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Origin and spatial distribution of gas at seismogenic depths of the San Andreas Fault from drill-mud gas analysis

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Abstract

Data are presented on the molecular composition of drill-mud gas from the lower sedimentary section (1800–3987 m) of the SAFOD (San Andreas Fault Observatory at Depth) Main Hole measured on-line during drilling, as well as C and H isotope data from off-line mud gas samples. Hydrocarbons, H_2 and CO_2 are the most abundant non-atmospheric gases in drill-mud when drilling seismogenic zones. Gas influx into the well at depth is related to the lithology and permeability of the drilled strata: larger formation gas influx was detected when drilling through organic-rich shales and permeable sand-stones. The SAF (San Andreas Fault), encountered between approximately 3100 m and 3450 m borehole depth, is generally low in gas, but is encompassed by two gas-rich zones (2700–2900 m and below 3550 m) at the fault margins with enhanced ²²²Rn activities and distinct gas compositions. Within the fault, two interstratified gas-rich lenses (3150–3200 m and 3310–3340 m) consist of CO_2 and hydrocarbons (upper zone), but almost exclusively of hydrocarbons (lower zone).

The isotopic composition indicates an organic source of hydrocarbons and CO_2 in the entire sedimentary section of the well. Hydrocarbons in sedimentary strata are partly of microbial origin down to ~2500 m borehole depth. The contribution of thermogenic gas increases between ~2500 m and 3200 m. Below ~3200 m, hydrocarbons fully derive from thermal degradation of organic matter. The lack of H₂ in the center of the fault and the high concentration of H₂ in the fractured zones at the fault margins are consistent with H₂ formation by interaction of water with fresh silica mineral surfaces generated by tectonic activities, however, this needs to be verified by laboratory experiments. Based on these studies, it is concluded that the fault zone margins consist of strata with enhanced permeability, separated by a low-permeability fault center.

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1. Introduction

In this paper, results are presented from a drillmud gas monitoring experiment carried out during drilling the SAFOD wells (San Andreas Fault Obser-

* Corresponding author. Fax: +49 331 288 1474. *E-mail address:* wiers@gfz-potsdam.de (T. Wiersberg). vatory at Depth) near the town of Parkfield (California) and the data discussed in the context of gas sources and the permeability structure of the San Andreas Fault (SAF) zone at seismogenic depths. The aim of the SAFOD project, funded and supported by Earthscope and the ICDP (International Continental Drilling Program), is to achieve a better understanding of the processes occurring in active

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plate-bounding fault systems at seismogenic depths. More information about SAFOD is available at www.icdp-online.de/sites/sanandreas/index.

Recently published results from the SAFOD Main Hole (Wiersberg and Erzinger, 2007) have shown that the contribution of mantle-derived fluids to the total fluid inventory of the well is small, and, as a consequence, their role with respect to fault weakening of the SAF has probably been over-estimated in the past (Kennedy et al., 1997); nevertheless it is still unclear from which principal sources the gases and fluids at focal depths of the SAF may derive.

Here data are presented on the gas composition as well as C and H isotope data from drill-mud gas. Mud gas was analysed in real time for its molecular composition during drilling of the SAFOD Main Hole in 2005/2006, off-line samples were later analysed for isotopes. Drill-mud gas as a carrier of information on the geochemistry of gases at depth has been used in some previous studies (Hilton and Craig, 1989; Aquilina and Brach, 1995; Aquilina et al., 1998; Erzinger et al., 2004, 2006; Wiersberg et al., 2004; Wiersberg and Erzinger, 2007). Although analysis of gas extracted from circulating drill-mud provides little information on absolute gas concentrations, it reveals valuable information on the gas composition at depth and can help to identify strata of different permeability with high spatial resolution. The molecular composition of mud gas can be indicative for the source of gas, but only isotope data can finally clarify its origin.

Fluids are suspected of being involved in processes occurring at seismogenic depths of active fault zones (Hickman et al., 1995). Many studies have been performed on soil gas (e.g. Wakita et al., 1980; Kita et al., 1980; Sugisaki et al., 1983; Sato et al., 1985; King, 1986; Ito et al., 1999; Lewicki et al., 2003) or gas from geothermal wells or springs along active fault zones (Giggenbach et al., 1993; Kennedy et al., 1997; Güleç et al., 2002; Kulongoski et al., 2003, 2005), but direct investigations on the composition of gases from focal depths are rare.

To present the authors' knowledge, only Arai et al. (2001) have developed a model for fluid migration in a fault zone by direct measurement of gases. These authors extracted gas from drill core samples of the Nojima fault zone in Japan and could identify CO_2 , CH_4 and H_2 as major non-atmospheric gaseous species. Hydrogen and CH_4 were enriched in the fracture zones around the fault core, whereas CO_2 was concentrated in the fault core. The high concentration of H_2 in the fractured zones at the margins of the fault core was interpreted as H_2 formation by interaction of water with fresh mineral surfaces generated by tectonic activities. Hydrogen anomalies are also reported from the SAF (Sato et al., 1985), but no isotope data has been published yet. Hence, the origin of H_2 occurring at the SAF is not fully understood.

2. SAFOD setting

The SAFOD wells were drilled in 2002 (Pilot Hole, PH) and 2004/2005 (Main Hole, MH) close to the town Parkfield in the Coast Range of central California, 1.8 km SW of the surface trace of the San Andreas Fault (SAF). The well site was selected for drilling because of the simultaneous occurrence of creep and repetitive seismicity at drillable depths, several historical M6 earthquakes, and an expected change in the lithology when crossing the SAF at depth (Hickman et al., 2004). In 2002, the straight SAFOD PH was drilled to 2168 m borehole depth. whereas the SAFOD MH was drilled in two phases. In the first phase, conducted in 2004, a hole was drilled down to 3051 m (MH-I). After a downtime of about nine months, the well was deepened to a final depth of 3987 m in 2005 (MH-II). During the drilling break, a M6.0 earthquake hit Parkfield on September 28, 2004.

