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Natural evidence for rapid abiogenic hydrothermal generation of CH_4

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Abstract

Although recent hydrothermal experiments imply that abiogenic methane (CH_4) generation from hydrothermal reduction of CO_2 can occur, evidence from natural systems was still lacking. Based on the chemical and isotopic equilibrium signatures of low-temperature fumarolic gas discharges, we are able to provide hard evidence for its natural occurrence, namely in three subduction-related bi-phase hydrothermal systems of the Mediterranean, whose temperatures range from 260 to 470 °C. The attainment of equilibrium and the time spans of recent volcanic dormancy allowed us to calculate minimum rates for chemical and isotopic equilibration. These are significantly higher than those previously reported and might be due to the presence of a saturated water vapor phase in the investigated systems. The fact that nature provides conditions enabling relatively fast production of hydrocarbons from CO_2 strongly supports the concerns that were recently raised from laboratory experiments. These address the use of the carbon isotope composition of reduced carbon in Archean sediments as a tracer of early life and the occurrence of CH_4 on extraterrestrial planets as a bioindicator. In view of the potential role of abiogenic CH_4 as a precursor of life, we also present an estimate of abiogenic hydrothermal CH_4 fluxes throughout the Archean. It is not expected that these fluxes exceeded 80 Mt/yr during the past 4.0 Ga. This, however, would have been enough to facilitate HCN production on the prebiotic Earth.

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1. INTRODUCTION

Methane (CH_4) may have contributed to the origin of life, both directly, i.e. as an educt for the synthesis of complex organic molecules (Zahnle, 1986) and indirectly, i.e. as a greenhouse gas that kept temperatures comfortable for early life (Pavlov et al., 2000; Catling et al., 2001). For a comprehensive understanding of the processes that lead to the formation of life and to the formation of habitable planets, the identification of the pathways that produce natural CH_4 is of particular importance. Generation of CH_4 by microbes (microbial CH_4) or by thermal decomposition of organic matter (thermogenic CH_4) is well documented (Schoell, 1980, 1988; Whiticar, 1999). Both of these pathways require organic carbon originating in the biosphere, either as catalyst or as reagent, and the evolved CH_4 is, therefore, often classified as "biogenic".

Possible processes of abiogenic CH_4 formation identified to date include the reduction of graphite (Holloway, 1984), the thermal decomposition of siderite (McCollom, 2003) and the reduction of gaseous or dissolved carbon oxides (Fischer, 1935; Berndt et al., 1996; Horita and Berndt, 1999; Foustoukos and Seyfried, 2004) according to

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (1)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2)$$

Reactions (1) and (2) are often categorized as Fischer–Tropsch-type (FTT) reactions, although (1) should be more properly referred to as the Sabatier process. Their occurrence within crustal domains at relatively low

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temperatures ($T < 500$ °C) has remained speculative. An abiogenic origin was proposed for the CH_4 emanating from mid-ocean ridges mainly because its ^{13}C-enriched carbon isotopic signature sets it apart from biogenic CH_4 (e.g., Welhan and Craig, 1983; Welhan, 1988; Charlou et al., 2002; Simoneit et al., 2004). Welhan and Craig (1983) noted that $CH_4/^3He$ ratios of the fluids venting from the East Pacific rise are similar to those of the basalts and, therefore, suggested that the CH_4 might have been extracted as an intrinsic mantle component from the basalts by the interaction with seawater. Charlou et al. (1998) noticed that at some locations along the Mid-Atlantic ridge CH_4 concentrations are decoupled from ^3He anomalies, implying that additional sources may contribute to CH_4 production, too. Recent hydrothermal experiments have confirmed that mid-ocean ridge hydrothermal systems may provide suitable conditions allowing for abiogenic generation of CH_4 from dissolved CO_2 at temperatures lower than 500 °C (Berndt et al., 1996; Horita and Berndt, 1999; McCollom and Seewald, 2001, 2007; Foustoukos and Seyfried, 2004).

Abiogenic generation of hydrocarbons has also been proposed for geological settings other than mid-ocean ridges. Szatmari (1989) postulated that abiogenic synthesis of hydrocarbons could occur in subduction zones. He observed that the distribution of hydrocarbons closely follows a Schulz-Flory distribution, which is typically observed if CH_4 and the higher hydrocarbons are generated according to FTT reactions. However, as later pointed out by Giggenbach (1997), the similarity in the distribution of hydrocarbons in natural gases to that in synthetic gas cannot be used to distinguish between FTT-synthesis and thermogenic decay of organic matter, because the "size distribution of polymers resulting from random formation of linkages is identical to that for random breaking of linkages". Taran and Giggenbach (2003) noticed that the mole fraction of CH_4 in gases released from subduction-related volcanoes tends to increase with N_2/Ar. Provided that N mainly originates from the decomposition of organic matter and that it is inert during metamorphic and hydrothermal processes, these observations suggest a thermogenic origin of the evolved CH_4. Sherwood-Lollar et al. (2002, 2006) used a formalism first developed by Des Marais et al. (1981) to identify the abiogenic nature of hydrothermal gases that are released from underground sites in Precambrian-aged rocks in Canada and South Africa. Here, the C_2–C_4 alkanes occur depleted in ^{13}C and enriched in ^2H relative to co-emitted CH_4. These isotopic signatures are in agreement with those derived from abiogenic polymerization reactions. However, as was stated by Sherwood-Lollar et al. (2002), the process that delivered the shortest chain molecule, CH_4, could not be identified.

In summary, although laboratory experiments imply that hydrothermal reduction of CO_2 to CH_4 may occur in nature, unambiguous evidence, i.e. evidence that is provided by the natural system itself, is still lacking. In this study we use both new gas data and gas data published by Tedesco (1996), Tedesco et al. (1998) and Fiebig et al. (2004) to give direct evidence for such an occurrence, namely in subduction-related bi-phase hydrothermal systems. The observation that natural systems provide conditions that allow for abiogenic hydrothermal generation of CH_4 from CO_2 has several implications for a broad number of disciplines in the Earth and planetary sciences, ranging from the fields of astrobiology, evolution of life and Earth's early atmosphere to the fields of geothermal energy exploration and volcanic risk evaluation.

