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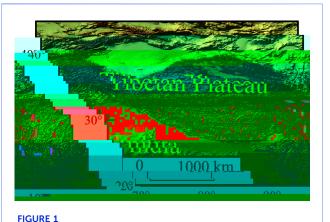
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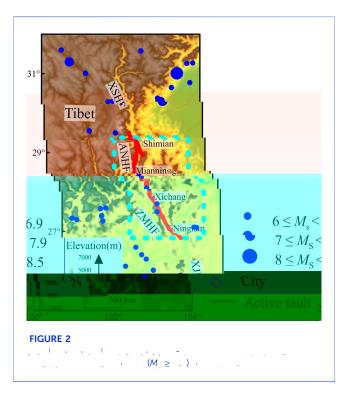
2022). In addition to human activities, natural factors (e.g., volcanic eruptions, biological respiration, seismic activity) will also contribute to the increase of greenhouse gas concentration in the atmosphere (Inguaggiato et al., 2012; Muirhead et al., 2020). Therefore, a great interest has been focused on studying of CO_2 Earth degassing. There are many targets for such research, such as the relationships between the CO_2 flux and the tectonic structures (Etiope et al., 1999; Jolie et al., 2015), the researches of volcanic degassing (Inguaggiato et al., 2012; Chen et al., 2019; Fischer and Aiuppa, 2020), and the quantification of deeply derived CO_2 discharging into the atmosphere (Lee et al., 2016; Viveiros et al., 2017; Jacome-Paz et al., 2020; Bekaert et al., 2021; Rahilly and Fischer, 2021).

However, the contribution of CO₂ released from nonvolcanic areas, particularly deep and large faults, is also worthy of attention (Fischer et al., 2019; Rahilly and Fischer, 2021; Zhang et al., 2021). Based on a study of ³He and CO₂ in springs and wells, Kennedy et al. (1997) estimated a mantlederived CO₂ flux of ~0.02 gm⁻² d⁻¹ for the entire San Andreas Fault system. The relationship between active crustal stress and soil CO₂ flux in southern Italy suggested that crustal stress associated with the seism genic process can effectively modulate the gas release in a seismically active area (Camarda et al., 2016). On the Chaozhou fault in China, significant anomalies in soil gas He and Rn were observed before the earthquake, which may reflect changes in the stress field before the earthquake (Fu et al., 2008); The sudden increase in CO₂ and Rn before the earthquake was observed on a fault in the earthquake cluster area in northwestern Bohemia, Czech Republic, which may indicate an increase in porosity and the opening of transport channels due to stress redistribution (Weinlich et al., 2006). Weinlich and others concluded that underground gas components can objectively and sensitively reflect the stress and tectonic activity changes of the earth's crust, and usually show various anomalies before or after the occurrence of earthquakes.

AZF is a seismic zone with vigorous seismic activity, which has high slip rates and developed fractures providing a channel for fluid migration deep and CO2 degassing. Therefore, the estimation of CO₂ degassing from the AZF is of great significance to understand the impact of the Earth's natural degassing on the environment. Yang et al. (2028) studied three characteristic points in AZF for soil gas CO2 concentration measurements. The results showed that the mean and maximum values of soil gas CO₂ concentration in the northern section of the ZMHF were much higher than those in the southern section of the ANHF. The soil gas CO₂ geochemistry produced different anomalous features, which, combined with the degree of occlusion in the AZF, reflect the gas-bearing characteristics of the AZF as well as the seismic hazard. However, there is no research on the characteristics of AZF soil gas CO2 flux and its causes.

Taken together, the relationship between soil gas CO_2 fluxes and active fault tectonic features is considered a hot topic for discussion in the field of geochemistry. In this paper, measurements of flux of soil gas CO_2 were performed at 1,483 sampling points along 67 profile lines oriented perpendicularly to the AZF. The geochemical characteristics





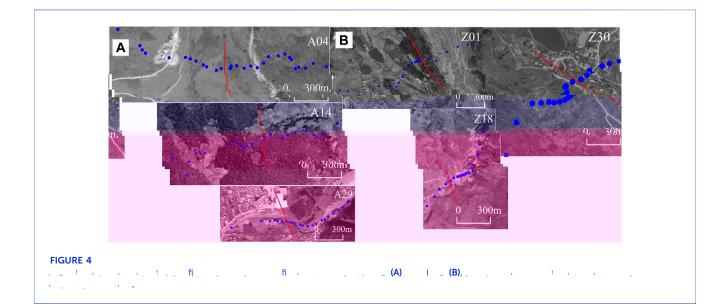
of soil gas CO_2 emissions in study areas and the association between the earthquakes and degassing process were investigated. This investigation aims to evaluate the total output of the CO_2 from the AZF and elucidate the tectonic association between the flux of soil gas CO_2 and the activity of earthquakes.