The SAFOD wells traverse 768 m of Tertiary and Quaternary sediments on the Pacific Plate, underlain by Mesozoic granites of the Salinian Block. At \sim 1445 m depth, the MH was deviated to the NE to intersect the SAF and penetrate into the North American Plate at seismogenic depth (Fig. 1). The geological setting around Parkfield is described in greater detail in Page (1981) and Irwin (1990).

In contrast to the Pilot Hole, which remained in crystalline rocks down to the bottom of the hole (BOH) at 2168 m, the MH encounters sedimentary strata below 1930 m that persist to the bottom at 3987 m depth. From 1930 to 3200 m, these sediments are mainly composed of arkosic sandstone with embedded clay (1930–2500 m) or embedded shale and clay (2700–3160 m), separated by shale units from 2540 m to 2690 m and 3150–3200 m. The section 3200–3340 m mostly consists of clay and sandstone. Shale and siltstones are the dominant strata from 3340 m to 3550 m. At 3550 m depth, a layer of clay marks the transition to a sequence of alternating sandstone, clay, and shale.



Fig. 1. Sketch of the SAFOD wells, drilled a few meters apart close to the town of Parkfield, CA.

The first occurrence of serpentinite in drill cuttings is reported from \sim 3320 m depth (Evans et al., 2005). Serpentinite is known from outcrops on the North American Plate as indicative for the Franciscan complex, but only traces of serpentine have been found in the SAFOD well. Hence, it is believed that the SAFOD MH probably did not penetrate into the Franciscan complex, but into the Great Valley Sequence. Observations on cuttings and a few core samples reveal the presence of sheared rocks at approximately 3100–3450 m depth in the SAFOD MH (Hickman et al., 2005; Solum et al., 2005).

3. Experimental set-up and data evaluation

Here only a short description of the on-line mud gas monitoring technique is given, it is described in more detail in Erzinger et al. (2006). Formationderived gases extracted from returning drill-mud are either liberated from the rock material that is crushed by the drill bit or flow into the well through faults and fractures from the wall rock. The former process releases mostly fluids and gases accumulated in the pore space of the drilled rock, whereas the amount of fluids entering the well through faults and fractures from surrounding rocks depends on the permeability of the drilled formation. The gasloaded drill-mud is mechanically degassed in a gas-water separator when returning from the borehole. In order to separate the gas from the mud prior to addition of air, the separator is installed directly above the drill-mud outlet pipeline in the "Possum Belly". The extracted gas phase is continuously piped into a laboratory trailer at ~ 30 m distance and analyzed in real-time by means of (1) a quadrupole mass spectrometer for N₂, O₂, H₂, H₂S, He, CH₄, CO₂, Ar; (2) a gas chromatograph equipped with a FID for saturated and non-saturated light hydrocarbons including *i/n*-C₄H₁₀; and (3) a Lucas-cell type detector for ²²²Rn. Gas samples are taken automatically for laboratory studies when a given concentration threshold at the mass spectrometer is exceeded.

Knowledge of the composition of air in waterbased bentonite drill-mud is necessary to estimate the proportions of gas from the formation relative to air. Air enters the mudflow line either at the mud pumps and is piped down the hole as bubbles, or is dissolved in the mud tanks; each process leads to a different molecular composition of the atmospheric component in the drill-mud. Depending on mud type, temperature and salinity, air dissolved in the drill-mud has a composition rather like air-saturated water, whereas air, piped down as bubbles, shows atmospheric composition. The N₂/Ar ratio can help to distinguish between the processes: N₂/ Ar ratios lower than the atmospheric value of \sim 84

reflect solubility-based fractionation due to the higher solubility of Ar in aqueous liquids. However, the possible occurrence of N₂ from the formation limits the use of the N₂/Ar ratio, and N₂-rich gases are described by Jenden et al. (1988) for the California Great Valley. Furthermore, input of Ar from the formation needs to be ruled out. Based on ⁴⁰Ar/³⁶Ar ratios indistinguishable from the atmospheric value $({}^{40}\text{Ar}/{}^{36}\text{Ar} = 295.5)$. Wiersberg and Erzinger (2007) could demonstrate that no Ar excess with respect to air is present in SAFOD drill-mud-gas samples. These authors have used ²⁰Ne/⁴⁰Ar ratios to discriminate between both sources of air in drill-mud, which circumvents the problem of an additional non-atmospheric N_2 source, and found only an air-like atmospheric composition $(^{20}\text{Ne}/^{40}\text{Ar}=0.00175\,\pm$ 0.0005, air value = 0.00177) in drill-mud gas from SAFOD with no evidence for solubility-based fractionation. The N₂/Ar ratios from the on-line monitoring experiment mostly range between 82 and 90, which is, according to the analytical uncertainties of this field experiment, air-like. Only in the interval between 2850 m and 2950 m depth are the values somewhat lower (down to \sim 70), which is probably an artifact due to analytical difficulties. Hence, N₂ and Ar in drill-mud gas from the SAFOD wells are mainly related to air bubbles, piped down the hole, instead of air dissolved in the drill-mud. Hydrogen, hydrocarbons, ²²²Rn and most of the CO₂ are released from the formation.

At SAFOD, O_2/Ar values down to ~9 were observed in drill-mud, whereas the atmospheric value is 22.5. Excess Ar is unlikely to cause the low O_2/Ar values; hence it is concluded that up to 60% of the O_2 in SAFOD drill-mud was lost by chemical reactions.

The air-like Ne/Ar and N₂/Ar ratios suggest quantitative extraction of all gases with similar solubility, such as H₂, He, N₂ and the lighter hydrocarbons. In contrast, the separation of CO_2 may not be quantitative, as its solubility in water-based drill-mud is much higher. Insufficient extraction could be indicated, e.g. by CO_2 concentrations lower than air.

