
SAFOD MH-II	3713	23/07/2005 15:56	159	50 113	316	322
SAFOD MH-II	3783	31/07/2005 17:25	42	112 368	2 658	336
SAFOD MH-II	3831	03/08/2005 17:44	21	162 759	7 606	438
SAFOD MH-II	3902	06/08/2005 13:23	23	120 600	5 278	316

* Depth is corrected according to Zoback et al., 2010

**POOH = Pull out of hole

*** Wiersberg and Erzinger, 2008