Geochemical characterisation and protolith restoration of metamorphic rocks at Lazishao graphite mine, Sichuan

Wenqi Cheng [2], Haijun Yu[1,2]*, Xue Wang [3], Decai Kong [2], Bo Long [2]

1.Sichuan Shu-Neng Mineral Co., Ltd., Leshan,Sichuan, 614600，China;
2. Mine bureau of sichuan province，106 geological team, chengdu,Sichuan, 611130，China;
3. Sichuan Shu-Dao Highway Group Co., Ltd. Chengdu,Sichuan,610000, China.
* Correspondence: yuhaijun0601@163.com

Abstract: This study determined the deposit characteristics and geochemical features of metamorphic rocks from the Lazishao graphite deposit in order to reconstruct the metamorphic protoliths and palaeo-sedimentary environment. The results show that the SiO_2 content of the metamorphic rocks is relatively higher (55.60% to 77.94%), while Na_2O is 0.22% to 1.85%, K_2O is 1.87% to 3.45%, $K_2O > Na_2O$, and $K_2O/Na_2O + K_2O > 0.5$. The fractionation degree of light rare earth elements (LREEs) is greater than that of heavy rare earth elements (HREEs), with LREE/HREE ratios of 3.09 to 8.77; La_N/Yb_N is 2.72 to 10.75, with a mean value of 9.69. The rocks have moderate negative Eu anomalies (δEu = 0.50 to 0.89, mean = 0.64). Ionic lithophile elements (e.g., Rb, Ba, and K) are relatively enriched, but Sr is relatively depleted. The graphite-bearing metamorphic rocks in the study area originated from sedimentary rocks, mainly mudstone and greywacke. The palaeo-sedimentary environment was a low-salinity terrestrial freshwater body in a cold or moderately cold climatic zone.

Keywords: graphite mine; deposit characteristics; geochemical characteristics; carbon source; Lazishao

1. Introduction

Graphite (also known as 'black gold') is one of China's strategic non-metallic mineral resources(Deng Shaojun, 2020). Graphite has electrical and thermal conductivities similar to those of metallic materials, and remarkable plasticity and expandability (Zhang Tengfei, 2015). It is widely used in various industrial fields, including metallurgy, mechanics, chemistry, and electricity, and has become a strategic resource for modern cutting-edge technologies (Zhang et al., 2013; Li et al., 2015; Jiang , 2016; Wang et al., 2017).

Graphite mines are widely distributed in China, although those with large-scale output are mainly concentrated in five regions: Shandong, Heilongjiang, Hunan, Inner Mongolia, and Sichuan. Graphite mines in Sichuan Province are mainly distributed in Nanjiang County of Bazhong City and Renhe District and Yanbian County of Panzhihua City. The national resource base (Nanjiang–Wangcang graphite mine) is in Sichuan Province and the graphite mineral resource exploration and development base is in Panzhihua City (Yu et al., 2017; Department of Natural Resources of Sichuan Province,2017). At present, ultra-large graphite deposits at Zhongba and Tianping in Panzhihua City have been discovered. The metallogenic age of graphite deposits in Panzhihua is mainly Palaeoproterozoic–Mesoproterozoic, and metallogenic processes included the deposition of graphitic rocks, regional metamorphism, and late-stage superposed contact metamorphism (Yu et al., 2020).

However, the microscopic characteristics, geochemistry, ore genesis, carbon source, and other deposit features of graphite mines in the region have not been thoroughly explored. In this study, we investigated the geochemistry of metamorphic rocks from the Lazishao graphite mine (Renhe District, Panzhihua City) in order to determine the metamorphic protoliths and palaeo-sedimentary environment. The results of this study provide a reference for analysing the metallogenic mechanism and genesis of sedimentary–metamorphic graphite deposits in the Panxi area of Sichuan Province and across China.

2. Regional geological background

2.1. Geotectonic position

The study area is in the central Yangzi Craton (Kangdian axis), east of the Songpan–Ganzi orogenic belt, and at the northeast tip of the Gondwana palaeo-continent. This region forms an important part of the Panxi metallogenic belt (Fig. 1a). The Kangdian basement fault uplift zone is a horst-like structure composed of Archaean to Early Mesozoic metamorphosed magmatic complexes with a banded distribution. Magmatic rocks are primarily Jinning granites of the Chengjiang period, whose extension is controlled by north–south trending faults. The primary metallogenic belt is the Fe–Cu–V–Ti–Ni–Sn–Pb–Zn–Au–Pt–rare earth–asbestos metallogenic belt along the Yangtze metallogenic province of the Kangdian fault uplift zone; the secondary metallogenic belt is the Cu–Ni–Pb–Zn–graphite sub-metallogenic belt of the Yanbian palaeo-forearc basin.

2.2. Geological characteristics of the mining area

The regional stratigraphy is simple, mainly consisting of the second member of the Lengzhuguan Formation (Kangding Group), the first member of the Neoproterozoic Guanyinya Formation, and the first member of the Cenozoic Yuanyongjing Formation. The second member of the Lengzhuguan Formation is the ore-bearing formation of the graphite deposits, whose lithology is mainly sericite (muscovite)–quartz schist and two-mica–quartz schist. During the massive intrusion of monzonitic granites in the Cryogenian, most schists of the Lengzhuguan Formation were removed, leaving only a small number of lenticular and strip-shaped outcrops of the Lengzhuguan Formation in the west(Fig. 1b).