2. GEOLOGICAL SETTINGS

At the venting surface, fumarolic gases often occur as mixtures of primary magmatic components with secondary hydrothermal components (Giggenbach, 1987). As our study addresses the potential hydrothermal origin of CH_4 in volcanic gases, we have exclusively sampled low-temperature volcanic gas emissions that lack typical magmatic components such as HF, HCl and SO_2. The absence of these "acid" components indicates that the ascending magmatic gases extensively interacted with an external hydrothermal phase in such a way that the latter dominates the magmatic component. Samples were taken from three volcanoes of the Mediterranean: Nisyros, Greece, Vesuvius and Ischia, Italy. Nisyros volcano belongs to the Hellenic volcanic arc, whereas Vesuvius and Ischia are part of the Neapolitan volcanic province. Geophysical and geochemical investigations clearly demonstrate the subduction-related origin of both volcanic systems (e.g., Le Pichon and Angelier, 1979; Keller, 1983; Tedesco, 1997). Volcanism at Ischia began more than 150,000 years ago, with the most recent volcanic event being the AD 1302 Arso eruption (Vezzoli, 1988; Civetta et al., 1991). The oldest magmatic products of Vesuvius are dated at 25,100 years (Delibrias et al., 1979). Its latest eruptive activity was in 1944. Nisyros volcano is considered to be younger than 150,000 years (Vougioukalakis, 1993). While its last magmatic activity is unknown, several phreatic events took place between 1871 and 1888 (Marini et al., 1993).

The volcanics at the three sites investigated cover a wide range of chemical composition. At Nisyros, erupted products correspond to the typical calc-alkaline series, ranging in composition from basaltic andesites to rhyolites (Vougioukalakis, 1993). In contrast, volcanic rocks at Ischia and Vesuvius belong to the alkali series. Those at Ischia consist of shoshonite and alkalitrachyte (Civetta et al., 1991), whereas the volcanics of Somma–Vesuvius exhibit large differences in silica saturation. Nearly SiO_2-saturated rocks such as leucite-basalts and trachytes are found as well as highly SiO_2-undersaturated rocks such as leucititic phonolithes and leucititic tephrites (Joron et al., 1987). All three volcanoes have in common the presence of hydrothermal aquifers, lying at a depth of 400–900 m at Ischia (Chiodini et al., 2004), 1–2 km at Nisyros (Chiodini et al., 1993) and 1–5 km at Vesuvius (Chiodini et al., 2001). Geochemical data indicate temperatures of 250–300 °C for Ischia, 320–360 °C for Nisyros and 450–470 °C for Vesuvius (Chiodini et al., 2001, 2004; Fiebig et al., 2004). For Nisyros, a reservoir temperature of 330–335 °C was confirmed by direct measurements during a drilling campaign in 1982 (Chiodini et al., 1993).

3. ANALYTICAL DETAILS

Fumarolic gases were collected as soda and dry gas samples following the procedures given by Giggenbach (1975) and Cioni and Corazza (1981). Carbon isotope analyses were performed at the University of Frankfurt using a Thermoquest/Finnigan MAT 253 mass spectrometer and the analytical setup described by Fiebig et al. (2004). Gas concentration analyses were carried out at the Osservatorio Vesuviano. Analytical details for compositional analyses are given by Fiebig et al. (2004). For the Ischia samples, CH_4 contents were too low to be analyzed with the Elemental Analyzer, so the GC/C/IRMS at the University of Lausanne was used instead. Gas sampling was performed using a gas-tight syringe and the carbon isotope composition of CH_4 was measured using a Hewlett-Packard 6890 gas chromatograph (GC) coupled to a Thermoquest/Finnigan MAT Delta S isotope ratio mass spectrometer via a combustion (C) interface III (GC/C/IRMS) under a continuous helium flow (Freedman et al., 1988; Hayes et al., 1990). Higher hydrocarbons than CH_4 were not detected. For isotopic analysis of CH_4, the GC was operated with a Carboxen™ 1006 PLOT capillary column ($30\ \mathrm{m} \times 0.53\ \mathrm{mm}$ internal diameter) and helium as carrier gas (linear flow velocity 3 ml/s). The samples were injected splitless at 230 °C. After an initial period of 5 min at 35 °C, the column was heated to 100 °C at 20 °C/min followed by an isothermal period of 20 min, and later heated to 220 °C at 20 °C/min and held at that temperature for 5 min. The CuO/NiO/Pt combustion reactor was set at 960 °C. The performance of the GC/C/IRMS system, including the GC and combustion furnace, was evaluated every 10 analyses by injection of methane and carbon dioxide of known $\delta^{13}C$ values. Each gas sample was analyzed three times and reproduced within $\pm 0.6‰$.

4. RESULTS

Chemical and carbon isotopic data for the fumarolic gas discharges are given in Table 1. The Nisyros data as well as a single gas sample analysis from Vesuvius (FC2**) are from Fiebig et al. (2004). Chemical and isotopic data for a sample from Ischia (ISDR*) was published by Tedesco (1996). For reasons of verification, FC2 and ISDR were sampled again in August 2005. Apparent chemical and isotopic equilibrium temperatures were computed using the H_2–H_2O–CO–CO_2–CH_4 geoindicator of Chiodini and Marini (1998) (Fig. 1) and carbon isotope fractionation factors of the redox pair CH_4–CO_2 (Horita, 2001). Note, that the H_2–H_2O–CO–CO_2–CH_4 geoindicator is a five-component system, but that apparent chemical equilibrium temperatures are near-exclusively dominated by the molar CO/CO_2 ratios of the samples. All data points plot inside the bi-phase stability field which is defined by the coexistence of saturated water vapor with its hydrothermal liquid, the latter exhibiting salinities of up to 3 m NaCl. The apparent chemical (T_{CO}) and isotopic temperatures ($T_{carb.}$) derived by these two mutually independent geothermometers are listed in Table 1 and it is evident that apparent isotopic and chemical temperatures roughly agree for all three locations.

5. DISCUSSION

The agreement of isotopic and chemical temperatures demonstrates that CO_2 and CH_4 can attain carbon isotopic equilibrium, as previously demonstrated by Fiebig et al. (2004). The recent study provides evidence that the temperature range of isotopic equilibration can be extended down to temperatures as low as ~260 °C. As already expressed by Giggenbach (1997), carbon isotopic exchange in the system CO_2–CH_4 cannot occur decoupled from chemical exchange, because such a scenario would require a statistically improbable process, i.e. the simultaneous breaking and reconstruction of two double and four single bonds. Therefore, the agreement of chemical (predominantly inferred from molar ratios of CO/CO_2) and isotopic temperatures (reflected by carbon isotope partitioning between CH_4 and CO_2), also provides evidence that natural occurrences of CO, CH_4 and CO_2 can attain chemical equilibrium within a temperature range of 260–470 °C under hydrothermal conditions.

5.1. Potential production pathways of the evolved CH_4

Biogenic pathways of CH_4 production comprise microbial reduction of CO_2 and thermogenic decay of organic matter, whereas potential sources of abiogenic CH_4 are the mantle, metamorphism of graphite, thermal decomposition of siderite and FTT reactions. In order to determine the equilibration mechanism, we can assess the extent to which our observations agree with the characteristics of each of these biogenic and abiogenic processes.