2 Geological setting

The AZF is the main active rift on the eastern boundary of the Sichuan-Yunnan block (Deng et al., 2003; Zhang et al., 2003). Under the combined effect of deep dynamic processes, large shear displacement and deformation zones are formed

near the Xianshui fault, the ANHF and the Xiaojiang fault, which control the tectonic pattern of the Sichuan-Yunnan region (Figure 1).

The ANHF starts from Shimian in the north, extending through Xichang to Huili (Figure 2), with an overall northsouth trend. The



3.2 Measurement methods of soil CO₂ flux

The details and principles of the closed-chamber method were described by Zhou et al. (2016). Analytical error associated with a single measurement was about $\pm 5\%$ and the reproducibility was about $\pm 10\%$ for the range of 100–10,000 gm⁻² d⁻¹.

Soil temperature at a depth of 10 cm was taken at every site, using a pocket digital thermometer (Henxin AZ8821), which has an accuracy of ± 0.1 °C. To minimize the inherent variability of gas flux due to soil water and humidity, sampling was performed during dry stable weather. Ambient air temperature and barometric pressure were recorded every 25 samples. Each survey was executed over three consecutive days, and under rain-free conditions, to avoid environmental effects. Both soil temperature and atmospheric pressure, recorded at every measurement, were used for calibrating soil flux values. At each observation site, the wind speed and barometric pressure was measured.

3.3 Measurement methods of carbon isotope

Four samples of CO_2 in soil gas from ANHF and four samples from ZMHF were collected for measurement of values of $\delta^{13}C_{CO2}$ (V-PDB). Glass bottles (500 mL) were used to collect soil gas in order to improve the accuracy of carbon isotopes. The gas samples were collected as follows: first, the glass bottle was filled with saturated brine and then inverted into a bucket filled with saturated brine and kept the glass bottle from tipping over. Soil gas is pumped into the glass bottle through a rubber hose. Until the filled saturated brine was replaced by gas in one-half of the bottle, the glass bottles were sealed in water with rubber blocks to avoid air contamination. All gas samples were analyzed at the Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Sciences. Carbon isotope analysis was performed using a Delta Plus XL mass spectrometer. It is manufactured by ThermoFinnigan Inc., consisting of the HP6890 gas chromatograph, combustion/conversion oven, interface and DeltaPlusXP mass

spectrometer (Li et al., 2017). The stable carbon isotope composition is generally expressed as δ^{13} C and has a precision of ±0.2‰.

4 Results

Overall, 734 points along 32 profiles across the ANHF and 728 points along 35 profiles across the ZMHF were sampled for the CO_2 flux analysis (Figure 5). There are two main patterns in the distribution of soil gas CO_2 fluxes on the AZF, one with anomalously high values near the fractures, which are mainly because the fault fractures are well developed at this location, creating many gas escape routes. The other is where the anomaly occurs on both sides of the fault, because the fault is mature and its fractured core is well developed, while the surrounding fragmentation is so high that a peak occurs above the lateral fault. This bimodal distribution is also observed in the San Andreas Fault profile (Kang et al., 2020).

In ANHF, the CO₂ flux in soil gas varied in the range of 0–1996.2 g m²d⁻¹, and the arithmetic mean values were 73.7 g ±2.36 m²d⁻¹ (Figure 6); In ZMHF, the CO₂ flux in soil gas varied in the range of 0–442.3 gm²d⁻¹, and the arithmetic mean values were 87.5 g ±4.21 m²d⁻¹. The $\delta^{13}C_{CO2}$ (V-PDB) were in the range of –25.0‰ ~ –19.7‰ (Table 1). The statistics data on the fluxes of CO₂ in soil gas from the AZF are listed in Table 2. The mean fluxes of CO₂ in each soil gas survey line were in the range of 7.23–272.22 gm⁻² d⁻¹ (Figure 7).

