Mantle-Derived Helium Distribution and Tectonic Implications in the Sichuan–Yunnan Block, China

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ABSTRACT: The geochemical characteristics of mantle degassing observed on the surface of the earth can indicate the origin and migration path of mantle fluids. Compared with the plate boundary tectonic environment, the intraplate tectonic environment does not have a large number of active volcanoes and active faults, and the observation of mantle volatiles in hot spring gas is relatively limited. We selected the Sichuan–Yunnan block to discuss mantle degassing based on the carbon and noble gas isotopes of the spring gases and previous studies on the fault slip rate and geophysical research. A total of five hot spring gas samples (including two free gases and three dissolved gases) were collected from the Sichuan–Yunnan block. Chemical and isotopic compositions were analyzed in N2-dominant hot spring gases. The 3He/4He ratio (0.068–0.541 Ra) indicates the occurrence of mantle-derived helium throughout the Sichuan–Yunnan block, which has been diluted by a crustal radiogenic 4He component. The occurrence of mantle-derived helium in the study areas ranges from 0.74 to 5.67%. The lower proportion of mantle-derived helium in YNWQ and HGWQ than that in other spring gases near the Jinghe-Qinghe fault may be caused by the smaller scale of fault around YNWQ and HGWQ than the Jinghe-Qinghe fault. The correlation between 4He, 20Ne, and N2 concentrations implies a common trapping mechanism for 4He, 20Ne, and N2 in hot spring gases. The 40Ar/36Ar ratios and N2/Ar ratios indicate that N2 and Ar are mostly meteoric, and YNWQ and HGWQ have more crustal-derived Ar contribution (40.56 and 51.49%, respectively). The δ13C(CO2) values calculated by Rayleigh fractionation and CO2 concentration suggest that CO2 has inorganic and organic origins. The plot of Rc/Ra versus δ13C(CO2) indicates that the spring gas CO2 origin in the Sichuan–Yunnan block is mainly derived from mixing of limestone and organic sediments with minor mantle CO2. The δ13C(CH4) versus CH4/3He values indicate that the origin of methane is thermogenic and microbial oxidation. The low mantle-derived helium distribution pattern is most likely controlled by the weak fault activity rate, the small fault scale, and not obvious magmatic activity in the Sichuan–Yunnan block.

1. INTRODUCTION

In recent years, extensive reports and studies have been conducted on the geochemical characteristics of geothermal fluids in the southeastern margin of the Qinghai–Tibet Plateau.1,2 The Sichuan–Yunnan block is close to Tengchong, Ning’er, and Pingbian volcanic fields in the southeastern margin of the Qinghai–Tibet Plateau. However, there are relatively few reports of noble gas and carbon isotopes of the geothermal fluids in the Sichuan–Yunnan block. The 3He/4He value between crustal helium (~10−8) and mantle-derived helium (~10−5) has a remarkable difference.3 Unlike rocks, natural fluids can integrate helium isotope ratios of mantle-derived and crustal-derived helium to varying degrees. Therefore, the 3He/4He ratio in fluids provides a possibility to indicate local to regional geological characteristics.3 Mantle volatiles are released through fractures and volcanic pipes connecting the mantle and the surface of the earth.3 When mantle fluids are ejected from the subsurface through hot springs, they can be blended with crustal fluids in faults or volcanic channels.1 In structurally stable regions, helium is formed by α decay of uranium and thorium series elements, while active extension or young volcanism areas are characterized by mantle-derived helium.4 Therefore, the overflow of mantle-derived fluids is mainly controlled by tectonism. The 3He/4He ratio has a significant positive correlation with the deformation rate of active crust.6 Therefore, the 3He/4He ratio is usually used to track mantle-derived materials.7 In addition, the correlation between the carbon isotopes of CO2 and CH4 and the abundance of 3He...
can indicate geochemical information related to their sources and carbon cycle. To discuss the mantle degassing mechanism in an intraplate tectonic environment, this paper studies the noble gas and carbon isotopic distributions of the geothermal fluids in the Sichuan–Yunnan block. By defining the relationship between the $^3\text{He}/^4\text{He}$ ratio and the abundance of main gases and carbon isotope data in the subsurface geothermal fluids, the correlation between the mantle degassing mechanism, tectonics, and magmatism is summarized.

2. GEOLOGICAL SETTINGS

The study area is located at the intersection of Yunnan and Sichuan Provinces, PR China and is geologically situated in the Sichuan–Yunnan block (Figure 1a). It is a part of the Yanyuan–Lijiang platform fold belt in the western margin of the upper Yangtze block. It is adjacent to Sanjiang structural belt in the west and Kangdian ancient land in the east. Ninglang-Yanyuan Basin is distributed in the study area (Figure 1b). The tectonic location of the Ninglang-Yanyuan Basin is a part of the southwest margin of the upper Yangtze block, which is mainly surrounded by the Jinhe-Qinghe fault, Xiaojinhe fault, Maijiaping fault, Guoboashan-Yanfeng fault, Woluo fault, and Baizidi-Yongsheng fault. The basement is the Proterozoic stratum, on which the Sinian, Lower Cambrian, Lower Ordovician–Lower Jurassic, and Paleogene sedimentary strata are deposited, missing the Middle-Upper Cambrian and Jurassic–Middle Cretaceous and Neogene, and the sedimentary stratum is more than 5000–10 000 m thick. Carbonate rocks (limestone, marble, and dolomite) are developed in the Upper Sinian, Middle-Upper Ordovician, Middle-Upper Silurian, Middle-Upper Devonian, Carboniferous, Permian Maokou formation, the upper of Middle Triassic, and the lower of Upper Triassic. The upper wall of the Jinhe-Qinghe thrust fault is the Sinian stratum, while the footwall is the Permian–Lower Jurassic strata in the Kangdian ancient land, and the upper wall of other faults is the Permian stratum and the footwall is the Triassic stratum in the other study areas. The study area mainly developed the Jinning, Caledonian Early Hercynian, late Hercynian, Indosinian, and Yanshanian magmatism. Except that the Late Permian Emeishan basalt of the Hercynian period erupted in a large area and had a huge thickness, other magmatic activities were mainly intrusive in the study area. The magmatic rocks in the Kangdian uplift and surrounding areas have high U and Th contents.

3. SAMPLES AND ANALYTICAL METHODS

Two free gases (YNWQ, YBWQ) and three dissolved gases (JHWQ, SSYQ, and HGWQ) were collected from the Sichuan–Yunnan block, China, in August 2020. The free gas is collected by a gas drainage method using a 500 mL glass bottle with a funnel on the mouth and then sealed with a rubber cap under water when the gas occupies about one-half of the bottle. The dissolved gases are collected using an injection bottle and then transferred into a 500 mL glass bottle. The collected gases were stored on dry ice and then analyzed in the laboratory.
of the volume of the glass bottle. The dissolved gas adopts the same glass bottle and rubber cap to start sampling when the hot spring water flows out of the spring mouth within 10 min to avoid air pollution and ensure temperature balance. When the glass bottle is filled with hot spring water, it is sealed under water with a rubber cap. YNWQ is close to the Xiaojinhe fault; YBWQ, JHWQ, and SSYQ are located in the Jinhe-Qinghe fault; and HGWQ is sited in the Kangdian uplift. Chemical compositions and carbon and noble gas isotopes were analyzed in the Key Laboratory of Petroleum Resources of Gansu Province, China.

