

## Article

# Genesis of the Graphite from the Tugeman Graphite Deposit, Xinjiang, China: Evidence for Carbon Isotope Refining by Fluids Associated with the Ductile Shear Zone

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**Abstract:** The Altun orogenic belt is situated along the northern boundary of the Tibetan Plateau. In this study, we present an analysis of the ore deposit, mineral composition, and carbon isotope signatures of the Tugeman graphite deposit within the Altun orogenic belt. The graphite in the Tugeman graphite deposit occurs within graphite-bearing schists and marble. Graphite enrichment is observed in the ductile shear zone. The carbon isotope values of graphite range between  $-18.90\text{‰}$  and  $-10.03\text{‰}$  (with an average value of  $-12.70\text{‰}$ ). These values differ significantly from those observed in organic matter and marine carbonates, suggesting the occurrence of a mixing process involving reduced carbon fluid derived from biological organic material during regional metamorphism as well as a potential influx of oxidized carbon fluid from external sources. In addition, the metamorphic temperature of Tugeman graphite calculated from Raman spectroscopy is between  $494\text{ °C}$  and  $570\text{ °C}$ , which indicates that the disordered material is transformed from greenschist-amphibolite facies metamorphism to moderate-crystalline graphite. Combining the geological and carbon isotope characteristics of the Tugeman graphite deposit, we argue that the Tugeman graphite deposit is a regional metamorphic graphite deposit of biogenic origin, and during the late stage of metamorphism, it underwent interaction with fluids.

**Keywords:** Altun orogenic belt; Tugeman; graphite deposit; carbon isotopes; fluid mixing



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## 1. Introduction

The distinctive characteristics of graphite have made it a valuable component in industrial materials. The rise of advanced materials like graphene has heightened interest in the availability of graphite resources [1–3]. China, the United States, and the European Union have all identified natural flake graphite deposits as a mineral that is critical to their supply chain [2,4,5].

In terms of graphite production and export, China holds the top position globally [3]. Recently, many graphite deposits have been discovered in Xinjiang province, including the Qitai County Huangyangshan, Yiwu County Tuerkuli, Qinghe County Kongkere and Sujiquan, Dabuxun, and Sandeke graphite deposits [6]. Although graphite deposits are

already mined in Xinjiang province, the metallogeny of these deposits is still poorly studied so far. A comprehensive examination of the mineralization process of graphite deposits has been of critical importance as industrial uses soar and the demand for the material rises quickly.

The application of carbon isotope analysis plays a significant role in discerning the carbon origins within diverse geological formations. This approach is extensively utilized in studying the genesis of diamond [7,8], the evolutionary processes of life on our planet [9–13], and the formation mechanisms of graphite [14–17], contributing to a comprehensive understanding of these complex phenomena. The temperature-dependent effects of fractionation and the carbon source have an impact on the composition of carbon isotopes [14]. With rising temperatures, the fractionation of carbon isotopes between the two phases reduces [18–21], and prograde metamorphism causes the metamorphic graphite to become heavier due to the release of isotopically light methane [14]. Carbon isotope exchange has been reported and efficiently used as a thermometer in all ranges of temperature conditions, up to ultra-high temperature conditions, except for a third carbon-bearing phase in the system, such as CO<sub>2</sub> fluid [20,22,23]. For instance, Ueno et al. [10] documented a distinct trend in the  $\delta^{13}\text{C}$  value of graphite during the metamorphic process, specifically noting an elevation from  $-14\text{‰}$  to  $-5\text{‰}$  as the rocks transformed from epidote-amphibolite facies to upper amphibolite facies. Each different carbon reservoir is distinguished by different carbon isotope values. In general, the carbon isotope values of organic matter, mantle, and marine carbonate range from  $-40\text{‰}$  to  $-17\text{‰}$  [24], from  $-7\text{‰}$  to  $-3\text{‰}$  [25], and from  $-2\text{‰}$  to  $+4\text{‰}$  [26], respectively. Carbon obtained from organic matter is lighter compared to carbon derived from the mantle or carbonates [14].

The carbon isotope information for graphite deposits and the ore-bearing khondalite series was summarized by Chen et al. [27]. These data show that: (1) the carbon isotope composition of graphite is correlated with the rock types; and (2) hydrothermal fluids exert a profound influence on the fractionation and homogenization of carbon isotope compositions of graphite and function as a pivotal medium for the circulation of carbon throughout geological systems.

Recently, Ai et al. [28] and Sun et al. [29] have conducted carbon isotopic studies on the Huangyangshan super-large graphite deposit in the Eastern Junggar orogenic belt. The results of these studies demonstrate a striking similarity in the  $\delta^{13}\text{C}$  value between the graphite deposit and the proximal strata, suggesting the source of carbon for the graphite deposit is likely to come from the organic carbon in the proximal strata.

The Tugeman graphite deposit was discovered by the No. 3 Geological Party, Xinjiang Bureau of Geology and Mineral Exploration and Development. The geological characteristics and prospecting indicators of ore deposits are the main contents of recent research. However, there are few studies on the genetic model and carbon source of graphite deposits.

This paper presents a comprehensive study of the geological and carbon isotope composition of graphite from the Tugeman graphite deposit. This study aims to enhance our understanding of the ore-forming conditions and characteristics of the Tugeman graphite deposit, which will undoubtedly facilitate the identification and discovery of graphite deposits in this region.