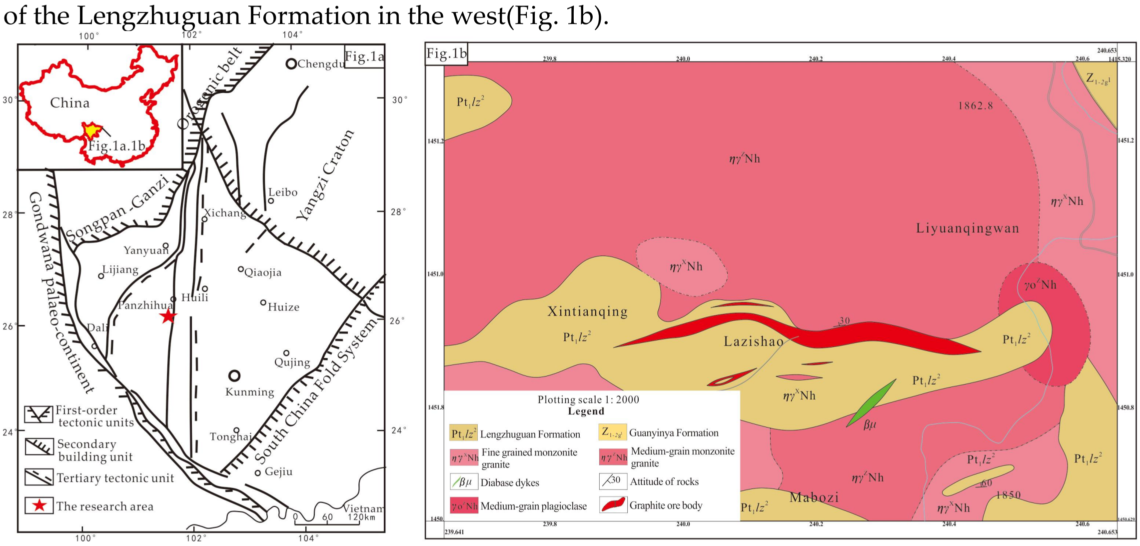

Fig.1 Geotectonic location and geological map of the research area(Wang Xue , 2014)

3. Petrographic characteristics

3.1. Ore types

Natural graphite deposits at Lazishao are mainly sericite–quartz schist; some graphite infills between quartz grains and some is arranged parallel to mica and quartz flakes, showing a schistose texture. Graphite flake sizes are 48–680 μm and the ore is a crystalline flake graphite.

3.2. Ore characteristics

The ore mineral is graphite; gangue minerals are mainly quartz, muscovite, and sericite, with occasional biotite and feldspar; metal minerals mainly include magnetite, hematite, limonite, pyrrhotite, and pyrite. Fresh graphite surfaces are black, and weathered surfaces are brownish-black. Granular minerals such as quartz (anhedral) and a small amount of feldspar (anhedral to subhedral) are distributed in the ore, while flaky minerals, including graphite and mica, have a directional arrangement among the granular minerals. Flaky minerals are less abundant than granular minerals, exhibiting a grano-lepidoblastic texture with a predominantly schistose structure (Fig. 2 and Fig. 3) following the banded structure. The graphite content is about 10% and mostly comprises individual flakes or flake aggregates. Graphite particles are generally 0.2 to 0.6 mm in length and 0.05 to 0.1 mm in width. Graphite is mostly in banded and directional, extending along the same direction as muscovite and biotite, and graphite grains are evenly distributed among the quartz grains (Fig. 4). Euhedral columnar minerals are occasionally seen. The quartz content is ~60%, and particles are anhedral and granular with a small grain size (< 0.8 mm), showing a mosaic structure. Quartz grains have been deformed under stress, with flattened and elongated morphology, displaying wavy extinction and optical anomalies; however, the long axis of quartz grains is still in a directional arrangement with flaky minerals. Mica is mostly muscovite and sericite, with a small amount of biotite. Muscovite and sericite (flake diameters 0.05 to 1.9 mm mm) have a silky lustre and typically represent 20% of the sample; the content of muscovite is higher than that of sericite. The biotite content is relatively low (generally 2% to 5%) and grains are unevenly distributed. Biotite particles are usually brown and flaky, generally 0.25 to 0.6 mm in diameter, and have a oriented arrangement. Metallic minerals account for 0.1% to 3% and are unevenly distributed in the ore. Magnetite accounts for ~90% of the metallic minerals, followed by pyrite, with occasional arsenopyrite and chalcopyrite. These minerals are generally interstitial to the particles of major minerals.