Chemical compositions were analyzed by a GC-9560-PDD gas chromatography (GC) instrument with a relative standard deviation of <5%, installed with a Porapak Q (2 m × 1.60 mm) column using He as the carrier gas. The oven temperature was programmed as follows: the initial temperature was set at 150 °C and maintained for 5 min and then the temperature was increased to 240 °C at 10 °C min⁻¹ and maintained for 12 min. The detector temperature was 250 °C.¹³

The carbon isotopes of spring gas were tested by a 6890A GC instrument linked to a Finnigan MAT Delta Plus XP mass spectrometer.¹⁴ The hydrocarbon compounds and CO₂ can be separated by an HP-Plot column using He as the carrier gas. The GC oven temperature was programmed as follows: the initial temperature was set at 35 °C and maintained for 3 min, increased to 80 °C at 8 °C min⁻¹, and then to 260 °C with 5 °C min⁻¹, maintained for 10 min. The individual compounds were oxidized to CO₂ in a high-temperature (940 °C) oxidation furnace (an oxidation ceramic microreactor loaded with twisted wires) and detected by a Delta Plus XP isotope mass spectrometer with uncertainties of ±0.5‰.¹⁴ The values of δ¹³C are reported relative to V-PDB (Vienna Pee Dee Belemnite) in per mill.¹⁵

Noble gas contents and isotope compositions were measured by a Noblesse SFT noble gas mass spectrometer.¹⁶ The analysis system is divided into four parts: sample introduction, sample purification, noble gas separation, and noble gas testing.¹⁷ The detailed processes of sample introduction are described in the refs 14, 16. The gas was purified first using a spongy titanium furnace at 800 °C to remove active gases (H₂O, hydrocarbons, CO₂, N₂, O₂, etc.). H₂ in the gas can be eliminated by Zr–Al getters running at room temperature. Purified noble gases were separated by a cryogenic trap (10−475 K) filled with activated charcoal. He, Ne, Ar, Kr, and Xe were released for analysis at the cryogenic trap temperatures of 15, 50, 100, 150, and 230 K, respectively. The details of analytical procedures were described in the refs 16.¹⁴ ⁴He, ²⁰Ne, ²¹Ne ⁴⁰Ar, and ³⁸Ar were examined with a Faraday collector, and ³He, ²²Ne, ³⁵Ar, Kr, and Xe isotopes were analyzed with an electron multiplier. Experimental uncertainties for the noble gas concentrations were <10%.¹⁶ The details of data correction are described in the refs 18, 19.

### 4. RESULTS

#### 4.1. Chemical Compositions and Carbon Isotopes.

The basic information and chemical compositions of the hot spring gases collected from the Sichuan–Yunnan block are presented in Table 1. These hot spring gases are dominated by N₂, which is present at a concentration ranging from 67.05 to 97.13%. This N₂-dominant hot spring gas differs from the CO₂-rich hot spring gas discovered in Tengchong and Wudalianchi volcanic areas.²¹ The O₂ content in HGWQ hot spring gas (9.80%) is higher than those in the other hot spring gases. The other components include CO₂, CH₄, N₂, Ar, Kr, and Xe, which are important tracers for understanding the origin and evolution of hot spring gases.

### Table 1. Chemical Compositions and Carbon Isotopes of Hot Spring Gases in the Sichuan–Yunnan Block

| No. | Sampling Site | Longitude (E) | Latitude (N) | Temperature (°C) | N₂ | CO₂ | O₂ | CH₄ | Ar | Kr | Xe | δ¹³C(CO₂) | δ¹³C(CH₄) |
|-----|---------------|--------------|--------------|------------------|----|-----|----|-----|----|----|----|-----------|-----------|
| 1   | YNWQ          | 100.704255   | 27.812170    | 27.41170         | 82 | 13.77 | 1.77 | 0.12 | 0.0032 | 13.5 | 4.1 | -3.3 | 0.0023 |
| 2   | YBWQ          | 101.265715   | 27.009167    | 27.001657        | 61 | 70.26 | 3.02 | 1.01 | 0.0002 | 12.8 | 3.9 | -19.4 | 0.0005 |
| 3   | JHWQ          | 101.951365   | 26.529469    | 26.727151        | 38 | 93.85 | 0.33 | 4.62 | 0.0001 | 13.5 | 1.4 | -18.0 | 0.0005 |
| 4   | SSYQ          | 101.351221   | 26.971885    | 26.7471845       | 16 | 97.13 | 0.11 | 4.07 | 0.0023 | 13.5 | 1.4 | -11.6 | 0.0003 |
| 5   | HGWQ          | 101.351365   | 26.529469    | 26.7471845       | 16 | 97.13 | 0.11 | 4.07 | 0.0023 | 13.5 | 1.4 | -11.6 | 0.0003 |

Note: The value of δ¹³C(CO₂) is measured using the samples. δ¹³C(CH₄) is the original value of δ¹³C(CO₂).

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gases (0.27–4.62%). However, CO₂ contents in YNWQ and YBWQ hot spring gases (12.77 and 30.92%, respectively) are higher than those in the other hot spring gases (0.09–1.45%). In addition, O₂ and CO₂ contents in N₂-rich hot spring gases are higher than those in the other major components (Table 1). The N₂/O₂ ratios (8.97–359.74) in the N₂-dominant gas are greater than N₂/O₂ ratios (3.71) in the N₂-dominant gas (Table 1). The contents of H₂ and CH₄ are very low (2–32 ppm and 0.10–1.24%, respectively) in these N₂-dominant hot spring gases.

The δ¹³C(CO₂) values analyzed using YNWQ and YBWQ hot spring gases (−9.0 and −5.0‰, respectively) are higher than other hot spring gases (−26.3 to −18.3‰) (Table 1). The δ¹³C(CO₂) values calculated by the Rayleigh fractionation in YNWQ and YBWQ hot spring gases (−8.3 and −4.1‰, respectively) are higher than other hot spring gases (−18.6 to −12.4‰) (Table 1). CO₂ contents and the δ¹³C values of CO₂ (Table 1) exhibit a positive correlation, indicating enriched ¹³C and depleted ¹²C with an increase of CO₂ contents. The δ²¹Ne/²²Ne values and CO₂ concentrations in YNWQ and YBWQ hot spring gases are more than −10‰ and 10%, respectively, indicating an inorganic origin. However, the δ²¹Ne/²²Ne values and CO₂ concentrations in other hot spring gases are less than −10‰ and 10%, respectively, indicating a predominantly organic origin. The δ¹³C values of CH₄ in YNWQ, YBWQ, JHWQ, and HGWQ hot spring gases are less than 0.029 except for YNWQ spring gas, indicating that ²¹Ne in these hot spring gases is mainly derived from atmospheric sources (9.8). The ²¹Ne/²²Ne values of the hot spring gases range from 9 to 19 ppm (Table 2). In Figure 2, the ²⁰Ne/²²Ne ratios from 9.3 to 10.6 in YNWQ, YBWQ, and HGWQ hot spring gases show slight deviations from the atmospheric ²⁰Ne/²²Ne ratios (9.8) and are lower than mantle ²⁰Ne/²²Ne ratios (12.5). However, ²⁰Ne/²²Ne ratios in JHWQ and SSYQ hot spring gases (9.8 and 9.9, respectively) are similar to the atmospheric ²⁰Ne/²²Ne ratios (9.8). The ²¹Ne/²²Ne values (0.0281–0.0328) of the hot spring gases vary from the atmospheric and crust values of ²¹Ne/²²Ne = 0.029 and 0.03–0.70, respectively. The ²¹Ne/²²Ne values of the hot spring gases are less than 0.029 except for YNWQ spring gas, indicating that ²¹Ne in these hot spring gases is mainly derived from atmospheric sources (9.8). The contribution of crustal helium to the hot spring gases in the Sichuan–Yunnan Block was estimated using ²³He/²²Ne and ²⁰Ne/²²Ne ratios from 9 to 19 ppm (Table 2). In Figure 2, the ²⁰Ne/²²Ne ratios from 9.3 to 10.6 in YNWQ, YBWQ, and HGWQ hot spring gases show slight deviations from the atmospheric ²⁰Ne/²²Ne ratios (9.8) and are lower than mantle ²⁰Ne/²²Ne ratios (12.5). However, ²⁰Ne/²²Ne ratios in JHWQ and SSYQ hot spring gases (9.8 and 9.9, respectively) are similar to the atmospheric ²⁰Ne/²²Ne ratios (9.8). The ²¹Ne/²²Ne values (0.0281–0.0328) of the hot spring gases vary from the atmospheric and crust values of ²¹Ne/²²Ne = 0.029 and 0.03–0.70, respectively. The ²¹Ne/²²Ne values of the hot spring gases are less than 0.029 except for YNWQ spring gas, indicating that ²¹Ne in these hot spring gases is mainly derived from atmospheric sources (9.8). 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from the atmosphere without evident crustal addition of 21Ne. Previously reported data also show the same isotopic pattern. 30 All of the Ne isotopic ratios can be accounted for by two processes: one is variable crustal radiogenic 21Ne addition to the air Ne, and the other is the mass fractionation process (Figure 2).

