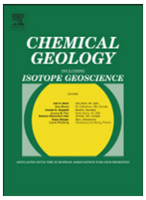
Chemical Geology 351 (2013) 66–75

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo



Carbon-bearing gas geothermometers for volcanic-hydrothermal systems

Jens Fiebig [a,*], Franco Tassi [b,c], Walter D'Alessandro [d], Orlando Vaselli [b,c], Alan B. Woodland [a]

[a] Institut für Geowissenschaften, Goethe-Universität, Altenhöferallee 1, 60438 Frankfurt am Main, Germany
[b] Department of Earth Sciences, University of Florence, Via La Pira 4, 50121 Florence, Italy
[c] CNR-IGG Institute of Geosciences and Earth Resources, Via La Pira 4, 50121 Florence, Italy
[d] Istituto Nazionale di Geofisica e Vulcanologia, Via Ugo la Malfa 153, 90146 Palermo, Italy

ARTICLE INFO

Article history:
Received 5 March 2013
Received in revised form 7 May 2013
Accepted 9 May 2013
Available online 21 May 2013

Editor: David R. Hilton

Keywords:
Hydrocarbons
Hydrothermal fluids
Volcanoes
Geothermometry

ABSTRACT

The genetic relationship between carbon-bearing species (CO, CO_2, CH_4, C_2H_6, C_3H_8, C_2H_4 and C_3H_6) was investigated in volcanic-hydrothermal gases emitted from Nisyros (Greece), Vesuvio, La Solfatara (Campi Flegrei) and Pantelleria (all Italy).

Apparent carbon isotopic temperatures of the CH_4–CO_2 system are ~360 °C at Nisyros, 420–460 °C at Vesuvio, ~450 °C at La Solfatara and ~540 °C at Pantelleria. These temperatures are confirmed by measured propene/propane and H_2/H_2O concentration ratios. CH_4 and CO_2 equilibrate in the single liquid phase prior to the onset of boiling, whereas propene and propane attain equilibrium in the saturated water vapor phase. Boiling in these high-enthalpy hydrothermal systems might occur isothermally. Once vapor has been extracted from the parental liquid, CO/CO_2 responds most sensitively to the temperature gradient encountered by the ascending gases. Our results imply that the CH_4–CO_2 isotopic geothermometer can provide reliable information about temperatures of deep hydrothermal liquids associated with volcanism. Propene/propane and H_2/H_2O concentration ratios should be measured along with the carbon isotopic composition of CO_2 and CH_4 to provide independent constraints on the geological significance of the apparent carbon isotopic temperatures.

1. Introduction

After their exsolution from magma on their way up to the surface, volcanic gases often come into contact with externally and internally derived waters. The chemical composition of gases that are emitted at the surface of these volcanic-hydrothermal systems depends on the chemical composition of the magma, pressure, temperature and redox conditions prevailing within the magma and within superposed hydrothermal reservoirs, the extent of vapor phase separation and the degree of vapor phase reequilibration potentially occurring after vapor extraction (e.g., Giggenbach, 1980, 1987; Symonds et al., 1994; Chiodini and Marini, 1998). Considering that a given number of redox pairs and their corresponding concentration ratios (such as H_2/H_2O, CO/CO_2, CH_4/CO_2, N_2/NH_3) attain a state of overall equilibrium within the hydrothermal reservoir at depth, equilibration temperatures, saturated water vapor pressures and the degree of steam separation can be derived from measured gas concentration data. For this purpose, Giggenbach (1980) compared theoretical and measured equilibrium constants for the two reactions:

$$CH_4 + 2H_2O = CO_2 + 4H_2 \tag{1}$$

$$2NH_3 = N_2 + 3H_2 \tag{2}$$

while Chiodini and Marini (1998) did the same for the following reactions:

$$CO_2 + H_2 = CO + H_2O \tag{3}$$

$$3CO_2 + CH_4 = 4CO + 2H_2O \tag{4}$$

with reaction (4) being a combination of reactions (1) and (3). Although methane represents a constituent of each of the two geothermometers defined by reactions (1) and (2) and reactions (3) and (4), respectively, and apparent equilibration temperatures derived from gas concentration data in many cases agree very well with temperatures measured directly in the associated hydrothermal reservoirs at depth, its equilibration behavior with respect to CO_2 has remained unclear (Chiodini and Marini, 1998). This is due to the circumstance that reactions (1) and (4) are much more sensitive to measured H_2/H_2O and CO/CO_2 concentration ratios than to CH_4/CO_2, making apparent equilibration temperatures derived from the comparison of theoretical calculations and analytical data relatively insensitive to measured CH_4/CO_2 concentration ratios (Taran, 1986). Contrasting views have been offered concerning the genetic relationship between CO_2 and CH_4. Taran and Giggenbach (2003) postulated that CH_4 and CO_2 do not occur in equilibrium in volcanic-hydrothermal systems. They did not observe any correlation between measured CH_4/CO_2 and sampling temperature for gases from geothermal wells and steam vents. Instead, they noticed a correlation between measured N_2/Ar ratios and CH_4 concentration. Provided that