## 2. Geological Setting

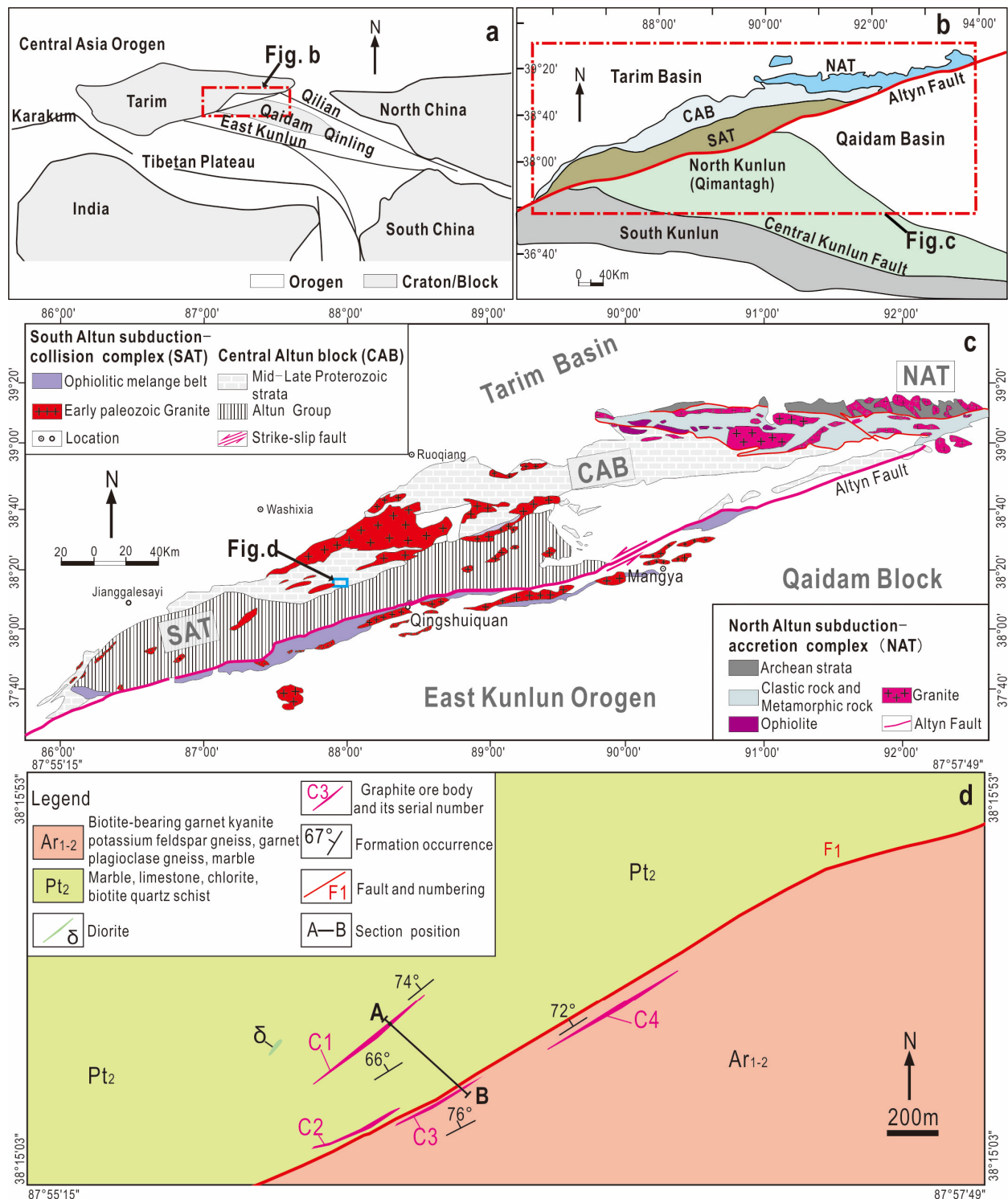
The Altyn Tagh extends east–west for c. 1000 km and is sandwiched between the Qilian and Kunlun Orogenic Belts and the Tarim and Qaidam blocks [30]. It is adjacent to the Tarim Basin on the north and delimited by the Altyn left-lateral strike-slip fault on the south. The Altyn Tagh has a complex history that includes the formation of an Archean–Paleoproterozoic continental nucleus [31,32], Mesoproterozoic passive margin development, Neoproterozoic rifting, early Paleozoic subduction and collision [33,34], late Paleozoic erosion and local shallow-marine sedimentation [35], Triassic extensional, and left-lateral strike-slip deformation during the Late Jurassic–Early Cretaceous [36–38]. These

processes resulted in the formation of a composite orogenic belt consisting of geological complexes that originated at different times and tectonic backgrounds [39,40].

The Altun orogenic belt consists of three tectonic units (Figure 1a): the North Altun subduction–accretion belt, the Central Altun block, and the South Altun subduction–collision belt. The North Altun subduction–accretion belt consists mainly of early Paleozoic ophiolites (e.g., the 490–450 Ma Qiashikasayi ophiolite; [41,42]), volcanic granitic rocks, high-pressure blueschists [43], flysch deposits, and I- and S-type granites (520–400 Ma; [44–48]).

The main rock types in the Central Altun block were formed in the Altun Group of the Paleoproterozoic and the Calymmian, Ectasian, and Stenian periods of the Mesoproterozoic and the Tonian period of the Neoproterozoic [49,50]. The Altun Group is a metamorphic complex dominated by amphibolite facies, which have long been regarded as part of the Tarim metamorphic basement [51]. The Mesoproterozoic–Neoproterozoic rocks are mainly composed of clastic rock, carbonate rock, and a small amount of volcanic rock, which was derived from the stable continental margin environment with shallow metamorphism, and the carbonate rocks contain stromatolites [51]. The degree of metamorphism of rocks is relatively low, and the aluminum-rich metamorphic rocks mainly consist of biotite, muscovite, garnet, plagioclase, K-feldspar, quartz, amphibole, and calcite, the metamorphic basic rocks consist of amphibole, pyroxene, plagioclase, and quartz. In addition, these rocks have undergone regional thermal flow dynamometamorphism of high greenschist facies—low amphibolite facies [52].

The South Altun subduction–collision belt features the Southern Altun HP-UHP metamorphic belt, which serves as a characteristic early Paleozoic subduction–collision belt. This metamorphic belt encompasses a range of rock types, such as garnet-bearing pelitic gneiss, kyanite–garnet, and granitic gneisses [53]. Furthermore, the presence of the Southern Altun ophiolite belt provides evidence of early Paleozoic subduction and collision within the Southern Altun region [53].



**Figure 1.** (a) Location of Altun Tagh and adjoining regions; (b) schematic distribution of main geotectonic units in Altun Tagh and East Kunlun; (c) geological sketch map of the Altun orogenic belt (the figures are modified after Li et al. [54]); and (d) Tugeman graphite deposit (after [55]).

### 3. Geology of the Tugeman Graphite Deposit and Petrography Descriptions

The Tugeman area is located in the middle of the Central Altun block, and the Tugeman graphite deposit was discovered in the southwestern part of the Tugeman area. The main outcropping strata in the Tugeman graphite ore district are the Archean Milan Group (Ar<sub>1-2</sub>) and the upper lithologic segment of the Yinggelike structure ophiolite mélangé

flysch sheet (Pt<sub>2</sub>). The Archaean Milan Group, with an area of ~1.5 km<sup>2</sup>, is exposed in the south of the study area. Its elongation direction is primarily NE–SW, where a fault contact occurs with the upper lithologic segment of the flysch of the overlying Yinggelike structure ophiolitic complex. The main lithology of the outcrop is marble with garnet plagioclase gneiss. The upper lithologic segment of the Yinggelike structure ophiolite complex flysch is largely exposed in the north of the study area, with an area of ~2.5 km<sup>2</sup>, extending in an NE–SW direction.

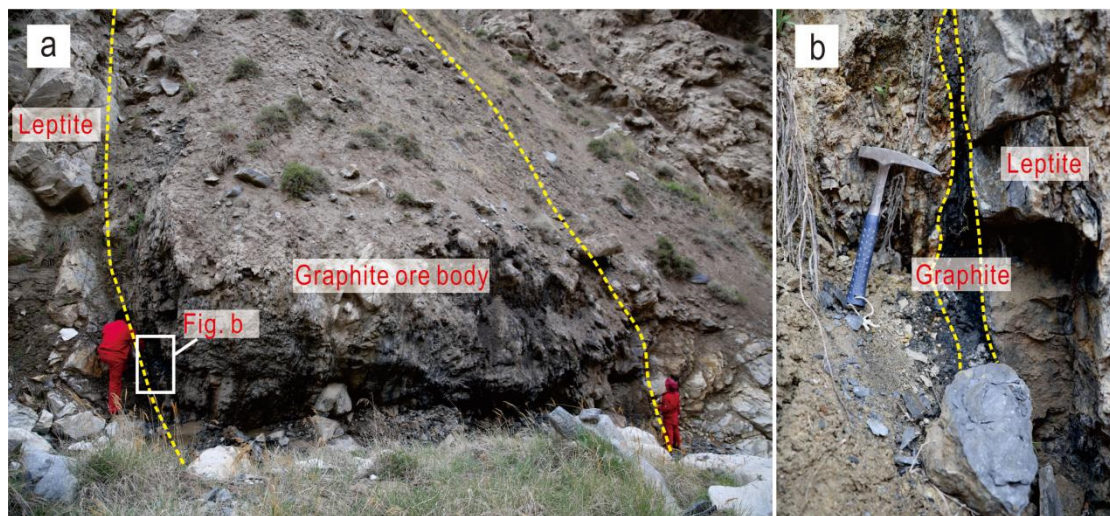
No obvious intrusive rocks are exposed in the study area. In the southern part of the mine area, there is an NE trending fault with a strike of N54E–S54W. The northern part of the fault contains the upper part of the ophiolite flysch of the Yinggelike structure and is made up of biotite plagioclase schist. The southern part of the fault contains the cleaved marble of the Archaean Milan Group. The fault fracture zone is about 50 m wide, and graphite mineralization is common in the fracture zone.