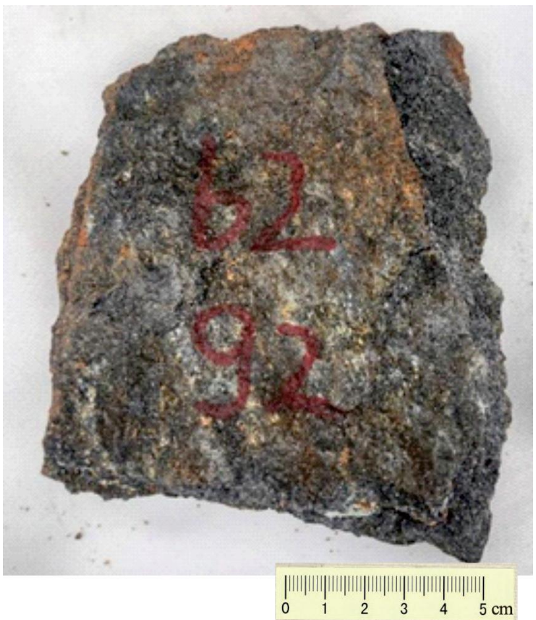

Fig.2 Graphite aligned along the foliation plane

Fig.3 Flake structure of graphite ore

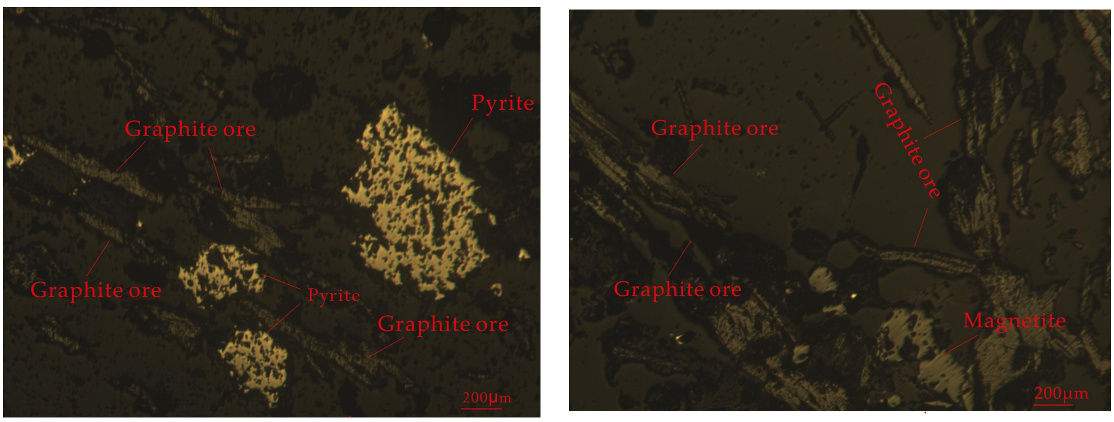

Fig.4 Oriented Graphite ore (polished section10×10)

3.3. Ore-fixed carbon content

The fixed carbon content of graphite ores in the study area ranges from 2.03% to 18.87%, and the average fixed carbon content of industrial-grade ores in the mining area is 5.16%, with the fixed carbon occurring in graphite. The fixed carbon content of muscovite (sericite)–quartz schist is mainly ~1%. There is little fixed carbon in the of granites and gangue rocks, and the distribution of fixed carbon content in the deposit is irregular.

3.4. Graphite flake size

Graphite flake size determines the quality of graphite products. Based on the analysis of 22 samples, graphite flakes in the mining area are generally between 0.048 and 0.68 mm. Graphite flakes of +100 mesh account for 17% to 80%, with an average of 52.4%; 100 to 80 mesh graphite flakes account for 9% to 28%, with an average of 19.4%; 80 to 50 mesh graphite flakes account for 5% to 35%, with an average of 19.8%; graphite flakes of > 50 mesh account for 3% to 38%, with an average of 13.3%. Graphite flake size increases with depth, making the deep orebody more economically valuable than the surface orebody.

4. Materials and methods

A total of 11 fresh samples were collected from drill holes, including seven graphite ore samples and four mica–quartz schist samples. Samples were analysed at the Mineral Testing Centre of Xichang, Sichuan Provincial Bureau of Geology and Mineral Exploration and Development (Table 1).

Table 1 Analysis of Lazishao Graphite Mine Samples

Analytical object	Analytical method	Analytical accuracy
Major elements	X-ray fluorescence spectrometry	Better than 0.1% to 1.0%
V_2O_5 and Fe_2O_3	Inductively coupled plasma–atomic emission spectrometry	Reproducibility up to 5%
Trace elements and rare earth elements	Inductively coupled plasma–mass spectrometry (ICP–MS)	Better than 10%

5. Results

5.1. Geochemical characteristics of major elements

Major element compositions of the graphite ore and mica–quartz schist are shown in Table 2. The SiO_2 content is generally high, ranging from 55.60% to 77.94%, with an average of 68.74%, which is higher than the average SiO_2 content in the upper crust (66%) (Deng Shaojun, et al.,2020). Na_2O show little variation, ranging from 0.22% to 1.85%, with an average of 0.68%, while K_2O ranges from 1.87% to 3.45%, with an average of 2.70%. In all samples, $K_2O > Na_2O$, and $K_2O/Na_2O + K_2O > 0.5$ (4.64–12.31, with an average of 8.32), indicating that the protoliths of the graphite deposit and mica–quartz schist were of normal sedimentary origin (He Tongxing et al.,1980). TiO_2 ranges from 0.14% to 1.36% (average of 0.44%), MgO ranges from 0.59% to 5.11%, and CaO ranges from 0.14% to 3.22%. In all samples, CaO < MgO, which also indicates that the metamorphic protoliths had a normal sedimentary origin (He Tongxing et al.,1980). The Fe_2O_3 content is 2.43% to 3.92%, with an average of 2.99%; FeO ranges from 0.50% to 5.50%, with an average value of 2.52; Al_2O_3 ranges from 5.45% to 14.81%, with an average of 9.96%. The SiO_2/Al_2O_3 ratio is between 3.75 and 13.84 (7.96–13.84 for the seven graphite ore samples and 3.75–4.69 for the four mica–quartz schist samples), with an average of 7.85%. This shows that the maturity levels of the seven graphite ore samples are similar, and those of the four mica–quartz schist samples are similar (Feng Wei, 2019). SiO_2 is significantly negatively correlated with Al_2O_3. P_2O_5 ranges from 0.072% to 0.92%, which is generally low, and MnO is between 0.010% and 0.090%, with a small variation range.

On Harker diagrams (Fig. 5), SiO_2 is negatively correlated with Al_2O_3, Na_2O, K_2O, TiO_2, CaO, MnO, MgO, and Fe_2O_3, and positively correlated with P_2O_5 and V_2O. On this basis, the chemical differentiation of the rocks is constrained by sedimentary differentiation (He et al.,1980; Long , 2016).