---

[*] Corresponding author. Fax: +49 69 79840185.
E-mail address: Jens.Fiebig@em.uni-frankfurt.de (J. Fiebig).

0009-2541/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemgeo.2013.05.006

elevated N_2/Ar ratios are indicative of thermal breakdown of organic matter, they concluded that CH_4 may derive from the same organic source as N_2 and that it does not equilibrate with CO_2 after its infiltration into the hydrothermal system. Analyzing hydrothermal gases emitted from high heatflow sedimentary basins, Giggenbach (1997) was able to correlate CH_4/CO_2 concentration ratios with measured temperatures and with the magnitude of carbon isotope fractionation between CH_4 and CO_2. He concluded that CH_4 and CO_2 approach chemical equilibrium with respect to redox conditions predicted by the mineral paragenesis fayalite–hematite–quartz (FHQ). Though being of a metastable nature (fayalite is not stable in the presence of quartz), this redox buffer was found to closely describe redox conditions in many volcanic-hydrothermal systems (e.g., Giggenbach, 1987; Chiodini and Marini, 1998). However, his data did not indicate attainment of isotopic equilibrium, because apparent carbon isotopic temperatures derived from carbon isotope partitioning between CO_2 and CH_4 were significantly higher than measured temperatures. He postulated that isotopic exchange rates might be 400 times slower than chemical reaction rates. Finally, Fiebig et al. (2004, 2007) observed that apparent carbon isotopic temperatures agree very well with apparent equilibration temperatures inferred from the geothermometer of Chiodini and Marini (1998) for hydrothermal gases discharged at Nisyros, Vesuvio and Ischia. These findings implied that CH_4 and CO_2 can indeed attain both chemical and isotopic equilibrium, at least in certain hydrothermal systems.

Along with CH_4, which often occurs in ppm concentrations, volcanic-hydrothermal gases can contain sub ppm quantities of n-alkanes higher than methane and n-alkenes (Capaccioni et al., 1993; Darling, 1998; Taran and Giggenbach, 2003). Sugisake and Nagamine (1995) observed that concentration ratios of methane, ethane and propane of samples with vent temperatures >300 °C plot close to equilibrium values predicted by reaction:

$$CH_4 + C_3H_8 = 2C_2H_6 \tag{5}$$

However, Giggenbach (1997) pointed out that reaction (5) implicitly assumes that the redox potential is internally controlled by the hydrocarbons. This is very unlikely since ethane and propane occur in too low concentrations to act as a redox buffer. Assuming more realistic conditions, with redox conditions being externally buffered by Fe^{2+} and Fe^{3+}-bearing minerals in contact with the fluids, Giggenbach (1997) concluded that the relative concentrations of the n-alkanes are instead governed by kinetic processes, making geothermometers based on n-alkane distribution ratios an improper tool for the determination of hydrothermal temperatures.

Alternatively, geothermometers involving alkene/alkane redox pairs seem to be more promising. Laboratory experiments suggest that the dehydrogenation reaction of alkanes to alkenes:

$$C_nH_{2n+2} = C_nH_{2n} + H_2 \tag{6}$$

proceeds relatively rapidly under hydrothermal conditions (Seewald, 1994, 2001). Metastable equilibrium between ethene and ethane was reached after a couple of days at 325 °C and redox conditions corresponding to the pyrite–pyrrhotite–magnetite buffer. This motivated others to investigate the equilibration behavior of alkene/alkane pairs in volcanic and hydrothermal gas discharges in more detail (Capaccioni and Mangani, 2001; Taran and Giggenbach, 2003, 2004; Capaccioni et al., 2004; Tassi et al., 2005, 2007, 2009; Zelensky and Taran, 2011). Taran and Giggenbach (2003, 2004) analyzed molar alkene/alkane ratios in magmatic gases discharging at White Island, New Zealand. For high temperature vents ($T > 600$ °C), measured ethene/ethane and propene/propane ratios matched those predicted for measured vent temperatures and redox conditions prevailing in the magmatic carrier gas (H_2S–SO_2 buffer). Some discharges even attained alkene/alkane equilibrium at discharge temperatures down to 100 °C (Taran and Giggenbach, 2004). In contrast, alkene/alkane patterns from volcanic-hydrothermal emissions (i.e., emissions lacking HCl, HF and SO_2) are more difficult to interpret because their concentration ratios often no longer correspond to vent temperatures (e.g., Capaccioni and Mangani, 2001; Capaccioni et al., 2004; Tassi et al., 2005). Obviously, alkene/alkane ratios are set at higher temperatures than the vent temperature. Capaccioni et al. (2004) postulated that C_3 and linear C_4 alkenes and alkanes in hydrothermal gases from El Chichon, Mexico equilibrate under temperature and redox conditions similar to those reflected by the CH_4/CO_2 pair, whereas ethene/ethane and branched butene/butane indicate different temperatures and/or redox conditions. In this respect, at least some of the alkene/alkane redox pairs may exhibit reactivities similar to the CH_4/CO_2 pair.

Here, we present a detailed investigation of the equilibration behavior of carbon-bearing gases (CO, CO_2, CH_4, C_2H_6, C_3H_8, C_2H_4 and C_3H_6) in volcanic-hydrothermal systems of the Mediterranean area. We demonstrate that carbon isotope partitioning between CO_2 and CH_4 as well as propene/propane concentration ratios yield consistent equilibration temperatures. Therefore, our data provides evidence that the CH_4–CO_2 carbon isotope geothermometer can be a useful indicator for hydrothermal aquifer temperatures at depth.

2. Volcanic-hydrothermal settings

All investigated volcanic systems except Pantelleria are situated along convergent plate boundaries within the Mediterranean Sea. Nisyros is part of the Hellenic volcanic arc (Fytikas et al., 1976), while La Solfatara (Campi Flegrei) and Vesuvio belong to the Neapolitan volcanic province (Scandone et al., 1991; Peccerillo, 2003). In contrast, Pantelleria is related to an extensional system, the so-called "Siciliy Rift Channel" (Civetta et al., 1988; Peccerillo, 2005; Panza et al., 2007). Volcanic products at all localities exhibit large variations in silica saturation, covering the entire calc-alkaline (Nisyros) and (per)alkaline series (Vesuvio, La Solfatara, Pantelleria).

The investigated volcanoes all have high-enthalpy hydrothermal aquifers situated above a relatively shallow magma chamber. Gas emissions do not contain acid components such as SO_2, HCl and HF, implying that the ascending magmatic gases are completely absorbed into the liquid phase hosted in the deepest parts of the hydrothermal systems (e.g., D'Alessandro et al., 1994; Chiodini and Marini, 1998; Chiodini et al., 2001). Some systems have been drilled for exploratory reasons. At Nisyros, temperatures of >330 °C were directly measured at the bottom of an aquifer located at 1800 m depth beneath the Lakki plain (e.g., Chiodini et al., 1993). The borehole lies <1 km from the fumarolic vents where gas samples were collected. At Pantelleria, maximum temperatures of 260 °C were measured for a reservoir at 1000 m depth beneath the Favare-zone (D'Amore et al., 1995), near the outlet of the Favare Grande fumarole sampled in this study. Detailed maps of fumarolic occurrences are provided by Fiebig et al. (2004) for Nisyros, Chiodini et al. (2001) for Vesuvio, D'Alessandro et al. (2009) for Pantelleria and Caliro et al. (2007) for La Solfatara. Vent temperatures of the investigated fumaroles are always close to the boiling point of liquid water. Exceptions are the Bocca Grande and Bocca Nuova fumaroles at La Solfatara, Campi Flegrei, whose outlet temperatures are significantly higher than 100 °C (Table 1).

3. Gas sampling, analysis and results

At Nisyros, samples were taken from Polybotes Mikros (PP), Stefanos (S), Alexandros (A) and Kaminakia (K) phreatic craters in September 2008, September 2009 and August 2010. The crater fumarole FC2 of Vesuvio was sampled in February 2010 and May 2011. During the latter campaign, three fumaroles from La Solfatara crater, Campi Flegrei, were probed, too [Bocca Grande (BG), Bocca Nuova (BN) and Pisciarelli]. At Pantelleria, gases were taken in July 2010 from Favara Grande fumarole. All these fumaroles were sampled