4.2.3. Argon. 40Ar contents in the hot spring gases are 908–1170 ppm, and 40Ar/36Ar ratios vary between 310.8 and 610.2 (Table 2). In Figure 3, 40Ar/36Ar ratios of the hot spring gases are higher than the atmospheric 40Ar/36Ar ratios (298). 31 Because of the minor mantle contribution proved by the 3He/4He ratio, therefore, excess 40Ar generally was derived from radioactive decay of 40K in the crust. Based on excess 40Ar to total 40Ar is 40.56 and 51.49% in YNWQ and HGWQ hot spring gases, respectively, and 6.86, 5.99, and 4.78% in YBWQ, JHWQ, and SSYQ hot spring gases, respectively.

5. DISCUSSION

5.1. Correlation between 4He, 20Ne, and N2 Contents in Hot Spring Gases. The contents of 20Ne and 4He show a positive correlation in hot spring gases except for SSYQ and JHWQ samples in the Sichuan–Yunnan block (Figure 4a). 20Ne is almost completely derived from the atmosphere and enters the subsurface by dissolving in groundwater. 33 4He is formed by a decay of uranium and thorium series elements. 35 Generally, there is no correlation between 4He and 20Ne from different sources, and they are also subject to variable dilution of main gas components in the later stage. The positive correlation between 4He and 20Ne in the sample indicates that 4He and 20Ne have mixed before the main gas component is charged. In addition, this correlation provides direct evidence of the important role of groundwater in the enrichment process of crustal-derived gas. Similar relationships exist between 4He/N2 and 20Ne/N2 (Figure 4b) and N2 and 4He concentrations (Figure 4c), implying a common trapping mechanism for 4He, 20Ne, and N2 in the geothermal fluids. Notably, 4He vs 20Ne, 4He vs N2, and 4He/N2 and 20Ne/N2 show two trend distributions in the hot spring gases; this is may be caused by the difference in 4He contents in the springs. The difference of 4He contents in the samples is mainly determined by the difference of U and Th concentrations in rocks in different regions. This also shows that the U and Th contents of rocks in SSYQ and JHWQ areas are lower than those in other sample distribution areas. However, 20Ne vs N2 shows only one trend (Figure 4d), indicating that 20Ne and N2 have the same source and geological migration pathway.

5.2. Origins of Gases Discharging from the Sichuan–Yunnan Block. 5.2.1. N2–Ar–He System. The magma fluids, crustal fluids, and atmospheric precipitation fluids have different distribution positions in N2–Ar–He triangle diagram; therefore, the N2–Ar–He triangle diagram is usually used to determine the source of the subsurface fluids. 36,37 The N2, He, and Ar contents of the three major sources of gas usually have the following distribution characteristics (Figure 5). The air and air-saturated water (ASW) usually have lower He contents, and N2/Ar ratios are 83 and 38, respectively. However, mantle-sourced gases usually have higher He contents and lower N2/Ar contents, with N2/He less than 200. 38 Arc-type gases usually have high N2 contents, N2/He greater than 1000, and N2/Ar greater than 200. The hot spring gases from the Sichuan–Yunnan block are distributed along between mantle–crustal-derived and air or ASW in Figure 5, and the N2/Ar values of samples are greater than that of air (83), except for the YBWQ hot spring gas, the N2/Ar ratio is 77 between air (83) and ASW (38). The excessively high N2/Ar ratio may be caused by excessive N2 addition or N2/Ar fractionation during the fluid migration process. 39 Compared with the hot spring gases from the Sichuan–Yunnan block, Tengchong and Wudalianchi gases show mantle–crustal-derived and air or ASW distribution, but Tengchong and Wudalianchi gases have higher mantle He and Ar concentrations. In addition, some Tengchong gases fall along the arc-type gas region.

5.2.2. Helium in Hot Spring Gases. Due to the different isotopic compositions of noble gases in the different geo-spheres, 4He/20Ne and 4He/3He can further reveal deep material information and the source of gas components. 35 As shown in Figure 6, a simple ternary mixture model including atmospheric (R0), mantle (≈8.0 R0), and crustal (0.02 R0) can be used to indicate the source of geothermal fluids in the...
The 4He/20Ne values range from 57.32 to 88.18 except for JHWQ and SSYQ hot spring gases with values of 3.25 and 1.97, respectively, and Rc/Ra ratios (0.068−0.541 Ra) all are less than 0.6 Ra. It can be clearly seen that all hot spring gases in the Sichuan−Yunnan block are scattered between air and crustal mixing lines. Therefore, all the hot spring gases are typical of a crustal origin. Usually, 3He/4He ratios of natural gases are greater than 0.1 Ra, suggesting the presence of mantle He components. The proportion of mantle He in YBWQ, JHWQ, and SSYQ hot spring gases are 3.90, 2.02, and 5.67%, respectively, and this result is consistent with the Jinhe-Qinghe fault cut through the lower crust. However, the proportion of mantle He in the YNWQ and HGWQ hot spring gases (0.74 and 1.25%, respectively) are relatively lower than that in the hot spring gases located in the Jinhe-Qinghe fault.

In addition, Wudalianchi, Changbai Mountain, and Tengchong hot spring gases are also plotted in Figure 6 for comparison. All Wudalianchi and Changbai Mountain hot spring gases have 3He/4He values greater than 1.0 Ra indicating that these spring gases are mainly derived from the mantle origin. The hot spring gases from Tengchong, Yunnan Province can be divided into CO2- and N2-rich gases. Generally, N2-rich gases have a higher crust source gas input, and CO2-rich gases have a higher mantle source gas input.

