Origin of carbon dioxide occurrences in Central Anatolia (Turkey)

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The occurrence of carbon dioxide (CO₂) in Central Anatolia has been well-known for 50 years. Four gas producing fields (Bozkar, Guneygaz, Karbogaz, and Terra) are located in the region. The aim of this study was to define the composition of these gas occurrences and to determine the gas origin. For this purpose, the molecular and isotopic composition of gas samples from production wells were investigated and interpreted. Gases from the region are rich in CO₂ (>80%). Carbon dioxide concentrations were found to vary from 80.7 to 94.3%. The total amount of methane components (CH₄) was less than 0.1%. The isotopic composition of CO₂, with values between −1.76 and 1.02‰, indicated abiogenic origin from limestone. The generation of CO₂ could largely result from the decarbonation of limestone. Helium isotopic values indicated that a minor amount of CO₂ originated from the mantle. δ¹³C values for methane from the Karbogaz Field suggested that the origin of the Aksaray Field methane is thermogenic.

Keywords: origin of gases, hydrocarbon gases, carbon dioxide, generation mechanism of CO₂, Central Anatolia, Turkey

INTRODUCTION

Central Anatolia is the most productive region in Turkey for carbon dioxide. Since 1980, several wells have been drilled for carbon dioxide production. The depth of carbon dioxide production wells varies between 50 and 450 m. Four CO₂ gas fields (Bozkar, Guneygaz, Karbogaz, and Terragaz) are currently in production (Fig. 1a).

In Central Anatolia, Upper Cretaceous–Eocene basement blocks belonging to the Eurasian and Afro-Arabian plates are covered by rocks of pyroclastic and volcanic deposits (Pearce *et al.*, 1990; Toprak and Göncüoğlu, 1993; Yılmaz *et al.*, 1998; Kuşçu *et al.*, 2007; Gevrek and Kazancı, 2000; Piper *et al.*, 2002). These units can briefly be summarized as follows: a) basement rocks (Cretaceous) composed of metamorphic and Cenozoic volcanic rocks; b) Lower Eocene limestone, gypsum, and anhydrite, followed by Cenozoic volcanism (Fig. 1a). Cenozoic volcanic activity is concentrated within a triangular zone between three major strike-slip faults (Ecemis, Kızıltırmak, and Tuzgölü) (Piper *et al.*, 2002). Cenozoic volcanism is represented by major central volcanoes, such as Erciyes, Hasan Dağ, and Melendiz Dağ; various volcanic rocks erupted from many monogenic centers. Cenozoic volcanic activity can largely be divided into three episodes as follows: a) basaltic andesitic volcanism (13.5–8.5 Ma), b) a rhyolitic and rhyodacite

ignimbrite eruption (11–2.8 Ma), and c) the formation of stratovolcanoes, such as Erciyes, Melendiz Dağ, and Hasan Dağ, as well as numerous small monogenic centers that erupted during the late Pliocene until recent times (Piper *et al.*, 2002).

The CO₂ produced from different geological units and reservoirs exhibits different chemical characteristics. Previously published water chemistry data are presented in Table 1. The Karbogaz Field (Aksaray) is located in the eastern corner of the Tuz Gölü Basin. Two superimposed aquifers are located within the field: the lower confined (gypsum, siltstone, and sandstone) and the upper unconfined (alluvium). The lower confined aquifer contains a high amount of dissolved CO₂ (20–30 mg/L) (Geosan, 1998). According to their chemical composition, the wellhead waters are defined as Na–Ca–HCO₃–Cl-type waters (Table 1). The wellhead waters within the Bozkar Field are defined as Na–Cl-type waters and the amount of dissolved CO₂ is 469.45 mg/L (Table 1). The Guneygaz–Kemerhisar Field, located to the south of the city Nigde, consists of two aquifers: tuffites and alluvium. The Kemerhisar region wellhead waters have a similar chemical composition to the Na–Cl-type water. While shallow reservoir water contains only small amounts of dissolved CO₂ (2–21 mg/L), the water within the tuffite aquifer has a high concentration of CO₂ (102.8–1,280.7 mg/L) (Table 1) (Geosan, 1998). In the Karaptınar Field (Konya Province), water samples indicate predominantly Na–Cl/Ca–Mg–HCO₃-type waters. The amount of dissolved CO₂ varies in the range from 395.11 to 1,041.24 mg/L (Table 1).

