

## Article

# Stable Isotope Evaluation of Geothermal Gases from the Kızıldere and Tekke Hamam Geothermal Fields, Western Anatolia, Turkey

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**Abstract:** Volatiles transported from the Earth's interior to the surface through permeable faults provide insights on the gas composition of deep reservoirs, mixing and migration processes, and can also be applied as gas-geothermometer. Here, we present carbon ( $\delta^{13}\text{C}$ ), hydrogen ( $\delta^2\text{H}$ ) and nitrogen ( $\delta^{15}\text{N}$ ) isotopic data of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2$  from gas samples collected from the Kızıldere and Tekke Hamam geothermal fields, located along the eastern segment of the Büyük Menderes Graben, Turkey. The stable isotopic composition of carbon ( $\delta^{13}\text{C}$ ) ranges from +0.30 to +0.99‰ (PDB) for  $\text{CO}_2$  from Kızıldere and is slightly more variable (−0.95 to +1.3‰) in samples from Tekke Hamam. Carbon isotope data in combination with  $\text{CO}_2/{}^3\text{He}$  data reveal that ~97% (Tekke Hamam) to ~99% (Kızıldere) of  $\text{CO}_2$  derives from limestone sources, with the residual  $\text{CO}_2$  being magmatic in origin with no evidence for  $\text{CO}_2$  from organic sources. The slightly higher contribution of limestone-derived  $\text{CO}_2$  in Kızıldere, compared to Tekke Hamam can be attributed to the higher temperatures of the Kızıldere reservoir and resulting amplified fluid–limestone interaction, as well as helium depletion during phase separation for Kızıldere samples. In contrast to the carbon isotopic composition of  $\text{CO}_2$ , the  $\delta^{13}\text{C}$  values of methane from Kızıldere and Tekke Hamam are clearly distinct and vary between −23.6 and −20.8‰ for Kızıldere and −34.4 and −31.7‰ for Tekke Hamam, respectively. The  $\delta^2\text{H}$ – $\text{CH}_4$  composition is also distinct, measured as −126.7‰ for Kızıldere and −143.3‰ for Tekke Hamam.  $\text{CO}_2$ – $\text{CH}_4$  carbon isotope geothermometry calculations based on the isotopic fractionation of  $\delta^{13}\text{C}$  between the dominant component  $\text{CO}_2$  and the minor component  $\text{CH}_4$  reveals temperatures 20–40 °C and 100–160 °C higher than the bottom–hole temperatures measured for Tekke Hamam and Kızıldere, respectively. Based on the  $\text{CO}_2$ – $\text{CH}_4$  carbon isotope disequilibrium, unusual high methane concentrations of ~0.3 to 0.4 vol.-% and  $\text{CH}_4/{}^3\text{He}$ – $\delta^{13}\text{C}$ – $\text{CH}_4$  relationships we suggest thermal decomposition of late (Tekke Hamam) to over-mature (Kızıldere) organic matter and, to some extent, also abiogenic processes as principal source of methane. The  $\text{N}_2/{}^{36}\text{Ar}$  ratios of most samples reveal the existence of a non-atmospheric nitrogen component within the gas mixture issuing from both fields, in addition to a constant contribution of atmospheric derived nitrogen accompanied into the system via the meteoric recharge of the geothermal system. Based on the  $\delta^{15}\text{N}$  isotopic ratios (varying between −4.44‰ and 4.54‰), the non-atmospheric component seems to be a mixture of both sedimentary (crustal organic) and mantle nitrogen. The thick Pliocene sedimentary sequence covering the metamorphic basement is the likely major source for the thermogenic content of  $\text{CH}_4$  and crustal  $\text{N}_2$  gas content in the samples.

**Keywords:** Kızıldere geothermal field; Tekke Hamam geothermal field; source of gas; stable isotopes; thermogenic methane; nitrogen; carbon dioxide



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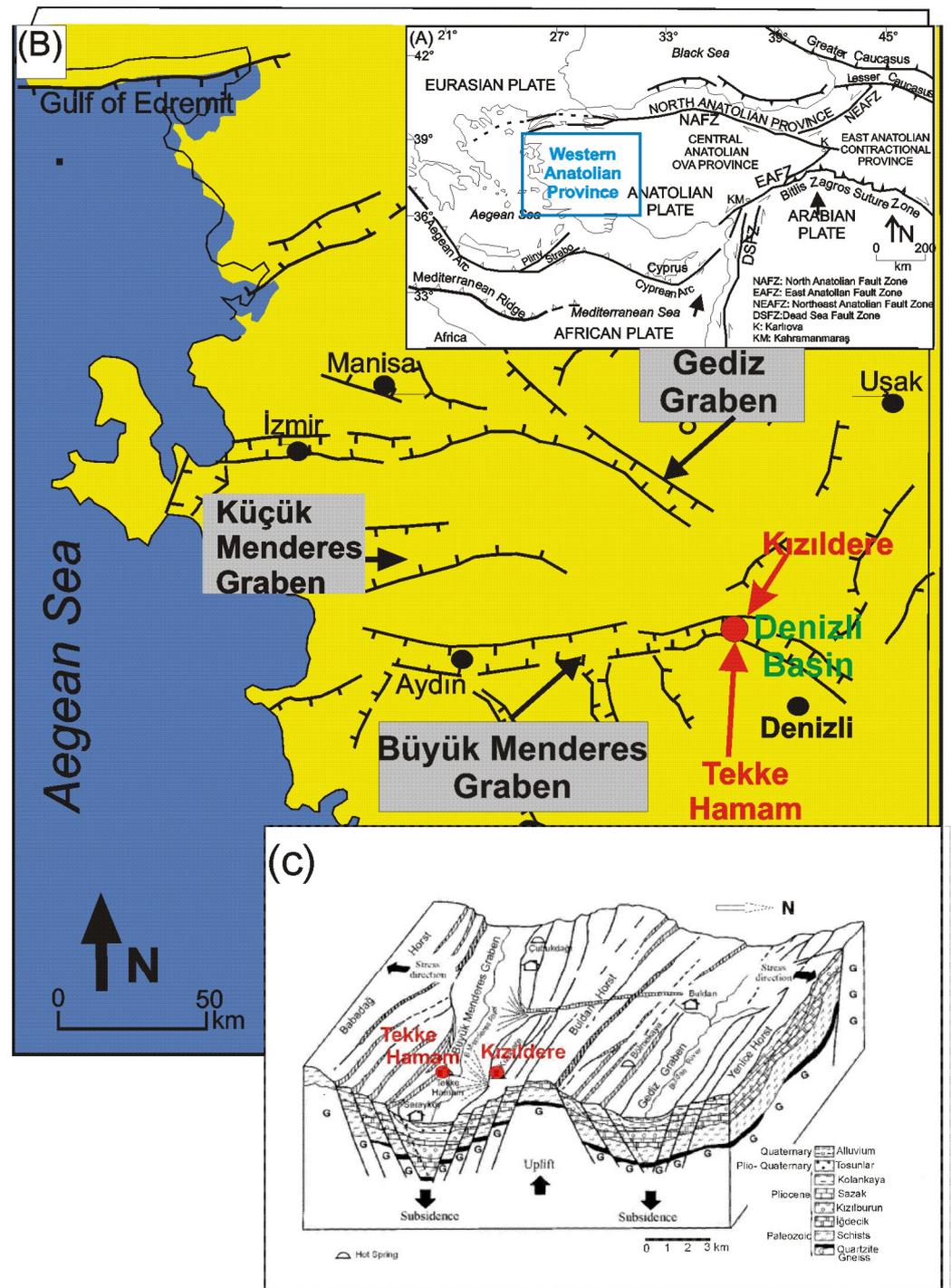
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## 1. Introduction

Stable isotopic evaluation of thermal fluids (water and/or gas), in the form of natural springs, mofettes, and well discharges, has been adopted as a major strategy for the delineation of (i) the possible sources of the fluids (mantle, crust, atmosphere), (ii) the accompanying physicochemical processes affecting the fluids (water-rock interaction, diffusion, isotopic fractionation), (iii) fluid migration along fault zones and the role of faults as conduit or barrier for fluid flow, and (iv) the deep geothermal reservoir temperature conditions within the subsurface. In this regard, several studies have carried out stable isotopic investigations in different geothermal settings throughout the world and presented the effective utilization of carbon ( $\delta^{13}\text{C}$ ), nitrogen ( $\delta^{15}\text{N}$ ), oxygen ( $\delta^{18}\text{O}$ ), and hydrogen ( $\delta^2\text{H}$ ), in addition to other parameters such as noble gases (e.g.,  $^3\text{He}$  and  $^4\text{He}$ ); gas compositional ratios ( $\text{CH}_4/\text{He}$ ,  $\text{CO}_2/{}^3\text{He}$ , and  $\text{N}_2/\text{Ar}$ ); and water chemistry [1–14].