5.2.3. CO2 and CH4 in Hot Spring Gases. The δ13C values of carbonaceous compounds in the hot spring gases contain abundant geochemical information. Generally, the different sources of CO2 have different carbon isotope distribution characteristics. The δ13C value of CO2 with the range of −10 to 0‰ and the CO2 contents greater than 15% can be regarded as an inorganic origin. However, CO2 contents and the δ13C values of CO2 less than 10 and −10‰, respectively, can be regarded as an organic origin. The δ13C value of CO2 is less than −14‰, which generally indicates the source of carbonaceous compounds in the hot spring gases.
organic matter, while the $\delta^{13}C$ value of marine limestone is usually 0 ± 3‰. If the mantle-derived fluids are effectively mixed through the lithosphere without significant fractionation, the CO$_2$/3He ratio in the surface fluids is between the mantle (2 × 10$^9$) and crustal (>10$^{10}$) values. For example, the samples from the Sichuan Basin and YNWQ and YBWQ spring gases have a CO$_2$/3He ratio between the mantle and crustal values (Figure 7). However, compared with the mantle and crustal end-member, the JHWQ, SSYQ, and HGWQ have significantly low CO$_2$/3He ratios (1.65 × 10$^8$, 5.05 × 10$^8$, and 3.48 × 10$^6$, respectively). He production within the crust is dominated by thermal neutron capture by $^6$Li in reaction $^6$Li($n$,$\alpha$)H-(β)$^3$He. Even if the Li content in surrounding rocks reaches 100 ppm, the local $^3$He/$^4$He ratio of radiogenic helium cannot exceed 0.1 R$_a$. Thus, $^3$He is mainly derived from the mantle, and it is impossible for $^3$He to be added during the upward migration of gas. $^3$He belongs to noble gas, and there is no correlation between the geothermal system and volcanic activity in the study area. Thus, except for dissolution, almost no process could alter $^3$He concentrations in the geothermal fluids. When the gas is released from the geothermal fluids, due to the solubility difference in the aqueous solution, CO$_2$ and He may be fractionated. Helium prefers to partition into exsolved vapor phase relative CO$_2$, rendering the residual phase CO$_2$/3He values elevated compared to the original values. The CO$_2$/3He ratio in the dissolved gases (JHWQ, SSYQ, and HGWQ) is lower than the bubbling gas (YNWQ and YBWQ), which is similar to the mantle CO$_2$/3He ratio (1–10 × 10$^9$). Therefore, hydrothermal degassing is not the cause of CO$_2$/3He ratio change.

In the ascending channel, calcite precipitates when the CO$_2$ partial pressure decreases, which leads to the decrease of CO$_2$/3He ratio and the $\delta^{13}C$(CO$_2$) changes. Based on the Rayleigh fractionation ($\delta^{13}C$(CO$_2$)$_o$ = $\delta^{13}C$(CO$_2$)$_o$ + $\epsilon$ ln $f$), the value of $\delta^{13}C$(CO$_2$)$_o$ is measured by the samples, the $\delta^{13}C$(CO$_2$)$_o$ is the original value of $\delta^{13}C$(CO$_2$) in the geothermal fluids, and $\epsilon$ is the carbon isotope fractionation degree for precipitation. The specific calculation method is shown in ref 59; the original value of $\delta^{13}C$(CO$_2$)$_o$ values ranges from −18.6 to −4.1‰. The gas plots below the crustal and mantle range in the CO$_2$/3He-$\delta^{13}C$(CO$_2$) space (Figure 7) imply the loss of CO$_2$ relative to He, as previously observed in numerous natural CO$_2$ accumulations. About 83.5, 49.5, and 99.5% of CO$_2$ has been lost in JHWQ, SSYQ, and HGWQ, respectively, assuming mantle-derived CO$_2$ with a typical magmatic range of 1–10 × 10$^9$. In addition, the loss contents of CO$_2$ reflected by the CO$_2$/3He values are positively correlated with the carbon isotope fractionation degree of CO$_2$. In Figure 8, the correlation of $R_c/R_a$ versus $\delta^{13}C$(CO$_2$) indicates that all spring gases from the Sichuan–Yunnan block are plotted within the two mixing lines (between mantle and limestone and between the mantle and organic sediments). The YNWQ and YBWQ spring gases contain 12.77 and

![Figure 6](https://doi.org/10.1021/acsomega.1c04533)

**Figure 6.** Plot of $R_c/R_a$ vs $^3$He/$^{30}$Ne ratios. Atmospheric: $^3$He/$^4$He = $R_a$, $^3$He/$^{30}$Ne = 0.318; crustal-derived: $^3$He/$^4$He = 0.02 $R_a$, $^3$He/$^{30}$Ne = 1000; mantle-derived: $^3$He/$^4$He = 8 $R_a$, $^3$He/$^{30}$Ne = 1000. All samples from the Sichuan–Yunnan block are scattered between air and crustal mixing lines, indicating helium of all of the hot spring gases is typical of a crustal origin. Wudalianchi data are from refs 41, 47; Changbai Mountains data are from ref 47; Tengchong data are from refs 46, 47.

![Figure 7](https://doi.org/10.1021/acsomega.1c04533)

**Figure 7.** Plot of $\delta^{13}C$(CO$_2$) vs CO$_2$/3He. Except for YNWQ and YBWQ spring gas, other sample data plot below standard mixing fields. Ranges of different sources are from refs 52, 60. The $\delta^{13}C$(CO$_2$) value of the sample with the frame is the initial value, and the $\delta^{13}C$(CO$_2$) value of the sample without the frame is the correction value. Sichuan Basin data are from ref 61.

![Image](https://doi.org/10.1021/acsomega.1c04533)
respectively, suggesting the CO2 is mainly derived from the limestone and organic sediments with minor mantle CO2. The JHWQ, SSYQ, and HGWQ spring gases have a δ13C(CO2) value of −18.9, −21.6, and −26.3‰, respectively, which are significantly less than those for typical inorganic carbon. Therefore, the spring gas CO2 origins in the Sichuan–Yunnan block are mainly derived from mixing of limestone and organic sediments with minor mantle CO2. The organic-rich shale and carbonate decomposition provides organic sediments and limestone-type carbon as two end-members of the crust that pollute the rising mantle volatiles. However, the δ13C(CO2) value and the 3He/4He ratio of the samples in the Sichuan Basin are less than −10‰ and 0.02 Ra, respectively, indicating that CO2 is mainly derived from the contribution of organic sediments CO2 (Figure 8). In addition, the δ13C(CO2) value and the 3He/4He ratio of the samples in the Quaternary volcanos (Wudalianchi, Tengchong, and Changbai Mountains) are greater than −10‰ and 1.0 Ra respectively, suggesting the CO2 is mainly derived from the contribution of mantle CO2 (Figure 8).

Generally, the formation of natural CH4 is reported in four ways: (a) biogenic methane formed by bacteria at a temperature less than 100 °C,62 (b) thermal decomposition of organic matter at a temperature greater than 100 °C,63 (c) degassing of the mantle,64 and (d) formation by chemical reactions, such as the Fischer–Tropsch synthesis reaction.65 In Figure 9, the plot of the δ13C(CH4) versus CH4/3He values can effectively identify the four origins of CH4.66 The HGWQ spring gas is located in the mixing between thermogenic methane and biogenic methane. The other spring gas methane is thermogenic methane, which tends to be a heavy carbon isotope. The hot spring gases have a tendency to approach the end components of the EPR (abiotic) (Figure 9), which suggests that microbial oxidation processes are likely to exist in geotherms.