5.1.1. Biogenic: microbial or thermogenic

The observed equilibrium along with the carbon isotopic composition of the evolved gases rule out a thermogenic or microbial production pathway of the evolved CH_4. Microbial reduction of CO_2 is a kinetically controlled process that does not yield an equilibrium signature between product CH_4 and educt CO_2 and, in addition, it does not occur at temperatures higher than 120 °C (Whiticar, 1999). Thermal decomposition of organic matter also represents a disequilibrium process (e.g., Berner et al., 1995). If the evolved CH_4 was generated directly by either of these two processes, the observed consistency of apparent temperatures would have to be fortuitous. However, such a coincidence is highly unlikely, as agreement of isotopic with chemical temperatures occurs for three different volcanic–hydrothermal systems, each possessing different reservoir temperatures. Unidirectional secondary oxidation of excess amounts of biogenic CH_4 to CO_2 can also be excluded. This process could provide near-equilibrium signatures only if virtually all the CO_2 is derived from the oxidation of biogenic CH_4. Otherwise, CO_2 of different origins would be mixed, leading to erroneous temperatures computed with the carbon isotope geothermometer. If the evolved CO_2 was due to unidirectional oxidation of biogenic CH_4, the measured CO_2/CH_4 ratios would indicate that the original CH_4 must have reacted nearly completely to CO_2. In this case, the evolved CO_2 should have inherited the carbon isotopic signature of the precursor CH_4. However, measured $\delta^{13}C_{CO_2}$

Table 1

Chemical and carbon isotopic composition of hydrothermal gases released from different arc volcanoes of the Mediterranean

Volcanic system	Sample	Date	T_{vent} (°C)	H_2O	CO_2	H_2S	H_2	N_2	CH_4	CO	He	Ar	O_2	$\delta^{13}C$ (CO_2)	$\delta^{13}C$ (CH_4)	$T_{carb.}$ (°C)	T_{CO} (°C)
Ischia	ISDR*	5/12/1988	117.0	998,600	1335	37	12.7	27.3	0.26	0.004	0.11	n.a.	n.a.	−4.3	−30.8	279	283
	ISDR 1	8/3/2005	99.7	997,250	2690	29	15.3	17.2	0.22	0.007	0.08	0.25	0	−4.0	−32.3	257 ± 10	288
Vesuvius	FC2**	5/10/2002	97.6	869,000	129,000	512	1080.0	196.0	55.20	48.800	0.69	0.26	0	−0.3	−16.4	469	450–470
	FC2	8/4/2005	94.8	928,600	70,300	273	690.5	117.6	34.78	25.044	0.37	0.68	0	0.1	−16.7	451	450–470
Nisyros	PP9N**	2/3/2002	99.2	990,000	6740	2900	134.0	6.0	10.60	0.108	0.21	0.03	0	−1.2	−23.4	340	323
	PP9S**	2/3/2002	99.4	991,000	6510	2710	103.0	5.4	7.50	0.062	0.16	0.04	0	−0.9	−23.0	345	305

Gas concentration data is given in µmol/mol and $\delta^{13}C$ values are relative to VPDB. * and ** mark data taken from Tedesco (1996) and Fiebig et al. (2004), respectively. Apparent carbon isotopic temperatures ($T_{carb.}$) were derived from carbon isotope partitioning between CO_2 and CH_4 using the empirical calibration of Horita (2001). For Ischia samples, the uncertainty in temperature estimation results from the precision of the analytical setup. Apparent chemical equilibrium temperatures (T_{CO}) were computed using the H_2–H_2O–CO–CO_2–CH_4 geoindicator (Fig. 1).

values (−4.3 to +0.1‰) are clearly outside the ranges usually observed for microbial ($\delta^{13}C \leqslant -50$‰; Whiticar, 1999) or thermogenic CH_4 ($\delta^{13}C = -50$‰ to −20‰; Whiticar, 1999).

5.1.2. *Abiogenic: CH_4 from the mantle*

As postulated by Welhan and Craig (1983), CH_4 emanating from midocean ridges might derive from the mantle, with its ultimate production pathway being unknown. If our CH_4 originated in the mantle, unidirectional oxidation of mantle CH_4 at the temperatures reflected by carbon isotope partitioning (260–470 °C) might account for an approach to equilibrium. As was already indicated for the secondary oxidation of excess amounts of biogenic CH_4, equilibrium could have only been approached if almost all CO_2 present was derived from the oxidation of mantle CH_4. This would imply that the C-bearing gases migrating from the mantle are dominated by CH_4. However, redox conditions and temperatures prevailing in the spinel–peridotite facies of the upper mantle imply that CO_2 rather than CH_4 is the dominant carbon-bearing species of gases exiting the mantle (e.g., Woodland and Koch, 2003; Woodland et al., 2006).

5.1.3. *Abiogenic: metamorphism of graphite*

Carbonate rocks are present beneath Vesuvius and Nisyros (Principe et al., 1987; Marini et al., 1993), and are probably also present under Ischia. These rocks may contain graphite. To evaluate if the evolved CH_4 and CO_2 could have been processed through metamorphism of graphite-bearing carbonates, the stability of graphite under the *P*, *T* and redox-conditions characteristic of the investigated volcanic–hydrothermal systems needs to be considered. Fig. 2 shows a correlation between carbon isotopic temperature and $\log(X_{CH_4}/X_{CO_2})$ values. Measured values are compared to those predicted by thermodynamic constraints under the assumption that a variety of mineral assemblages can control redox conditions (details are given in the Appendix A). All data points form a near-horizontal array and one may, therefore, speculate that CH_4 concentrations were frozen in (quenched) from high temperatures. However, interpreting the array as reflecting a quenching process is incorrect. It would require that carbon isotopic exchange between CO_2 and CH_4 occurred decoupled from chemical exchange, but as was already explained, such a process is extremely unlikely. Rather, it becomes obvious that there is no unique oxygen buffer that governs the equilibration between CO_2 and CH_4. Within the hydrothermal reservoirs of Nisyros and Vesuvius, oxygen fugacities are closely reflected by the metastable mineral assemblage of fayalite–hematite–quartz (FHQ). This buffer has been found to exert control of redox conditions in many mature volcanic–hydrothermal and geothermal systems worldwide (Giggenbach et al., 1986; Giggenbach, 1987; Giggenbach, 1993, 1997; Chiodini and Marini, 1998). The Ischia data deviate significantly from the FHQ buffer line plotting at lower $\log(X_{CH_4}/X_{CO_2})$ values. Obviously, equilibrium at Ischia was attained at conditions more oxidizing than the FHQ reaction.