The graphite ore body occurs in the fracture zone that flanks the F1 fault on both sides, and the ore-bearing lithology is mainly schist and marble. There are four graphite ore bodies in the study area (namely C1, C2, C3, and C4; Table 1). The resources of the four graphite ore bodies can reach 1,836,700 tons, and the average grade of the deposit is 5.03%, which is a small crystalline graphite deposit.

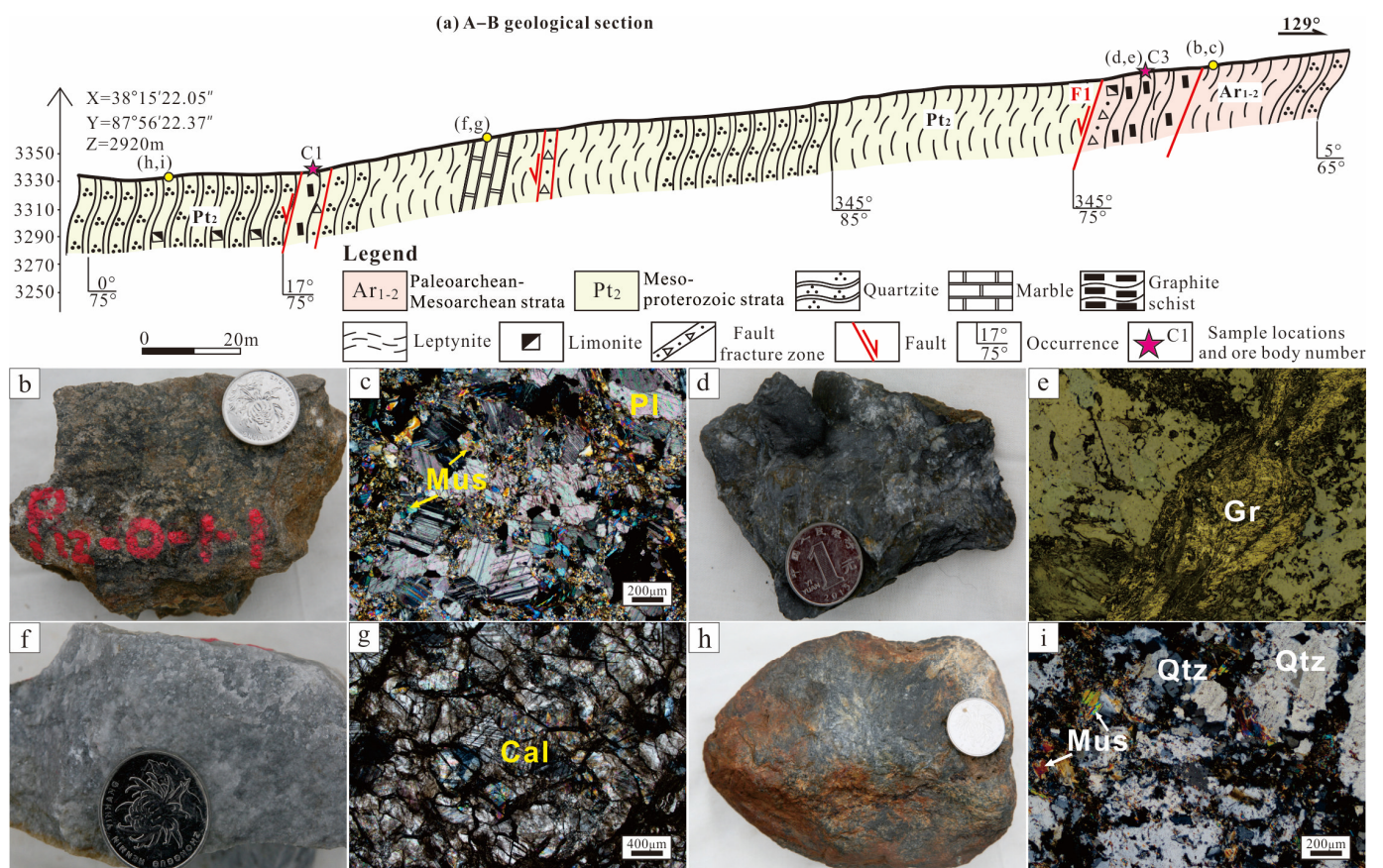
**Table 1.** Geological characteristics of the graphite ore body from the Tugeman area.

| Graphite Ore Body | Long (m) | Thickness (m) | Fixed Carbon Grade | Ore-Bearing Lithology | Occurrence          | Types of Graphite          | Other Features                                                               |
|-------------------|----------|---------------|--------------------|-----------------------|---------------------|----------------------------|------------------------------------------------------------------------------|
| C1                | 550      | 2.91          | 5.24%–6.35%        | Schist and marble     | 308°–325° / 75°–78° | Flake-crystalline graphite | Graphite distribution along foliation, accompanied by pyrite in graphite ore |
| C2                | 394      | 3.45          | 4.64%–7.46%        | Schist and marble     | 304°–325° / 75°–82° | Flake-crystalline graphite | Graphite distribution along foliation, accompanied by pyrite in graphite ore |
| C3                | 386      | 2.64          | 2.95%–3.96%        | Schist and marble     | 310°–318° / 70°–73° | Flake-crystalline graphite | Graphite distribution along foliation, accompanied by pyrite in graphite ore |
| C4                | 603      | 2.54          | 2.95%–5.59%        | Schist and marble     | 300°–315° / 71°–77° | Flake-crystalline graphite | Graphite distribution along foliation, accompanied by pyrite in graphite ore |

Graphite is mainly present in the Tugeman graphite deposit within graphite-bearing schists and marble, and the occurrence of graphite in these rocks is predominantly characterized by disseminated flakes (Figure 2). The graphite-bearing schists are mainly composed of feldspar (20%–30%), quartz (40%–45%), biotite (20%–30%), muscovite (15%–20%), graphite (5%–10%), and pyrite (1%–3%, Figure 3d,e). Tugeman graphite is generally a flake-crystalline graphite with an irregular distribution along foliation. The thickness is generally smaller than 1 mm, and the thickness of the graphite aggregates is generally smaller than 10 mm.



**Figure 2.** (a) Field photograph of the C1 graphite ore body; (b) Field photograph of the contact relationship between C1 graphite ore body and country rock.



**Figure 3.** (a) The A-B geological section in the Tugeman graphite deposit; (b,c) hand specimen and microphotograph of leptynite; (d,e) hand specimen and microphotograph of graphite-bearing schist; (f,g) hand specimen and microphotograph of marble; and (h,i) hand specimen and microphotograph of limonite quartzite. The coin in the picture is 2.5 cm in diameter. Gr = graphite; Qtz = quartz; Cal = calcite; Pl = plagioclase; Mus = muscovite.