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Fig. 1. (a) Location map of the study area, indicating the examined gas fields. The sample origin sites are indicated by stars. (b) A cross section A–A' across the gas fields Terragaz and Bozkar and major central volcanoes, such as Erciyes and Hasan Dağ, prepared from a subsurface map.

Table 1. The chemical composition and properties of water samples collected from Central Anatolia (as compiled by Camur and Mutlu (1996), Geosan (1998), and Mutlu and Güleç (1998))

Location	Sample name	Determined water type	TDS mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Cl mg/l	HCO ₃ mg/l	SO ₄ mg/l	CO ₂ mg/l
Karbogaz (Aksaray)	K1	Na–Ca–HCO ₃ –Cl	2307.9	312	35	264	63	446	1091.9	96	161.22
Bozkar (Kayseri)	B1	Na–Cl	8991.8	2251	97	348	264	4205	1634.8	192	469.45
Guneygaz (Kemerhisar)	G1	Na–Cl	16310.5	4646	343	250	380	8106	1433.5	1152	102.77
Guneygaz (Kemerhisar)	G2	Na–Cl–HCO ₃	35313.1	10948	483	154	441	13685	7692.1	1910	1280.67
Terragaz (Karapınar)	T1	Na–Ca–Cl–HCO ₃	5102.6	690	66	460	170	1355	1805.6	556	395.11

Table 2. He, Ne, Kr, Xe, and C isotopic compositions and calculated R/R_A values for Central Anatolian gases (data taken from Ercan *et al.*, 1995; Nagao *et al.*, 1989)

Locality	Latitude	Longitude	³ He/ ⁴ He ($\times 10^{-6}$) ^a	R/R_A ^b	Air-corrected R/R_A ^c	⁴ He/ ²⁰ Ne	⁴ He	²⁰ Ne	⁸⁴ Kr	¹³² Xe	$\delta^{13}\text{C}_{\text{CO}_2}$
Avanos	38°43′	34°51′	1.73 ± 0.12	1.24	1.34	0.8	1	0.41	1.8	22	0.8
Ürgüp	38°38′	34°55′	3.10 ± 0.12	2.23	2.25	18	19	0.33	1.8	2.1	0.7
Ziga (Aksaray)	38°16′	34°17′	2.03 ± 0.05	1.46	1.59	1.1	1.9	0.55	1.7	1.7	0.7
Ziga (Aksaray)	38°16′	34°17′	2.05 ± 0.14	1.47	1.58	1.3	2.1	0.51	1.7	2.2	0.5
Karapınar (Terragaz)	37°46′	33°43′	1.59 ± 0.06	1.14	1.14	23	27	0.37	2	2.3	–1.5
Kemerhisar (Guneygaz)	38°48′	34°36′	2.54 ± 0.05	1.83	1.83	170	220	0.4	1.7	1.9	1.6

^a ⁴He/²⁰Ne ratios and He concentrations are those corresponding to minimum and maximum ³He/⁴He ratios.

^b R/R_A values were directly quoted from the original reference, where available, or were calculated by normalizing the ³He/⁴He ratios given in the original reference to the atmospheric-He value (1.39×10^{-6}). The ratios from Pfister *et al.* (1997) were obtained by extrapolation from the R/R_A vs. $\delta^{13}\text{C}$ plot presented in Güleç *et al.* (2002).

^c Air-corrected R/R_A ratios were obtained from those in column 6, based on the assumption that all the neon in the samples is of atmospheric origin (the ⁴He/²⁰Ne ratio of air-saturated water is considered as 0.24). The R/R_A ratios from Pfister *et al.* (1997) were assumed to be air-corrected ratios (Güleç *et al.*, 2002).