Kızıldere and Tekke Hamam geothermal fields are two of the most significant high-enthalpy fields located along the eastern segment of the Büyük Menderes Graben in Western Anatolia (Figure 1). The Kızıldere geothermal field, situated along the northern flank of the graben, is a major field supplying fluids for both power generation and direct use applications, such as greenhouse heating, district heating, and  $\text{CO}_2$  gas production. The Kızıldere geothermal field currently houses two geothermal power plants: the Kızıldere power plant I in operation since 1984 (total installed capacity: 17.4 Mwe) and the Kızıldere Power plant II in operation since 2013 (installed capacity of 80 Mwe), both owned by the Zorlu Energy Group since the privatization of the field in 2008 [15]. A total of 44 production and reinjection wells have been drilled in the site since 1968, with depths varying between 370 and 2872 m. The reservoir temperatures vary between 155 °C and 245 °C [16,17]. The Tekke Hamam geothermal field, on the other hand, located along the southern flank of the graben, is a site full of gas discharging mofettes, mud pools, and thermal springs, which are mainly used for health tourism facilities [18].

Until now, several studies have concentrated on the geochemical evaluation of the thermal fluids emerging from the Kızıldere and/or Tekke Hamam geothermal sites [17,19–33], in addition to other fields located in the Western Anatolian Province. These studies were mainly concerned with (i) the delineation of the source of the fluids via the adoption of both chemical (major and trace element chemistry) and isotopic (stable and noble gas isotopes) parameters, (ii) the identification of the possible physicochemical processes that alter the pristine fluid composition within the subsurface and during their ascent to the surface, (iii) the real-time monitoring of the gases emerging from the sites and their possible correlations with the ongoing seismicity of the region, and (iv) the estimation of reservoir temperatures via the utilization of both chemical and gas geothermometers. In this study, we present stable isotopic data of  $\text{CO}_2$  ( $\delta^{13}\text{C}\text{-CO}_2$ ) and of two of the minor gas components issuing from Kızıldere and Tekke Hamam: methane and nitrogen ( $\delta^{13}\text{C}\text{-CH}_4$ ,  $\delta^2\text{H}\text{-CH}_4$  and  $\delta^{15}\text{N}\text{-N}_2$ ), in addition to gas compositional data of the samples, collected during two separate sampling campaigns conducted in November 2007 and August 2008. The aim of this study is to (i) identify possible sources of these gaseous components via the coupled evaluation of  $^{13}\text{C}\text{-}^2\text{H}\text{-}^{15}\text{N}$  isotopic compositions and mixed elemental–nuclide gas ratios (such as  $\text{CO}_2/{}^3\text{He}$ ,  $\text{N}_2/{}^{36}\text{Ar}$ ,  $\text{CH}_4/{}^3\text{He}$ , and  $\text{CH}_4/\text{C}_2\text{H}_6+\text{C}_3\text{H}_8$ ); (ii) estimate the possible reservoir temperature based on isotope geothermometry calculations ( $\delta^{13}\text{C}$  geothermometry for  $\text{CO}_2\text{-CH}_4$ ); and (iii) compare the findings with previous geothermometry estimations and the observed bottom–hole temperatures.



**Figure 1.** (A) Tectonic Map of Turkey, modified from [18], (B) simplified map of major structural elements in Western Anatolian Province, including the locations of the Kızıldere and Tekke Hamam geothermal fields, and (C) simplified diagram showing the geological framework of the fields, modified from [20].

## 2. Geological Framework

The Western Anatolian Province (WAP) of Turkey is a region of intense seismic activity that constitutes one of the most important structural features representing the neotectonics period of Turkey [34–36]. Located within the Alpine–Mediterranean belt, the WAP represents a site of horst–graben structures formed in relation to the N–S-directed continental extension prevailing in the region since at least the latest Oligocene–Early Miocene [37]. The high-angle boundary fault network of the horst–graben structures in WAP, in addition to the Neogene–Quaternary volcanism, leads to the widespread occurrences of geothermal manifestations, located mostly within moderate to high enthalpy geothermal fields.

This study focuses on two of the most significant geothermal fields situated in the WAP: the Kızıldere and Tekke Hamam high enthalpy geothermal fields, located west of the city of Denizli in the Denizli Basin, which also hosts several other geothermal fields (e.g., Pamukkale, Yenice, Gölemezli, and Karahayit) of moderate-to-high enthalpy [38,39]. The Denizli Basin, a result of extensional tectonics characterizing the area, is approximately 70 km in length and 50 km in width, mainly located at the junction of the E–W trending Büyük Menderes Graben and the nearly NW–SE trending Gediz graben, two major tectonic remnants of the extension prevailing in the area [40–42]. Geothermal activity within the Denizli Basin mainly manifests itself along the NW–SE trending normal fault patterns, which act as major circulation pathways for the deep rising thermal fluids within the horst–graben-related fault–fracture network, heated by shallow magma bodies within the thinned crustal lithosphere of the extensional regime [43].

The Kızıldere and Tekke Hamam geothermal fields share the same lithostratigraphic sequences. The basement rocks in the area are represented by Paleozoic or older Menderes Massif Metamorphics, which is defined as a well developed metamorphic core complex composed of a crystalline core and a metasedimentary cover series [36,44–47]. The Precambrian to early Paleozoic core of the massif, which forms the basement, is mainly composed of augen gneiss, migmatites, metagranite, gabbro, and medium to high grade metamorphic schists. The cover is represented by two major Paleozoic units: (i) the Ortaköy formation, composed of mainly schist with garnet, muscovite, and biotite, and (ii) the İğdecik formation, which is mainly an alternation of marble, micaschist, and quartzite. The metamorphic complex is overlain unconformably by the Pliocene fluvial-lacustrine sedimentary formations, which are divided into four major rock series, namely from bottom to top: the Kızılburun (alternation of conglomerate, sandstone, and claystone); Sazak (limestone, marl, siltstone, and claystone alternation); Kolankaya (alternation of marl, sandstone, and siltstone); and Tosunlar (conglomerate, sandstone, and claystone) formations [40,42,48]. Quaternary alluvium, terrace deposits, and travertines cover the Pliocene sedimentary formations. Three major levels act as reservoirs in the field: (i) the low-lying gneiss levels of the Menderes massif have been identified as the deepest reservoir in the field, (ii) the intensely fractured and faulted İğdecik formation acts as a major reservoir feeding most of the wells drilled in the area, and (iii) the limestone levels of the Sazak formation act as the shallow reservoir with a rather limited lateral continuity [40,49]. The horst–graben of the area constitute the major recharge zones, with the graben bounding fault zones providing the pathways for the recharge of the thermal reservoirs [20,50].

## 3. Gas Sampling and Analysis

Gas samples were collected from the Tekke Hamam and Kızıldere geothermal fields during two sampling campaigns. Stable isotope analysis of carbon dioxide, methane, and nitrogen ( $\delta^{13}\text{C-CO}_2$ ,  $\delta^{13}\text{C-CH}_4$ ,  $\delta^2\text{H-CH}_4$ , and  $\delta^{15}\text{N-N}_2$ ) was conducted on a total of five pool samples from Tekke Hamam (Umut-1 (a,b), Umut-2, Umut-4, and Umut-5) and four production wells from Kızıldere (KD-6, KD-13 (a,b), and KD-15), in addition to the chemical composition analysis. The gas samples from the Tekke Hamam geothermal site were collected as free gas phase utilizing an inverted funnel dipped inside the bottom of the pools to capture the bubbles released there. Gas sampling in Kızıldere, on the other hand, was performed after separation of the wellhead fluid into a gas and a water phase by means

of a steam separator. Copper tubes, as well as glass tubes equipped with two stopcocks, served as sample devices. The gas was allowed to flow through the sampling devices at least for 10 min and the sample volume was replaced at least 20 times by formation gas before the sample was collected. A water trap at the sample outlet acted as a unidirectional no-return valve to minimize air contamination.