Besides on-line drill-mud gas monitoring and -sampling, formation fluids and gases were also taken at SAFOD under in-situ conditions by downhole fluid sampling (Thordsen et al., 2005). These samples were collected at the beginning of the SAFOD-II drilling operations in June 2005 from 3051 m depth and in March 2006 after reaching the final borehole depth of 3987 m. Both sampling operations were performed after the well was cased and several months of downtime to promote fluid flow and accumulation in the borehole through the open hole section at the bottom. Headspace gas from downhole samples is more dominated by hydrocarbons when compared with drill-mud gas samples from corresponding depths; they furthermore contain minor H_2 and virtually no CO_2 . The higher CO₂ concentration found in drill-mud gas could be due to one or a combination of the following: (1) higher temperatures when extracting the gas from drill-mud; (2) different chemical composition of the solvents (formation fluids vs. water-based bentonite drilling mud) and (3) the generally different gas extraction techniques. The higher concentration of H₂ in drill-mud gas is difficult to explain, however, both drill-mud gas and downhole fluid samples show higher H₂ concentrations on the Pacific Plate, compared with the North American Plate.

3.1. Off-line isotope analysis

 δ^{13} C and H/D determinations were commercially carried out by INC Leipzig (Center of Non-Classical Chemistry e.V.) with a MAT 252 isotope ratio mass spectrometer and at GCA Isolab Sehnde (Geo Chemical Analysis) with an Europa Scientific PDZ 2020 mass spectrometer. Prior to gas inlet, hydrocarbons were separated in a gas chromatograph, combusted to CO₂, and carried by He to the mass spectrometer. δ^{13} C isotope data from hydrocarbon and CO₂ are given relative to the δ^{13} C of the PDB-carbonate standard, H/D isotope data are given relative to SMOW (Standard Mean Ocean Water). The reproducibility of the isotope values is better than ±0.4‰ for δ^{13} C and ±3‰ for HD.

4. Results

Methane, CO₂, C₂H₆ and C₃H₈ were analyzed for C isotopes (δ^{13} C) and CH₄ and H₂ for H isotopes (H/D) in 22 drill-mud gas samples with sufficient gas concentrations. The molecular composition of the off-line gas samples as well as isotopic data are shown in Table 1; the complete on-line gas monitoring record is available upon request to the authors.

Two types of samples have been investigated in this study: samples taken during drilling and samples taken after downtime, when drilling was interrupted, e.g. for changing the drill bit ("Trip gas"). Pulling out the drill string causes a temporary reduction in the downhole pressure and induces

| Table 1 | | | |
|-----------------------------------|---|--------------------------------------|--------------------|
| Molecular and isotope composition | $(\delta^{13}C, H/D)$ of 22 drill mud gas samples | s from the lower sedimentary section | on of the SAFOD-MH |

| Sample# | depth | Ar | CH_4 | CO_2 | H_2 | He | N_2 | O_2 | H/D | $\delta^{13}C$ | $\delta^{13}C$ | $\delta^{13}C$ | $\delta^{13}C$ | H/D | pН | Т |
|---------|-------|---------|---------|---------|---------|--------|---------|---------|----------|----------------|----------------|----------------|--------------------|-------------------|------|------|
| | (m) | (vol.%) | (vol.%) | (vol.%) | (vol.%) | (ppmv) | (vol.%) | (vol.%) | (CH_4) | (CH_4) | (C_2H_6) | (C_3H_8) | (CO ₂) | (H ₂) | | (°C) |
| 1 | 1861 | 0.99 | 0.051 | (0.10) | 0.10 | 6.7 | 80.6 | 18.2 | n.a. | -49.6 | n.a. | n.a. | -17.7 | n.a. | n.a. | n.a. |
| 2 | T2117 | 1.02 | 0.079 | 0.82 | 3.6 | 9.0 | 82.6 | 11.9 | n.a. | -39.3 | n.a. | n.a. | -19.8 | n.a. | 8.0 | 55 |
| 3 | 2266 | 1.00 | 0.088 | 0.72 | 0.65 | 8.4 | 80.0 | 17.5 | n.a. | -50.6 | n.a. | n.a. | -16.7 | n.a. | 8.0 | 60 |
| 4 | T2403 | 1.07 | 0.087 | 0.52 | 1.4 | 7.4 | 80.9 | 16.0 | n.a. | -48.6 | n.a. | n.a. | -16.9 | n.a. | 8.1 | 57 |
| 5 | 2482 | 1.03 | 0.11 | 0.42 | 0.5 | 3.2 | 79.5 | 18.4 | -302 | -58.1 | n.a. | n.a. | -15.1 | n.a. | 8.1 | 64 |
| 6 | 2618 | 0.99 | 0.27 | 0.45 | 0.31 | 5.8 | 79.8 | 18.2 | -205 | -34.5 | -24.0 | n.a. | -14.9 | n.a. | 7.8 | 63 |
| 7 | T2665 | 1.10 | 0.25 | (0.23) | 4.0 | 6.2 | 79.0 | 15.5 | -291 | -41.9 | n.a. | n.a. | -14.6 | n.a. | n.a. | n.a. |
| 8 | 2724 | 0.98 | 0.41 | 0.51 | 1.06 | 5.1 | 79.0 | 18.0 | -284 | -39.8 | n.a. | n.a. | -16.3 | n.a. | 7.6 | 66 |
| 9 | 2830 | 0.99 | 1.2 | 0.58 | 2.15 | 5.9 | 79.3 | 15.7 | -181 | -38.8 | -29.3 | -26.4 | -18.0 | n.a. | 7.4 | 68 |
| 10 | 2849 | 0.96 | 0.44 | 0.39 | 1.86 | 5.3 | 77.9 | 18.4 | -212 | -39.4 | -30.2 | -27.1 | -21.0 | n.a. | 7.5 | 66 |
| 11 | T2864 | 0.96 | 0.19 | 0.27 | 0.81 | 5.1 | 78.2 | 19.5 | -188 | -43.1 | n.a. | n.a. | -19.3 | n.a. | 7.6 | 67 |
| 12 | 2910 | 1.03 | 0.23 | 0.47 | 0.46 | 4.2 | 79.4 | 18.4 | n.a. | -33.6 | -27.2 | -26.3 | -21.5 | n.a. | 7.5 | 66 |
| 13 | T3051 | 0.67 | 21.2 | (0.12) | 10.5 | 55.0 | 58.1 | 9.4 | -173 | -38.0 | -28.7 | -26.0 | -21.7 | -618 | n.a. | n.a. |
| 14 | 3182 | 0.94 | 2.2 | (2.7) | 0.03 | 6.0 | 78.8 | 15.3 | n.a. | -34.5 | -28.2 | -26.3 | -17.0 | n.a. | n.a. | n.a. |
| 15 | 3343 | 1.10 | 2.5 | (1.6) | 0.01 | 5.8 | 72.2 | 22.2 | n.a. | -36.3 | -28.0 | -27.2 | -26.0 | n.a. | n.a. | n.a. |
| 16 | T3433 | 0.94 | 5.9 | 5.0 | 13.3 | 10.0 | 72.2 | 2.6 | -155 | -37.2 | -28.1 | -26.6 | -21.4 | -659 | 8.1 | 63 |
| 17 | 3579 | 1.08 | 2.6 | 1.9 | 0.24 | 8.5 | 89.4 | 4.8 | n.a. | -35.1 | -27.6 | -26.1 | -17.9 | n.a. | 8.1 | 68 |
| 18 | 3700 | 0.93 | 1.4 | 2.1 | 1.28 | 6.7 | 79.6 | 14.6 | n.a. | -36.6 | -30.1 | -28.7 | -21.7 | -665 | 8.2 | 69 |
| 19 | T3781 | 0.76 | 16.9 | 5.0 | 1.1 | 9.0 | 65.8 | 10.5 | -162 | -34.1 | -28.7 | -28.1 | -21.0 | -646 | 7.9 | 67 |
| 20 | T3862 | 0.96 | 9.5 | 3.8 | 2.7 | 8.0 | 72.6 | 10.3 | n.a. | -34.1 | -27.3 | -26.7 | -20.9 | n.a. | 8.0 | 69 |
| 21 | T3903 | 0.83 | 28.9 | 7.4 | 2.4 | 48.0 | 58.5 | 2.0 | -153 | -35.0 | -27.5 | -26.9 | -22.4 | -708 | 8.2 | 70 |
| 22 | T3903 | 0.74 | 28.7 | 7.6 | 1.7 | 40.0 | 59.0 | 2.3 | -133 | -35.0 | -27.5 | -26.9 | -22.5 | -662 | 8.2 | 70 |