30.92% CO2, respectively, with δ13C(CO2) values of −9.0 and −5.0‰, respectively, which are overlapping that for typical magmatic CO2. However, considering the outcrops of organic-rich shale and carbonate rocks in the Sichuan–Yunnan area and the relatively low 3He/4He ratio, CO2 is mainly contributed by limestone mixed with minor mantle and organic CO2. The JHWQ, SSYQ, and HGWQ spring gases from the Sichuan–Yunnan block with low CO2 contents and δ13C(CO2) values are −18.9, −21.6, and −26.3‰, respectively, which are significantly less than those for typical inorganic carbon. Therefore, the spring gas CO2 origins in the Sichuan–Yunnan block are mainly derived from mixing of limestone and organic sediments with minor mantle CO2. The organic-rich shale and carbonate decomposition provides organic sediments and limestone-type carbon as two end-members of the crust that pollute the rising mantle volatiles. However, the δ13C(CO2) value and the 3He/4He ratio of the samples in the Sichuan Basin are less than −10‰ and 0.02 Ra, respectively, indicating that CO2 is mainly derived from the contribution of organic sediments CO2 (Figure 8). In addition, the δ13C(CO2) value and the 3He/4He ratio of the samples in the Quaternary volcanos (Wudalianchi, Tengchong, and Changbai Mountains) are greater than −10‰ and 1.0 Ra respectively, suggesting the CO2 is mainly derived from the contribution of mantle CO2 (Figure 8).

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5.3. Mantle Helium Distribution in an Intracontinental Crust and Its Tectonic Implications. Assuming that the upward transmission rate of helium along the stratum in the study area is equal to that in Southern California (147 mm a−1),65 it takes 4.4 Ma for helium to pass through the 40 km crust. At the same time, helium is in the whole granite (Dhufl = 5 × 10−7 m2 a−1)53 migration distance is only 1 mm, indicating the importance of faults for the upward transport of helium. Deep and large faults are one of the important channels through which mantle fluids pass through the crust, and the ratio of 3He/4He can reflect the rate of mantle fluids passing through fault zones.68 Usually, 3He/4He ratio in the volcanic areas is higher than that in the areas without magmatic activity.64 The high 3He/4He ratios are usually related to subsurface melting or magmatism.69 The 3He/4He ratio has a significant positive correlation with the deformation rate of the active crust.6 Therefore, the migration of mantle helium in the crust may be influenced by the scale of fault, fault activity rate, and magmatic activity in the Sichuan–Yunnan block.

The hot spring gas is mainly distributed along the fault in the Sichuan–Yunnan block. YNWQ is close to the Xiaojinhe fault, YBWQ, JHWQ, and SSYQ are close to the Jinhe-Qinghe fault, and HGWQ is located in the Kangdian uplift. The Moho depth of the Yunnan block is 50–60 km.70,71 In addition, there is a low-velocity zone within ∼30 km in central Yunnan.72 According to the previous structural geological profile,70–72 the stratigraphic contact relationship on both sides of the Jinhe-Qinghe fault is that the Sinian Dengying formation (Zbd) in the north is thrust napped onto the Triassic Jurassic formation (T1J1) in the south (Figure 1c). Based on the characteristics of the surface geological structure and deep electrical anomaly, it is considered that the Jinhe-Qinghe fault is a lithospheric fault passing through the Moho surface (Figure 10).35 Therefore, the contribution ratio of mantle-derived helium of hot spring
gases (the proportions of mantle-derived helium in YBWQ, SSYQ, and JHWQ samples are 3.90, 5.67, and 2.02%, respectively) near the Jinhe-Qinghe fault is higher than that of hot spring gases distributed in other fault zones (the proportions of mantle-derived helium in YNWQ and HGWQ are 0.74 and 1.25%, respectively). In addition, the lower proportion of mantle-derived helium in YNWQ and HGWQ than other spring gases near the Jinhe-Qinghe fault may be caused by the smaller scale of fault around YNWQ and HGWQ than the Jinhe-Qinghe fault.

Although a large amount of mantle-derived helium exists in Tengchong, Pingbian, and Ning'er volcanic areas, there is low mantle-derived helium observed in the Sichuan–Yunnan block. Compared with the mantle-derived helium of typical intraplate volcanic areas in China, the maximum proportion of mantle-derived helium in Tengchong, Changbai Mountain, Hainan, and Wudalianchi volcanic fields can reach 65.6, 80, 15.6, and 38%, respectively. However, the proportion of mantle-derived helium (0.74–5.67%) in the Sichuan–Yunnan block is significantly lower. In addition, when the mantle volatiles was transported along the deep fault in the granitic crust, the first decay of uranium and thorium series elements produces 3He, which is added to mantle fluids. Therefore, the 3He/4He ratio in hot spring gas shows a certain functional relationship with uranium and thorium contents in rock, indicating the time of extracting 4He into the fluids and passing through the crust. Geochronological evidence shows that the Mesozoic granites in the Sichuan–Yunnan block have high U and Th contents. Therefore, mantle-derived helium is diluted by the radiogenic 4He produced in the crust. Besides, the slow transport of mantle-derived helium in deep faults (e.g., the average flow rate of the Karakoram fault is 19 mm a\(^{-1}\)) will lead to more time mixing of crustal helium and mantle-derived helium.

Fault activity and deformation have a positive correlation with the migration of mantle-derived helium in the crust. The increase of fault slip rate can significantly improve and maintain the high permeability of fault. According to the statistical relationship of the helium isotope (\(R_0\)) and the strike-slip rate (mm a\(^{-1}\)) of the S-wave low-speed anomaly occurring in the 70 km deep region (\(^3\)He/\(^4\)He (\(R_0\) = strike-slip rate of fault × 0.127 + 0.551, \(R_2 = 0.869\)), the results show that the strike-slip rates of the Xiaojinhe fault, Jinhe-Qinghe fault, and Kangdian uplift are 0.10, 1.03–3.82, and 0.42 mm a\(^{-1}\), respectively. The fault activity rate calculated by \(^3\)He/\(^4\)He is consistent with the current activity rate characterization of main faults in the Sichuan–Yunnan region through GPS. Therefore, the crustal deformation rate is positively correlated with the migration rate of mantle fluids in the crust. According to the above analysis, the low fault activity rate, the small fault scale, and the not obvious magmatic activity result in the low proportion of mantle-derived helium of the geothermal fluids in the Sichuan–Yunnan block.