5 Discussion

5.1 Sources of CO₂ degassing

The CO_2 in subsurface fluids can be classified into two categories based on the type of parent material formed, organic and inorganic. The organic mainly formed by organic matter decomposition and bacterial activity, and the inorganic mainly from mantle/magmatic activity, thermal decomposition of carbonate rocks and dissolution



of carbonate rocks (Wycherley et al., 1999). Different types of CO₂ exhibit different carbon isotopic signatures. $\delta^{13}C_{CO2}$ (V-PDB) vs. 1/CO₂ is regarded to be an indicator for gas sources region (Sano and

Marty, 1995; Yuce et al., 2017; Chen et al., 2020). The values of end members for $\delta^{13}C_{CO2}$ of mantle and crust are –6.5‰ and 0‰, respectively, while for atmospheric and biogenic end members

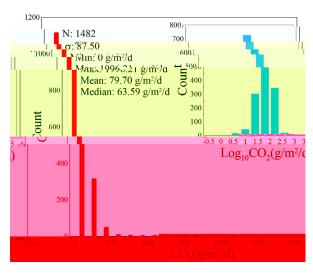


FIGURE 6

$$\label{eq:flow} \begin{split} & \left\{ f_{i}^{(1)} = \inf_{i \in I} \left\{ e_{i}^{(1)} e_{i}^{(1)} e_{i}^{(2)} e_{i}^{(1)} e_{i}^{(2)} e_$$

TABLE 1	Values	of	Soil	gas	CO ₂	carbon	isotope.
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Name	Line number	Concentration (%)	δ ¹³ C-CO ₂ (‰)
Soilgas01	ANH15	2.7	-22.3
Soilgas02	ANH20	4.8	-23.9
Soilgas03	ANH26	1.2	-20.8
Soilgas04	ANH27	1.2	-22
Soilgas05	ZMH03	1.7	-25.6
Soilgas06	ZMH06	1.3	-22.8
Soilgas07	ZMH20	0.7	-19.7
Soilgas08	ZMH34	3.1	-25

are –7‰ and –26‰, respectively (Dai, 1995; Sano and Marty, 1995; Dogan et al., 2009).

From Figure 8, it can be seen that the values of $\delta^{13}C_{CO2}$ values of the hot spring gas and soil gas samples are located in the composition mixing range between the mixed end of the crustal mantle and the biological end. The $\delta^{13}C_{CO2}$ values of the soil gas samples are located between the hot spring gas and the end of biological, which indicates that the CO₂ in the surface AZF mainly originates from the biological and the mixed end of the crustal mantle. Compared to the shallow depth of soil air circulation, the circulation of hot spring gas can reach depths of tens of kilometers. The CO₂ in soil gas is closer to the end of biological, which indicates that the oxidation of organic matter during aerobic microbial respiration plays the most important role in the production of CO₂ in soil gas.

Based on the above results, an attempt is made to explain the conceptual model of CO_2 sources and transport in the active fault zone of AZF. Fluids from the crust and mantle that accumulate in the lower crust and upper mantle rise through deep faults with a small amount of crust- and mantle-derived gas diffusing into near-surface soil gas. Although biogenic CO_2 is the primary source of soil

gas, crust-derived and mantle-derived CO_2 may be a secondary source. In addition, air can intrude into faulted soil gas due to fluctuations in air pressure (Tamir et al., 2012; Chen et al., 2020).

5.2 Contribution to the atmosphere from CO_2 degassing in the AZHF

Global warming, which has received widespread social attention, is thought to be closely related to the rapid increase in atmospheric CO₂ concentrations over the past 100 years (Joos et al., 1999; solomon et al., 2009; Italiano et al., 2010). However, many scientists currently question the warming caused by increasing atmospheric CO₂ concentrations, and the main debate focuses on what are the main drivers of warming; how accurate predictions of future climate trends based on existing climate models; and what is the magnitude of the impact of climate change (Italiano et al., 2009; Iqbal et al.,2009), all of which are subject to considerable uncertainty. There is a great deal of uncertainty in these issues. Therefore, it is necessary not only to reduce greenhouse gas emissions caused by human activities, but also to study the contribution of natural factors to atmospheric greenhouse gases, so as to distinguish between natural and anthropogenic factors leading to changes in atmospheric greenhouse gas concentrations, and to correctly understand the impact of Earth degassing on the increase of atmospheric greenhouse gas concentrations. In addition, the degassing areas of seismically active fracture zones are also "natural analogue" sites for studying the leakage of CO2 geological storage, especially the risk of sudden leakage of stored gases to the biosphere (Jing et al., 2019).