## 4. Analytical Methods

### 4.1. Carbon Isotope Test

The carbon isotopes of graphite were analyzed using a Delta V Advantage isotope ratio mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) at the Laboratory for Stable Isotope Geochemistry, Institute of Geology and Geophysics, Chinese Academy of Sciences. Sample powders were decarbonated by pouring them into 6 N HCl for 24 h. After neutralization, the dried samples were transferred into tin capsules and underwent combustion within the EA autosampler. The CO<sub>2</sub> gas that was produced was fed into the mass spectrometer to measure its isotopic composition. Isotopic values of organic carbon are quantified using the Vienna Pee Dee Belemnite (VPDB) standard ( $\delta^{13}\text{C}_{\text{carb}}$ ) and expressed in per mil notation (‰) and calculated by the formula  $\delta^{13}\text{C}_{\text{‰}} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 10^3$ , where  $R = {}^{13}\text{C}/{}^{12}\text{C}$ . Sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) with a known isotopic composition was used as the standard to monitor the analytical quality. Repeated measurements ( $n = 9$ ) obtained a reproducibility ( $2\sigma$ ) of  $\pm 0.15\text{‰}$ . For detailed analytical procedures, please refer to Zhu et al. [17].

### 4.2. Raman Spectroscopy Test

The micro-Raman microscopy analysis was conducted utilizing the DXR3xi Raman spectrometer, manufactured by Thermo Fisher Scientific (Waltham, MA, USA), with a 50× objective lens. The analysis focused on a graphite sheet contained within a meticulously prepared, polished thin section at Sanming University. The experimental setup entailed specific conditions as follows: the excitation source emitted light with a wavelength of 532 nm, facilitating the collection of Raman signals within the spectral range spanning from 50 to 3400 cm<sup>−1</sup> while maintaining a laser power of 40 mW. To ensure accuracy and precision, the spectrometer underwent regular calibration using a silicon standard, performed prior to each analysis. The spectrum was evaluated and decomposed using Peak Fit Version 4.12 (SeaSolve Software, Inc., San Jose, CA, USA).

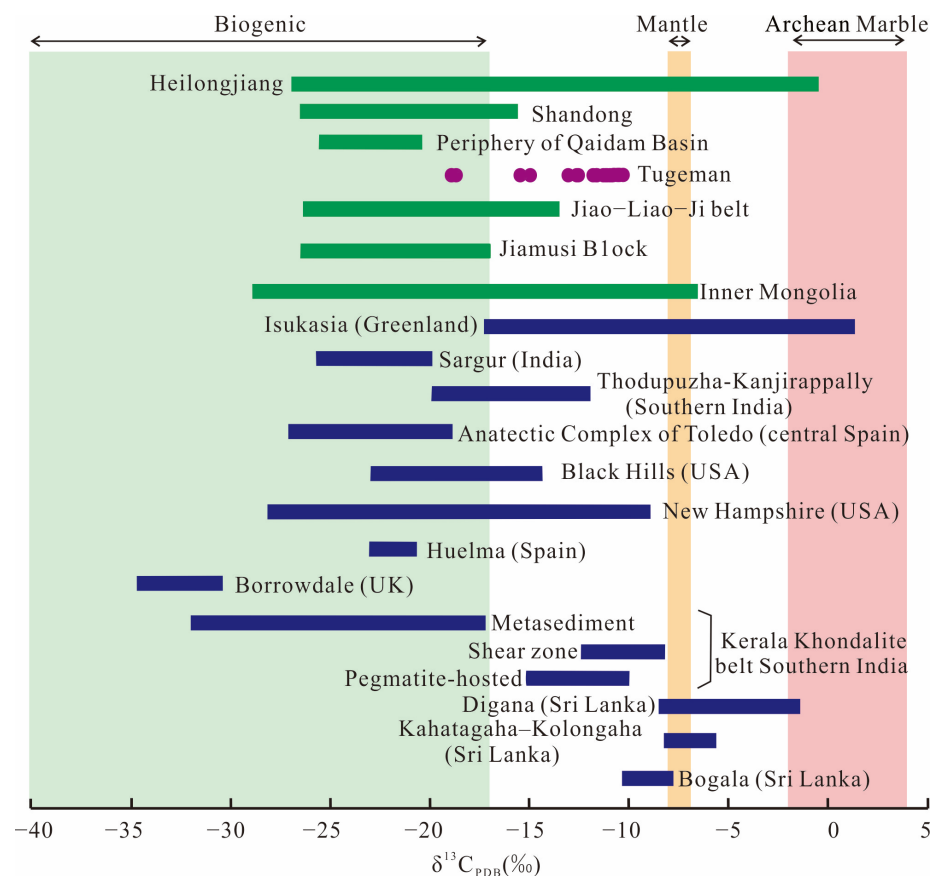
## 5. Results

### 5.1. Carbon Isotope Compositions of Graphite

Since C1 and C2 orebodies are in Pt<sub>2</sub> (the C1 and C2 orebodies have similar characteristics), and C3 and C4 orebodies are in Ar<sub>1–2</sub> (the C3 and C4 orebodies have similar characteristics), we selected C1 and C3 orebodies for the carbon isotope test. Table 2 and Figure 4 present a comprehensive overview of the carbon isotope results pertaining to graphite samples derived from C3 and C1 ore bodies. Among them, twelve samples (denoted as G1–G12) were obtained from the graphite ore body C3, while eight samples (identified as G13–G20) originated from the graphite ore body C1. This study presents a comparative analysis of the carbon isotopic compositions of graphite deposits in various geographical locations, including two graphite metallogenic belts surrounding the North China Craton [15,27], as well as groundwater, terrestrial carbonate, and atmospheric CO<sub>2</sub> [56]. Additionally, comparisons are made with graphite deposits from Heilongjiang [57,58], Shandongsheng [59], the periphery of the Qaidam Basin [56], Isukasia (Greenland) [10,60], Sargur (India) [61], Thodupuzha-Kanjirappally (Southern India) [62], the Anatectic Complex of Toledo in Central Spain [63], the Kerala Khondalite Belt in Southern India [64–66], Borrowdale in the UK [67–69], Huelma in Spain [68,70], New Hampshire in the USA [71,72], and the Black Hills in the USA [73,74].