The gas production in various wells in the Central Anatolian gas fields mainly consists of CO₂ and a negligible amount of hydrocarbon gases. The hydrocarbon and CO₂ gases within the gas fields are likely to have different formation mechanisms and origins. Ercan *et al.* (1995) collected six noble gases from Central Anatolia (He, Ne), which were measured with a noble gas spectrometer (Table 2). Abundances and isotopic ratios were measured with the Finnigan Mat-250 instrument at the laboratory of Kobe, The University of Tokyo. Ercan *et al.* (1995) suggested that Central Anatolian He gases are derived from the mantle. Using ³He/⁴He and ⁴He/²⁰Ne (neon) ratios and assuming that the samples were safely collected, the gases were evaluated to have a mixture of air, crustal, and mantle source. Although noble gases, such as He and Ne, were studied in detail, CO₂, the major constituent of gas fields, was only addressed for its origin with a very general approach. Additionally, Güleç *et al.* (2002) also discussed the origin of He gases and found evidence that mantle-derived He is a plausible explanation. The maximum proportion of mantle-derived helium varies between 15 and 30% within the Central Anatolian volcanic province.

In a recent study, Mutlu *et al.* (2008) identified that the proportion of mantle-derived helium varies between 5 and 20% within Western Anatolia.

To contribute to a realistic evaluation of the carbon dioxide potential of Central Anatolia, we sought to determine the origin of gases and to define their possible generation mechanisms. Therefore, as a first attempt, the molecular and isotopic compositions of the gases were investigated and the data were interpreted in terms of geological background.

We also discuss the origin of helium, based on data compiled from previously published papers (Ercan *et al.*, 1995; Nagao *et al.*, 1989; Güleç *et al.*, 2002) (Table 2).

METHODS

Fourteen gas samples were taken from several gas fields (Fig. 1a) from different depth intervals using gas cylinders. Generally, the reservoir to be found water and CO₂ mixing with pressure and springs out from wellhead. The gases were extracted from the separator and stored in a tank and samples from the tank were transferred into gas-tight cylinders. With the exception of Karapınar mineral water, which is produced from a well, the location had a free gas phase that was sampled for gas analysis (Fig. 2). Karapınar samples were extracted from the headspace of the glass bottles using a syringe and directly injected into a Gas Chromatograph Isotope Ratios mass

spectrometer (GC-IRMS).

The sample measurements were performed by an Agilent-6890N gas chromatograph (GC) equipped with an flame ionization detector (FID) and thermal conductivity detector (TCD) to determine the type of hydrocarbons, their molecular composition, and the amount of CO₂ gas in the samples. The gases were separated on the TCD detector by means of a GC equipped with an HP-Plot/Q (30 m; 0.542 mm; 40.00 µm) and an HP-molsieve (30 m; 0.539 mm; 50.00 µm) column. Helium was used as the carrier gas. The hydrocarbon gases were deeply devised by an FID detector with an HP-AL/S (50 m; 0.534 mm; 15.00 µm) column. The measurement results were evaluated by GC Chemstation software.

For the determination of the molecular composition of the gases, a correction was applied in order to eliminate admixtures of air. The air correction was calculated from the equation

$$N_{2\text{corrected}} = N_{2\text{measured}} - (O_{2\text{measured}} \times 3.7). \quad (1)$$

Stable isotope analyses of the gases were performed using a GV-IsoPrism High Performance instrument with a continuous-flow GC-IRMS at the Turkish Petroleum Company (TPAO). The analytical precision was $\pm 0.3\text{‰}$ for methane and carbon dioxide and $\pm 0.5\text{‰}$ for higher components ($>C_2$). The isotopic results are reported in δD and $\delta^{13}C$ notation in parts per mil (‰), relative to the Pee Dee Belemnite (PDB) standard for carbon and the Standard Mean Ocean Water (SMOW) for hydrogen, as

$$\delta_{\text{sample}} = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1000(\text{‰}) \quad (2)$$

where R denotes the ratios C^{13}/C^{12} or D/H , respectively.

RESULTS

The molecular and isotopic composition of gases

Fourteen gas samples from the four gas fields, Bozkar (Kayseri), Karbogaz (Aksaray), Terragaz (Karapınar), and Güneygaz (Kemerhisar-Niğde) (Fig. 1a), were analyzed for their molecular and isotopic composition. The concentrations of hydrocarbon gases, C_1 , C_{2+} , non-hydrocarbon gases, and carbon dioxide (CO₂) were determined. As indicated by carbon dioxide concentrations from 80.7 to 94.3%, the gas samples were rich in carbon dioxide ($>80\%$). The total amount of CH₄₊ components was less than 0.1% (Table 3).