Analytical uncertainties of gas concentrations are <10% for He and <5% for other gases. Reproducibility of the isotope values is better than $\pm 0.4\%$ for δ^{13} C and $\pm 3\%$ for HD.

 $(CO_2) =$ uncertain due to unknown pH.

n.a. = not analyzed.

T = Trip gas sample.

Temperature = surface temperature of returning drill mud.

formation fluids and gases to flow into the borehole. When mud circulation restarts after "tripping back" the hole, the formation gas-loaded drill-mud returns to the surface. Twenty-two off-line mud gas samples are reported in Table 1; 10 were taken after pipe tripping and are denoted with "T".

Fig. 2 shows depth profiles for the most abundant non-atmospheric gases found in drill-mud of the lower sedimentary section of the SAFOD MH (hydrocarbons, CO₂ and H₂), together with the 222 Rn activity, the sum of all non-atmospheric gases (formation gas) as well as a simplified lithology. Drill-mud gas data from the upper 1900 m of the MH are in good agreement with data from the PH data (Erzinger et al., 2004) and are therefore not discussed here.

During drilling MH-I, the concentration of CH_4 reached up to 4 vol.%, CO₂ up to 1.5 vol.% and H₂ up to 10 vol.%. The maximum concentration of He in drill-mud was low (≤ 8 ppmv), whereas Rn activity reached values of up to 4400 Bq/m³. Correlated H_2 and CO₂ peaks occurred in the depth intervals 2070-2200 m and approx. 2700-2900 m. The Rn activity also peaked in the lower interval. An increase in hydrocarbons below ~ 2500 m corresponds with a change from a clay to a more sandstone and shaledominated lithology. The hydrocarbon composition became enriched in heavier hydrocarbons: the $CH_4/$ $(C_2H_6 + C_3H_8)$ ratio dropped from >100 to <50 (Fig. 3). Fig. 3 shows furthermore a shift in the isotopic composition of CH₄ from δ^{13} C values as light as -58% to values between -43% and -35% (PDB). This shift reflects a change from gas having a microbial contribution when drilling through silt and clay to more thermogenic gas in shales and sandstones. In the interval 2700–2900 m, the concurrent peaks in H₂ and CO2 correspond with high Rn activity and abundant hydrocarbons (Fig. 2). In this interval, there is a clear correlation between the intersected strata and the CH₄ concentration, as hydrocarbon concentrations increase in permeable sandstone layers and decrease in shaly rocks.

The principal formation gas components found in drill-mud during drilling of the MH-II are the same as during drilling of the MH-I. Maximum concentrations were about 1 vol.% for H₂, 5 vol.% for CO₂ and up to 20 vol.% CH₄; the Rn activity reached maximum values of ~800 Bq/m³. With the exception of the depth interval 3150–3200 m, the molecular composition of hydrocarbons is uniform over the MH-II, as shown by a relatively constant CH₄/ (C₂H₆ + C₃H₈) ratio of ~20 (Fig. 3). Such low values

as well as C isotopes reveal an origin of the hydrocarbons exclusively by thermal degradation of organic matter. The 3160-3200 m depth interval, dominated by shaly rock, contains high amounts of hydrocarbons (4 vol.% CH₄) and CO₂ (2.5 vol.%). The lowest $CH_4/(C_2H_6 + C_3H_8)$ ratios (<5) in the entire well were found in this interval. From 3200 to 3310 m, the strata are dominated by silt, which can explain the low hydrocarbon concentrations. From 3310 m to 3550 m depth, both the lithology (partly metamorphic shale and silt) and mud gas composition are relative homogenous. The mud gas is composed of 0.5 vol.% CH₄, 1 vol.% CO₂, low H₂ and He concentrations and low Rn activity. An interstratified sandstone layer at 3340 m depth shows high concentrations of hydrocarbons (8 vol.% CH₄), but no significant change in the concentrations of other gases. It is assumed that this permeable, maybe fractured sandstone acts as a reservoir rock that traps hydrocarbons derived from nearby mature rocks. At 3550 m depth, a layer of clay marks the transition from the partly metamorphic shale to a sequence of alternating sandstone, clay and shale. In this sequence, the formation gas content began to increase. For the first time, considerable amounts of H₂ and Rn were detected in drill-mud gas from the MH-II.