**Table 2.** Carbon isotope values of the graphite-bearing rocks in the Tugeman graphite deposit.

| Serial No.                   | Samples No. | Mineral  | $\delta^{13}\text{C} \text{ ‰ (VPDB)}$ |
|------------------------------|-------------|----------|----------------------------------------|
| Samples from the C3 ore body |             |          |                                        |
| 1                            | G1          | Graphite | −11.05                                 |
| 2                            | G2          | Graphite | −10.03                                 |
| 3                            | G3          | Graphite | −10.60                                 |
| 4                            | G4          | Graphite | −10.32                                 |
| 5                            | G5          | Graphite | −10.71                                 |
| 6                            | G6          | Graphite | −10.50                                 |
| 7                            | G7          | Graphite | −10.86                                 |
| 8                            | G8          | Graphite | −12.35                                 |
| 9                            | G9          | Graphite | −10.22                                 |
| 10                           | G10         | Graphite | −12.43                                 |
| 11                           | G11         | Graphite | −10.94                                 |
| 12                           | G12         | Graphite | −11.58                                 |
| Samples from the C1 ore body |             |          |                                        |
| 13                           | G13         | Graphite | −18.66                                 |
| 14                           | G14         | Graphite | −14.83                                 |
| 15                           | G15         | Graphite | −15.35                                 |
| 16                           | G16         | Graphite | −11.41                                 |
| 17                           | G17         | Graphite | −18.90                                 |
| 18                           | G18         | Graphite | −11.39                                 |
| 19                           | G19         | Graphite | −12.87                                 |
| 20                           | G20         | Graphite | −18.90                                 |

**Figure 4.** Carbon isotope composition of graphite in various graphite deposits. The carbon isotopic characteristics of graphites from Heilongjiang [57,58], Shandongsheng [59], Periphery of Qaidam

Basin [56], Jiao–Liao–Ji belt [75], Jiamusi Block, Inner Mongolia [15,27], Isukasia (Greenland) [10,60], Sargur (India) [61], Thodupuzha-Kanjirappally (Southern India) [62], Anatectic Complex of Toledo (Central Spain) [63], Kerala Khondalite Belt, Southern India [64–66], Borrowdale (UK) [67–69], Huelma (Spain) [68,70], New Hampshire (USA) [71,72], Black Hills (USA) [73,74], Bogala (Sri Lanka) [25,76,77], Kahatagaha-Kolongaha (Sri Lanka) [76], and Digana (Sri Lanka) [25,78] are shown for comparison.  $\delta^{13}\text{C}$  value ranges of biogenic, mantle, and carbonate materials sourced from [24,25,79]. The data for graphite deposits from China (green) and other countries (blue) are displayed in the Supplementary Table S1.

The carbon isotopic values ( $\delta^{13}\text{C}$ ) exhibited considerable variability in the graphite samples obtained from Tugeman, ranging from  $-18.90\text{‰}$  to  $-10.03\text{‰}$  (average of  $-12.70\text{‰}$ , standard deviation of 2.92). The  $\delta^{13}\text{C}$  values of graphites from the C3 ore body range from  $-12.43$  to  $-10.03\text{‰}$  (average of  $-10.97\text{‰}$ , standard deviation of 0.75), and the carbon isotopic composition ( $\delta^{13}\text{C}$ ) of graphite in the C1 ore body exhibits a marginal reduction when compared to the graphite sample in the C3 ore body, varying from  $-18.90$  to  $-11.39\text{‰}$  (average of  $-15.29\text{‰}$ , standard deviation of 3.04).

## 5.2. Graphite Raman Spectroscopy

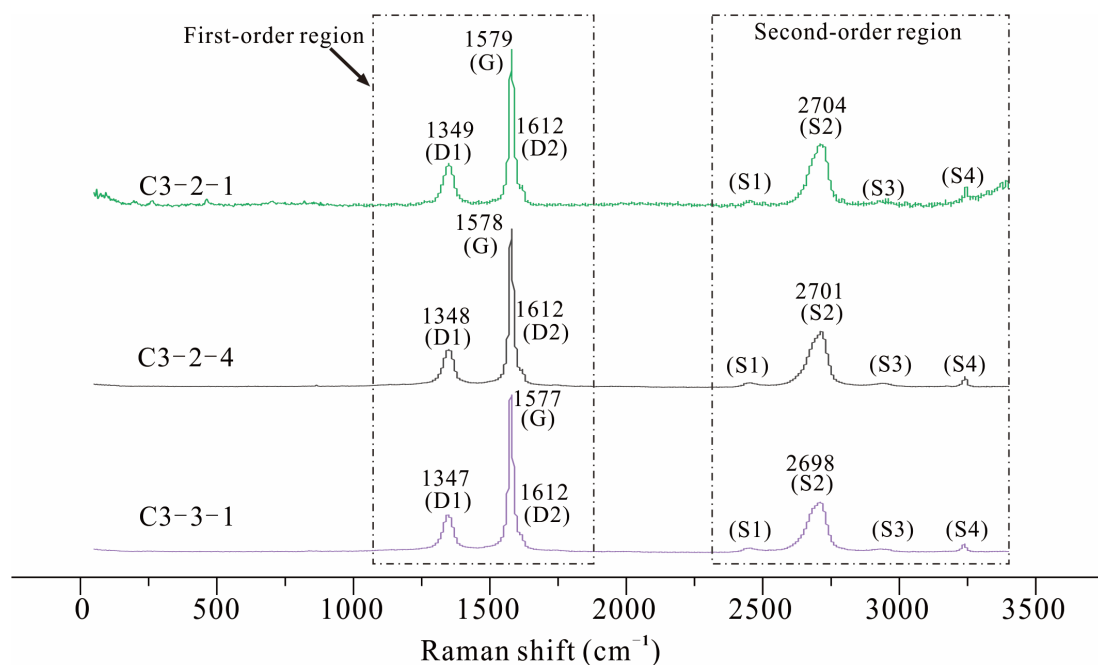
Figures 5 and 6d exhibit the Raman spectra analysis of graphite particles derived from the Tugeman graphite deposits. Raman spectra encompass both first- and second-order regions, as depicted in Figure 5 [80,81]. The first-order Raman spectra reveal the presence of three prominent peaks, namely D1, D2, and G, in the Tugeman graphite deposits (Figures 5 and 6d). D1 peaks are observed within the range of  $1346$  to  $1352\text{ cm}^{-1}$ , while G peaks exhibit a narrow range of  $1571$  to  $1580\text{ cm}^{-1}$ . A faint D2 peak can be observed adjacent to the lower-right side of the G peak, ranging from  $1610$  to  $1622\text{ cm}^{-1}$  (Table 3). The ID/IG (R1;  $\text{Intensity}_{\text{D1-band}}/\text{Intensity}_{\text{G-band}}$ ) for the C3 and C4 ore bodies varies between 0.25 and 0.27 (average value of 0.26) and 0.11 and 0.30 (average value of 0.24), respectively. The D1/(D1 + G + D2) (R2) peak area ratio varies between 0.32 and 0.33 (average value of 0.33) and 0.16 and 0.33 (average value of 0.28) for the C3 and C4 ore bodies, respectively. Furthermore, the Tugeman graphite sample demonstrates four peaks in the second-order regions, namely S1, S2, S3, and S4 (Figure 5). Among these, S2 manifests as the most intense peak within the range of  $2697$ – $2719\text{ cm}^{-1}$  (Table 3). On the other hand, the intensities of S1 and S3 are exceptionally low, nearly approaching zero (Figure 5). Since the D3 and D4 peaks are usually present in poorly crystallized graphite [80,81], and the S2' peaks are only present in highly crystallized graphite [82], the absence of the D3 ( $1320$  to  $1350\text{ cm}^{-1}$ ), D4 ( $1500$  to  $1550\text{ cm}^{-1}$ ), and S2' ( $2681$  to  $2690\text{ cm}^{-1}$ ) [56] peaks in the Tugeman graphite deposit indicates that the graphite obtained from the Tugeman graphite deposit does not correspond to either poorly crystalline or highly crystalline graphite [80–82]. Therefore, we conclude that the degree of graphite crystallization within Tugeman graphite deposits is moderate. The full width at half maximum (FWHM) of the G peak, as determined using the Lorentz function, ranges from  $23$  to  $29\text{ cm}^{-1}$ , while the FWHM of the S2 peak varies from  $67$  to  $82\text{ cm}^{-1}$  (Table 3).