The annual contribution of CO₂ degassing from the fault zone to the atmosphere is equal to the amount of the annual average released flux each section of the fault zone multiplied by the area of each section of the fault zone. Based on the AZF and degassing characteristics, the AZF was divided into 5 segments, and the average value of the length and degassing flux of each segment was calculated based on the measurements (Table 3). The width of the fracture zone of the fault is generally tens of meters to hundreds of meters, and the surface avoidance zone of the active fault is more than 50 m (Xu et al., 2002). After the Wenchuan Ms8.0 earthquake, the width of the surface fracture zone of Longmenshan fault is about 200 m (Zhou et al., 2017), Several earthquakes of magnitude 6 or greater have occurred in the history of AZF, with the strongest one occurring north of Xichang with a magnitude of 7.5. The flux data from all sampling points on the AZF were superimposed on a single graph, which could be seen that the outliers with more than double the variance are concentrated within 200 m (Figure 8). High values of soil gas are usually exhibited near the fracture zone (Yuce et al., 2017; Jacome-paz et al., 2020), So the width of AZF was supposed as 200 m in this study.

By calculating the average flux of each survey line of ANHF and ZMHF, the annual contribution of ANHF and ZMHF zone to the atmosphere is 1.2 \pm 0.4 Mt (Table 3). The total flux of greenhouse gases from typical Cenozoic volcanic areas in Chinese Mainland to the atmosphere is about 8.13 Mt \cdot a⁻¹ equivalent to about 6% of the total greenhouse gas emissions caused by global (10² ~ 10³ Mt \cdot y⁻¹) volcanic activities (Guo et al., 2014). The annual emission of AZF is relatively small compared with that of typical volcanoes in China.

Line number	Length of survey lines(m)	Number of measuring points	Mean	Maximum	Minimum	
			(gm ⁻² d ⁻¹)	(gm ⁻² d ⁻¹)	(gm ⁻² d ⁻¹)	
ANH01	555	28	93.84	201.1	28.83	
ANH02	425	29	125.46	688.52	0	
ANH03	475	28	74.59	160.54	0	
ANH04	539	30	73.68	224.64	18.75	
ANH05	1,146	27	79.31	266.41	19.09	
ANH06	367	23	54.28	131.93	0	
ANH07	125	13	34.75	100.83	13.43	
ANH08	428	39	114.6	213.49	43.42	
ANH09	1,149	29	32.03	76.18	0	
ANH10	106	29	272.22	1996.21	0	
ANH11	885	29	37.09	187.28	0	
ANH12	235	11	121.74	288.98	60.84	
ANH13	441	14	81.89	231.64	19.99	
ANH14	756	19	40.46	77.51	20.15	
ANH15	255	25	7.23	42.84	0.66	
ANH16	878	39	52.05	112.9	14.76	
ANH17	2,272	42	62.47	143.65	11.77	
ANH18	472	20	35.86	62.45	8.29	
ANH19	1,695	32	56.29	239.49	16.9	
ANH20	439	21	52.48	173.13	23.6	
ANH21	1,339	28	73.23	173.01	0	
ANH22	1,677	36	68.98	169.38	20.5	
ANH23	718	20	65.25	154.77	12.05	
ANH24	1984	21	73.77	179.87	20.61	
ANH25	1,130	24	33.5	100.81	13.67	
ANH26	123	8	77.34	329.95	22.36	
ANH27	663	18	66.63	144.66	26.03	
ANH28	928	13	112.51	196.19	45	
ANH29	760	23	59.37	109.2	27.75	
ANH30	535	18	92.92	212.61	34.27	
ANH31	296	14	26.44	57.2	0	
ANH32	173	14	66.73	135.01	22.57	
ZMH01	1,204	23	53.79	124.74	13.87	
ZMH02	367	16	55.42	101.61	14.11	
ZMH03	707	27	113.35	241.06	26.62	
ZMH04	354	18	46.87	77.92	23.38	
ZMH05	1,056	25	88.52	232.36	24.32	

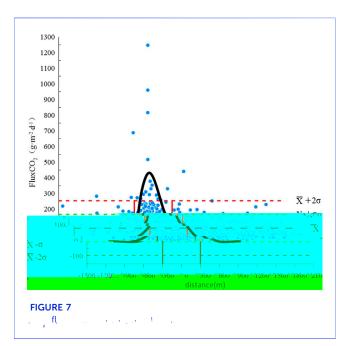
TABLE 2 The value of each measurement line on AZF.