The total gas analysis was performed with a quadrupole mass spectrometer (Pfeiffer Omnistar) for N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>S, He, and Ar with detection limits of 1 part per million by volume for H<sub>2</sub>, CH<sub>4</sub>, and Ar, and 10 ppmv for O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub>. Isobaric interferences with oxygen on the diagnostic mass over charge ratios [ $m/z$ ] = 32, 33, and 34 increase the detection limit for H<sub>2</sub>S to values of 200 ppmv [29]. Hydrocarbons were analyzed with a gas chromatograph (SRI- 8610) equipped with a flame ionization detector. Detection limits for the hydrocarbons are 1 ppmv. The stable isotope measurements on CH<sub>4</sub> and N<sub>2</sub> (<sup>13</sup>C, <sup>2</sup>H, <sup>15</sup>N) were conducted via isotope ratio mass spectrometry. Stable isotope measurements were carried out at INGV-Palermo (Istituto Nazionale di Geofisica e Vulcanologia—Sezione di Palermo) laboratories. Stable carbon and hydrogen isotope compositions of CH<sub>4</sub> and CO<sub>2</sub> were measured using a Delta Plus XP IRMS equipped with a Thermo TRACE GC interfaced with Thermo GC/C III and Thermo GC/TC. <sup>13</sup>C/<sup>12</sup>C ratios are reported as  $\delta^{13}\text{C}$  values ( $1\sigma = 0.1\text{‰}$ ) against VPDB standard and <sup>2</sup>H/<sup>1</sup>H ratios are reported as  $\delta^2\text{H}$  values ( $1\sigma = 1\text{‰}$ ) against VSMOW standard. Nitrogen isotope composition ( $\delta^{15}\text{N}$ ) was determined by using a Delta Plus XP stable isotope ratio mass spectrometer coupled with a Thermo TRACE Gas Chromatograph and a Thermo GC/C III interface, following the method proposed in [51].  $\delta^{15}\text{N}$  values ( $1\sigma = 0.2\text{‰}$ ) are reported against Air.

## 4. Results and Discussions

### 4.1. Relative Concentrations and Chemical Composition of the Gas Samples

The chemical composition of samples taken from the Kızıldere and Tekke Hamam geothermal fields during November 2007 and September 2008 are given in Table 1. The main component of the gas samples taken from the Kızıldere and Tekke Hamam geothermal fields is represented by CO<sub>2</sub>, changing between 96.1 and 98.4 vol.% for Kızıldere and 84.4 and 96.9 vol.% for Tekke Hamam geothermal field. Other gas components, from the highest to the least are: N<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub>, O<sub>2</sub>, Ar, H<sub>2</sub>, and He. CH<sub>4</sub> is a minor component varying around 1620 and 4300 ppmv for Kızıldere and 2844 and 4496 ppmv for Tekke Hamam. The nitrogen content varies between 1.09 and 2.91 vol.% for Kızıldere and between 1.63 and 12 vol.% for Tekke Hamam, while oxygen varies between 0.19 and 0.72 vol.% for Kızıldere and between 0.16 and 3.14 vol.% for Tekke Hamam, suggesting that air contamination is negligible in most of the samples. All argon contents are much lower than the air value of 0.934%, while He abundances are ranging from 3.8 to 4.8 ppmv for Kızıldere and from 4.5 to 5.6 ppmv for Tekke Hamam, similar to that of air (5.24 ppmv, [52]). All of the gas samples, except for Umut-4a, have low amounts of O<sub>2</sub> (<1 vol.%), which points to only little atmospheric contamination during sampling for most of the samples. Umut-4a sample, on the other hand, with its high O<sub>2</sub> content, accompanied by N<sub>2</sub>/O<sub>2</sub> ratio similar to that of air (N<sub>2</sub>/O<sub>2</sub><sub>air</sub>: 3.727) depicts the presence of air contamination. Based on the gas chromatographic analysis of the light hydrocarbons, the CH<sub>4</sub>/(C<sub>2</sub>H<sub>6</sub> + C<sub>3</sub>H<sub>8</sub>) ratios vary between 101 and 860 for Kızıldere and between 36 and 43 for Tekke Hamam. The N<sub>2</sub>/Ar ratios vary between 106 and 255 for Kızıldere and between 82 and 107 for Tekke Hamam, both fields exhibiting N<sub>2</sub>/Ar ratios exceeding the value characteristic for atmospheric contributions (N<sub>2</sub>/Ar~84; [53]).

**Table 1.** Chemical compositions of gas samples from Kızıldere and Tekke Hamam geothermal fields.

	Sample	Sampling Date	Ar (ppmv)	CH <sub>4</sub> (ppmv)	CO <sub>2</sub> (vol.%)	H <sub>2</sub> (ppmv)	He (ppmv)	N <sub>2</sub> (vol.%)	O <sub>2</sub> (vol.%)	Kr (ppmv)	H <sub>2</sub> S (ppmv)	CH <sub>4</sub> (ppmv)	C <sub>2</sub> H <sub>6</sub> (ppmv)	C <sub>3</sub> H <sub>8</sub> (ppmv)	CH <sub>4</sub> /[C <sub>2</sub> H <sub>6</sub> + C <sub>3</sub> H <sub>8</sub> ]	N <sub>2</sub> /Ar
Kızıldere	KD-6a	November 2007	69	2750	98.4	30	3.8	1.09	0.19	0.9	12	1620	11	5	101	158
	KD-13b	September 2008	274	2540	96.1	176	4.1	2.91	0.72	1.1	26	2962	7	3	296	106
	KD-15a	November 2007	49	4090	98.1	26	4.8	1.25	0.18	1.1	39	4301	4	1	860	253
Tekke Hamam	Umut-1a	November 2007	153	3390	96.9	103	5.3	1.63	0.16	1.1	9140	4496	80	45	36	107
	Umut-2a	November 2007	207	3700	97.2	27	5.3	1.92	0.16	1.0	3430	3731	65	40	36	92
	Umut-4a	November 2007	1330	2680	84.4	20	4.5	12	3.14	0.9	n.d.	2844	37	33	41	90
	Umut-5b	September 2008	288	4100	96.2	38	5.6	2.37	0.16	1.1	8770	3910	55	36	43	82

n.d.= not detected.

#### 4.2. Isotopic Composition of the Gas Samples

The isotopic composition of CO<sub>2</sub> ( $\delta^{13}\text{C-CO}_2$ ), CH<sub>4</sub> ( $\delta^{13}\text{C-}\delta^2\text{H-CH}_4$ ) (expressed as per mil (‰) vs. PDB, Pee Dee Belemnite) and N<sub>2</sub> ( $\delta^{15}\text{N-N}_2$ ) (expressed as per mil (‰) vs. air), along with the gas ratios to the other components of the gas mixture (CO<sub>2</sub>/<sup>3</sup>He, CH<sub>4</sub>/<sup>3</sup>He, and N<sub>2</sub>/<sup>36</sup>Ar) are presented in Table 2. A total of 6 samples were analyzed for  $\delta^{13}\text{C}$  on carbon dioxide and methane, along with a total of 9 samples analyzed for  $\delta^{15}\text{N-N}_2$ . The  $\delta^2\text{H}$  analysis of CH<sub>4</sub>, on the other hand, was conducted for two samples (KD-13a and Umut-4a).

**Table 2.** Isotopic composition of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> of gas samples from Kızıldere and Tekke Hamam, along with their CH<sub>4</sub>/<sup>3</sup>He, CO<sub>2</sub>/<sup>3</sup>He, and N<sub>2</sub>/<sup>36</sup>Ar ratios.