The $\delta^{13}C$ values of carbon dioxide in the Terragaz and Bozkar Fields varied in the range from -1.48 to -1.76‰ and 0.89 to 1.02‰ , respectively. The $\delta^{13}C$ composition of CO₂ in the Karbogaz and Güneygaz Fields varied from

Fig. 2. Gas well and separator from Karapınar fields.

-0.03 to -0.36‰ and 0.81 to 0.99‰ , respectively. The $\delta^{13}C$ value of methane from the Karbogaz Field ranged between -23.9 and -24.2‰ (Table 3).

The origin of gases

To determine the origin of the hydrocarbon and carbon dioxide gases, different formation mechanisms were considered, which are separately discussed below.

The origin of methane Since the Karbogaz Field was the only site with a methane concentration within the detection limits of the GC-IRMS instrument, methane isotopic composition was only determined for this field. The origin of the hydrocarbon gases and possible processes for their generation were first investigated with the help of a Bernard diagram (Bernard *et al.*, 1978), which uses the molecular composition, the C_1/C_2+C_3 ratio, and $\delta^{13}C$ values of methane. Data points for all the samples were plotted within the zone for thermal gas generation (Fig. 3a). Since both the isotopic and molecular composition of the gases can be impacted by migration or by the mechanism of gas generation (Whiticar, 1994; Hunt, 1996; Prinzhofer and Pernaton, 1997), another classification (according to Schoell, 1980) was applied using a genetic plot of the $\delta^{13}C$ and δD of methane (Fig. 3b). As shown in Fig. 3b, gases from the Karbogaz Field were plotted within the thermal zone. An altered hydrocarbon isotopic composition was also observed for gaseous hydrocarbons generated from peat and lignite during high-pressure and high-temperature pyrolysis (Jiang *et al.*, 2000). Suitable geological settings with high-pressure regimes that produce these types of gases are commonly found in basins near continental margins (Du *et al.*, 2003). The methane isotopic composition indicated that the Karbogaz Field hydrocarbon gases are of thermogenic origin (Figs. 3a and b).

Table 3. The molecular and isotopic composition of gases from various gas fields in Central Anatolia

Locality (Company)	Sample number	Well name	Latitude	Longitude	Production depth (m)	CO ₂ production (Ton/Day)	CO ₂ (%)	N ₂ (%)	CH ₄ (%)	C ₂ H ₆ (%)	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰ vs. PDB)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰ vs. PDB)	$\delta\text{D}_{\text{CH}_4}$ (‰ vs. PDB)
Erciyes (Bozkar)	B1		36S0701561	4286237	150–185	100	89.1	10.9	0.001	<0.0001	n.d.	1.02	n.d.
	B2		36S0701380	4286254	185–220		88.3	11.7	0.001			0.97	
	B3		36S0701138	4286260	360–400		94.3	5.7	0.001			1.02	
	B4		36S0701227	4286118	220–250		91.4	8.6	0.001			0.91	
Kemerhisar (Guneygaz)	G1	Bahceli	36S642424	4186297	250–280	25	89.3	10.7	0.001	<0.0002	n.d.	0.81	n.d.
	G2	Bahceli	36S642424	4186297	250–280		90.5	9.5	0.001			0.85	
	G3	Havuzlu	36S0641595	4184250	220–260		91.2	8.8	0.001			0.99	
Karapinar (Terragaz)	T1		36S0558359	4181577	50–75	5	94.3	5.7	0.001	<0.0001	n.d.	–1.48	n.d.
	T2		36S0558368	4181551	75–90		92.1	7.9	0.001			–1.76	
	T3		36S0558381	4181586	100–108		91.3	8.7	0.001			–1.56	
Aksaray (Karbogaz)	K1	A1	36S0583697	4244886	250–290	70	80.3	19.6	0.1	<0.0001	–23.9	–0.03	–128.4
	K2	A3	36S0583673	4244868	300–330		86.4	13.6	0.01		n.d.	0.31	–129.6
	K3	A9	36S0583669	4244858	410–450		93.3	6.73	0.1		–24.2	0.36	–133.5
	K4	A9	36S0583669	4244858	290–320		82.1	17.9	0.01		n.d.	–0.01	–129.4

n.d.: not determined.