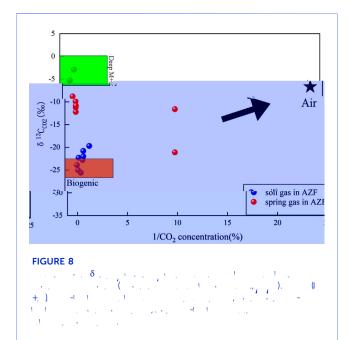
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only 8 active volcanoes in China (Liu., 1999), than 200 active fault zones in the intraplate area d (Deng et al., 2003), among which the Tanlu t zone, Haiyuan fault zone and Xianshuihe fault 1000 km long. The total emission of CO_2 from would be huge, which may be higher than that s in China. Only a few of researches were aimed missions from faults in the world (Table 4), but ugh. From a public health risk assessment perspective, detailed $\rm CO_2$ degassing maps should also be performed to evaluate the potential for $\rm CO_2$ release from fault.

5.3 Diffuse degassing in the ANHF and ZMHF

It is well known that understanding of crustal dynamics and degassing processes can be improved by studying soil gas in fracture zones (Ciotoli et al., 2016). Soil gas CO_2 flux is an important





indicator of crustal stress accumulation and fault activity (Irwin and Barnes, 1980; Zhou et al., 2010; Yuce et al., 2017). Changes in tectonic stress leads to expansion or contraction of bedrock, altering the degree of water-rock response and thus affecting CO_2 degassing. The strength of degassing along active faults is related to seismic activity, which can reflect the state of stress accumulation to some extent (Rovira and Vallejo, 2008; Manaker et al., 2008). Hence, there could be some degree of correlation between CO_2 emissions and historical earthquakes and nowadays earthquakes.

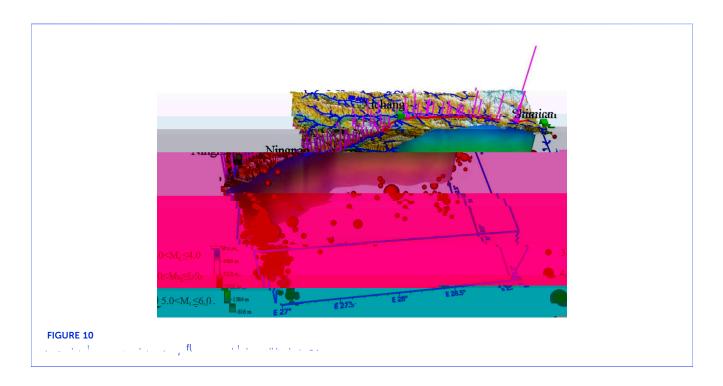
According to the location and magnitude of historical strong earthquakes on the fault zone, the seismic gap on the fault zone, and the spatial distribution of current seismic activity, the soil gas flux on the AZF has obvious segmented features (Yu et al., 2014; Yu et al., 2018; Wen, 2000; Zhou et al., 2017; Chen et al., 2019; Walia et al., 2010).

In this paper, our results show that high soil gas CO₂ fluxes are found in the northern section of ANHF, southern section of AMHF and the central section of AZF (Figure 9), which well correlates with the sites that have high seismic activities. Notably, the higher soil gas concentration values in the northern section of the ANHF relative to the southern section of the ANHF, combined with the high flux values at point A (Figure 9), may indicate that the higher degree of fracture fragmentation in the area leads to elevated bedrock permeability, which promotes CO₂ migration from deeper to the surface. B point (Figure 9) is located at the intersection of ANHF and ZMHF. On the one hand, the area has a high stress background value under the interaction of multiple sets of ruptures (Wen, 2000); on the other hand, the study shows that the area is highly occluded and belongs to the seismic gap area for both historical and presentday earthquakes (Deng et al., 2003). Therefore, the fault fragmentation in this area is low, the fracture is not fully developed, and the overall soil gas CO₂ flux values are in the middle. C point (Figure 9) is characterized by the same high seismic activity, but the soil gas CO₂ flux is weaker than point A. This may be due to the "Y" shaped intersection of the ZMHF, Daliangshan fault, and Xiaojiang fault in the southern section, which may not have the tectonic conditions for high stress concentration. Although the frequency of seismic activity is high and the magnitude is large, the stress drop value of the earthquake source is generally in the middle. Therefore, the degree of fault fragmentation in this area is weak, resulting in relatively low bedrock permeability and fewer soil gas CO₂ migration channels.