	Sample	Sampling Date	$\delta^{15}\text{N}$ (‰ vs. Air)	$\delta^{13}\text{C-CO}_2$ (‰ vs. PDB)	$\delta^{13}\text{C-CH}_4$ (‰ vs. PDB)	$\delta\text{D-CH}_4$ (‰ vs. PDB)	CH <sub>4</sub> / <sup>3</sup> He	* CO <sub>2</sub> / <sup>3</sup> He	N <sub>2</sub> / <sup>36</sup> Ar
Kızıldere	KD-6a	November 2007	4.23	0.34	−20.8		$5.31 \times 10^8$	$1.90 \times 10^{11}$	$4.97 \times 10^4$
	KD-13a	November 2007	4.54	0.30	−23.2	−126.7	$7.42 \times 10^8$	$2.86 \times 10^{11}$	$6.27 \times 10^4$
	KD-13b	September 2008	−2.61				$7.42 \times 10^8$ *	$2.86 \times 10^{11}$ +	$2.91 \times 10^4$
	KD-15a	November 2007	−4.44	0.99	−23.6		$1.23 \times 10^9$	$2.95 \times 10^{11}$	$4.32 \times 10^4$
Tekke Hamam	Umut-1a	November 2007	2.75				$3.52 \times 10^8$	$1.01 \times 10^{11}$	$3.20 \times 10^4$
	Umut-1b	September 2008	1.80	−0.95	−34.4		$3.52 \times 10^8$ *	$1.01 \times 10^{11}$ +	$2.65 \times 10^4$
	Umut-2a	November 2007	1.16	-	-			$1.11 \times 10^{11}$	$2.36 \times 10^4$
	Umut-4a	November 2007	0.960	−0.74	−31.7	−143.3	$2.58 \times 10^8$	$8.14 \times 10^{10}$	$2.28 \times 10^4$
	Umut-5b	September 2008	−0.702	1.3	−32.0		$3.48 \times 10^8$	$8.56 \times 10^{10}$	$2.46 \times 10^4$

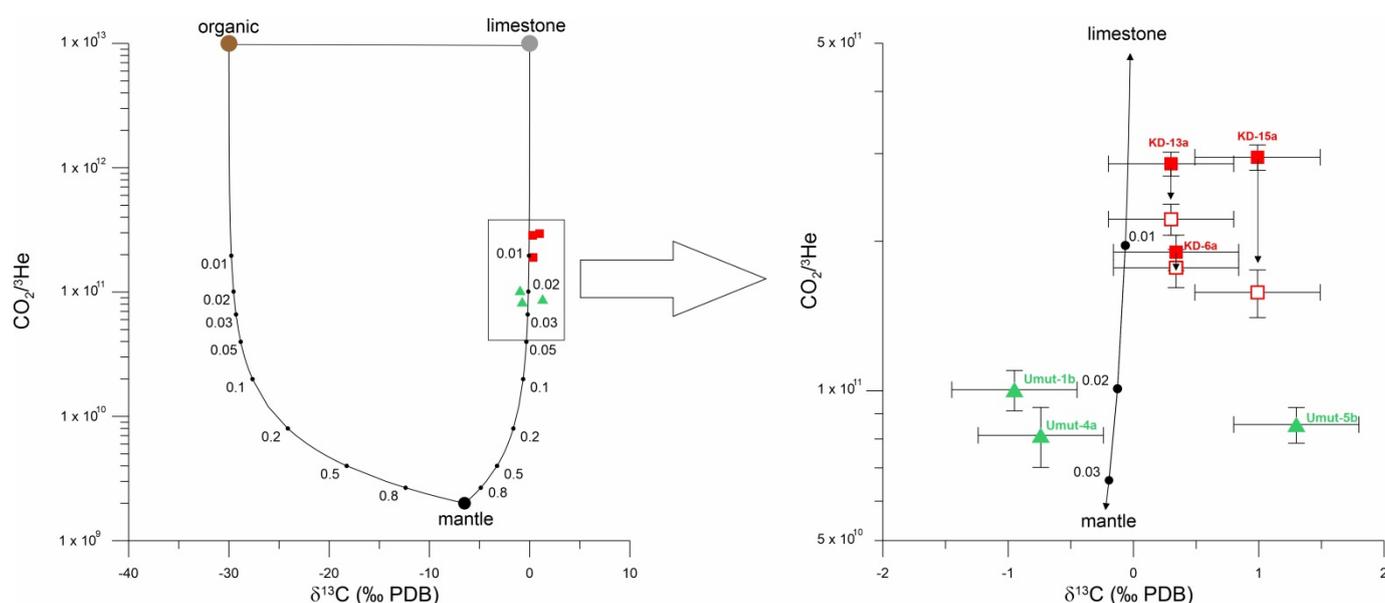
\* Data taken from [29]. + Calculated by using KD-13a, respectively, Umut-1a chemical composition data, assuming that the chemical and noble gas composition of samples from the same location does not change significantly over time.

The  $^{13}\text{C}$  isotope values of  $\text{CO}_2$  fall between 0.30 and 0.99 (‰ VPDB) for the samples from the Kızıldere geothermal field and between  $-0.95$  and  $1.30$  (‰ VPDB) for Tekke Hamam. The  $\delta^{13}\text{C}$  isotope ratio of  $\text{CH}_4$  varies between  $-23.6$  and  $-20.8$ ‰ for Kızıldere and between  $-34.4$  and  $-31.7$ ‰ for Tekke Hamam. The  $\delta\text{D}$  values of  $\text{CH}_4$  for sample KD-13a from Kızıldere is  $-126.7$ ‰ and for Tekke Hamam sample Umut-4a is  $-143.3$ ‰. The  $\delta^{15}\text{N}$  isotope values vary broadly between  $-4.44$  and  $4.54$ ‰ for Kızıldere and narrowly for Tekke Hamam between  $-0.702$  and  $2.75$ ‰. The measured  $\text{CO}_2/{}^3\text{He}$  ratios from both fields are greater than the average mantle value of  $2 \times 10^9$  [29]. The  $\text{CH}_4/{}^3\text{He}$  ratios are above values characteristic for abiogenic gases ( $\text{CH}_4/{}^3\text{He} \sim 10^6$ ; [54]). The  $\text{N}_2/{}^{36}\text{Ar}$  ratios are mostly greater than that of air ( $2.47 \times 10^4$ , [55]).

#### 4.3. Origin of $\text{CO}_2$

It is generally known that gas emanations in tectonically or volcanically active areas are typically characterized by carbon dioxide ( $\text{CO}_2$ ) as the main gaseous component. The  $\text{CO}_2$  originates in different proportions from a magmatic source, as well as from the interaction of geothermal fluids or magma with the surrounding host rock. Host rocks with potential for  $\text{CO}_2$  release are limestone and sediments enriched in organic material.  $\text{CO}_2$  deriving from these three sources (magmatic, limestone, and organic-rich sediments) shows distinctly different  $\delta^{13}\text{C}$  isotopic composition, with  $\delta^{13}\text{C}$  values (all values relative to PDB, average values in brackets) ranging from  $-20$ ‰ to  $-40$ ‰ ( $-30$ ‰) for organic-rich sediments,  $-9$ ‰ to  $-4$ ‰ ( $-6.5$ ‰) for MORB and  $-2$ ‰ to  $+2$ ‰ ( $\pm 0$ ‰) for limestone [56]. However, in order to characterize and quantify mixtures of  $\text{CO}_2$  from these reservoirs, a further, additional parameter is required, in the composition of which the reservoir fluids also must differ. For this purpose, [56] introduced the  $\text{CO}_2/{}^3\text{He}$  ratio as additional proxy with  $\text{CO}_2/{}^3\text{He} = 1\text{--}2 \times 10^9$  for mantle-derived  $\text{CO}_2$  as typically observed in MORB and  $\sim 10^{13}$  for  $\text{CO}_2$  from crustal reservoirs (organic-rich sediment, limestone). It should be noted that the  $\text{CO}_2/{}^3\text{He}$  ratio for the limestone endmember in the study area is probably in the range of  $2 \times 10^{12}$ , as pointed out by [29], rather than  $10^{13}$ . However, for ease of comparison with other data sets, the subsequent estimates are based on an assumed  $\text{CO}_2/{}^3\text{He}$  ratio endmember composition for the limestone of  $10^{13}$ .