Fig. 3. (a) The genetic characterization of gas occurrences in the Karbogaz Field according to the molecular ratio (C_1/C_2+C_3) versus the $\delta^{13}\text{C}$ isotopic composition of methane. (b) The origin of the Karbogaz Field gases according to the CD diagram of gases (Whiticar, 1994).

The origin of carbon dioxide Within the literature, various mechanisms have been suggested for CO₂ formation. The mechanisms and their controlling factors can be summarized as follows:

- The bacterial or thermal degradation of organic matter. For this case, the $\delta^{13}\text{C}$ composition of the resulting CO₂ is less than –8‰ (Schoell, 1983; Whiticar, 1994; Clayton, 1995; Thrasher and Fleet, 1995; Hunt, 1996).
- Magmatic origin/degassing of the mantle. For this mechanism, the $\delta^{13}\text{C}$ of the formed CO₂ is between –4 and –7‰ (Baker *et al.*, 1995; Clayton *et al.*, 1990; Clayton, 1995; Dai *et al.*, 1996; Hunt, 1996; Wycherley *et al.*, 1999).
- Thermal decarbonation of carbonate rocks at temperatures of approximately 250°C (Schoell, 1980; Baker *et al.*, 1995; Thrasher and Fleet, 1995; Dai *et al.*, 1996; Boz *et al.*, 2004). In this case, the $\delta^{13}\text{C}$ composition of carbon dioxide is between 1 and –3‰ (Shangguan and

Fig. 4. He isotopic ratios vs. $\delta^{13}\text{C}_{\text{CO}_2}$, assuming that the course of CO_2 is a mixture of mantle-derived CO_2 and CO_2 produced either from organic or inorganic sedimentary material (the mixing curves are based on end-member values from Sano and Marty, 1995). Carbon dioxide isotopic zonation according to Jenden *et al.* (1993) and Hoşgörmüş *et al.* (2008). AO: aerobic hydrocarbon oxidation; KD: kerogen decarboxylation; AC: alteration of marine carbonates; BSM: biodegradation and secondary methanogenesis. The He isotopic ratio data are from Guleç *et al.* (2002). Western Anatolia data taken from Mutlu *et al.* (2008); WA1 Tuzla (spring), WA2 Kestanbol-1 (well), WA3 Kestanbol-2 (spring), WA4 Çan (well), WA5 Gönen (well), WA6 Manyas (well), WA7 Hisaralan (spring), WA8 Seferihisar (spring), WA9 Balçova (well), WA10 Germencik (spring), WA11 Germencik2 (spring), WA12 Kızılder (well), WA13 Gazlıgöl (well), WA14 Ömer (well). Eastern Anatolia data from Mutlu *et al.* (2012); EA1 Ayrancı-Çaldıran, EA2 Buğulu-Çaldıran, EA3 Çamlık-Başkale, EA4 Çaybağı-Saray, EA5 Çukur-Güroymak, EA6 Diyardin, EA7 Diyardin2, EA8 Germav-Hizan, EA9 Kokarsu-Bitlis, EA10 Nemrut caldera, EA11 Patnos-Ağrı, EA12 Taşkaptı-Erciş, EA13 Tutak-Van, EA14 Yurtbaşı-Gürpınar.

Zhang, 1990).

The variation of the isotopic composition of the Central Anatolian CO_2 gases between -1.76 and 0.99‰ indicates that these gases were not formed as a result of the bacterial or thermal degradation of organic matter. Furthermore, the CO_2 content in the gas fields is higher than 80%. The amount of CO_2 of organic origin is generally much lower (Tissot and Welte, 1984; Wycherley *et al.*, 1999). While hydrocarbon gases are generated by the thermal degradation of organic matter, some organic CO_2 can also be formed. However, the amount is much smaller than the CO_2 formed by other mechanisms, such that no significant deviation is encountered in the isotopic composition. If the quantity of organic CO_2 is equivalent or nearly equivalent to the amount of CO_2 formed by an-

Fig. 5. The maturity (vitrinite reflectance) trend versus depth for the borehole Aksaray-1.