6. CONCLUSIONS

The N\(_2\)-dominant component (67.05–97.13%) were observed in the hot spring gas samples. contents of the YBWQ sample (67.05%). The helium isotope of all hot spring gases shows 0.068–0.541 \(R_b\) and the percentages of atmospheric, crustal, and mantle-derived helium range 0.33–16.14, 78.2–98.9, and 0.74–5.67%, respectively. The \(N_2\)–Ar–He triangle diagram and \(^{40}\)Ar/\(^{39}\)Ar ratios indicate that \(N_2\) and Ar are mostly meteoric, and YNWQ and HGWQ have more crustal-derived Ar contribution (40.56 and 51.49%, respectively). The low CO\(_2\)/\(^3\)He ratio (e.g., 3.48 × 10\(^{-6}\) in HGWQ) is probably accussed by the loss of CO\(_2\) by calcite precipitation. The \(\delta^{13}\)C(CO\(_\text{2}\)) values calculated by Rayleigh fractionation and the CO\(_2\) concentrations suggest that YNWQ and YBWQ are consistent with the inorganic origin and JHWQ, SSYQ, and HGWQ are consistent with the organic origin. The plot of \(R_0/\ R_b\) versus \(\delta^{13}\)C(CO\(_\text{2}\)) indicates that the spring gas CO\(_2\) origin in the Sichuan–Yunnan block is mainly derived from mixing of limestone and organic sediments with minor mantle CO\(_2\). The \(\delta^{13}\)C(CH\(_\text{4}\)) versus CH\(_\text{4}\)/\(^3\)He values indicate that the origin of methane is thermogenic and microbial oxidation. Mantle helium contents in YBWQ, SSYQ, and JHWQ samples near the Jinhe-Qinghe fault are 3.90, 5.67, and 2.02%, respectively, and higher than those in hot spring gases distributed in other fault zones. Such distribution patterns and low mantle-derived helium proportions are most likely controlled by the low fault activity rate, the small fault scale, and the not obvious magmatic activity in the Sichuan–Yunnan block.
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Notes
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REFERENCES
(1) Zhang, L.; Guo, Z.; Sano, Y.; Zhang, M.; Sun, Y.; Cheng, Z.; Yang, T. Flux and genesis of CO2 degassing from volcanic-geothermal fields of Gulu-Yadong rift in the Lhasa terrane, South Tibet: Constraints on characteristics of deep carbon cycle in the India-Asia continent subduction zone. J. Asian Earth Sci. 2017, 149, 110–123.
(2) Zhou, X.; Wang, W.; Chen, Z.; Yi, L.; Liu, L.; Xie, C.; Cui, Y.; Du, J.; Cheng, J.; Yang, L. Hot Spring Gas Geochemistry in Western Sichuan Province, China After the Wenchuan Ms 8.0 Earthquake. Terr. Atmos. Ocean. Sci. 2015, 26, 361–373.
(3) Mamyrin, B. A.; Tolstikhin, I. N. Helium Isotope in Nature; Elsevier, 1984; p 273.
(4) Sheng, X.; Zheng, G.; Xu, Y. Helium, Argon and Carbon Isotopic Compositions of Spring Gases in the Hainan Island, China. Acta Geol. Sin. 2012, 86, 1513–1523.
(5) Rizzo, A. L.; Caracausi, A.; Chavagnac, V.; Nomikou, P.; Polymenakou, P. N.; Mandalakis, M.; Kotoulas, G.; Magoulas, A.; Castillo, A.; Lampridou, D.; Maruscak, N.; Sonke, J. E. Geochemistry of CO2-Rich Gases Venting From Submarine Volcanism: The Case of Kolumbo (Hellenic Volcanic Arc, Greece). Front. Earth Sci. 2019, 7, No. 60.
(6) Kennedy, B. M.; van Soest, M. C. Flow of mantle fluids through the ductile lower crust: helium isotope trends. Science 2007, 318, 1433–1436.
(7) Hilton, D. R.; Porcelli, D. Noble Gases as Mantle Tracers. In Treatise on Geochemistry; Richard, W. C.; Heinrich, D. H.; Karl, K. T., Eds.; Elsevier Ltd: London, UK, 2003; pp 277–318.
(8) Zhang, Z.; Yang, W.; Li, X.; Song, Y.; Jiang, Z.; Luo, Q. Geochemical Characteristics of the Middle Devonian Dacozit-Tanshanping Shale Strata in the Yanyuan Basin, Southwest China: Implications for Organic Matter Accumulation and Preservation. Geoﬂuids 2021, 1–24.
(9) He, W.; Tang, T.; Yue, M.; Deng, J.; Pan, G.; Xing, G.; Luo, M.; Xu, Y.; Wei, Y.; Zhang, Z.; Xiao, Y.; Zhang, K. Sedimentary and Tectonic Evolution of Nanhan-Permian in South China. Earth Sci. 2014, 39, 929–953.
(10) Wang, Z.; Deng, M.; Cheng, J.; Zhang, H. Influence of Fault and Magmatism on Oil and Gas Preservation Condition, to the West of Kangdian Ancient Continent: Taking Yanyuan Basin as an Example. Earth Sci. 2018, 43, 3616–3624.
(11) Yao, J.; Li, J.; Zhou, J.; Chen, Z.; Yao, H. LA-ICP-MS zircon U-Pb dating of migmatite in Dattian, Panzhihua City, and its geological significance. Geol. Bull. China 2017, 36, 381–391.
(12) Yin, M.; Xu, Z.; Song, H.; Zhang, S.; Zhang, C.; Li, T.; Tian, J. Significant geological events related to uranium mineralization in the Dattian area, Xikang-Yunnan Geo-Axis. Geol. Explor. 2021, 57, 14–29.
(13) Li, L.; Liu, Y.; Wang, X.; Zhang, M.; Cao, C.; Xing, L.; Li, Z. Development of a Combined Device with High Vacuum and Pulsed Discharge Gas Chromatography and Its Application in Chemical Analysis of Gases from Rock Samples. Rock Miner. Anal. 2017, 36, 222–230.
(14) Cao, C.; Zhang, M.; Li, L.; Wang, Y.; Li, Z.; Du, L.; Holland, G.; Zhou, Z. Tracing the sources and evolution processes of shale gas by coupling stable (C, H) and noble gas isotopic compositions: Cases from Weiyuan and Changning in Sichuan Basin, China. J. Nat. Gas Sci. Eng. 2020, 78, No. 103304.
(15) Li, Z.; Wang, X.; Li, L.; Zhang, M.; Tao, M.; Xing, L.; Cao, C.; Xia, Y. Development of new method of 63/64Cu measurement for trace hydrocarbons in natural gas using solid phase micro-extraction coupled to gas chromatography isotope ratio mass spectrometry. J. Chromatogr. A 2014, 1372, 228–235.
(16) Cao, C.; Zhang, M.; Tang, Q.; Yang, Y.; Lv, Z.; Zhang, T.; Chen, C.; Yang, H.; Li, L. Noble gas isotopic variations and geological implication of Longmaxi shale gas in Sichuan Basin, China. Mar. Pet. Geol. 2018, 99, 38–46.
(17) Zhang, W.; Li, Y.; Zhao, F.; Han, W.; Li, Y.; Wang, Y.; Holland, G.; Zhou, Z. Using noble gases to trace groundwater evolution and assess helium accumulation in Weihe Basin, central China. Geochim. Cosmochim. Acta 2019, 251, 229–246.
(18) Zhang, T.; Zhang, M.; Bai, B.; Wang, X.; Li, L. Origin and accumulation of carbon dioxide in the Huanghua depression, Bohai Bay basin, China. AAPG Bull. 2008, 92, 341–358.
(19) Zhang, M.; Tang, Q.; Hu, P.; Ye, X.; Cong, Y. Noble gas isotopic constraints on the origin and evolution of the Jinchuan NieCue(PGE) sulﬁde ore-bearing ultramafic intrusion, West. China. Chem. Geol. 2013, 339, 301–312.
(20) Zhang, M.; Guo, Z.; Sano, Y.; Zhang, L.; Sun, Y.; Cheng, Z.; Yang, T. Magma-derived CO2 emissions in the Tengchong volcanic ﬁeld, SE Tibet: Implications for deep carbon cycle at intra-continent subduction zone. J. Asian Earth Sci. 2016, 127, 76–90.
(21) Xu, S.; Zheng, G.; Nakai, S.; Wakiha, G.; Wang, X.; Guo, Z. Hydrothermal He and CO2 at Wudalianchi intra-pla-te volcano, NE china. J. Asian Earth Sci. 2013, 62, 526–530.
(22) Thrasher, J.; Fleet, A. J. Predicting the Risk of Carbon Dioxide Pollution in Petroleum Reservoirs. In Organic Geochemistry: Development and Applications to Energy, Climate, Environment and Human History; Grimalt, J. O.; Dorronsoro, C., Eds.; Proceedings of the 17th
International Meeting on Organic Geochemistry, San Sebastian, Spain, 1995; pp 1086–1088.
(23) Sano, Y.; Marty, B.; Burnard, P. Noble Gases in the Atmosphere. In The Noble Gases as Geochemical Tracers; Burnard, P., Ed.; Springer: Berlin, Heidelberg, 2013; pp 17–31.
(24) Mamyrin, B. A.; Anufriev, G. S.; Kamenski, I. L.; Tolstikhin, I. N. Determination of the isotopic composition of atmospheric Helium. Geochim. Int. 1970, 7, 498–505.