Several processes can alter the  $\text{CO}_2/{}^3\text{He}$  ratio in hydrothermal fluids. Phase separation may influence the  $\text{CO}_2$  [8,57] or the helium component, where the higher soluble  $\text{CO}_2$  preferentially remains in the liquid phase, whereas the less-soluble helium is preferentially separated into the gas phase. [29] interpreted the low helium concentrations (0.7–2.2 ppmv) and low helium isotopic ratios ( ${}^3\text{He}/{}^4\text{He} = 0.96\text{--}2.06$  Ra) of Kızıldere geothermal fluids, both of which showing a negative correlation to temperature by tapping of a remaining liquid phase after phase separation and the consequent depletion of helium in the liquid phase. Other processes that have the potential to alter the  $\text{CO}_2/{}^3\text{He}$  ratio in hydrothermal fluids are abiogenic reduction of  $\text{CO}_2$  to  $\text{CH}_4$  in the presence of reducing agents [58,59], and calcite precipitation [8,60]. Hydrothermal phase separation involving  $\text{CO}_2$ , and calcite precipitation may also impact on the  $\delta^{13}\text{C}$  isotopic composition. The  $\text{CO}_2/{}^3\text{He}$  ratios of fluid samples from Kızıldere range from  $1.8$  to  $9.2 \times 10^{11}$  and from  $0.7$  to  $1.1 \times 10^{11}$  for fluid samples from Tekke Hamam [29], higher than the average mantle value of  $\sim 2 \times 10^9$  [61]. Kızıldere samples cover a wider range of  $\text{CO}_2/{}^3\text{He}$  ratios, while ratios from Tekke Hamam are lower and more uniform. The  $\delta^{13}\text{C}$  isotope values of  $\text{CO}_2$  fall between 0.30 and 0.99 (‰ VPDB) for the samples from the Kızıldere geothermal field (wells KD -6, KD-13 and KD-15) and between  $-0.95$  and  $+1.30$  (‰ VPDB) for Tekke Hamam (mofettes Umut-1, -4 and -5), respectively. In a  $\text{CO}_2/{}^3\text{He}$  vs.  $\delta^{13}\text{C}\text{-CO}_2$  diagram (Figure 2), the data of our study plot on or close to a mixing hyperbola between magmatic  $\text{CO}_2$  and  $\text{CO}_2$  from interaction of geothermal fluids with limestone. There is no evidence for contributions of  $\text{CO}_2$  from organic-rich sediments. The diagram indicates that  $\sim 97\%$  of  $\text{CO}_2$  from samples from Tekke Hamam and  $\sim 99\%$  of  $\text{CO}_2$  from Kızıldere samples derives from fluid–limestone interactions, and only a small contribution is mantle-derived.



**Figure 2.** Diagram of  $\text{CO}_2/{}^3\text{He}$  (data from 29) vs.  $\delta^{13}\text{C}$  ( $\text{CO}_2$ , ‰ PDB) including organic, limestone and magmatic endmembers (see text for values) from [56] and mixing hyperbolas. Kızildere samples: red squares, Tekke Hamam samples: green triangles. Right site: close up showing Kızildere samples corrected for He phase separation effects (open squares). See text for details.

Our findings are in good agreement with [62] who proposes carbonate–magma interaction as dominant process that accounts for  $\text{CO}_2$  in Kızildere geothermal fluids. Ref. [27] suggested that 73–97% of  $\text{CO}_2$  in gas and water samples from western Anatolia derives from carbonates. Similar is reported by [63] from central Anatolia with a contribution of  $\text{CO}_2$  from fluid–limestone interaction of more than 90%.

Two different processes may account for the slightly different  $\text{CO}_2/{}^3\text{He}$  ratios observed in Kızildere and Tekke Hamam geothermal fluids: depletion of helium in the liquid phase after phase separation, as reported by [29] for Kızildere samples, and the higher fluid temperatures at Kızildere which result in amplified fluid–limestone interaction. To estimate the relevance of the first process, a correction to the  $\text{CO}_2/{}^3\text{He}$  ratio was applied to the Kızildere samples by calculating  ${}^3\text{He}$  concentrations based on an assumed original  ${}^3\text{He}/{}^4\text{He}$  ratio of 2.2 Ra (Ra = atmospheric  ${}^3\text{He}/{}^4\text{He}$  ratio), as proposed by [29] rather than the observed  ${}^3\text{He}/{}^4\text{He}$  ratios in Kızildere (0.96–2.06 Ra, 29). The such-like corrected  $\text{CO}_2/{}^3\text{He}$  ratios for Kızildere samples are between 1.6 and  $2.2 \times 10^{11}$  ( $1.5\text{--}4.7 \times 10^{11}$  for the entire dataset published by 29) which is still higher than the  $\text{CO}_2/{}^3\text{He}$  ratios of Tekke Hamam fluid samples ( $0.7\text{--}1.1 \times 10^{11}$ ). Therefore, we assume that the higher temperature of geothermal fluids in Kızildere reservoir leads to increased extraction of  $\text{CO}_2$  from the limestone source.

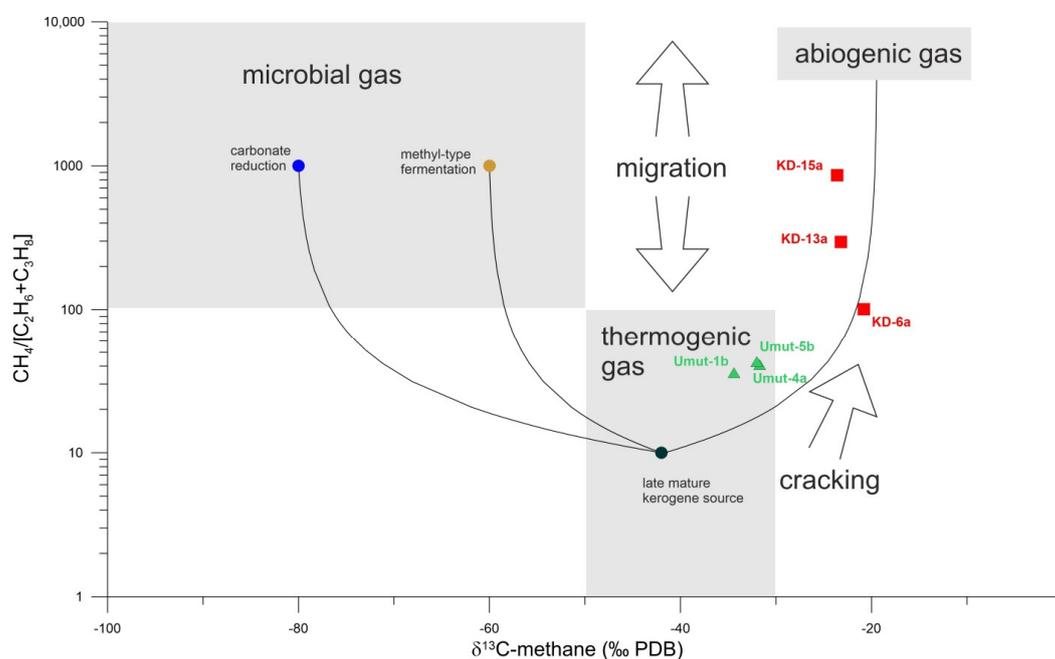
#### 4.4. Origin of Hydrocarbons

In hydrothermal fluids, methane and heavier hydrocarbons in general may derive from two possible sources: biogenic or abiogenic [64]. Biogenic methane is basically produced by microbial or thermal degradation of organic matter [65–67]. Microbial methane production such as those from wetlands and rice paddies, is peaking at temperatures lower than 50 °C, and can be related to several processes, including fermentation of acetate, dominant in freshwater sediments, and reduction of  $\text{CO}_2$  dominant in sulfate-free zone of marine sediments [68]. The thermogenic originated methane is related to the decomposition of organic matter within sediments at temperatures peaking around 150 °C [69,70]. Abiogenic methane, on the other hand, which is methane that is not directly related to an organic precursor, generally derives from sources and processes such as (i) migration from the mantle or magmatic bodies, (ii) metamorphism of graphite bearing

carbonate rocks, (iii) iron carbonate decomposition, (iv) Fischer–Tropsch-type reactions, (v) abiogenic reduction of CO<sub>2</sub> in volcanic-hydrothermal systems, and (vi) high temperature hydrothermal serpentinization of mafic and ultramafic rocks [7,59,60,71–74]. Except for (i), all abiogenic reactions require hydrogen as reducing agent.