In order to prove if graphite is stable at the temperature and redox conditions provided by the three investigated

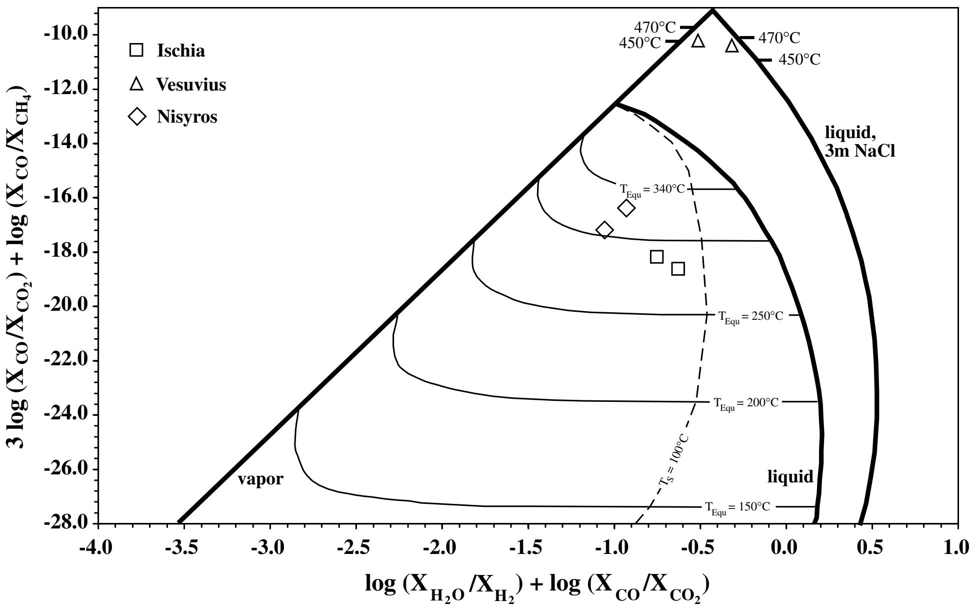

Fig. 1. Comparison between measured and theoretical data for the biphase H_2–H_2O–CO–CO_2–CH_4 system (Chiodini and Marini, 1998). Equilibration temperatures (T_{equ}) and vapor separation temperatures (T_s) were computed assuming adiabatic boiling. For Vesuvius, equilibrium temperatures can only be graphically approximated because of unknown temperature–enthalpy relationships for 3 m NaCl and its corresponding saturated vapor phase.

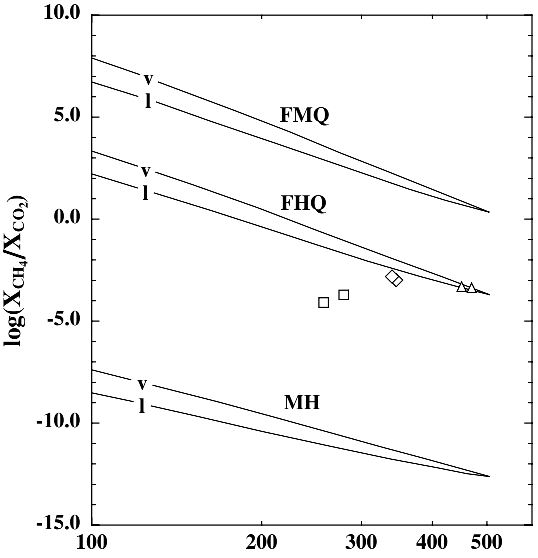

Fig. 2. Comparison between measured CH_4/CO_2 ratios and those predicted by the redox buffer reactions fayalite ↔ magnetite + quartz (FMQ), fayalite ↔ hematite + quartz (FHQ) and magnetite ↔ hematite (MH), at the temperatures reflected by carbon isotope partitioning between CO_2 and CH_4. Theoretical values refer to the saturated vapor phase in equilibrium with a 3 m NaCl solution. For each buffer, both the vapor and liquid composition is shown. Note, that the effect of vapor separation affects CH_4/CO_2 molar ratios by less than 1log-unit. For symbols see Fig. 1.

Table 2

Apparent carbon isotopic temperatures, corresponding oxygen fugacities of the investigated hydrothermal systems and those required for the stability of graphite

Volcanic system	Sample	$T_{carb.}$ (°C)	$\log f_{O_2}$ (system)	$\log f_{O_2}$ (graphite)
Ischia	ISDR*	279	−34.2	−37.4
	ISDR 1	257	−35.7	−38.8
Vesuvius	FC2**	469	−23.7	−25.7
	FC2	451	−24.5	−26.5
Nisyros	PP9N**	340	−30.5	−33.3
	PP9S**	345	−30.1	−33.1

Oxygen fugacities were calculated from (A.11) and (A.14), respectively. * and ** mark calculations that are based on chemical and isotopic data of Tedesco (1996) and Fiebig et al. (2004) (Table 1).

volcanic–hydrothermal systems, oxygen fugacities of each system, f_{O_2} (system), are compared to those necessary for graphite stability, f_{O_2} (graphite) (see Appendix B for details). Table 2 indicates that $\log f_{O_2}$ (system) is always significantly higher (two to four log-units) than the stability of graphite requires. The more oxidizing conditions cannot be explained by vapor separation effects. Vapor–liquid distribution coefficients of CO and H_2 are nearly identical in the temperature range of 260–470 °C (Chiodini et al., 2001). Hence, $\log f_{O_2}$ (graphite) values computed from Eq. (A.14), but corrected for the effects of boiling, would not deviate significantly from those reported in Table 2. In contrast to X_{H_2}/X_{CO} ratios, the effects of vapor separation on X_{CH_4}/X_{CO_2} ratios are larger due to the enhanced solubility of CO_2 in the liquid phase (Chiodini et al., 2001). However, as illustrated in Fig. 2, boiling can only lower X_{CH_4}/X_{CO_2} ratios of the vented gases by up to 1 log-unit, irrespective of the rock buffer system. Hence, X_{CH_4}/X_{CO_2} ratios corrected for the effects of boiling might be up to 1 log-unit higher than those measured. From Eq. (A.11), this can affect calculated $\log f_{O_2}$ (system) values by only −0.5 log-units at most. Thus, under the P, T and redox conditions characteristic of the investigated hydrothermal reservoirs, all graphite would be oxidized to CO_2 and there would be no graphite available for CH_4 formation. As a consequence, graphite can not be directly involved in the process of CH_4–CO_2 equilibration.