5. Discussion

Gases at seismogenic depths of SAFOD may derive from different sources. Faulkner and Rutter (2001) have shown that meteoric water containing atmospheric gases must overcome hydrostatic pressure and reach lithostatic pressure to get carried downward, which is not very likely for seismogenic depths at SAFOD. Organic gases (hydrocarbons, CO_2), generated by thermal degradation or biodegradation of organic matter, could be either produced insitu or migrate from a mature source at greater depth. Thermometamorphic gases from mineral reactions, geothermal gases from fluid-rock interaction, and mechanochemical gases, generated on fresh mineral surfaces, need to be taken into consideration. Wiersberg and Erzinger (2007) could identify a small contribution of mantle-derived gases to the total gas inventory migrating through permeable strata from great depth. Gas released from intrusive magmatic bodies seems unlikely at SAFOD, because the latest magmatic activities along the SAF happened 8-15 Ma ago and thus magma should now be almost completely degassed (Kennedy et al., 1997).



Fig. 2. Depth profiles (on-line data) for the most abundant non-atmospheric gases found in drill-mud of the lower sedimentary section (below 1800 m) of the SAFOD MH, including hydrocarbons, CO₂, H₂, the ²²²Rn activity, the sum of all non-atmospheric gases (formation gas) as well as a simplified lithology. Data are fitted by running average over 5 m intervals.



Fig. 3. Isotopic δ^{13} C–CH₄ and molecular (CH₄/(C₂H₆ + C₃H₈) composition of hydrocarbons versus depth of the SAFOD MH. Molecular and isotopic gas composition of bacterial and thermogenic hydrocarbons from Whiticar (1994).

5.1. Hydrocarbons

The high amounts of CH_4 and other hydrocarbons at SAFOD as well as their molecular and isotopic composition can only be explained by breakdown of organic matter (e.g. Whiticar, 1994). Two types of degradation of organics account for hydrocarbons in the SAFOD wells: thermal degradation, leading to thermogenic gas and biodegradation, producing microbial gas. The produced hydrocarbon gases differ in their molecular as well as isotopic composition. The

biodegradation of organic matter is kinetically controlled, resulting in a very light C and H isotopic composition of the produced gas. Microbial gas can further be subdivided into gas from bacterial carbonate reduction and from bacterial methyl-fermentation; both show distinct δ^{13} C and H/D values (Fig. 4). Bacterial gas consists almost exclusively of CH₄ with a ratio CH₄/ (C₂H₆ + C₃H₈) > 100, whereas thermogenic gas contains more heavy hydrocarbons, resulting in a ratio of CH₄/(C₂H₆ + C₃H₈) < 100. Gas formation by thermal degradation is thermodynamically



Fig. 4. Diagram of δ^{13} C–CH₄ vs. H/D–CH₄. Isotopic composition of distinct sources after Whiticar (1994).

controlled; therefore $\delta^{13}C$ and H/D values of thermogenic gas are higher than those of microbial gas.

Both the molecular and the isotopic composition of hydrocarbons show a similar depth trend (Fig. 3). Hydrocarbons are partly of microbial origin down to \sim 2500 m borehole depth. The contribution of thermogenic gas increases between \sim 2500 m and 3100 m. Below \sim 3100 m, hydrocarbons derive from thermal degradation of organic matter. Furthermore, C and H isotopes imply that the microbial component is produced by methylfermentation rather than carbonate reduction (Fig. 4). In particular the sample from 2482 m depth is clearly characterized by a high contribution of gases from methyl-fermentation, which is indicated also by its C isotope fractionation between CO_2 and CH_4 (see below). The molecular composition (CH₄/C₂H₆ + C₃H₈ \sim 10–25) and isotopic composition (δ^{13} CH₄ from -34‰ to -38‰) are relatively constant below approx. 3200 m depth, whereas He isotopes differentiate between the North American Plate (below 3450 m) and the transition zone (3100-3450 m, Wiersberg and Erzinger, 2007). The distinct distributions of mantle-derived He and hydrocarbons at depth call for a different origin of these gases. Hydrocarbons extracted from SAFOD drill-mud show a trend of less negative δ^{13} C values with increasing molecular mass, typical for thermogenic hydrocarbons. Abiogenic alkanes do not show such trends (Sherwood Lollar et al., 2002).

5.2. Carbon dioxide

Like hydrocarbons, CO_2 in crustal fluids may derive from different sources, which can be distinguished by different C isotope values (e.g. Whiticar, 1994; Wycherley et al., 1999). Carbon dioxide from the mantle and from degassing magmatic bodies is isotopically heavy, ranging in δ^{13} C from -4% to -7%. The C isotope signature of CO₂ from interaction of water with carbonates depends on the isotopic composition of the source rock, but generally covers a range from $\delta^{13}C = -2\%$ to -12%. Carbon dioxide from breakdown of organic material has a δ^{13} C range of -20% to -40%. Atmospheric CO₂, dissolved at the mud tanks and piped down the hole, is another possible source of CO₂ in drill-mud. Carbon dioxide in air from Parkfield has a δ^{13} C value of -8.9‰ and a concentration of 365 ppmv (Lewicki et al., 2003).