Fig. 6. Plot of $\text{CO}_2/{}^3\text{He}$ vs. $\delta^{13}\text{C}(\text{CO}_2)$ for the Central Anatolian gas samples. The end-member compositions for sedimentary organic carbon (S), mantle carbon (M), and limestones (L) are $\delta^{13}\text{C}(\text{CO}_2) = -30, -6.5, \text{ and } 0\text{‰}$ and $\text{CO}_2/{}^3\text{He} = 1 \times 10^{13}, 2 \times 10^9, \text{ and } 1 \times 10^{13}$, respectively (Sano and Marty, 1995). ASRY: Aksaray; KPNR: Karapınar; KHSR: Kemerhisar sample (modified from Mutlu *et al.*, 2008).

other mechanism, the CO_2 isotopic composition should be close to that of the CO_2 of organic origin ($\delta^{13}\text{C} < -8\text{‰}$) (Schoell, 1983; Whiticar, 1994; Clayton, 1995; Thrasher and Fleet, 1995; Hunt, 1996). The CO_2 isotopic values of the Central Anatolian gas fields suggest that

either the gases were not formed as a result of the bacterial or thermal degradation of organic matter or that the contribution by organic-origin CO₂ is so small that it did not cause an isotopic deviation.

During the Middle Miocene–Holocene, several phases of volcanic activity occurred in Central Anatolia; namely, basaltic-andesitic volcanism during the mid-late Miocene, a rhyolitic and rhyodasitic ignimbrite eruption and the formation of stratovolcanoes, such as Erciyes, Melendiz Dağ, and Hasan Dağ, and the activity from several small monogenetic volcanic centers that have erupted from the late Pliocene to the present (Piper *et al.*, 2002). As a result, the CO₂ in the Central Anatolian gas fields is expected to be of mantle-derived magmatic origin and it may have been formed as a result of volcanic activity. In general, $\delta^{13}\text{C}$ values close to 0‰ do not typically represent magmatic CO₂, which is usually lighter (–4 to –8‰) (Macpherson and Matthey, 1994). However, the isotopic composition of CO₂ within the study area ranged between –1.76 and 1.02‰, which differed from the mantle-derived magmatic-origin CO₂ isotopic composition of $\delta^{13}\text{C}$ by –4 to –7‰ and was much heavier (Rigby and Smith, 1981; Koncz, 1983; Clayton *et al.*, 1990; Baker *et al.*, 1995; Thrasher and Fleet, 1995; Dai *et al.*, 1996). On the other hand, the high *R/Ra* ratios in Fig. 4 indicate mantle-He contributions in regions of historically active volcanoes. Therefore, a minor amount of CO₂ of magmatic origin cannot be excluded. Previous studies showed that large volumes of carbon dioxide (over 20 v/v% CO₂) are a relatively uncommon occurrence in sedimentary basins. However, in regions where large volumes do occur, the stable carbon isotope ratio of CO₂ is generally in the range of $\delta^{13}\text{C}_{\text{CO}_2}$ 0 to –10‰ PDB (Wyckley *et al.*, 1999). These isotopic values are considered to indicate an inorganic origin, principally from either magmagenesis or contact metamorphism of carbonates.

Carbon dioxide with $\delta^{13}\text{C}_{\text{CO}_2}$ values in the range of –4 to –7‰ and particularly large accumulations of carbon dioxide (i.e., >15 v/v%) are considered to represent an inorganic origin, such as the decarbonation of carbonates. High temperatures are required for the thermal decarbonation of carbonate rocks (Boz *et al.*, 2004). At temperatures higher than 250°C, calcite is found to undergo thermal decarbonation and to form CO₂ (Boz *et al.*, 2004).

The following reactions indicate how CO₂ can be formed in the presence of high temperatures as a result of the thermal decarbonation of limestone:

In our study area, some carbonate rock has been reported within the Miocene-aged basement of the volcanic rocks covering large areas in the surface.

To determine whether the limestone sequence in the region underwent the necessary high temperatures required for thermal decarbonation, we examined the organic maturity trends in deep wells. Vitrinite reflectance values of organic matter from the Aksaray-1 well (near the study area) drilled by TPAO ranged between 0.5 and 0.7 (%Ro) (Fig. 5). The data indicated an early maturation stage for organic matter and that the sequence did not experience high thermal overtime stress. Therefore, the temperatures required for carbonate decarbonation were definitely not reached at these depths. On the other hand, when the volcanic history of the basin was taken into consideration, the data indicated that portions of the sequence could have been affected by the higher temperatures caused by volcanic activity. Volcanic fluids and volcanic melt rising along main fault lines may have led to a local rise in temperature. Therefore, in volcanically active regions where igneous intrusive rocks intersect limestone, CO₂ can be formed from the thermal decarbonation of limestone due to high temperatures (>250°C).