5.1.4. Abiogenic: thermal decomposition of carbonates

Recently, CH_4 and CO_2 were produced experimentally from siderite (McCollom, 2003). Throughout this process, CO_2 might have been generated by the thermal decomposition of siderite and then be reduced by H_2. However, mechanisms different from that, e.g., generation of CH_4 through direct reduction of siderite by H_2, can not be excluded, as was already indicated by McCollom (2003). In order to determine if the major C-bearing source in our case could be siderite or related carbonate, we followed an approach of Sano and Marty (1995), who demonstrated that the relative contributions of sedimentary, mantle and limestone sources to overall CO_2 production can be identified using a correlation between $CO_2/^3He$ ratios and the carbon isotopic composition of CO_2. He-isotope data for samples PP9S and ISDR* were given by Fiebig et al. (2004) and Tedesco (1996), respectively (Table 3). Although He-isotope data are not available for any of our samples from Vesuvius, Tedesco (1997) and Tedesco et al. (1998) reported $\delta^{13}C_{CO_2} = 0‰$ and a He-isotope value of $2.51R/R_a$ for the crater fumaroles sampled in September 1990. Federico et al. (2002) reported the He-isotopic composition of Vesuvius groundwater sampled during 1997 and 1999, and they demonstrated that the groundwater was fed by a magmatic component whose He- and C-isotopic composition was indistinguishable from that of the crater fumaroles as measured 1990. Chiodini and Marini (1998) published compositional data for the crater fumarole gases sampled between 1996 and 1999. If compared to our data, it becomes obvious that there have been no significant changes, either in vent temperatures or in the chemical composition of the emitted gases. Additionally, the carbon isotopic composition of CO_2 reported by us is still within the range observed by Tedesco (1997). Therefore, it seems reasonable to assume that no input of fresh magma at shallow depths has occurred since 1990 and that the He-isotope data of Tedesco et al. (1998) can be combined with our compositional and carbon isotopic data. Inspection of Fig. 3 reveals that the evolved CO_2 at all three sites is a mixture of marine limestone-derived CO_2 with mantle CO_2. The extent of mixing varies from location to location. Vesuvius and Ischia data plot exactly on the mixing trend defined by the endmember values of −6.5‰ for mantle CO_2 and 0‰ for limestone CO_2. Beneath Vesuvius, more than 95% of the CO_2 derives from the decomposition of marine limestones, whereas their contribution to the CO_2 emitted at Ischia is less than 30%. Nevertheless, for both locations carbon isotopic temperatures agree perfectly with those determined by the H_2–H_2O–CO–CO_2–CH_4 geoindicator (Table 1). This is contrary to what is expected if the evolved CH_4 were directly generated from the thermal decomposition of carbonates. If CH_4 simply originated from such a process, mixing between mantle CO_2 and CO_2 and CH_4 deriving from the thermal decomposition of carbonates must have occurred. Through this process, the carbon isotopic composition of the total CO_2 at Ischia would have been lowered by approximately 4‰ compared to purely marine limestone-derived CO_2. In order to determine the temperature at which marine limestone underneath Ischia could have decomposed to CO_2 and CH_4, the carbon isotope fractionation defined by CH_4 and the bulk CO_2 must be corrected for the contribution of mantle CO_2. As a consequence, the apparent isotopic temperature corresponding to thermal decomposition would be ~230 °C. It is, however, the higher "bulk CO_2" temperature of ~280 °C that agrees perfectly with the

Table 3
Helium isotopic composition and $CO_2/^3He$ ratios of Vesuvius, Nisyros and Ischia fumaroles

Location	Sample	R/R_a	$CO_2/^3He$
Ischia	ISDR*	3.95	2.2E+09
Nisyros	PP9S**	5.06	5.7E+09
Vesuvius	Crater, FC2	2.51	5.4E+10

Ischia data (ISDR*) was taken from Tedesco (1996), Nisyros data (PP9S**) from Fiebig et al. (2004).
For Vesuvius, $CO_2/^3He$ ratios were calculated using the mean of the He- and CO_2 molar ratios of Table 1 and He isotope data provided by Tedesco et al. (1998), according to $CO_2/^3He = X_{CO_2}/(1.4 \times 10^{-6} * R/R_a * X_{He})$. For further discussion see text.

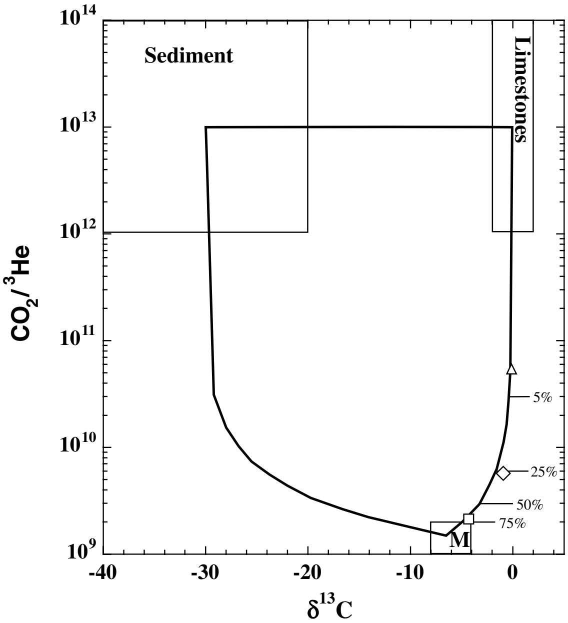

Fig. 3. Correlation between $CO_2/^3He$ ratios and carbon isotopic composition of the fumaroles. Corresponding data are listed in Tables 1 and 3. For Vesuvius, the averages of molar ratios of CO_2 and He for FC2 were combined with He-isotopic data of crater fumaroles from Tedesco et al. (1998). Endmember values for $CO_2/^3He$ ratios and $\delta^{13}C_{CO_2}$ for sediments, marine limestones and the mantle (M) were taken from Sano and Marty (1995). All data points plot along a mixing curve represented by gases originating from the mantle and marine limestones. For symbols see Fig. 1.

apparent chemical temperatures derived from the H_2–H_2O–CO–CO_2–CH_4 geoindicator (Table 1). Therefore, it is not reasonable to assume that the evolved CH_4 was directly processed through the thermal decomposition of marine limestones.

5.1.5. Abiogenic reactions involving CO_2

We have demonstrated that neither organic matter, nor graphite nor carbonates were directly involved in the generation of the evolved CH_4. If equilibrium would have been approached by a unidirectional process, the only carbon source that is in agreement with our data is that of CO_2, which, in turn, derives from the mantle and from marine carbonates. The finding that varying amounts of mantle CO_2 and limestone-derived CO_2 are mixed underneath Ischia and Vesuvius, but that apparent isotopic temperatures agree perfectly with apparent chemical temperatures demonstrates that *both* mantle CO_2 *and* limestone-derived CO_2 are reduced to CH_4 at the indicated reservoir temperatures. Alternatively, these two types of CO_2 could have mixed prior to reduction. Of course, we cannot exclude that initially minor amounts of biogenic or mantle-/limestone-/graphite-derived CH_4 were present and that these finally equilibrated in a reversible fashion with the mixed aliquots of CO_2. However, along with the oxidation of CH_4, this process would also require the reverse reaction to occur, i.e. the reduction of CO_2 to CH_4. In any case, our data provides hard evidence for the occurrence of abiogenic hydrothermal reduction of CO_2 to CH_4 in these natural hydrothermal systems.