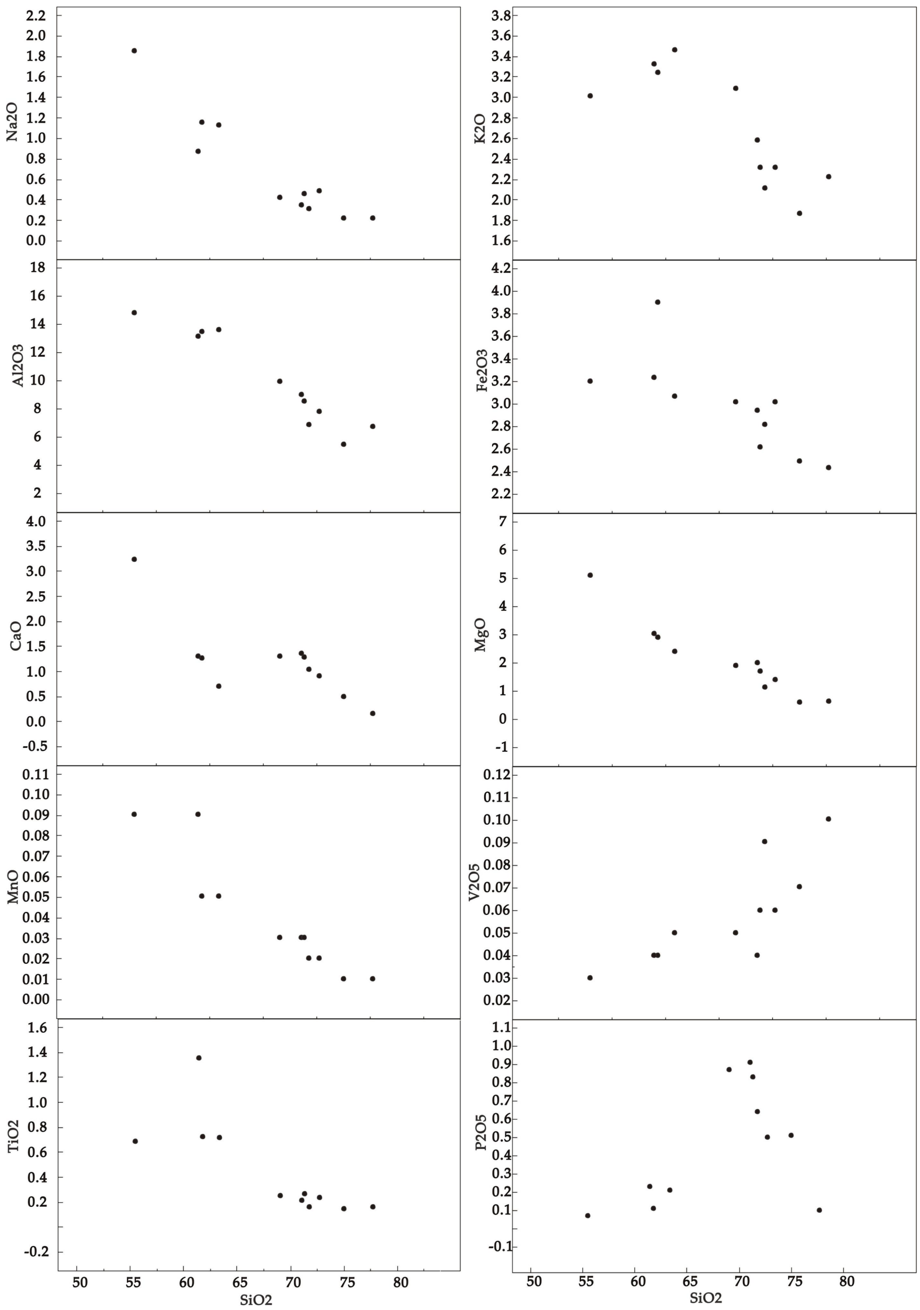

Fig.5 Harker diagrams for the Lazishao Graphite mine

Table 2 Results of major elements analysis of Lazishao graphite deposit metamorphic rocks（*wt.%*）

sample number	sample type	Na_2O	K_2O	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	V_2O_5	TiO_2	P_2O_5	FeO	H_2O^+	loss on ignition	TOTAL
LZS-BZY-01	mica–quartz schist sample	1.85	3.01	55.60	14.81	3.20	3.22	5.11	0.087	0.035	0.68	0.072	5.09	2.58	4.77	100.11
LZS-BZY-02	mica–quartz schist sample	1.16	3.26	62.21	13.49	3.92	1.27	2.89	0.046	0.043	0.72	0.11	4.00	2.00	5.38	100.50
LZS-SMK-01	graphite ore sample	0.34	2.61	72.00	9.05	2.97	1.37	2.00	0.027	0.039	0.21	0.92	1.50	1.42	6.72	101.18
LZS-SMK-02	graphite ore sample	0.48	2.33	73.50	7.84	3.04	0.91	1.40	0.023	0.062	0.23	0.50	1.33	0.70	8.60	100.95
LZS-SMK-03	graphite ore sample	0.22	2.22	77.94	6.72	2.43	0.14	0.61	0.010	0.10	0.16	0.10	0.59	0.96	7.98	100.18
LZS-SMK-04	graphite ore sample	0.22	1.87	75.41	5.45	2.50	0.48	0.59	0.013	0.071	0.14	0.51	0.50	0.70	12.02	100.47
LZS-SMK-05	graphite ore sample	0.42	3.10	69.63	9.98	3.03	1.31	1.91	0.026	0.048	0.25	0.88	1.33	1.38	7.40	100.69
LZS-SMK-06	graphite ore sample	0.31	2.12	72.28	6.90	2.83	1.04	1.14	0.021	0.090	0.16	0.64	1.42	1.00	10.64	100.59
LZS-SMK-07	graphite ore sample	0.45	2.33	72.19	8.56	2.64	1.29	1.72	0.027	0.058	0.26	0.84	1.92	1.40	7.38	101.07
LZS-BZY-03	mica–quartz schist sample	1.12	3.45	63.18	13.53	3.05	0.69	2.37	0.049	0.046	0.71	0.21	4.59	1.94	4.68	99.62
LZS-BZY-04	mica–quartz schist sample	0.88	3.36	62.16	13.25	3.27	1.30	3.05	0.090	0.039	1.36	0.23	5.50	2.16	4.44	101.09