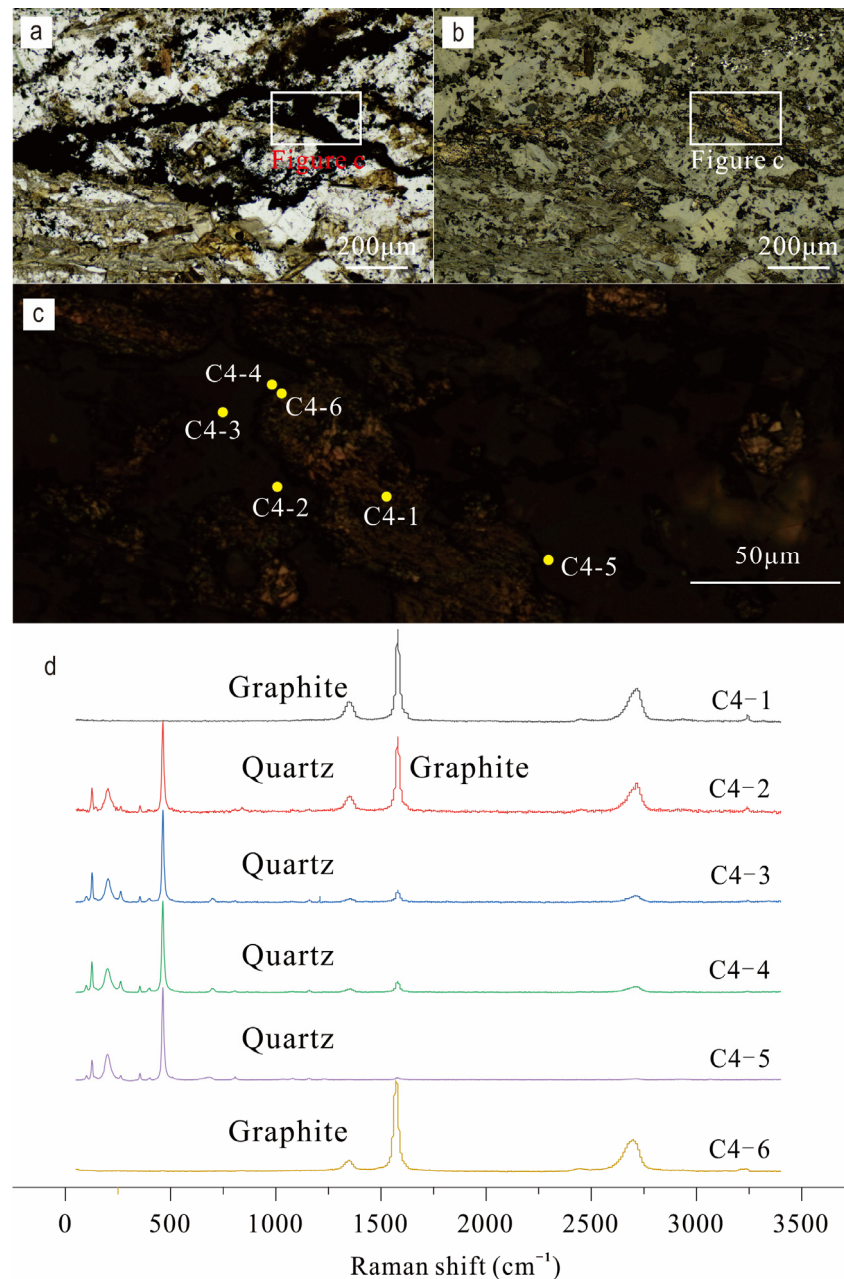
**Table 3.** Quantitative parameters of Raman spectroscopy of graphite samples in the Tugeman flake-graphite deposit.

| Sample | D1-Bands/cm <sup>-1</sup> |           |      |            |               | G-Band/cm <sup>-1</sup> |      |            | D2-Bands/cm <sup>-1</sup> |           |      |            |
|--------|---------------------------|-----------|------|------------|---------------|-------------------------|------|------------|---------------------------|-----------|------|------------|
|        | Peak Position             | Band Area | FWHM | Peak Value | Peak Position | Band Area               | FWHM | Peak Value | Peak Position             | Band Area | FWHM | Peak Value |
| C4-1   | 1352                      | 2150      | 52   | 39         | 1576          | 4301                    | 27   | 148        | 1622                      | 1175      | 71   | 16         |
| C4-2   | 1349                      | 649       | 54   | 11         | 1579          | 1365                    | 24   | 54         | 1612                      | 230       | 34   | 6          |
| C4-3   | 1350                      | 441       | 48   | 9          | 1580          | 759                     | 25   | 29         | 1616                      | 139       | 29   | 4          |
| C4-4   | 1350                      | 841       | 47   | 17         | 1579          | 1441                    | 24   | 56         | 1615                      | 264       | 34   | 7          |
| C4-6   | 1346                      | 2714      | 56   | 46         | 1571          | 12,985                  | 29   | 417        | 1610                      | 1243      | 30   | 39         |
| C3-2-4 | 1348                      | 25,045    | 53   | 441        | 1578          | 43,385                  | 23   | 1762       | 1612                      | 7434      | 32   | 220        |
| C3-2-1 | 1349                      | 2482      | 49   | 48         | 1579          | 4347                    | 23   | 175        | 1612                      | 741       | 29   | 24         |
| C3-3-1 | 1347                      | 13,307    | 54   | 233        | 1577          | 24,681                  | 25   | 933        | 1612                      | 3699      | 29   | 118        |

| S2-band/cm <sup>-1</sup> |           |      |            | ID/IG              | D1/(G + D1 + D2)          |  | S2/G       | Peak Metamorphic Temperature/°C |             |
|--------------------------|-----------|------|------------|--------------------|---------------------------|--|------------|---------------------------------|-------------|
| Peak Position            | Band Area | FWHM | Peak Value | R1 Intensity Ratio | R <sub>2</sub> Area Ratio |  | Area Ratio | Formula (1)                     | Formula (3) |
| 2719                     | 5051      | 75   | 63         | 0.26               | 0.28                      |  | 1.17       | 516                             | 527         |
| 2705                     | 1697      | 80   | 20         | 0.21               | 0.29                      |  | 1.24       | 512                             | 523         |
| 2704                     | 1336      | 78   | 16         | 0.30               | 0.33                      |  | 1.76       | 494                             | 503         |
| 2702                     | 2599      | 81   | 30         | 0.30               | 0.33                      |  | 1.80       | 494                             | 503         |
| 2697                     | 7209      | 67   | 102        | 0.11               | 0.16                      |  | 0.56       | 570                             | 590         |
| 2701                     | 57,821    | 82   | 663        | 0.25               | 0.33                      |  | 1.33       | 494                             | 503         |
| 2704                     | 6075      | 77   | 74         | 0.27               | 0.33                      |  | 1.40       | 495                             | 504         |
| 2698                     | 29,031    | 82   | 331        | 0.25               | 0.32                      |  | 1.18       | 499                             | 508         |

**Figure 5.** Representative characteristics of the Raman spectra of graphite samples in the Tugeman graphite deposit. The first- and second-order regions are marked by the dashed lines.



**Figure 6.** Microphotograph (a–c) and Raman spectra (d) of graphite-bearing schist of the C4 ore body in the Tugeman graphite deposit. a—plane-polarized; b and c—reflected light.