(25) Sano, Y.; Wakita, H. Geographical distribution of $^{3}$He/$^{4}$He ratios in Japan: Implications for arc tectonics and incipient magmatism. J. Geophys. Res.: Solid Earth 1989, 90, 8729–8741.
(26) Bottomley, D. J.; Ross, J. D.; Clarke, W. B. Helium and Neon isotope geochemistry of some ground waters from the Canadian Precambrian Shield. Geochim. Cosmochim. Acta 1984, 48, 1973–1985.
(27) Ballentine, C. J.; Bernard, M.; Sherwood, L. B.; Martin, C. Neon isotopes constrain convection and volatile origin in the Earth's mantle. Nature 2005, 433, 33–38.
(28) Sarda, P.; Staudacher, T.; Allègre, C. J. Neon isotopes in submarine basalts. Earth Planet. Sci. Lett. 1988, 91, 73–88.
(29) Kennedy, B. M.; Hyagon, H.; Reynolds, J. H. Crustal neon: a striking uniformity. Earth Planet. Sci. Lett. 1990, 98, 277–286.
(30) Zhou, Z.; Ballentine, C. J.; Kipfer, R.; Schoell, M.; Thibodeaux, S. Noble gas tracing of groundwater/coalbed methane interaction in the San Juan Basin USA. Geochim. Cosmochim. Acta 2005, 69, 5413–5428.
(31) Mark, D. F.; Stuurt, F. M.; de Podesta, M. New high-precision measurements of the isotopic composition of atmospheric argon. Geochim. Cosmochim. Acta 2011, 75, 7494–7501.
(32) Battani, A.; Sarda, P.; Prinzhofer, A. Basin scale natural gas source, migration and trapping traced by noble gases and major elements: the Pakistan Indus basin. Earth Planet. Sci. Lett. 2000, 181, 229–249.
(33) Ballentine, C. J.; Burgess, R.; Marty, B. Tracing fluid origin, transport and interaction in the crust. Rev. Mineral. Geochim. 2002, 47, 539–614.
(34) Graham, D. W. Noble Gas Isotope Geochemistry of Mid-ocean Ridge and Ocean Island Basalts: Characterization of Mantle Source Reservoirs. In Noble Gases in Geochemistry and Cosmochemistry; Porcelli, D.; Ballentine, C. J.; Weiller, R., Eds.; Reviews in Mineralogy and Geochemistry; Mineralogical Society of America: Washington, DC, 2002; pp 247–319.
(35) Andrews, J. N. The isotopic composition of radiogenic helium and its use to study groundwater movement in confined aquifers. Chem. Geol. 1985, 49, 339–351.
(36) Giggenbach, W. F.; Matsuo, S. Evaluation of results from Second and Third IAVCEI Field Workshops on Volcanic Gases, Mt Usu, Japan, and White Island, New Zealand. Appl. Geochim. 1991, 6, 125–141.
(37) Giggenbach, W. F.; Glover, R. B. Tectonic regime and major processes governing the chemistry of water and gas discharges from the rotorua geothermal field, New Zealand. Geothermics 1992, 21, 121–140.
(38) Fischer, T. P.; Giggenbach, W. F.; Sano, Y.; Williams, S. N. Fluxes and sources of volatiles discharged from Kudryavy, a subduction zone volcano, Kurile Islands. Earth Planet. Sci. Lett. 1998, 160, 81–96.
(39) Blomgren, V.; Crosse, L. J.; Karlstrom, K. E.; Fischer, T. P.; Darrah, T. H. Hot spring hydrochemistry of the Rio Grande rift in northern New Mexico reveals a distal geochemical connection between Valles Caldera and Ojo Caliente. J. Volcanol. Geotherm. Res. 2019, 387, No. 106663.
(40) Giggenbach, W. F. In The Composition of Gases in Geothermal and Volcanic Systems as a Function of Tectonic Setting, Proceedings of International Symposium on Water Rock Interaction, Roterdam, 1992; pp 873–878.
(41) Du, J.; Li, S.; Liu, L.; Ren, J.; Zhao, Y.; Sun, R.; Heshun, D. Geochemistry of gases from Wudalianchi volcanic district northeast China. Geochimica 1999, 28, 171–176.
(42) Shangguan, Z.; Bai, C.; Sun, M. Mantle-derived magmatic gas releasing features at the Rehai area, Tengchong county, Yunnan Province, China. Sci. China, Ser. D: Earth Sci. 2000, 43, 132–140.
(43) Hoke, L.; Lamb, S.; Hilton, D. R.; Poreda, R. J. Southern limit of mantle-derived geothermal helium emissions in Tibet: implications for lithospheric structure. Earth Planet. Sci. Lett. 2000, 180, 297–308.
(44) Marty, B.; O’Nions, R. K.; Oxburgh, E. R.; Martel, D.; Lombardi, S. Helium isotopes in Alpine regions. Tectonophysics 1992, 206, 71–78.
(45) Wang, Q. Crust-Mantle Electrical Structure and Dynamics of Xiaojinhe-Qinghe Tectonic Belt in the Central Sichuan-Yunnan Block; Chengdu University of Technology, 2020; pp 38–56.
(46) Zhao, C.; Ran, H.; Wang, Y. Present-day mantle-derived helium release in the Tengchong volcanic field, Southwest China: Implications for tectonics and magmatism. Acta Pet. Sin. 2012, 28, 1189–1204.
(47) Shangguan, Z.; Zhao, C.; Gao, L. Carbon isotopic compositions of the methane derived from magma at the active volcanic regions in China. Acta Pet. Sin. 2006, 22, 1458–1464.
(48) Dai, J.; Yang, S.; Chen, H.; Shen, X. Geochemistry and occurrence of inorganic gas accumulations in Chinese sedimentary basins. Org. Geochem. 2005, 36, 1664–1688.
(49) Bergfeld, D.; Goff, F.; Janik, C. J. Carbon isotope systematics and CO2 sources in the Geysers-Clear Lake region, northern California, USA. Geothemics 2001, 30, 303–331.
(50) Craig, H. The geochemistry of the stable carbon isotopes. Geochim. Cosmochim. Acta 1953, 3, 53–92.
(51) Xu, S.; Zheng, G.; Wang, X.; Wang, H.; Nakai, S.; Wakita, H. Helium and carbon isotope variations in Liaodong Peninsula, NE China. J. Asian Earth Sci. 2014, 90, 149–156.
(52) Marty, B.; Jambon, A. C./$^{3}$He in volatile fluxes from the solid Earth: implications for carbon geodynamics. Earth Planet. Sci. Lett. 1987, 83, 16–26.
(53) Ballentine, C. J.; Burnard, P. Production of noble gases in the continental crust. Rev. Mineral. Geochim. 2002, 47, 481–538.
(54) Tao, H.; Wang, Q.; Yang, X.; Jiang, L. Provenance and tectonic setting of late Carboniferous clastic rocks in west Junggar, Xinjiang, China: a case from the Hala-alt Mountains. J. Asian Earth Sci. 2013, 64, 210–222.
(55) Xu, S.; Zheng, G.; Zheng, J.; Zhou, S.; Shi, P. Mantle-derived helium in foreland basins in Xinjiang, Northwest China. Tectonophysics 2017, 694, 319–331.
(56) Dubacq, B.; Bickle, M. J.; Evans, K. A. An activity model for phase equilibria in the H2O-CO2-NaCl system. Geochim. Cosmochim. Acta 2013, 110, 229–252.
(57) Gillillan, S. M. V.; Lollar, B. S.; Holland, G.; Blaghurn, D.; Stevens, S.; Schoell, M.; Cassidy, M.; Ding, Z.; Zhou, Z.; Lacrampe-Couloume, G.; Ballentine, C. J. Solubility trapping in formation water as dominant CO2 sink in natural gas fields. Nature 2009, 458, 614–618.
(58) Clark, I. D.; Fritz, P. Environmental Isotopes in Hydrology; Lewis Publishers: New York, 1997; pp 55–61.
(59) Zhang, W.; Du, J.; Zhou, X.; Wang, F. Mantle volatiles in spring gases in the Basin and Range Province on the west of Beijing, China: Constraints from helium and carbon isotopes. J. Volcanol. Geotherm. Res. 2016, 309, 45–52.
(60) Sano, Y.; Marty, B. Origin of carbon in fumarolic gas from island arcs. Chem. Geol. 1995, 119, 265–274.
(61) Zhang, M.; Guo, Z.; Xu, S.; Barry, P. H.; Sano, Y.; Zhang, L.; Halldorsson, S. A.; Chen, A.; Cheng, Z.; Liu, C.; Li, S.; Lang, Y.; Zheng, G.; Li, Z.; Li, L.; Li, Y. Linking deeply-sourced volatile emissions to plateau growth dynamics in southeastern Tibetan Plateau. Nat. Commun. 2021, 12, No. 4157.
(62) Schoell, M. Multiple origins of methane in the Earth. Chem. Geol. 1988, 71, 1–10.
(63) Des Marais, D. J.; Donchin, J. H.; Nehring, M. L.; Truesdell, A. H. Molecular carbon isotopic evidence for the origin of geothermal hydrocarbons. Nature 1981, 292, 826–828.
(64) Poreda, R. J.; Craig, H.; Arnorsson, S.; Welhan, J. A. Helium isotopes in Icelandic geothermal systems: I. $^{3}$He, gas chemistry, and $^{13}$C relations. Geochim. Cosmochim. Acta 1992, 56, 4221−4228.