The isotopic values of the CO₂ formed by thermal decarbonation are similar to those of limestone (Shangguan and Zhang, 1990). Therefore, the isotopic composition of carbon dioxide within the study area (–1.76 to 1.02‰) indicates that these gases can originate from limestone. A similar origin for carbon dioxide in other regions has also been proposed by various authors (Botz *et al.*, 1996; Fiebig *et al.*, 2004; D'Alessandro *et al.*, 2008; Tassi *et al.*, 2013). Carbon dioxide with isotopic values $\delta^{13}\text{C}$ ranging from –2 to 2‰, –1 to 2‰, and –5 to +4‰ has been reported by Javoy *et al.* (1986), Hunt (1996), and Minissale *et al.* (1997), respectively. Since the isotopic composition of CO₂ can be affected by mixing from other sources, a classification that uses genetic plots of $\delta^{13}\text{C}$ and the He isotopic ratios of gases, according to Jenden *et al.* (1993) and Hosgormez *et al.* (2008), was also applied. In Fig. 4, gas data from central Anatolia are plotted within the mixing zone between carbonate and mantle origins. A shift in the respective values of high *R/Ra* ratios is obvious and suggests mixing of carbonate-origin CO₂ with mantle-origin CO₂. Based on the magnitude of the shift in the $\delta^{13}\text{C}$ values for CO₂, it can be inferred that the amount of mantle-origin CO₂ is low in the Central Anatolian gas fields (Fig. 4). This suggests that at least a high proportion of the CO₂ emissions is derived from the breakdown of basement carbonates, either from heating by or direct reaction with magma (Fig. 1b).

In order to examine in detail the deep magmatic and near-surface physical degassing processes in Central

Anatolia, we have calculated the $\text{CO}_2/{}^3\text{He}$ ratio of the gases. The three-component mixing model, reported by Sano and Marty (1995), was used to calculate the relative quantities of carbon sources contributing to arc magmas. As shown in Fig. 6, MORB (M), marine limestones (L), and organic sediments (S) were used to estimate the fraction of each C source for the gas samples.

A quantitative assessment of the various contributions to the carbon inventory is determined as an; the L source contributes >90%, the S source <5%, and the M source <5%. It is clear that carbon derived from marine limestone is the principal contributor to the carbon budget in all cases (>90% of the total). These values are in the same order as reported by Mutlu *et al.*, 2008 and 2012 (Fig. 4).

CONCLUSION

The present study sought to determine the origin and formation mechanisms of gases in Central Anatolia and led to the following results:

1. As indicated by both the molecular and isotopic compositions, hydrocarbon gases in the Karbogaz Field are thermogenic. Relatively heavy isotopic values of methane suggest possible secondary effects, such as generation from high-pressure and high-temperature pyrolysis of peat and lignite.

2. Carbon isotopic data indicate that CO_2 is mainly formed from the decarbonation of limestone. Furthermore, helium isotopic values suggest that minor amounts of CO_2 are derived from the mantle. Therefore, the CO_2 gas in Central Anatolia is produced from multiple sources.

3. A dominant limestone component has been established for the CO_2 source with contributions from each of the sedimentary and mantle components not exceeding about 10% of the total inventory. It is apparent that limestone is the major contributor to the carbon inventory of all samples (>90%), followed by sedimentary organic and mantle sources.

4. According to the thermal history of the basin, well data on temperature, and the maturity of organic matter, it can hardly be concluded that the temperatures (>250°C) required for decarbonation were regionally reached. However, such temperatures could be reached locally at the contact zones of limestone with uprising volcanic bodies.

5. The CO_2 formed at the contact metamorphism zones of limestone migrated along fracture zones, dissolved in water upward, until its movement was stopped by impermeable beds, such as evaporites. Hence, the present CO_2 occurrences are located just below these impermeable beds.

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