## 6. Discussion

### 6.1. Carbon Source of the Tugeman Graphite Deposit

Anomalously high carbon burial played a crucial role in reducing friction strength and lubricating compressive deformation, which allowed crustal thickening to build Palaeoproterozoic mountain belts [83,84]. The earth's carbon reservoirs primarily consist of three principal sources: organic matter, sedimentary carbonates, and mantle-derived igneous carbon [14,16,85]. Each of these sources is distinguished by a different isotopic value. Organic matter typically has carbon isotope ratios between  $-40\text{‰}$  and  $-17\text{‰}$  [24], with an average  $\delta^{13}\text{C}$  value of  $-27\text{‰}$  [9]. The  $\delta^{13}\text{C}$  values of marine carbonate rocks generally tend to be relatively heavier, falling within the range of  $-2\text{‰}$  to  $+4\text{‰}$  [26,86]. In comparison to marine carbonates, mantle-derived carbon has a somewhat lower carbon isotope composition ( $\delta^{13}\text{C} = -5\text{‰} \pm 2\text{‰}$ ) [25].

The origin of graphite has been explored in many studies using carbon isotope analysis [15,16,27,85]. For instance, Chen et al. [27] conducted a comprehensive analysis of the carbon isotope characteristics within the North China Craton. Their study revealed substantial variability in the carbon isotope values of graphite deposits in Jiamusi ( $\delta^{13}\text{C} = -24.4 \sim -16.8\text{‰}$ ) and Inner Mongolia ( $\delta^{13}\text{C} = -25.66 \sim -6.42\text{‰}$ ), as depicted in Figure 4. Notably, the carbon isotopic composition of these deposits exhibits similarities with the graphite found in the Kerala Khondalite Belt [75]. Furthermore, graphite deposits from New Hampshire (USA) [71], Huelma (Spain) [68], Borrowdale (UK) [67–69], and Black Hills (USA) [74] all have biogenic carbon isotope signatures (Figure 4).

Based on an investigation of carbon isotope compositions of graphite from diverse graphite-bearing rock types in the Kerala Khondalite Belt of Southern India, it has been observed that the graphitization process of organic matter within sedimentary deposits, subjected to regional high-grade metamorphism, yields graphite with lighter and more widely dispersed isotopic signatures ( $\delta^{13}\text{C} = -32.09 \sim -17.51\text{‰}$ ) in metapelites [14,64,65]. Conversely, graphite occurring within pegmatites and shear zones typically exhibits heavier carbon isotopes, with  $\delta^{13}\text{C}$  values ranging from  $-15.1$  to  $-10.0\text{‰}$  and  $-12.4$  to  $-8.2\text{‰}$ , respectively [16,64] (Figure 4). This graphite is believed to be the result of precipitation from  $\text{CO}_2$ -rich fluids derived from igneous rocks [64], and other studies suggest  $\text{CO}_2$  is derived from carbonates during decarbonation reactions [87]. The graphite in the Heilongjiang graphite-bearing magnetite deposit has heavy graphite carbon isotope values ( $-7.4$  to  $-1.0\text{‰}$ ), which is interpreted to be a result of metamorphic decomposition of primarily deposited siderite under strong reducing conditions [57] (Figure 4). The heavier  $\delta^{13}\text{C}$  values ( $-9.25$  to  $-5.61\text{‰}$ ) of Sri Lankan graphite confirm that graphite mineralization is not associated with granulite facies metamorphism of supracrustal rocks but likely represents a magmatic origin, which is the precipitation reaction between carbon dioxide and methane in the C-O-H fluid [76]. The graphite in the Isukasia metasediments also has heavy graphite carbon isotope values ( $-17.3$  to  $+1.8\text{‰}$ ; [10]; Figure 4). Regarding the reason for the heavy carbon isotope value of graphite, Ueno et al. [10] proposed two explanations: (1) graphite exchanges isotopes with carbonate or  $\text{CO}_2$ -rich fluids; and (2) regional metamorphism.

In some cases, the bimodal distribution of  $\delta^{13}\text{C}$  values indicates the potential presence of multiple graphite carbon sources within a given mineral deposit [58]. Graphite deposits exhibiting distinct  $\delta^{13}\text{C}$  values, diverging from those associated with organic matter and global marine carbonates, suggest the occurrence of a mixing phenomenon involving COH fluids released through organic matter degassing as well as  $\text{CO}_2$ -rich fluids derived from sedimentary carbonate layers during periods of intense metamorphism [10,15].

Because the Tugeman graphite deposit occurs in the shear zone, the  $\delta^{13}\text{C}$  value of the graphite ranges from  $-18.9\text{‰}$  to  $-10.0\text{‰}$  (Figure 4). These carbon isotopic characteristics are consistent with those of Thodupuzha-Kanjirappally and shear zones (Figure 4) [64], displaying values marginally above the average  $\delta^{13}\text{C}$  of organic matter and below the average  $\delta^{13}\text{C}$  of marine carbonate rocks worldwide. Therefore, the slightly higher  $\delta^{13}\text{C}$  value than the average value of organic matter may be due to the effect of tectonic activities, which promote the occurrence of migmatization and eventually lead to a more enriched  $\delta^{13}\text{C}$  carbon isotope. However, the  $\delta^{13}\text{C}$  values of the C3 ore body are higher than those of the C1 ore body, which may be caused by the fact that there are more shear zones near the C3 ore body than the C1 ore body.

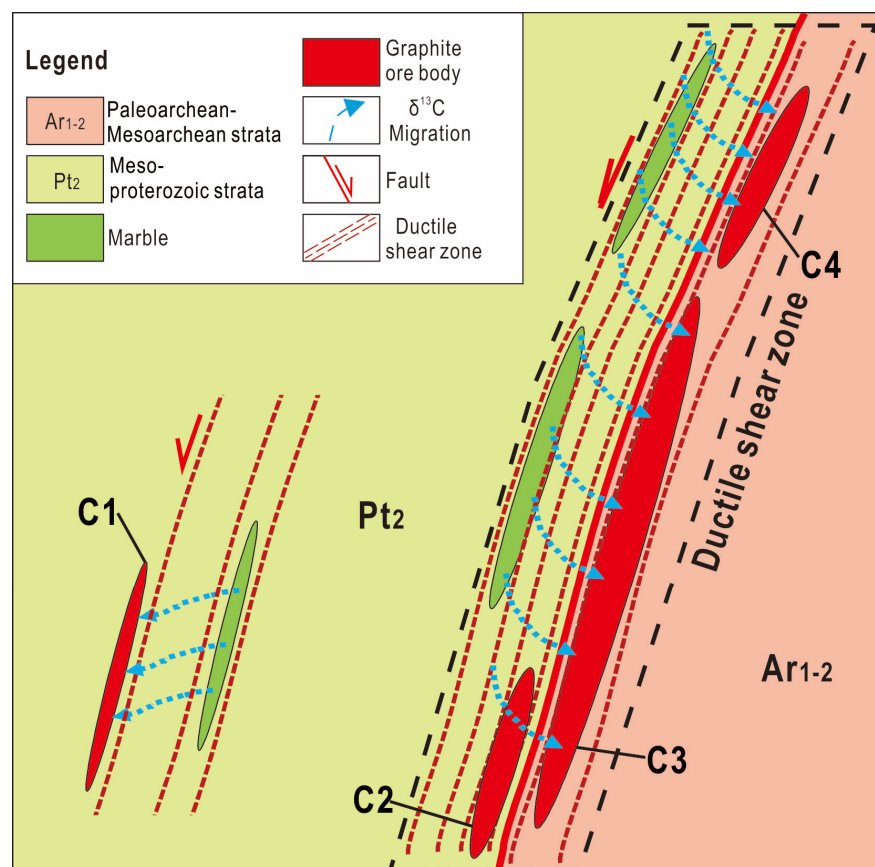
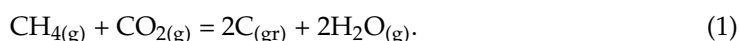
## 6.2. Metallogenic Process of the Tugeman Graphite Deposit