Table 3 Rare earth elements analysis results of Lazishao graphite deposit metamorphic rocks andrelevant parameter value（ppm）

sample number	sample type	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	LREE	HREE	LREE/HREE	La_N/Yb_N	δEu	δCe
LZS-BZY-01	mica–quartz schist sample	36.6	70.1	8.64	32.6	6.36	1.33	4.49	0.96	6.68	1.62	4.31	0.71	4.09	0.64	179.13	155.63	23.50	6.62	6.42	0.72	0.93
LZS-BZY-02	mica–quartz schist sample	61.1	114	14.3	51.6	9.87	1.69	6.94	1.44	9.90	2.43	6.12	1.01	5.58	0.85	286.83	252.56	34.27	7.37	7.85	0.59	0.91
LZS-SMK-01	graphite ore sample	35.6	88.3	10.3	41.0	9.54	1.59	7.43	1.69	12.4	3.24	8.5	1.41	8.40	1.32	230.72	186.33	44.39	4.20	3.04	0.56	1.12
LZS-SMK-02	graphite ore sample	26.9	36.9	7.52	31.8	7.44	1.30	6.10	1.37	10.0	2.65	6.8	1.12	7.10	1.06	148.06	111.86	36.20	3.09	2.72	0.57	0.63
LZS-SMK-03	graphite ore sample	19.7	27.3	5.06	20.5	4.45	1.13	2.99	0.59	4.65	1.09	2.80	0.56	3.32	0.50	94.64	78.14	16.50	4.74	4.26	0.89	0.65
LZS-SMK-04	graphite ore sample	30.2	35.5	7.94	33.1	7.05	1.29	4.55	1.00	5.05	1.11	2.82	0.44	2.51	0.40	132.96	115.08	17.88	6.44	8.63	0.65	0.55
LZS-SMK-05	graphite ore sample	47.6	112	13.4	52.8	11.6	2.16	8.54	1.86	12.7	3.14	7.7	1.27	7.43	1.18	283.38	239.56	43.82	5.47	4.60	0.63	1.07
LZS-SMK-06	graphite ore sample	27.2	39.1	8.12	34.4	8.00	1.29	6.42	1.27	8.50	2.06	4.99	0.79	4.76	0.66	147.56	118.11	29.45	4.01	4.10	0.53	0.64
LZS-SMK-07	graphite ore sample	40.5	82.6	11.3	45.2	9.89	1.43	7.12	1.50	10.4	2.59	6.6	1.12	6.53	1.07	227.85	190.92	36.93	5.17	4.45	0.50	0.93
LZS-BZY-03	mica–quartz schist sample	56.5	106	13.3	49.7	9.48	1.76	6.43	1.26	8.01	1.81	4.46	0.68	3.77	0.57	263.73	236.74	26.99	8.77	10.75	0.65	0.92
LZS-BZY-04	mica–quartz schist sample	45.4	89.0	11.5	42.8	8.76	1.91	6.24	1.29	8.71	2.12	5.55	0.84	4.69	0.71	229.52	199.37	30.15	6.61	6.94	0.75	0.93

Table 4 Trace element analysis results of Lazishao graphite deposit metamorphic rocks（ppm）

sample number	sample type	Rb	Ba	Th	U	K	Ta	Nb	La	Ce	Sr	Nd	P	Zr	Hf	Sm	Ti	Y
LZS-BZY-01	mica–quartz schist sample	162.00	620.00	10.40	1.82	25000.00	1.47	10.50	36.60	70.10	80.80	32.60	316.80	255.00	6.11	6.36	4100.00	40.00
LZS-BZY-02	mica–quartz schist sample	167.00	800.00	18.60	2.65	27100.00	1.66	14.60	61.10	114.00	40.90	51.60	484.00	276.00	6.00	9.87	4300.00	61.60
LZS-SMK-01	graphite ore sample	136.00	530.00	9.62	4.02	21700.00	1.93	6.82	35.60	88.30	13.90	41.00	4048.00	267.00	6.12	9.54	1300.00	78.20
LZS-SMK-02	graphite ore sample	103.00	480.00	9.47	7.56	19300.00	1.61	6.52	26.90	36.90	12.00	31.80	2200.00	141.00	3.65	7.44	1400.00	66.70
LZS-SMK-03	graphite ore sample	84.10	330.00	6.15	6.27	18400.00	1.80	6.28	19.70	27.30	9.25	20.50	440.00	154.00	4.17	4.45	1000.00	26.90
LZS-SMK-04	graphite ore sample	70.00	420.00	6.41	4.88	15500.00	0.38	3.34	30.20	35.50	11.10	33.10	2244.00	181.00	3.45	7.05	840.00	29.50
LZS-SMK-05	graphite ore sample	142.00	650.00	11.50	6.41	25700.00	0.94	8.03	47.60	112.00	27.40	52.80	3872.00	244.00	6.50	11.60	1500.00	74.30
LZS-SMK-06	graphite ore sample	79.00	400.00	8.30	5.44	17600.00	0.64	4.81	27.20	39.10	8.80	34.40	2816.00	171.00	3.41	8.00	1000.00	50.60
LZS-SMK-07	graphite ore sample	102.00	460.00	8.66	4.57	19300.00	1.35	8.68	40.50	82.60	17.70	45.20	3696.00	201.00	5.51	9.89	1600.00	63.20
LZS-BZY-03	mica–quartz schist sample	184.00	850.00	14.20	3.57	28600.00	10.70	17.00	56.50	106.00	56.00	49.70	924.00	314.00	4.00	9.48	4300.00	44.90
LZS-BZY-04	mica–quartz schist sample	195.00	670.00	11.50	2.83	27900.00	1.56	16.50	45.40	89.00	63.50	42.80	1012.00	253.00	3.06	8.76	8200.00	52.10

