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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).