Graphite deposits can be categorized into three types based on their primary host rock types: regional metamorphic type, contact metamorphic type, and hydrothermal type [88]. Regional metamorphism mainly occurs in the orogenic belt, so the study of the orogenic belt has become one of the focuses of the genetic research of graphite deposits [83,84]. The host rock of the graphite deposit in the Tugeman area comprises a series of metamorphic rocks formed by regional metamorphisms, such as schist, marble, and leptynite [55]. The

ore body occurrence is consistent with the country rock and the flake graphite's overall zonal distribution along schistosity.

In addition to experiencing initial formation and subsequent metamorphic alteration, ore deposits are prone to being influenced by other metamorphic and deformation processes [89]. Within the mineralization system, the enrichment and/or thickening of mineralization can be attributed to internal and external ductile reactivation [90].

The formation of graphite involves either “graphitization” of biogenic material during metamorphism or precipitation from C-bearing fluids. Under geologically reasonable metamorphic conditions, GCOH fluids (graphite-saturated C-O-H fluid) are basically composed of H<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub> [91,92]. Solid carbon (graphite) can be precipitated from C-bearing fluids such as those containing CO<sub>2</sub>, CO, and/or CH<sub>4</sub> in crustal environments [91,93–96]. Studies of carbonaceous material found in natural fluid inclusions have also been reported [97,98]. Graphite can precipitate out in the fluid inclusion by changing the pressure, temperature, hydrogen fugacity ( $f_{H_2}$ ), and oxygen fugacity ( $f_{O_2}$ ) of the natural C-O-H fluid inclusions [99,100]. In addition, <sup>12</sup>C-enriched CH<sub>4</sub> and <sup>13</sup>C-enriched C (solid) can be formed by devolatilization reactions of organic matter [75]. The  $\delta^{13}C$  values (ranging from −18.9‰ to −10.0‰) of the Tugeman graphite deposit are different from those of organic matter, indicating a mixture of reduced carbon fluids derived from biogenic organic matter and oxidized carbon fluids during regional metamorphism. Consequently, we propose that the migration of oxidized components (CO<sub>2</sub>), combined with the mixing of reduced components (methane and other organic matter), resulted in the precipitation of graphite veins along fault orientations (Figure 7). The graphite may have formed as a result of the following chemical reaction:



**Figure 7.** The sketch formation of the deformation and mineralized structure in the Tugeman graphite deposit.

Based on an integration of the carbon isotope composition and the characteristics of the host rock in the Tugeman graphite deposit, it is inferred that the Tugeman graphite deposit is a regional metamorphic graphite deposit of organic origin, and the characteristics of superposition fluid and tectonic transformation are obvious in the later period of the deposit. Among them, the two fluid mixing reactions (1) in the late stage of the Tugeman graphite deposit are similar to the main formation mechanism of the Sri Lanka graphite deposit, which is known for its high purity and crystallinity [76].

### 6.3. Degree of Metamorphism in Graphite

The transition from low-crystalline carbonaceous materials to well-crystallized graphite involves a number of stages. As metamorphism progresses, the degree of structural disorder in carbonaceous material will decrease. This structural development is considered an irreversible process, rendering the material unaffected by retrograde metamorphism [101,102]. Consequently, the temperature recorded by the material reflects the maximum temperature value within the metamorphic thermal history. Raman spectroscopy serves as an in situ, nondestructive analytical technique capable of elucidating the crystal characteristics of graphite across different metamorphic grades [103]. After undergoing various metamorphic grades, graphite granules' Raman spectrum peaks change [82,104], primarily affecting the D1, G, and S1 bands as metamorphism intensifies [102]. The R1 and R2 ratios allow the determination of peak metamorphic conditions [82,101], as both R1 and R2 decrease with increasing metamorphic grade [26,84]. The R1 (<0.5) and R2 (<0.5) ratios of the C3 and C4 ore bodies indicate a higher degree of graphitization. Previous research has demonstrated the efficacy of Raman spectroscopy in determining the peak temperature of carbonaceous materials [101]. In this study, alongside qualitative observations of the Raman spectrum of graphite, the peak temperature was quantitatively determined using the calculation formula proposed by Beyssac et al. [101], as it is best suited for regional metamorphic terrain [105]. The formula is as follows:

$$T (^{\circ}\text{C}) = -445 \times R2 + 641, \quad (2)$$

where the area ratio is:

$$R2 = [D1 / (G + D1 + D2)]. \quad (3)$$

Additionally, for the sake of facilitating comparative analysis, we have incorporated the temperature estimation calculation proposed by Aoya et al. [106]. The formula is as follows:

$$T (^{\circ}\text{C}) = 91.4R2^2 - 556.3R2 + 676.3. \quad (4)$$

The geothermometer utilized in this study has an estimated error range of  $\pm 50^{\circ}\text{C}$ . Applying the formula to five graphite samples derived from the Tugeman graphite deposit, the determined peak temperatures range from 494 to 570  $^{\circ}\text{C}$  (Table 3). According to Stüwe [107], this temperature falls within the range of the lower amphibolite facies and the greenschist facies. This is basically consistent with the early metamorphic conditions (580–520  $^{\circ}\text{C}$ ) and the retrograde temperature of the late greenschist facies (500–450  $^{\circ}\text{C}$ ) obtained by Liu et al. [39] in the northern Altun high-pressure metamorphic rock belt. Consequently, considering the qualitative analysis of Raman spectra alongside the quantitative data analysis, it can be inferred that the graphite within the study area originates from the metamorphism occurring within the greenschist-lower amphibolite facies.

## 7. Conclusions

1. The graphite enrichment zone in the Tugeman region predominantly occurs within the ductile transition zone. The carbon isotopic values of graphite exhibit a significant range ( $\delta^{13}\text{C} = -18.90$  to  $-10.03\text{‰}$ ) with an average of  $-12.70\text{‰}$ , suggesting the formation of graphite through a mixture of reduced carbon fluids derived from biogenic organic matter and oxidized carbon fluids;

2. Considering the characteristics of the ore body as well as mineral and graphite carbon isotope characteristics, the Tugeman graphite deposit is a regional metamorphic graphite deposit of organic origin, and the characteristics of superposition fluid and tectonic transformation are obvious in the later period of the deposit;

3. The graphite within the Tugeman graphite deposit is formed under the conditions of greenschist-lower amphibolite facies metamorphism, with peak temperatures ranging from 494 °C to 570 °C.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13101328/s1>, Table S1: Carbon isotope composition of graphite from representative graphite deposits around the world. References [10,15,16,22,25,27,56–65,67–78,83,87,100,105,108–119] are cited in the supplementary materials.

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