The interpretation of CO₂ concentration data from circulating drill-mud has to overcome some difficulties. Under the given temperature and salinity of the drill-mud, CO₂ is more soluble in waterbased liquids than other formation-derived gases. Dissolved CO₂ chemically reacts with water to form HCO_3^- and CO_3^{2-} , where the proportions of the involved species CO_2 , HCO_3^- and CO_3^{2-} depend on the pH, the temperature, and the chemical composition of the solvent. The solubility of gaseous CO_2 in drill-mud at the temperature of returning drill-mud is lower than under standard conditions. At a temperature of 60 °C, the average temperature of returning drill-mud at SAFOD, the solubility of CO_2 in water is only 18% of the CO_2 solubility under standard conditions (Carroll et al., 1991). The solubility of CO₂ in SAFOD drill-mud is even lower, because the extraction of gas takes place at pressure lower than atmospheric and the drill-mud is somewhat saline (2 g/kg NaCl-equivalent, Wiersberg and Erzinger, 2007).

Carbon dioxide concentrations in drill-mud lower than atmospheric have generally been observed at SAFOD when drilling cement, i.e. after setting a casing, which causes a very high pH of the drill-mud. These data have not been taken into consideration for the discussion of different molecular and isotopic composition of CO_2 from drill-mud gas on the Pacific Plate and the North American Plate.

In a diagram of δ^{13} C vs. 1/[CO₂] (Fig. 5), the drill-mud gas data show a somewhat linear correlation, implying mixing between a highly abundant,



Fig. 5. Diagram of δ^{13} C vs. 1/[CO₂]. Parkfield air values from Lewicki et al. (2003). A linear fit without 3 data points from the narrow interval 2849–2910 m reveals an intercept of –22‰ with a R^2 value of 0.85.

isotopically light component with a low-abundant, isotopically heavy component. This correlation becomes better without 3 data points from the narrow interval 2849–2910 m, where analytical difficulties are indicated also during the detection of other gases (i.e. N₂/Ar ratios). A linear fit of the reduced dataset reveals an intercept of $-22\%_0$, with a R^2 value of 0.85 for the fit. The isotopically heavy component could be of atmospheric origin, although a linear correlation between Parkfield air (Lewicki et al., 2003) and the data from drill-mud gas is not indicated, because the concentration of CO₂ in SAFOD drill-mud gas could be higher than the Parkfield air value of 365 ppmv.

The intercept value of -22% represents the minimum δ^{13} C value of the isotopically light component. Its maximum δ^{13} C value can be estimated based on C isotope fractionation between dissolved CO₂ and HCO₃⁻, which is -4.6% at 60 °C (Mook et al., 1974). Thus, δ^{13} C of CO₂ from depth is probably in the range between -22% and -17% PDB. Such δ^{13} C values are very similar to values reported by Lewicki et al. (2003). These authors have performed soil gas studies and found δ^{13} C values for CO₂ from -16% to -23% along the San Andreas Fault, which were interpreted as indicating a shal-

low biogenic source of CO₂, maybe derived from C3 plants, sometimes mixing with CO₂ from an isotopically enriched source. Such a source is unlikely for CO₂ from seismogenic depths at SAFOD. An alternative explanation, namely CO₂ from dissolution of carbonates, requires multiple re-equilibration steps between HCO₃⁻ and CO₂ to obtain such low values (Weinlich, 2005). Furthermore, low δ^{13} C values from multi-step fractionation should be concurrent with depletion in CO₂, opposite to the relationship observed in this study.

The source of CO_2 can be clarified by the C isotope fractionation between CO₂ and CH₄. The fractionation factor α of most samples (α (CO₂-CH₄) = $(\delta^{13}CO_2 + 1000)/(\delta^{13}CH_4 + 1000))$ is in a range typical for thermogenic natural gas (<1.03-1.001; Whiticar, 1994). The fractionation between CO_2 and CH_4 correlates negatively with depth (Fig. 6), which implies decreasing fractionation with increasing temperature due to improved thermal degradation of organic matter with depth. In the shallower part of the investigated section, mixing with microbial gas, probably from methyl fermentation, is indicated (see also Fig. 3). In particular the C isotope fractionation between CH₄ and CO₂ in samples from 2266 m to 2482 m depth implies admixture of CO₂ from methyl fermentation ($\alpha = 1.033 - 1.046$).

Based on measured C isotopic fractionation between CO_2 and CH_4 , equilibrium exchange in the system CO_2 – CH_4 would require equilibrium temperatures between 311 °C and 598 °C (Richet et al., 1977) for all SAFOD drill-mud gas samples



Fig. 6. Isotopic fractionation α (CO₂-CH₄) vs. depth.

with the exception of three samples from 2266 to 2482 m depth, much higher than observed at SAFOD (Williams et al., 2004). However, the proportions and isotopic exchange between CH_4 and CO_2 in a low-temperature environment such as SAFOD are not in thermodynamic equilibrium, but most likely kinetically controlled (Horita, 2001). Non-equilibrium ¹³C isotopic fractionation between CH_4 and CO_2 from the Nojima fault zone is reported from Arai et al. (2001), who proposed different origins for both species.

5.3. Hydrogen

A striking observation is the high concentration of H_2 measured during drilling of the deeper part of the SAFOD well. Hydrogen appears in particular in the fractured zones around the fault center, whereas only little H_2 is present in the fault core. Similar observations have been made by Arai et al. (2001), who attribute the high concentration of H_2 in the fracture zones at the margins of the fault core to H_2 formation at newly formed mineral surfaces generated by tectonic activities. It is out of the aim of this contribution to clarify the origin of apparent H_2 at SAFOD, nevertheless a brief discussion of possible sources that may account for H_2 in drill-mud gas follows.

5.3.1. Artificial hydrogen

At SAFOD, most H_2 appears at seismogenic depths concurrently with CO₂, Rn and hydrocarbons. These gases clearly derive from the formation and enter the borehole through permeable strata. The contribution of gases produced artificially at the drill bit by so-called "bit metamorphism" (e.g. Whiticar, 1994) is therefore negligible. Artificial H_2 may explain the constant increase of the H_2 background during the drilling phase I, but hardy accounts for the observed spike-like gas peaks.