(65) McCollom, T. M.; Seewald, J. S. A reassessment of the potential for reduction of dissolved CO$_2$ to hydrocarbons during serpentinization of olivine. Geochim. Cosmochim. Acta 2001, 65, 3769−3778.

(66) Wen, H.; Sano, Y.; Takahata, N.; Tomonaga, Y.; Ishida, A.; Tsubaki, K.; Kagoshima, T.; Shirai, K.; Ishibashi, J.; Yokose, H.; Tsunogai, U.; Yang, T. Helium and methane sources and fluxes of shallow submarine hydrothermal plumes near the Tokara Islands, Southern Japan. Sci. Rep. 2016, 6, No. 34126.

(67) Kulongoski, J. T.; Hilton, D. R.; Barry, P. H.; Esser, B. K.; Hillengonds, D.; Belitz, K. Volatile fluxes through the Big Bend section of the San Andreas Fault, California: helium and carbon-dioxide systematics. Chem. Geol. 2013, 339, 92−102.

(68) Kennedy, B. M.; Kharaka, Y. K.; Evans, W. C.; Ellwood, A.; DePaolo, D. J.; Thordsen, J.; Ambats, G.; Mariner, R. H. Mantle fluids in the San Andreas fault system, California. Science 1997, 278, 1278−1281.

(69) Zhang, M.; Guo, Z.; Sano, Y.; Zhang, L.; Sun, Y.; Cheng, Z.; Yang, T. Magma-derived CO$_2$ emissions in the Tengchong volcanic field, SE Tibet: Implications for deep carbon cycle at intra-continent subduction zone. J. Asian Earth Sci. 2016, 127, 76−90.

(70) Jiang, W.; Zhang, J.; Tian, T.; Wang, X. Crustal structure of Chuan-Dian region derived from gravity data and its tectonic implications. Phys. Earth Planet. Inter. 2012, 212−213, 76−87.

(71) Dong, X.; Yang, D.; Niu, F. Passive adjoint tomography of the crustal and upper mantle beneath eastern Tibet with a W2 norm misfit function. Geophys. Res. Lett. 2019, 46, 12986−12995.

(72) Burchfiel, B. C.; Chen, Z. Tectonics of the Southeastern Tibetan Plateau and its Adjacent Foreland; The Geological Society of America: Memori 210, 2012; pp 37−52.

(74) Wei, F.; Xu, J.; Shangguan, Z.; Pan, B.; Yu, H.; Wei, W.; Bai, X.; Chen, Z. Helium and carbon isotopes in the hot springs of Changbaishan Volcano, northeastern China: A material connection between Changbaishan Volcano and the west Pacific plate? J. Volcanol. Geotherm. Res. 2016, 327, 398−406.

(75) Burnard, P.; Bourlange, S.; Henry, P.; Geli, L.; Tryon, M. D.; Natal' in, B.; Sengör, A. M. C.; Ozeren, M. S.; Çagatay, M. N. Constraints on fluid origins and migration velocities along the Marmara Main Fault (Sea of Marmara, Turkey) using helium isotopes. Earth Planet. Sci. Lett. 2012, 341−344, 68−78.

(76) Klemperer, S. L.; Kennedy, B. M.; Saxtry, S. R.; Makovsky, Y.; Harinarayana, T.; Leech, M. L. Mantle fluids in the Karakoram fault: helium isotope evidence. Earth Planet. Sci. Lett. 2013, 366, 59−70.

(77) Tanikawa, W.; Sakaguchi, M.; Tadai, O.; Hirose, T. Influence of fault slip rate on shear-induced permeability. J. Geophys. Res. 2010, 115, No. B07412.

(78) Wang, Y.; Liu, Y.; Zhao, C.; Li, Q.; Zhou, Y.; Ran, H. Helium and carbon isotopic signatures of thermal spring gases in southeast Yunnan, China. J. Volcanol. Geotherm. Res. 2020, 402, No. 106995.

(79) Wang, Y.; Wang, E.; Shen, Z.; Wang, M.; Gan, W.; Qiao, X.; Meng, G.; Li, T.; Tao, W.; Yang, Y.; Cheng, J.; Li, P. GPS-constrained inversion of present-day slip rates along major faults of the Sichuan-Yunnan region, China. Sci. China, Ser. D: Earth Sci. 2008, 51, No. 1267.