5.2. Implications

5.2.1. Kinetic parameters of the abiogenic hydrothermal reduction of CO_2 to CH_4

We have demonstrated that CH_4 can be generated from CO_2 under hydrothermal conditions. Giggenbach (1997) used a pseudo-first order rate law in order to describe the conversion of CO_2 to CH_4 in a single-liquid phase. He considered experimental data of Berndt et al. (1996), who studied the formation of hydrocarbons during the serpentinization of olivine, reporting 1% conversion of CO_2 to CH_4 after 1658 h at 300 °C. With the assumption that this simulated natural process has the same activation energy as the technical Fischer–Tropsch process, Giggenbach (1997) derived the pre-exponential factor of the Arrhenius equation, allowing computation of the reaction half-time for chemical exchange, τ_c (in years), as a function of temperature:

$$\log \tau_c = -6.69 + 4440/T \tag{3}$$

Later on, McCollom and Seewald (2001) performed experiments under conditions almost identical to those of Berndt et al. (1996). They found only 0.04% conversion of CO_2 to CH_4 after more than 2500 h. Their results implied that the experiments of Berndt et al. (1996) suffered from severe thermogenic contamination. As a consequence, Eq. (3) does not correctly describe abiogenic hydrothermal production rates of CH_4. Considering the reaction yields of McCollom and Seewald (2001) Eq. (3) becomes

$$\log \tau_c = -5.06 + 4440/T \tag{4}$$

Assuming that chemical equilibrium is approached after four reaction half times (>90% conversion of CO_2 to CH_4), Eq. (4) predicts that it would haven taken ~40 years at Vesuvius (~460 °C), ~600 years at Nisyros (~340 °C) and ~5000 years at Ischia (~270 °C) to approach chemical equilibrium. Provided that the isotopic exchange rate is ~400 times slower than the chemical exchange rate (Giggenbach, 1997), it should have taken ~16,000 years underneath Vesuvius, ~240,000 years underneath Nisyros and ~2 Ma underneath Ischia to approach isotopic equilibrium.

For Vesuvius, the computed isotopic equilibration time is much longer than the recent period of volcanic dormancy, and, for Nisyros and Ischia, calculated equilibration times even exceed volcanic age constraints. These findings strongly imply that equilibrium was approached much more rapidly than predicted by Eq. (4). In this respect, it has to be noticed that Eq. (4) is only valid if the reduction of CO_2 proceeds in the single-liquid water phase. However, in contrast to the experimental conditions chosen by McCollom and Seewald (2001), a saturated water vapor phase is present in the investigated hydrothermal systems (as indicated by the position of data points inside Fig. 1). Significantly enhanced reaction kinetics in the system CO_2–CH_4 in the presence of a saturated water vapor phase are likely and agrees with the conclusions of McCollom and Seewald (2006). Therefore, it is reasonable to assume that the reduction of CO_2 to CH_4 in our hydrothermal systems occurred in the saturated water vapor phase.

Rate constants for isotopic exchange in the saturated water vapor phase can be obtained if we assume that both chemical and isotopic exchange follows a first order rate law. The Arrhenius equation can then be solved for the activation energy and for the pre-exponential factor using known reservoir temperatures and the time constraints provided by the most recent eruptions. We assume that isotopic equilibrium was approached by the forward reaction (1) within 58 years underneath Vesuvius and 114 years underneath Nisyros (as defined by the time difference between the dates of the first sampling campaigns listed in Table 1 and the dates for the most recent magmatic or phreatic eruptions). In addition, we assume that close isotopic equilibrium can be attained after four reaction half-times (>90% exchange). From that it follows that the isotopic reaction half-time τ_i corresponds to ~15 years and ~30 years for Vesuvius and Nisyros, respectively. The rate constant, k_i, for isotopic exchange is given by

$$k_i = \ln 2/\tau_i \tag{5}$$

Determining k_i for two different temperatures (460 and 340 °C) permits us to solve for the pre-exponentional factor A and the activation energy, E_a, in the Arrhenius equation

$$\log k_i = A - E_a/2.303RT \tag{6}$$

This yields

$$\log k_i = 0.18 - 1099/T \tag{7}$$

Inserting (7) into (5), the reaction half-time for isotopic exchange, τ_i, is defined through

$$\log \tau_i = -0.34 + 1099/T \qquad (8)$$

At 270 °C, the temperature of the Ischia hydrothermal system, the corresponding isotopic reaction half-time would be ~50 years. Accordingly, CH_4 and CO_2 would have required ~200 years to approach isotopic equilibrium. This is well within the time interval constrained by the last magmatic event. Considering the hypothesis of Giggenbach (1997) that chemical equilibration occurs at any temperature 400 times faster than isotopic equilibration, it would follow for the reaction half-time τ_c describing chemical exchange

$$\log \tau_c = -2.94 + 1099/T \qquad (9)$$

Accordingly, the reaction nearly attains completion (>90% conversion) within less than a single year at the temperatures reflected by the investigated hydrothermal systems, 270–460 °C. Eq. (9) predicts that CH_4 generation should occur relatively rapidly even at temperatures as low as 100 °C ($\tau_c = 1$ yr).

The enhanced reaction rates of CO_2 and CH_4 under bi-phase hydrothermal conditions have to be considered when computing residence times or cooling rates of geothermal fluids from chemical and isotopic data of discharged fluids (e.g., Giggenbach, 1980). It should be noted that the time constraints that can be derived from Eqs. (8) and (9) are maximum estimates. Chemical and isotopic exchange may even proceed faster than predicted by (8) and (9). If the generation of CH_4 from CO_2 under bi-phase hydrothermal conditions is an instantaneous process, carbon isotope partitioning between CO_2 and CH_4 may even be used to monitor actual temperatures of volcanic aquifers, which would be of importance for the evaluation of volcanic activity.