5.3.2. Geothermal and organic hydrogen

Hydrothermal fluids typically contain an assemblage of gases including CO_2 , CH_4 and H_2 . Waterrock interaction including Fischer-Tropsch-like reactions, and serpentinization of ultramafic rocks have been considered as gas sources (e.g. Sherwood Lollar et al., 1993, 2002; Horita and Berndt, 1999; Horita, 2001; Sleep et al., 2004). Surface outcrops of serpentine are a common feature on the North American Plate, but to the authors' knowledge, not known from the Pacific Plate around Parkfield. Small amounts of serpentine are reported from drill cuttings from 3320 m depth (Evans et al., 2005), but the occurrence of serpentine at SAFOD is not related to any significant H_2 anomalies in drill-mud gas. The highest concentrations of H_2 were found on the Pacific Plate between 2800 m and 2900 m depth some 100 m distant from the first occurrence of serpentine. Assuming that H_2 found on the Pacific Plate is formed by sepentinization of ultramafic rocks on the North American plate would require fluid migration through the SAF, which is unlikely.

The molecular and isotope composition of the hydrothermal gases have been commonly used as gas geothermometers (e.g. Richet et al., 1977; D'Amore and Panichi, 1979; Giggenbach, 1980; Evans et al., 1988; Horibe and Craig, 1995). Although CH₄-H₂ equilibrium temperatures calculated from Bottinga (1969) and Horibe and Craig (1995) roughly match formation temperatures at SAFOD, the proportions and isotope ratios of C-H-O gases in low-temperature environments are considered to be mainly controlled by kinetic effects (e.g., thermal or microbial degradation of organic matter, Horita, 2001). As shown before, the C isotope composition of CH₄ and CO₂ and the isotopic fractionation demonstrate only a biologic and mostly thermogenic source for these gases. If H₂ in SAFOD drill-mud gas were of biologic origin, H₂ concentrations should be distinctly lower than those of hydrocarbons, the opposite to that observed.

5.3.3. Radiolytic hydrogen

The energy released from the decay of U, Th and K causes dissociation of water into fragments, which later recombine to form, e.g. H₂. The isotope fractionation between H₂O and H₂ from such processes is $\alpha = 2.05 \pm 0.07$ (Lin et al., 2005). Hydrogen in SAFOD drill-mud gas would require water with H/D values of -215% to -400% to generate such a depleted H/D isotopic composition, out of the range of any known sedimentary, magmatic, or juvenile waters (Hoefs, 1980).

5.3.4. Mechanochemical hydrogen

Several laboratory studies have shown that freshly generated silicate mineral surfaces can catalyse the synthesis of H₂ from water (Kita et al., 1982; Saruwatari et al., 2004). Because reactive mineral surfaces can be generated in the rupture zone around the fault core, H₂ soil gas studies at fault zones has been carried out in the past to identify active faults (e.g. Wakita et al., 1980; Kita et al., 1980; Sugisaki et al., 1983; Sato et al., 1985; King, 1986; Ito et al., 1999; Arai et al., 2001). To distinguish between mechanochemically generated H_2 and H_2 from other sources such as serpentinization or organic, Kita et al. (1980) used D/H ratios in soil gas from the Yamasaki fault. Those authors could rule out a significant contribution of biogenic or hydrothermal H_2 and found H/D values in a range between -770% and -470%. These values correspond to a maximum depth of 12 km for H_2 generation, in relatively good agreement with the foci of microearthquakes. If such a mechanism could also account for the high amounts of H_2 at SAFOD needs to be verified by laboratory experiments.

5.4. Radon and helium

Radon and He derive from the same principal source, the radioactive decay of U and Th. However, Rn itself is radioactive. The most stable Rn isotope is 222 Rn with a half-life of 3.8 d. Its short half-life hampers Rn accumulation in pore space fluids of rocks. In the absence of unusually high concentrations of U or Th in the drilled rocks, increased Rn activity in drill-mud gas indicates fluid flow through permeable strata. Due to its low mobility, Rn migration is mostly controlled by active fluid flow. In contrast to Rn, He is very mobile and is accumulated in the pore space after diffusing from its source, the crystal lattice of U and Th-containing minerals. Helium migra-

tion and loss is not only controlled by diffusion, but like Rn, also by convective and advective fluid flow in rocks with interconnected pore space. Enhanced concentrations of He in formation fluids with low Rn activity is more indicative of high rock porosity, whereas abundant Rn in formation fluids suggests active fluid flow through permeable strata. Aquilina and Brach (1995) and later Aquilina et al. (1998) have used Rn and the He–Rn pair to distinguish fluids trapped in pore space from fluids that actively circulating through permeable strata when deepening the GPK-1 well at Soultz-sous-Forêts (Alsace, France) and when drilling the Balazuc-1 borehole at the northeastern edge of the SE Basin (France), respectively.

Fig. 7 shows depth profiles of He concentration and ²²²Rn activity data from drill-mud gas, together with the [U + 0.24Th] concentration data from geophysical logging (doi:10.1594/GFZ.SDDB.1082-1085), which accounts for the current production of ⁴He. Due to analytical difficulties, the He data shown in Fig. 7 are taken form 47 off-line drill-mud gas samples, collected from the gas line and later analysed in GFZ laboratories. Only He and Rn analysed during drilling but not during pipe tripping are discussed in the following.

The He concentrations detected in drill-mud gas range from 4 ppmv to 13 ppmv. A significant



Fig. 7. Helium, 22 Rn and [U + 0.24Th] depth profiles. Helium data from off-line drill-mud gas samples. [U + 0.24Th] from geophysical logging (doi:10.1594/GFZ.SDDB.1082-1085).

contribution of this He is of atmospheric origin (Wiersberg and Erzinger, 2007), hence the amount of intrinsic He produced in-situ in the formation is generally low at seismogenic depths of SAFOD. A rough correlation between the amount of He in drill-mud and the concentration gas of [U + 0.24Th] is indicated on the Pacific Plate and the SAF. Down to 2300 m depth, both show an increasing trend, reaching concentrations of 8 ppmv He and 12 ppm [U + 0.24Th]. Below 2300 m, the He concentration drops, reaching minimum values on the Pacific Plate at 2900 m. Also [U + 0.24Th] generally decreases below 2300 m depth, but peaks with maximum concentrations of ≥ 20 ppm between 2500 m and 2700 m. These maxima do not correspond to any He or Rn anomalies. Helium remains low down to \sim 3450 m, but shows somewhat higher concentration between 3150 m and 3200 m and around 3300 m depths. At 3450 m depth, the He concentration again starts to increase, reaching a concentration of 13 ppmv at ~3900 m on the North American Plate. Also [U + 0.24Th] concentrations increase below 3600 m, however, maximum concentrations of 10 ppm are distinctly lower than on the Pacific Plate.