sample number	sample type	Yb	Lu	Ni	Cr	Co	al	fm	c	alk	si	Zr	Zr/TiO2	al-alk	La/Th	Rb/Sr	Sr/Ba	/
LZS-BZY-01	mica–quartz schist sample	4.09	0.64	48.90	322.00	25.40	14.79	16.67	3.22	4.86	25.92	255.00	375.00	9.93	3.52	2.00	0.13	/
LZS-BZY-02	mica–quartz schist sample	5.58	0.85	69.80	89.20	22.50	13.42	14.71	1.26	4.39	28.89	276.00	383.33	9.03	3.28	4.08	0.05	/
LZS-SMK-01	graphite ore sample	8.40	1.32	77.40	39.90	29.70	8.94	9.37	1.35	2.92	33.21	267.00	1271.43	6.02	3.70	9.78	0.03	/
LZS-SMK-02	graphite ore sample	7.10	1.06	108.00	62.30	17.50	7.77	8.75	0.90	2.79	33.98	141.00	613.04	4.98	2.84	8.58	0.03	/
LZS-SMK-03	graphite ore sample	3.32	0.50	28.70	51.40	17.60	6.71	6.07	0.14	2.44	36.31	154.00	962.50	4.27	3.20	9.09	0.03	/
LZS-SMK-04	graphite ore sample	2.51	0.40	78.20	62.80	16.30	5.42	6.08	0.48	2.08	35.02	181.00	1292.86	3.34	4.71	6.31	0.03	/
LZS-SMK-05	graphite ore sample	7.43	1.18	98.20	65.40	28.00	9.91	9.27	1.30	3.50	32.27	244.00	976.00	6.41	4.14	5.18	0.04	/
LZS-SMK-06	graphite ore sample	4.76	0.66	112.00	48.80	17.10	6.86	8.18	1.03	2.42	33.53	171.00	1068.75	4.44	3.28	8.98	0.02	/
LZS-SMK-07	graphite ore sample	6.53	1.07	99.20	43.00	21.00	8.47	8.85	1.28	2.76	33.33	201.00	773.08	5.71	4.68	5.76	0.04	/
LZS-BZY-03	mica–quartz schist sample	3.77	0.57	63.80	92.70	23.90	13.58	13.16	0.69	4.58	29.60	314.00	442.25	9.00	3.98	3.29	0.07	/
LZS-BZY-04	mica–quartz schist sample	4.69	0.71	65.70	74.50	25.30	13.11	15.01	1.29	4.19	28.70	253.00	187.41	8.92	3.95	3.07	0.09	/

5.2. Geochemical characteristics of rare earth elements

Rare earth element (REE) data of the 11 samples are shown in Table 3. Total REE (ΣREE) ranges from 94.64 to 286.83 ppm, with an average of 202.22 ppm; total light REE (ΣLREE) ranges from 78.14 to 252.56 ppm, with an average of 171.3 ppm; total heavy REE (ΣHREE) ranges from 16.50 to 44.39 ppm, with an average of 30.92 ppm. The LREE/HREE ratio is 3.09 to 8.77, and La_N/Yb_N = 2.72 to 10.75, with an average of 9.69. These results indicate a degree of fractionation between LREEs and HREEs, suggesting that the metamorphic protoliths were sedimentary rocks. Eu anomalies (δEu) range from 0.50 to 0.89, with a mean value of 0.64, and there are no significant δCe (0.55–1.12) anomalies.

Chondrite-normalised LREE patterns (Fig. 6) are right-skewed, while HREE curves are relatively gentle. All samples show significant negative Eu anomalies, and LREE contents are much higher than those of chondritic standard values, consistent with the REE distribution pattern in the khondalite series at the margin of the Yangzi plate. This indicates that the metamorphic protoliths were sedimentary rocks and claystone; the low-maturity metamorphic rock series originated from continental crust basement with protoliths composed of sandy and argillaceous clastic sediments of early Proterozoic immature source areas (Liu Xinxin, 2015).

North American shale-normalised REE patterns (Fig. 7) show relatively gentle curves, with individual samples showing negative Ce anomalies. There are also slightly positive Ho anomalies, relative LREE enrichment, relative HREE depletion, negative Eu anomalies, and slightly negative Ce anomalies. Such characteristics are consistent with river, lagoon, and marginal sea sediments (Deng , 2020 ; Wildman T R et al., 1973; Zhao , 1997; Piper D Z, 1985; Goldstein S J et al., 1988; Murray R W et al., 1991; Sholkovitz E R, Jacobson S B et al.,1994).