5.2.2. Abiogenic fluxes of CH_4 from hydrothermal sources during the Archean

CH_4 may have played an important role in the evolution of life. Zahnle (1986) suggested that photochemically induced reactions might have generated HCN from N_2 and small amounts of CH_4. In turn, HCN could then have been a precursor of aminoacids. HCN generation would have worked efficiently in an atmosphere containing tens to hundreds of ppm of CH_4. Later on, in the Late Archean prior to the Great Oxidation Event (GOE) at 2.3 Ga, elevated atmospheric CH_4 concentrations of 100–1000 ppm probably compensated for the lower luminosity of the young sun and kept Earth from freezing (Pavlov et al., 2000; Kasting, 2005). The greenhouse CH_4 is assumed to have derived mainly from biogenic sources (Catling et al., 2001). Methanogens would have reduced atmospheric CO_2 both directly by the consumption of H_2 and indirectly by the decomposition of organic matter originating from photoautotrophic cyanobacteria (Hayes, 1994).

With our evidence for abiogenic generation of CH_4 in modern volcanic–hydrothermal systems it is of great interest to estimate the levels of atmospheric CH_4 these sources could have provided in the low-oxygen atmosphere of the Archean. Modern abiogenic generation of CH_4 can potentially occur in hydrothermal systems associated with convergent or divergent plate boundaries and plumes. There is growing evidence that these different types of volcanism were already active during large parts of the Archean (Polat et al., 2002; Bedard, 2006; Westerlund et al., 2006), at least up to 3.8 Ga ago. In these environments, the availability of reducing agents such as ferrous iron ultimately limits the production of CH_4. The redox state of Archean basaltic rocks can be assumed to be similar to that of modern basalts because their major source, the upper mantle, has remained constant within ±0.5 log-units since 4.0 Ga (Delano, 2001). Estimates of Archean fluxes of abiogenic CH_4 can be determined from modern magma emplacement rates at arcs, ridges and plumes and the Fe^{2+} contents of basaltic rocks. Modern magma emplacement rates at arcs, ridges and plumes amount to 5.7×10^{13} kg/yr (Lecuyer and Ricard, 1999). Considering the Fe^{2+} content of basaltic rocks (6 wt%), this corresponds to a Fe^{2+} production rate of 3.4×10^{12} kg/yr. Since more than 95% of this Fe^{2+} is produced at midocean ridges (Lecuyer and Ricard, 1999), we will make the simplifying assumption throughout the following that all Fe^{2+} is produced in midocean ridge environments. This rate might have been elevated by a factor of 5–10 during the early Archean, due to the higher thermal state of the early Earth (Kasting, 2005), yielding a production rate of $(1.7–3.4) \times 10^{13}$ kg/yr. At midocean ridges, the reduction of CO_2 to CH_4 can be modelled in terms of the serpentinization of olivine and the formation of magnetite:

$$\begin{aligned} &6Mg_2SiO_4 + 9Fe_2SiO_4 + 11H_2O + 1.5CO_2 \\ &\quad = 4Mg_3Si_2O_5(OH)_4 + 7SiO_2 + 6Fe_3O_4 + 1.5CH_4 \qquad (10) \end{aligned}$$

In this case, 12 mole of Fe^{2+} are needed to produce 1 mole of CH_4, and accordingly 400–800 Mt CH_4 could have been generated abiogenically each year.

It should be noted that this rate is an uppermost estimate that considers neither reaction geometries (3D-distributions of Fe^{2+}, CO_2 and H_2O) nor reaction kinetics. The extent to which these parameters can limit abiogenic CH_4 production rates can be assessed by comparing hypothetical and real fluxes of CH_4 from modern midocean ridges. Currently, ~80 Mt of CH_4 could be generated each year, if the entire amount of available Fe^{2+} would be used for the reduction of CO_2 by the serpentinization of olivine and if the reduction proceeds rapidly. However, real CH_4 production rates are 0.1 Mt/yr, which is three orders of magnitude smaller (Welhan and Craig, 1979). This difference can be understood in terms of: (1) the limited availability of water in the oceanic crust, which leads to only 12% of total Fe^{2+} being converted to Fe^{3+} at ridges (Lecuyer and Ricard, 1999); and (2) sluggish reaction rates in the absence of a saturated water vapor phase. According to Eq. (4), a conversion of 1% of CO_2 to CH_4 per year corresponds to reaction temperatures of 360–380 °C. These temperatures are slightly lower than the critical temperature of seawater and reasonably reflect the superconvective temperature range that is required for the attainment of modern penetration depths of seawater (Kasting et al., 2006).

It is unlikely that modern reaction geometries and kinetics correctly describe midocean ridge hydrothermal environments of the Archean. Kasting et al. (2006) postulated that ridgecrests were shallower during the Archean. If ridgecrest depths were less than 2.4 km, the onset of boiling would have inhibited seawater to penetrate to depths exceeding 600 m (Kasting et al., 2006). According to Eq. (9), the production of a saturated water vapor phase would have enhanced reaction kinetics in a way that the reaction could go to completion within a single year. However, the penetration depth only would have been ~10% of the modern value (e.g., 5 km according to Kasting et al., 2006). Assuming that the total Fe^{2+} contained in the upper 600 m of the oceanic crust was oxidized by saturated water vapor, our uppermost estimate for the Archean abiogenic CH_4 flux, therefore, must be reduced to 40–80 Mt/yr. Following photochemical calculations of Pavlov et al. (2001) and Kasting (2005), such a flux of abiogenic CH_4 could have provided an atmospheric mixing ratio of up to 20 ppm. This would have been enough for the effective production of HCN, but is less than what is required for the onset of the Archean greenhouse. Our estimate, therefore, is consistent with the hypothesis that the onset of the Archean greenhouse was dominated by CH_4 emissions from biogenic sources.

5.2.3. CH_4 as indicator of extraterrestrial life

For astrobiologists, CH_4 is of interest because of its potential as an indicator of life on other planets. Our study implies that abiogenic generation of CH_4 can proceed relatively rapidly if saturated water vapor is present. As a consequence, hydrothermal sources of CH_4 have to be considered, as pointed out by Formisano et al. (2004), who detected relatively small (~10 ppbv) CH_4 occurrences on Mars. Unless hydrothermal source fluxes and its impact on atmospheric CH_4 mixing ratios can be constrained, CH_4 should not be used as a bioindicator.

5.2.4. Carbon isotopes as indicator of early life

Several studies propose that Earth's earliest life may be as old as 3.9 Ga (Schidlowski, 1988; Mojzsis et al., 1996; Rosing, 1999). Evidence is based on reduced carbon in Archean sediments from Isua and Akilia being depleted in ^{13}C by 15–50‰ relative to VPDB. Our study provides evidence for the natural occurrence of a methanation mechanism that fractionates carbon isotopes abiogenically by at least as much as −30‰ with respect to mantle carbon. McCollom and Seewald (2006) demonstrated experimentally that semi-volatile and non-volatile organic compounds can occur as byproducts during the methanation of CO_2. Moreover, they demonstrated that these can be similarly depleted in ^{13}C as the co-generated CH_4. Isua and Akilia sediments were originally deposited in the vicinity of submarine volcanic edifices, parts of which (Isua) were recently ascribed to subduction-related volcanism (Polat et al., 2002). Thus the possibility that the reduced carbon contained in the metamorphosed Archean sediments represents the mature remnants of abiogenically generated organic compounds can no longer be excluded.