When comparing He and Rn data, a more or less negative correlation between approximately 1800 m and 3000 m borehole depth can be observed. Around \sim 2200 m depth, the Rn activity is minimum, whereas He concentration reaches maximum values on the Pacific Plate, which can be explained by drilling through porous, but low permeability strata. From 2200 to 2700 m depth, Rn activity constantly increases with depth, whereas the He concentration in drill-mud gas drops. The highest Rn activity of \sim 4400 Bq/m³ found in SAFOD drill-mud gas was found at 2700 m and 2850 m depths, whereas minimum He concentrations (4 ppmv) were found at 2900 m. Boness and Zoback (2006) report an increasing number of bedding planes per 10 m intervals in the SAFOD-MH between roughly 2300 m and 2900 m, with a maximum number of features around 2850 m, which implies that Rn-rich fluids entered the SAFOD borehole through bedding plane fractures. From approx. 3000 m to 3500 m depth, average Rn activity and He concentration were low. Below 3500 m, Rn and He start to increase, reaching maximum He concentration of 13 ppmv and maximum ²²²Rn activity of 700-800 Bq/m³ around 3900 m depth. These results suggest that the drilled lithology has improved porosity and permeability.

5.5. The spatial distribution of gas at seismogenic depths and its implication for fluid flow at the SAF

Models of fluid-flow in fault zones involve areas of different permeability controlling fluid migration within a fault (e.g. Byerlee, 1990, 1993; Sibson, 1991; Rice, 1992; Faulkner and Rutter, 2001). Our investigations of drill-mud gas from seismogenic depth imply a low-permeable fault core surrounded by more permeable strata at SAFOD, and hampered horizontal fluid flow at focal depths of the San Andreas Fault near Parkfield.

A ternary diagram ($CO_2-H_2-CH_4$) of drill-mud gas from the SAFOD-MH (Fig. 8) shows that the relative proportions of the main formation gases differ significantly on the Pacific Plate (down to approx. 3100 m) when compared with the North American Plate (below approx. 3450 m, see Fig. 2). The Pacific Plate is characterized by a higher contribution of H₂, whereas the North American Plate contains more CH₄ and CO₂. Also the Rn activity shows maximum values between 2700 and 2900 m and around 3900 m depth, but is surprisingly low in the depth interval 3000–3500 m, suggesting that the fault core at SAFOD has low permeability.

Although the center of the fault is generally low in gas, two sections within the fault core from \sim 3150 m to 3200 m and from \sim 3310 m to 3340 m show higher gas concentrations. The gas kick at 3340 m, very close to the active section of the SAF (3309 m), is almost exclusively composed by hydrocarbons. It is proposed that these hydrocarbons are trapped in permeable, probably fractured sandstone, which is surrounded by less permeable strata. Based on these observations, it is suggested that the Pacific Plate and the North American Plate represent individual hydrologic systems with little tendency for fluid mixing in the San Andreas Fault. This interpretation is in good agreement with results from He isotope studies, carried out on the same drill-mud gas samples (Wiersberg and Erzinger, 2007). The contribution of mantle-derived He at SAFOD differs on the Pacific Plate and the North American Plate, but is generally low: approx. 5% in the Pacific Plate and the SAF and up to 12% in the North American Plate, increasing with greater distance from the center of the fault on the North American Plate. The overall low fraction of mantle-derived He was interpreted as a product of low vertical permeability of the SAF and suggests that the SAF does not play a significant role as a conduit for fluids from depth.



Fig. 8. Ternary diagram (CO₂-H₂-CH₄) of drill-mud gas (on-line data) from the SAFOD-MH.

6. Conclusions

The most abundant formation-derived gases in drill-mud gas returning from seismogenic depths of the SAF during drilling of the SAFOD Main Hole are hydrocarbons, CO₂ and H₂. The molecular composition of hydrocarbons as well as C and H isotopes of CH₄ imply mixing between microbial and thermogenic gas down to $\sim 2900 \text{ m}$ depth. Below, hydrocarbons are produced by thermal degradation of organic matter only. Carbon isotopes also suggest an organic origin of CO₂. The C isotope fractionation between CH₄ and CO₂ indicates common sources for both species. Hydrogen could be generated mechanochemically on fresh mineral surfaces, generated by seismic movement. The proportions of these gases are different on the Pacific Plate and the North American Plate. Helium and Rn negatively correlate on the Pacific Plate, are both low in the SAF, and positively correlate on the North American Plate. The Rn activity shows maximum values between 2700 and 2900 m and around 3900 m depth, suggesting that permeable strata surround a low-permeable fault core.

Based on distinct gas compositions on both the Pacific and the North American Plate, it is suggested that the SAF acts as a barrier for horizontal fluid flow and more permeable rocks at the fault zone margins surround the generally low-permeable core of the SAF. In the fault core, some gas-rich sections are interstratified at \sim 3150–3200 m and \sim 3310–3340 m depths. Also these sections have distinct gas compositions; hence it is supposed that they represent isolated permeable gas lenses, trapping gas from surrounding source rocks.

The distinct gas composition of the lenses and the fact that most formation gas in the investigated section of the well is produced in-situ or in nearby sources indicates that vertical fluid flow through the SAF is less important. Evidence for only minor gas migration from greater depth in particular on the Pacific Plate is also displayed by the low contribution of mantle-derived He (Wiersberg and Erzinger, 2007).

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