The stable isotopic composition of methane ( $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$ ), along with the chemical composition of higher mass hydrocarbons (e.g., C<sub>2</sub>H<sub>6</sub> (ethane), C<sub>3</sub>H<sub>8</sub> (propane), C<sub>4</sub>H<sub>10</sub> (butane)) and their respective ratios (C<sub>1</sub>/[C<sub>2</sub> + C<sub>3</sub>], C<sub>1</sub>: CH<sub>4</sub>; C<sub>2</sub>: C<sub>2</sub>H<sub>6</sub>; C<sub>3</sub>: C<sub>3</sub>H<sub>8</sub>), has been used as a valuable tool for the elucidation of the possible sources of methane [67]. Typical  $\delta^{13}\text{C}$  values for microbial methane vary in a wide range between  $-110$  and  $-60\%$  [67,75] whereas the C<sub>1</sub>/[C<sub>2</sub> + C<sub>3</sub>] ratio exhibit values greater than 1000 [76]. Thermogenically produced methane is characterized by more enriched  $\delta^{13}\text{C}$  isotopic values, typically changing between  $-50$  and  $-20\%$ , with C<sub>1</sub>/[C<sub>2</sub> + C<sub>3</sub>] ratio lower than 100 [65,67,77]. In contrast to biogenic methane, abiogenic methane, emanating from sediment free mid ocean ridge systems were suggested to have enriched  $\delta^{13}\text{C}$  values ( $>-24\%$  V-PDB), and hydrocarbon concentration ratios higher than 1000 [78–81] due to exchange with mantle carbon at high temperatures.

The CH<sub>4</sub> content of the Kızildere and Tekke Hamam gases generally vary between 1600 and 4500 ppmv which is very low compared to the dominant CO<sub>2</sub> characteristic of the gases (reaching up to 98 vol.%), but surprisingly high compared to typical high-enthalpy geothermal gases of magmatic origin. The relatively high content of CH<sub>4</sub> and C<sub>1</sub>/[C<sub>2</sub> + C<sub>3</sub>] values observed in most of the gas samples from both fields were previously attributed to an input of possibly thermogenic methane [29], given the fact that methane from pure magmatic gases is very low, almost free of methane [82]. The  $\delta^{13}\text{C}$  isotopic composition, together with the gas compositional ratio of hydrocarbons C<sub>1</sub>/[C<sub>2</sub> + C<sub>3</sub>], also underpins the organic nature for the source of methane (Tables 1 and 2). Figure 3 shows the distribution of the gas samples on a modified so-called “Bernard diagram”.



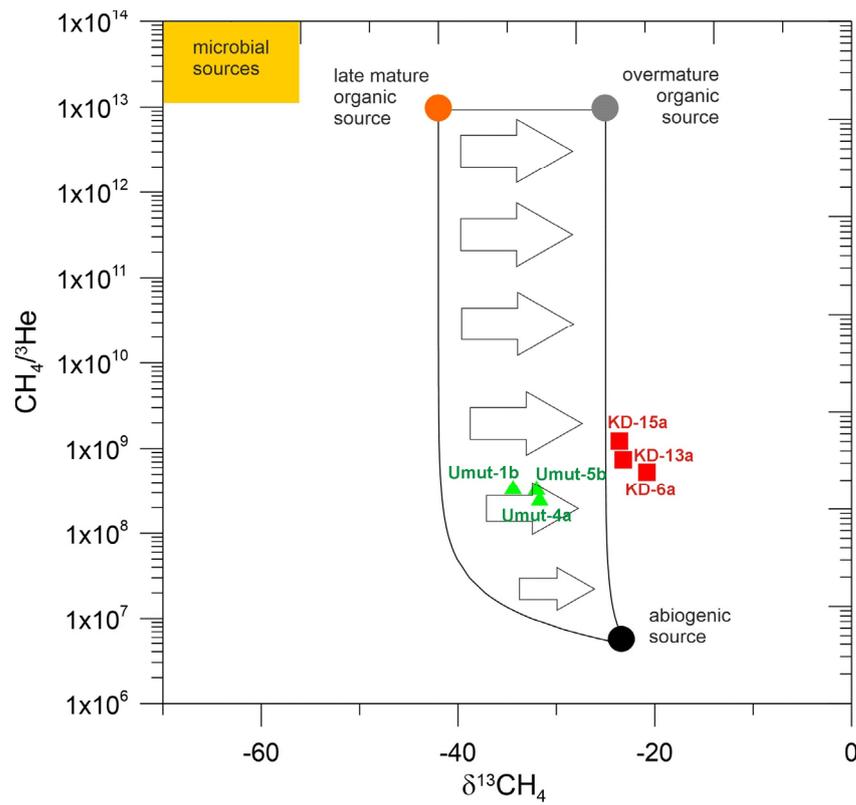
**Figure 3.** CH<sub>4</sub>/[C<sub>2</sub>H<sub>6</sub> + C<sub>3</sub>H<sub>8</sub>] vs.  $\delta^{13}\text{C}$  diagram (“Bernard-diagram”) including mixing lines of hydrocarbons from late mature kerogene source (black circle) with microbial gas from carbonate reduction (blue circle) and methyl-type fermentation (brown circle, values from [67]), as well as mixing with abiogenic hydrocarbons. Tekke Hamam samples plot in the thermogenic field, but show

indication for mixing with abiogenic gas or with gas from secondary cracking. In comparison, samples from Kızıldere are more depleted in ethane and propane and  $\delta^{13}\text{C}$ -methane is isotopically heavier, demonstrating a higher contribution of the abiogenic/secondary cracking component.

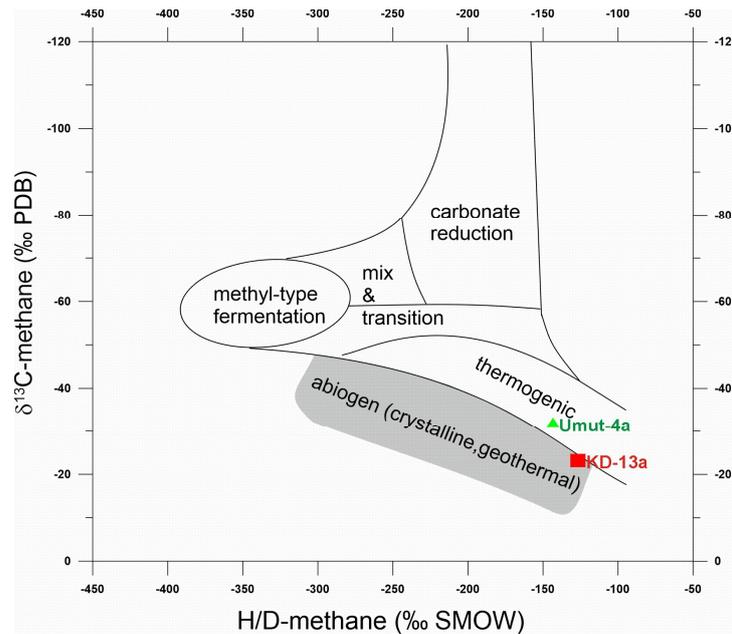
As can be seen from the diagram, both Kızıldere and Tekke Hamam samples localize along the thermogenic methane field ( $\delta^{13}\text{C}$  isotopic values changing between  $-34$  and  $-20\text{‰}$ ), possibly suggesting high temperature gas release from organic rich sediments. The possibility of a microbial methane source was previously eliminated based on the high amounts of higher mass hydrocarbons ( $\text{C}_2+$ ), as these species are not characteristic of microbial activity, and therefore cannot be observed in high temperature systems. The diagram also presents a different distribution for the geothermal fields. The samples from Tekke Hamam have hydrocarbon ratios varying tightly around 40 ( $\text{C}_1/\text{C}_2 + \text{C}_3 < 100$ ), and  $\delta^{13}\text{C}$  values more to the negative side, which is in conformity with methane produced via thermal degradation of organic matter. The gas samples from Kızıldere, on the other hand, display a scattered distribution of hydrocarbon gas ratio (mostly above 100), with  $\delta^{13}\text{C}$  values lying along the transition zone from thermogenic to abiogenic origin. The wide scatter in the hydrocarbon ratio probably suggests the existence of additional temperature dependent secondary processes such as (i) cracking of long chain hydrocarbons and/or (ii) enhanced production of methane from overmature kerogen at high temperatures, as was suggested in previous studies [29,83], both of which would also affect the  $\delta^{13}\text{C}$  isotopic values of methane towards more heavy values. [84] report methane concentrations (0.013–2.53 vol.-% with average value of 0.82 vol.-%) and  $\delta^{13}\text{C}$  isotopic composition of methane ( $-40$  to  $-26.8\text{‰}$  PBD) from the Acoculco caldera geothermal system in Mexico, similar to the values of the present study, and attributes these findings with a deep thermogenic origin of methane. [63] found up to 0.1 vol.-% methane with  $\delta^{13}\text{C}$  values of  $-24\text{‰}$  (PBD) in geothermal gas emanations in Central Anatolia, which the authors also interpreted with a thermogenic origin.