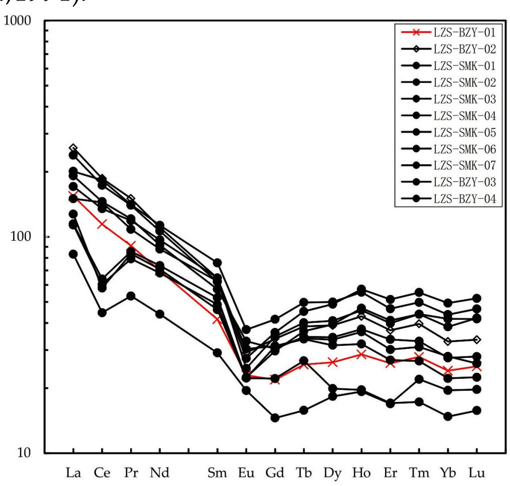

Fig.6 Chondrite-normalized REE patterns for Lazishao Graphite mine(Boynton W V, 1984)

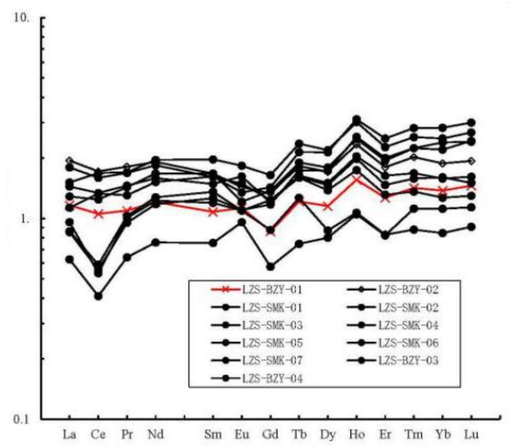

Fig.7 North American Shale normalized REE patterns for Lazishao Graphite mine(Haskin L A, et al., 1968)

5.3. Geochemical characteristics of trace elements

Trace element data are shown in Table 4. Large ion lithophile element (LILE) Rb ranges from 70 to 195 ppm, with an average of 129.0 ppm; Ba ranges from 330 to 850 ppm, with an average of 564.5 ppm; K ranges from 15,500 to 28,600 ppm, with an average of 22,372.73 ppm; Sr ranges from 8.80 to 80.8 ppm, with an average of 31.0 ppm. High field strength element (HFSE) Th varies little, ranging from 6.15 to 18.6ppm, with an average of 10.4 ppm; Nb ranges from 3.34 to 71.0 ppm, with an average of 9.40 ppm; Ta is relatively low, ranging from 6.15 to 18.6 ppm, with an average of 10.4 ppm; P varies widely from 316.8 to 4048.0 ppm, with an average of 2004.8 ppm; Zr ranges from 141 to 314 ppm, with an average of 223.0 ppm; Hf ranges from 3.06 to 6.50 ppm, with an average of 4.73 ppm; La/Th ranges from 2.84 to 4.71, with a mean value of 3.75. As Sr is relatively enriched in marine sedimentary environments, the Rb/Sr ratio can be used to distinguish marine and terrestrial sediments (Liang Shuai, 2015). Here, Rb/Sr ranges from 2.00 to 9.78 (with a mean value of 6.01); all values are > 1, indicating that the sediments are well sorted and probably originated from a terrestrial depositional environment. Sr/Ba varies in a relatively small range of 0.02 to 0.13, with a mean value of 0.05.

A spider diagram of trace element ratios relative to original mantle source values (Fig. 8) shows relative LILE enrichment (e.g., Rb, Ba, and K) and obvious Sr depletion. HFSE, such as Nb and Ta, show slight depletion, while Zr, Hf, and Th are relatively balanced, with gentle curves. The content of all elements, except Sr and Ti, are higher than the original mantle source values.

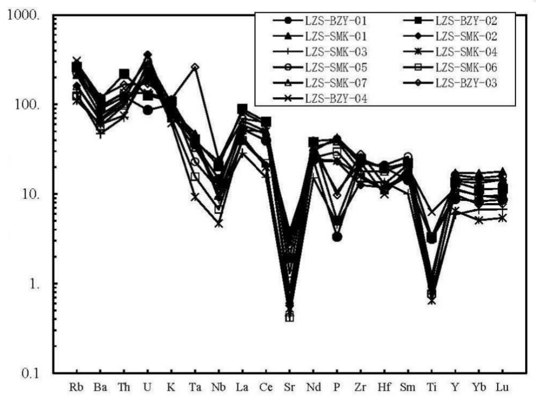

Fig 8 Trace elements primitive mantle standard element cobweb diagram of Lazishao graphite deposit(Sun S S, Mc Donough W F. 1989)

6. Discussion

6.1. Metamorphic protoliths

The Lazishao graphite deposit has undergone multiple phases of tectonic deformation and metamorphism, with superposed foliations and mineral assemblages. As such, accurate recreation of metamorphic protoliths cannot be accomplished merely based on geological features in the field, mineral assemblages, or mineralogical characteristics; geochemical data are also needed.

Owing to strong activity of the major components (e.g., SiO_2), their contents can change during multi-phase metamorphism, reducing the accuracy of protolith recreation. Instead, Winchester et al. (1980) chose relatively inactive elements (Zr, Ti, and Ni) to construct a Zr/TiO_2–Ni diagram. As shown in Fig. 9, data from the four mica–quartz schist samples and seven graphite ore samples were projected into the zone of sedimentary rocks on a Zr/TiO_2–Ni diagram, suggesting that the metamorphic protoliths of the Lazishao graphite deposit were sedimentary rocks, and that graphite-bearing metamorphic rocks in the study area are para-metamorphic.

Simonen (1953) used an Al+fm−C+alk−Si diagram to demonstrate the chemical characteristics of different metamorphic rocks, and showed wide variations in Al, fm, C, and alk. Simonen's diagram can effectively eliminate the effects of Si variation on protolith restoration. Numerous studies have verified that Simonen's diagram performs well in the determining metamorphic protoliths.

Based on the data in Table 4, Simonen's diagram was plotted for the Lazishao graphite deposit (Fig. 10). Volcanic rocks plot in the centre, argillaceous sedimentary rocks plot in the upper left, sandy sedimentary rocks plot in the upper right, and calcareous sedimentary rocks plot in the lower left. There is no evident boundary between argillaceous sedimentary and sandy sedimentary rock zones. All 11 samples projected into the argillaceous sedimentary rock zone, confirming that the protoliths of the metamorphic rocks in the study area were sedimentary and that the metamorphic rocks are para-metamorphic.