6. CONCLUSIONS

There has been a long and outstanding debate whether CH_4 can be generated abiogenically from CO_2 under natural hydrothermal conditions. Our study provides definitive evidence for its occurrence. Evidence comes from three volcanic–hydrothermal systems that are situated along convergent plate boundaries. These settings were not previously expected to produce abiogenic CH_4.

In these three systems, the evolved CH_4 is generated from mixed aliquots of limestone- and mantle-derived CO_2 in a bi-phase hydrothermal environment. The reaction attained or at least approached equilibrium. This is contrary to what is expected from the time constraints defined by the most recent volcanic eruptions and a recently elaborated kinetic model that describes the conversion of CO_2 to CH_4 within liquid water. The chemical composition of the gases indicates the presence of a saturated water vapor phase at all three sites and the reaction is suggested to take place in this phase. Based on the periods of volcanic dormancy we developed a kinetic model from which minimum chemical and isotopic equilibration times under bi-phase hydrothermal conditions could be constrained. We conclude that CH_4 might be generated from CO_2 at temperatures even as low as 100 °C, with chemical reaction half-times in the order of 1 year.

The fact that nature provides conditions under which the abiogenic methanation of CO_2 proceeds relatively rapidly and that the abiogenic methanation process itself causes large fractionation of carbon isotopes has important geochemical consequences. For example, the occurrence of CH_4 in planetary atmospheres cannot be used as an indicator for biogenic activity unless hydrothermal source fluxes and its impact on atmospheric CH_4 mixing ratios can be constrained. Further, that the carbon isotopic composition of reduced carbon in Archean sediments must be interpreted with caution. It is well known from laboratory experiments that higher hydrocarbons occur as byproducts of the hydrothermal methanation of CO_2 and these can be as depleted in ^{13}C as the co-generated CH_4. Therefore, the reduced carbon in Archean sediments may represent the mature remnants of these byproducts rather than the remnants of early life.

Abiogenic CH_4 probably played an important role in the evolution of the early life. The abiogenic source flux depends on several factors such as the availabilities of Fe^{2+}, CO_2 and H_2O and on reaction kinetics. Extrapolating modern Fe^{2+} production rates from global volcanism to the likely conditions of the early Archean (up to 4.0 Ga ago), a maximum estimate of 40–80 Mt/yr is obtained for abiogenic CH_4 production. This might have provided atmospheric CH_4 mixing ratios that were sufficient for an effective generation of HCN through photolytic reaction of CH_4, but were not enough to produce an atmospheric greenhouse.

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APPENDIX A. COMPUTING THEORETICAL $\log(X_{CH_4}/X_{CO_2})$ VALUES

For the vapor (v) phase, theoretical values were obtained by computing ($\log X_{CH_4}/X_{CO_2}$) values of reaction (1) according to

$$\log(X_{CH_4}/X_{CO_2})_v = \log K_1 + 4\log(X_{H_2}/X_{H_2O}) + 2\log f_{H_2O} \tag{A.1}$$

and setting X_{H_2}/X_{H_2O} ratios corresponding to conditions of the fayalite–magnetite–quartz (FMQ), fayalite–hematite–quartz (FHQ) or magnetite–hematite (MH) oxygen buffers. The temperature dependence of X_{H_2}/X_{H_2O} and K_1 were given by Giggenbach et al. (1986) and Giggenbach (1987):

$$\log(X_{H_2}/X_{H_2O})_{FMQ} = 162/T - 1.95 \tag{A.2}$$

$$\log(X_{H_2}/X_{H_2O})_{FHQ} = 73/T - 2.85 \tag{A.3}$$

$$\log(X_{H_2}/X_{H_2O})_{MH} = -251/T - 4.66 \tag{A.4}$$

$$\log K_1 = 8821/T - 9.665 \tag{A.5}$$

f_{H_2O} is the fugacity of saturated water vapor. The hydrothermal fluids beneath Nisyros and Vesuvius are saline solutions with up to 3 m NaCl (Chiodini et al., 1993, 2001). Chiodini et al. (2001) provide a relation to account for the effect these salts have on f_{H_2O}:

$$\log f_{H_2O} = 5.462 - 2047/T \tag{A.6}$$

The effects of vapor separation on X_{CH_4}/X_{CO_2} ratios of the liquid (l) phase (CH_4 and CO_2 dissolved in 3 m NaCl) were also calculated according to

$$\log(X_{CH_4}/X_{CO_2})_l = \log K_1 + 4\log(X_{H_2}/X_{H_2O}) + 2\log f_{H_2O} + \log B_{CO_2} - \log B_{CH_4} \tag{A.7}$$

where B_{CO_2} and B_{CH_4} are the vapor–liquid distribution coefficients of CO_2 and CH_4, respectively. For 3 m NaCl, their temperature dependence was recently constrained by Chiodini et al. (2001)

$$\log B_{CO_2} = 5.079 - 0.01038\ (T - 273) \tag{A.8}$$

$$\log B_{CH_4} = 6.482 - 0.01315\ (T - 273) \tag{A.9}$$

APPENDIX B. COMPUTING f_{O_2} (SYSTEM) AND f_{O_2} (GRAPHITE)

Considering the reaction

$$CO_2 + 2H_2O = CH_4 + 2O_2 \tag{A.10}$$

oxygen fugacities (f_{O_2}) for each hydrothermal system can be computed according to:

$$\log f_{O_2}(\text{system}) = 1/2\log K_{A10} - 1/2\log(X_{CH_4}/X_{CO_2}) + \log f_{H_2O}, \tag{A.11}$$

The temperature dependence of the equilibrium constant K_{A10} was given by Chiodini and Marini (1998)

$$\log K_{A10} = 0.527 - 42007/T \tag{A.12}$$

If graphite were present, oxygen fugacities can also be computed from:

$$\text{C (graphite)} + O_2 = CO_2 \tag{A.13}$$

according to:

$$\log f_{O_2}(\text{graphite}) = \log f_{CO_2} - \log K_{A13} \tag{A.14}$$

The following expressions for f_{CO_2} and K_{A13} can be obtained from Chiodini and Marini (1998) and Giggenbach (1987):

$$\log f_{CO_2} = -2.485 + 2248/T - \log(X_{H_2}/X_{CO}) + \log f_{H_2O} \tag{A.15}$$

$$\log K_{A13} = 20713/T - 0.295 \tag{A.16}$$

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