The heavier  $\delta^{13}\text{C}$  isotopic values, together with hydrocarbon ratios greater than 100, however, can also be explained by an abiogenic component (e.g., 58,59) that can be evaluated based on the correlation between  $\delta^{13}\text{C}$ - $\text{CH}_4$  isotopic ratios and the elemental ratio of  $\text{CH}_4$  to  $^3\text{He}$ , which is a major tracer for fluids from the mantle [85]. Figure 4 shows the relationship between  $\delta^{13}\text{C}$ - $\text{CH}_4$  and  $\text{CH}_4/{}^3\text{He}$  ratios, which was used in studies before [54,86]. Thermogenic and abiogenic methane have been assigned values of  $\text{CH}_4/{}^3\text{He}$  in the range of  $10^{13}$  and  $5 \times 10^6$ , respectively [54]. The samples from our study reveal  $\text{CH}_4/{}^3\text{He}$  ratios between  $5 \times 10^8$  and  $1.3 \times 10^9$  for Kızıldere fluids and somewhat lower values ( $2\text{--}3 \times 10^8$ ) for those of Tekke Hamam, respectively. Both Kızıldere and Tekke Hamam gases display mixture between two possible end members: thermogenic methane from organic sources of different maturity, and abiogenic methane. The comparison of  $\delta^{13}\text{C}$  and H/D values of methane (Figure 5) show similar behavior. Given that the  $\text{CO}_2$  content in Western Anatolian thermal fluids have been shown to be a mixture of dominant crustal (limestone) and minor mantle contribution, based on the  $\delta^{13}\text{C}$ - $\text{CO}_2$  and  $\text{CO}_2/{}^3\text{He}$  ratios of gases (see Figure 2), it is possible that the  $\text{CH}_4$  content can also be represented by a mixture of a dominant crustal (thermogenic) and minor mantle (abiogenic) source.

Based on the geodynamic setting of our study area, the organic source material of thermogenic methane is most likely hosted in the thick Pliocene sedimentary cover. The minor abiogenic origin for methane, on the other hand, can be related to either (i) mantle source (contributing up to  $\sim 4\%$  of total- $\text{CO}_2$  [27] and 35% of total-He [29] gas inventories in Western Anatolian fluids), or (ii) inorganic reactions, such as Fischer–Tropsch.



**Figure 4.** Correlation diagram between  $\delta^{13}\text{C}$  of methane and  $\text{CH}_4/{}^3\text{He}$  ratios, modified from [54].  $\delta^{13}\text{C}$  values of methane from kerogen endmembers with different maturities from [68],  $\delta^{13}\text{C}$  values of abiogenic methane and  $\text{CH}_4/{}^3\text{He}$  ratios from [54]. Kızıldere samples: red squares. Tekke Hamam samples: green triangles. Both Tekke Hamam and Kızıldere sample show mixing between abiogenic and thermogenic methane. Tekke Hamam samples contain methane from a less mature organic source. Arrows indicate increasing thermal maturity of the source of thermogenic methane.



**Figure 5.** Diagram between  $\delta^{13}\text{C}$  and H/D values of methane (“Schoell-diagram”, 66). Kızıldere sample (red square) plots on the mixing line between thermogenic and abiogenic methane. Tekke Hamam sample (green triangle) in the thermogenic field.

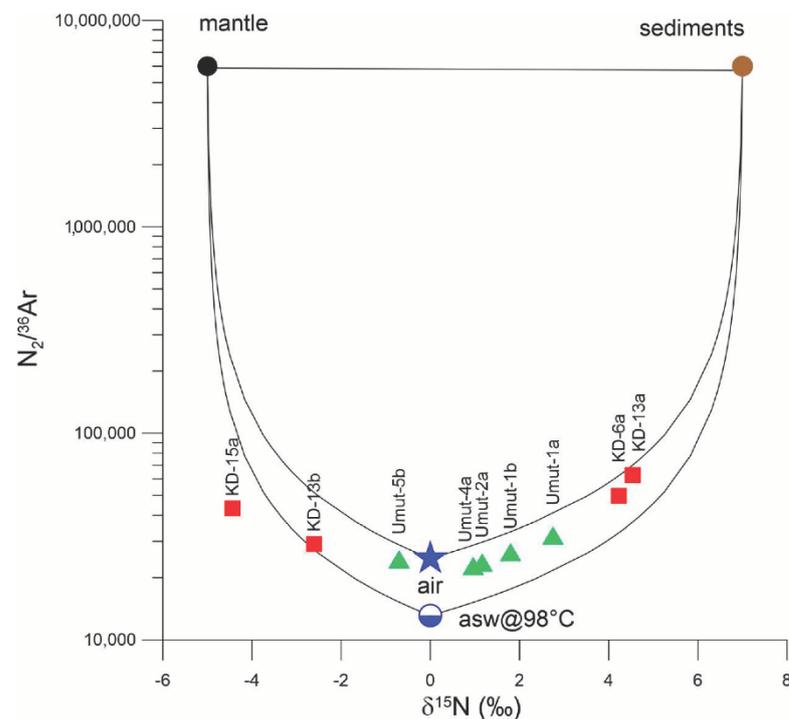
#### 4.5. Origin of N<sub>2</sub>

Nitrogen constitutes the major component of air and is found as a trace component within rocks. N<sub>2</sub>, like O<sub>2</sub> and Ar, can be considered to be derived from the atmosphere upon dissolution in groundwater during meteoric recharge of geothermal systems. Other than atmospherically derived nitrogen, non-atmospheric components of nitrogen within thermal fluids can be present due to contributions from different sources, such as sedimentary rocks containing organic matter, inorganic nitrogen in sediments, metamorphism of sedimentary rocks and mantle derived nitrogen [87–89].

The gas samples taken from Kızıldere and Tekke Hamam geothermal fields have N<sub>2</sub> values varying between 1.09 and 2.91 vol.%, and between 1.63 and 12 vol.%, respectively, with N<sub>2</sub> being the second dominant component after CO<sub>2</sub>. The ratio of N<sub>2</sub> to Ar and O<sub>2</sub> can be used as an initial parameter for the delineation of a possible existence of a—nitrogen component within a thermal fluid. Especially, the ratio of N<sub>2</sub> to Ar has been used as an indicator for the origin of nitrogen in natural gases [90], volcanic gases [91,92] and sedimentary rocks [93]. The N<sub>2</sub>/Ar ratio of the gases from Kızıldere and Tekke Hamam vary between 106 and 253, and between 82 and 107, respectively. Given that the N<sub>2</sub>/Ar ratio of air saturated water and air is 38 (at 20 °C) and 83.6 [53], respectively, it is apparent that nearly all of the gas samples exhibit a contribution from a non-atmospheric nitrogen component, in addition to N<sub>2</sub> derived from atmosphere upon dissolution through the recharge of the thermal reservoir or air by contamination during sampling. Only for the samples Umut-4a and Umut-5b, exhibiting N<sub>2</sub>/Ar values similar to that of air, can a sole atmospheric nitrogen origin be suggested; therefore, eliminating any source of non-atmospheric contribution within these samples. Particularly, the N<sub>2</sub>/O<sub>2</sub> ratio of sample Umut-4a (close to the value of air: 3.7) shows that there is also a considerable amount of air contamination, possibly due to improper sampling of this gas. Both samples also exhibit δ<sup>15</sup>N (‰ vs. air) values close to air, with δ<sup>15</sup>N = +0.96‰ for Umut-4a and −0.702‰ for Umut-5b, respectively.