The higher degree of active fault fragmentation and the increased permeability of bedrock and soil, provide an upward

Number	Number of survey lines	Name	length (km)	Size (10 ⁶ m ²)	Mean flux (gm ⁻² d ⁻¹)	emission (t·y ⁻¹)
1	16	ANHF Northern Section	60	12	80.95	354,561
2	16	ANHF Southern Section	65	13	63.99	303,632.6
3	13	ZMHF Northern Section	48	9.6	73.29	256,808.1
4	12	ZMHF Middle Section	26.5	5.3	77.04	149,033.9
5	10	ZMHF Southern Section	22.5	4.5	100.48	165,038.4
Total	67		222	44.4	395.75	1,229,074

TABLE 3 CO₂ emissions by segment.



cross-faults on the local stress field and seismic hazard needs to be considered when discussing the seismic activity and stress distribution characteristics in this multi-cross-fault region.

The northern section of the ANHF meets the Xianshuihe fault and the Daliangshan fault at an acute angle, which has local conditions of high stress concentration, high seismic activity, large magnitude, and high source stress, so the soil gas CO₂ flux is the highest (Figure 10) (Wang et al., 1998; Toda et al., 2008); the ANHF and ZMHF meet at an obtuse angle, which has weak seismic activity and low source stress in general, so the soil gas CO₂ flux is the lowest; the southern section of the AZF, ZMHF meets the Xiaojiang fault and the Daliangshan fault at an obtuse angle, which may not have high source stress (Xu et al., 2022) (Figure 10). The southern section of AZF, ZMHF and Xiaojiang fault and Daliangshan fault meet at an obtuse angle, so they may not have the tectonic condition of high stress concentration, and although the seismic activity is frequent, the source stress is relatively not high (Wu, 2020). Therefore, the overall performance of soil gas CO₂ flux is at medium level.

It has been suggested that degassing features similar to the AZF can be found in worldwide geologic extensional contexts (Apollaro et al., 2012), and spatial variations in CO_2 emissions from deep sources may be attributed to tectonic activity (Irwin and Barnes, 1980). In addition, it has also been demonstrated that areas with enhanced crustal permeability may show precursors of CO_2 degassing activity. Therefore, the geochemical exploration method proposed in this paper for AZF would be applied to other CO_2 degassing areas on Earth (Martinelli and Dadomo, 2017). Meanwhile, tectonic activity in possible future earthquakes can be monitored by implementing soil gas CO_2 flux and concentration measurements on active faults.

7 Conclusion

In this study, geochemical characteristics and causes of the fluids released from the AZF were systematically analyzed, and the seismic activity of various segments of the AZF was discussed. The main conclusions are as follows:

- The investigation of carbon isotopic of underground fluid in AZF highlighted that: there are multiple sources of underground fluids in AZF; Soil gas CO₂ was demonstrated to be mainly biogenesis in AZF, while the spring gas is mainly of crustal and mantle origin.
- (2) Soil gas CO_2 emissions surveys in this study and previous studies reveal a substantial range of average soil CO_2 fluxes (1996.2 gm⁻² d⁻¹) for the AZF, which may have close affinities with the influence of regional fault systems and the seismic activity. Total soil CO_2 output of the AZF is about 1.2 Mt a⁻¹, suggesting high CO_2 outgassing flux of the eastern boundary of the Chuan-Dian rhombic block. There are many longer fracture zones than AZF in the worldwide, so more attention should be given to CO_2 emissions from faults.
- (3) The variation of CO₂ emissions in the study area is consistent with the strength of regional seismicity, and CO₂ fluxes are also relatively low in areas with weaker tectonic stresses. These results indicate that seismicity and regional stress are the major triggering mechanism for CO₂ emissions from the AZF.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

Author contributions

XZ, YL, and JD conceived the study. FL performed the literature review with support from YY, JT, JL, MH, OY, and SZ. KL, BY, ZZ, and YW participated in data processing. All authors contributed to interpretation and writing of the manuscript.

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Conflict of interest

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2023.1117862/ full#supplementary-material

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