The stable isotopic composition of nitrogen δ<sup>15</sup>N (‰ vs. Air) has been used as a tracer for the delineation of the possible non-atmospheric nitrogen components present within terrestrial fluids issuing from various tectonic settings [94,95]. Nitrogen derived from (i) sediments (inorganic) of continental crust and/or subducted oceanic slab have δ<sup>15</sup>N values around +7‰, [55], (ii) mantle derived N<sub>2</sub>, including unaltered ocean crust and N<sub>2</sub> degassed from the upper mantle exhibit δ<sup>15</sup>N values close to −5‰, [89], (iii) nitrogen related to organic sources of different degrees of maturity have values in the negative range, reaching −19‰ [96]. Since the isotopic characteristics of different nitrogen reservoirs within the subsurface coincide at some level, it is the general trend to compare the δ<sup>15</sup>N isotopic values with those of the elemental ratios, such as N<sub>2</sub>/<sup>36</sup>Ar [54,55] and N<sub>2</sub>/<sup>3</sup>He [95] for the delineation of the possible nitrogen sources.

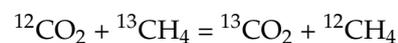
Figure 6 shows the diagram of δ<sup>15</sup>N vs. N<sub>2</sub>/<sup>36</sup>Ar ratio, with the possible end members (Air, Air Saturated Water, Mantle, Sediment; the endmember values for both δ<sup>15</sup>N and N<sub>2</sub>/<sup>36</sup>Ar are taken from [55]). Both Kızıldere and Tekke Hamam gases are located inside a mixing zone of the end member components (air, mantle, sediment), therefore calling for the existence of both sedimentary and mantle contributions for the gases, in addition to a constant atmospheric component that entered the geothermal system via reservoir recharge. The wide distribution of the Kızıldere gas samples (δ<sup>15</sup>N: −4.44 and 4.54‰ vs. air), showing values similar to that of both sedimentary and mantle nitrogen sources, however, possibly necessitates further arguments regarding possible physicochemical processes affecting the gases on their journey from the deep source to the surface. Especially, the effects of isotopic fractionation in relation to gas ascent in Kızıldere can be acting on these gases to a varying degree. In this context, it seems remarkable that samples from the Kızıldere well 13 show significant variations from +4.51‰ in November 2007 (sample Kızıldere-13a) to −2.61‰ in September 2008.



**Figure 6.**  $N_2/^{36}Ar$  ratios vs.  $\delta^{15}N$  diagram, with possible endmembers air, air-saturated water (asw@98 °C = air-saturated water at 98 °C. The  $N_2/^{36}Ar$  ratio in air-saturated water is lower than in air, which is due to the higher solubility of argon in water compared to nitrogen), mantle, and organic-rich sediments (modified from [54]). Most Kızildere and all Tekke Hamam gas samples fall inside a mixing zone of both atmospheric endmembers and one deep endmember. Kızildere samples: red squares, Tekke Hamam samples: green triangles.

#### 4.6. Reservoir Temperature Evaluation

The temperature of deep geothermal reservoir conditions can be highlighted based on temperature dependent isotopic fractionation between different compounds in geothermal fluids [97]. Various geothermometers have been designed based on the concept of isotopic fractionation, among which the  $CO_2$ - $CH_4$  isotope geothermometer has been used widely and reliably until now [5,9,97]. This geothermometer, based on the calculated carbon isotope fractionation factors between  $CO_2$  and  $CH_4$  via spectroscopic data [98] assumes that (i) carbon isotope fractionation reaches equilibrium between  $CO_2$  and  $CH_4$ , and (ii) there exists a symbiotic relationship between  $CO_2$  and  $CH_4$ . The results of this geothermometer generally yield temperatures 50–150 °C higher than those encountered in drillholes [99].



The temperature estimations, according to the temperature dependent relation of the  $CO_2$ - $CH_4$  isotope geothermometer given below indicates temperatures 20–40 °C higher at Tekke Hamam (compared to wells with temperatures reaching 170 °C, [18]) and 100–160 °C at Kızildere than measured bottomhole temperatures (Table 3).

$$T = 22166 / (13.86 + ^{13}C(CO_2-CH_4)) - 273$$

**Table 3.** Results of isotope geothermometry calculations for Kızıldere and Tekke Hamam gas samples.

	Sample	$\delta^{13}\text{C-CO}_2$ (‰ vs. VPDB)	$\delta^{13}\text{C-CH}_4$ (‰ vs. VPDB)	Bottom– Hole Temp (°C)	CO <sub>2</sub> –CH <sub>4</sub> Isotope Geother- mometer	Hydrocarbon Composition Geothermometer [29]
					Calculated Temp (°C)	Calculated Temp (°C)
Kızıldere	KD-6a	0.34	−20.8	194	347	224
	KD-13a	0.3	−23.2	198	309	250
	KD-15a	0.99	−23.6	208	294	274
Tekke Hamam	Umut-1b	−0.95	−34.4	-	195	-
	Umut-4a	−0.74	−31.7	-	219	-
	Umut-5b	1.3	−32.01	-	197	-

Compared to previous temperature calculations performed by [29] via the use of hydrocarbon gas ratio geothermometry [83], the obtained results are higher for Kızıldere. The greater temperature discrepancy between the measured temperatures and those derived from carbon isotopes at Kızıldere could be due to one or a combination of the following processes: (i) a faster ascent through wellbores at Kızıldere that hampers equilibrium achievement more than at Tekke Hamam, where fluids ascent slowly through fractures and faults, (ii) catalytic effects: Higher concentration of sulphuric species in geothermal gases from Tekke Hamam suggests a stronger interaction with metal sulphides that may act as catalysts, and (iii) secondary cracking processes of hydrocarbons that would alter the pristine  $\delta^{13}\text{C}$  signature of CH<sub>4</sub> towards higher values. Overall, the results obtained by this geothermometer possibly reflect temperatures at deeper levels than those penetrated by the drillholes.

## 5. Conclusions

In this study, we presented the stable isotopic evaluation of the gases (CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>) sampled from two neighboring geothermal fields located within the Büyük Menderes Graben, Turkey. Our findings are presented as follows:

- (i) The carbon isotopic ( $\delta^{13}\text{C}$ ) composition of CO<sub>2</sub>, together with its ratio to <sup>3</sup>He, points to a dominant limestone source and an accompanying minor magmatic component for gas samples collected from both fields.
- (ii) The carbon isotopic ( $\delta^{13}\text{C}$ ) composition of CH<sub>4</sub>, representing a minor gas component in the gas samples, reveals a dominant thermogenic character, with additional secondary processes (e.g., cracking of long chain hydrocarbons or input of abiogenic methane from deep sources), particularly effective on gas samples collected from the Kızıldere geothermal field.
- (iii) The nitrogen isotopic ( $\delta^{15}\text{N}$ ) composition, along with its elemental ratio to Ar, has pointed out to the existence of a non-atmospheric nitrogen component within both fields, possibly representing a mixture of crustal and mantle sources.
- (iv) The thick sedimentary cover, overlying the deep metamorphic basement, is the likely source for both the dominant CO<sub>2</sub> and the minor CH<sub>4</sub> and N<sub>2</sub> components issuing from both fields. A wider array of sampling points for both gas and isotopic compositions will better address the likely sources of the gases issuing from both fields.
- (v) The isotope geothermometry calculations have revealed a big temperature difference for Kızıldere and a rather small difference for Tekke Hamam. The difference that is more prominent for Kızıldere can possibly highlight the lack of equilibrium conditions due to fast gas ascent through the wellbores of Kızıldere and/or secondary cracking processes for hydrocarbons, which would alter the pristine  $\delta^{13}\text{C}$  signature of CH<sub>4</sub> towards higher values.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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