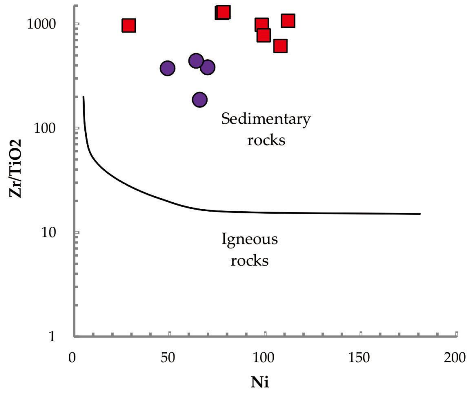

Fig 9 Diagram of Zr/TiO2-Ni of Lazishao graphite deposit(Wang Renmin et al., 1986)

（●are mica–quartz schist samples,■ are graphite ore samples）

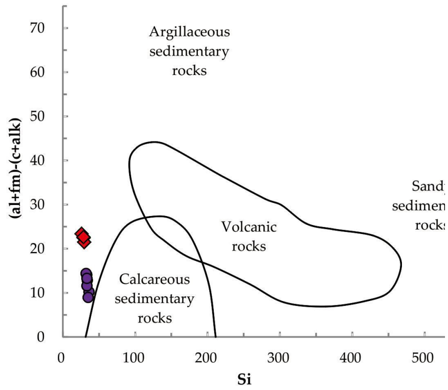

Fig 10 Diagram of al+fm-c+alk-Si of Lazishao graphite deposit(Wang Renmin et al., 1986)

（●are graphite ore samples, ◆are mica–quartz schist samples）

REEs are incompatible; that is, they cannot enter the crystal structures of rock-forming minerals or form independent mineral phases. As such, REEs are relatively stable and are not easily altered by metamorphism or metasomatism, making them suitable for reconstructing metamorphic protoliths (Meng Hui, 2015). On a La/Yb-ΣREE diagram (Fig. 11) (Allegre C T, 1978), the 11 samples mostly plot in the shale, claystone, and sandstone zones, providing further evidence that the protoliths of graphite-bearing metamorphic rocks in the study area were sedimentary rocks, and that the metamorphic rocks are para-metamorphic.

Leake (1969) proposed the (Al−alk)−C diagram to distinguish metasedimentary and metavolcanic rocks. On an (Al−alk)−C diagram (Fig. 12), the Lazishao graphite samples plot in the feldspathic claystone and greywacke zones, confirming that the metamorphic protoliths were feldspathic claystone and greywacke sedimentary rocks.

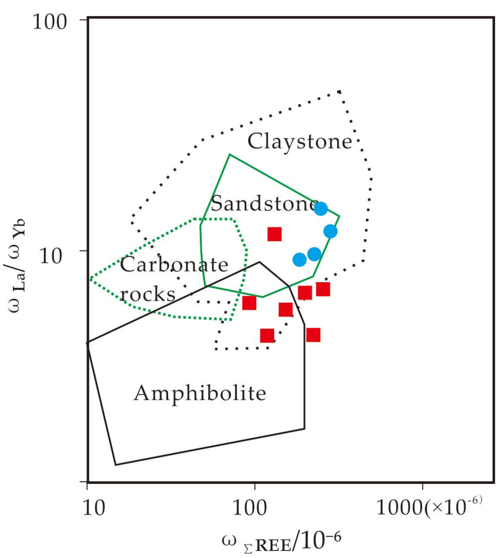

Fig 11 Diagram of La/Yb-ΣREE of Lazishao graphite deposit(Wang Renmin et al., 1986)

（●are mica–quartz schist samples,■ are graphite ore samples）

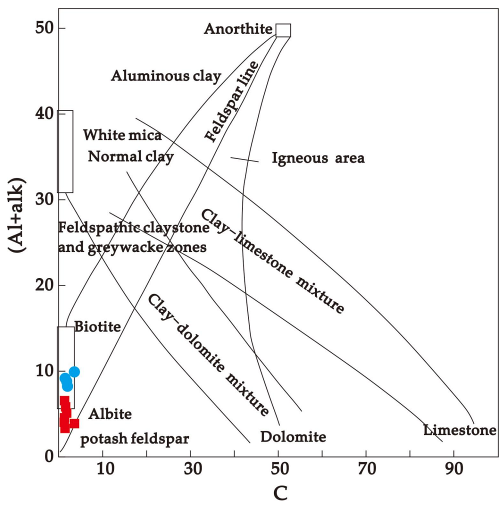

Fig 12 Diagram of (al-alk)-c of Lazishao graphite deposit(Wang Renmin et al., 1986)

（●are mica–quartz schist samples,■ are graphite ore samples）

In summary, the protoliths of metamorphic rocks in the Lazishao graphite deposit were sedimentary rocks, primarily comprised of mud shale and mixed greywacke.

6.2. Palaeo-sedimentary environment

Rocks formed in different depositional environments differ in terms of mineral composition and the contents and ratios of specific elements (Zhao Zhenhua, 1997). Since the protoliths of the Lazishao graphite deposit were mainly mud shale and greywacke, we infer that the corresponding depositional environment was a terrestrial or low-energy static shallow water environment.

The ternary diagram of claystone composition in different climatic zones and the Ba–Sr diagram proposed by Melezhik and Predovsky (1982) are widely used for distinguishing claystone depositional environments and palaeo-climatic conditions (Fig. 13). Here, the sample predominantly plot in the terrestrial facies zone of a cold or moderately cold climate of the ternary diagram; this is supported by the relatively high SiO_2 and K_2O, which are indicative of cold or moderately cold climate. On a Ba–Sr diagram (Fig. 14), almost all sample points plot in the freshwater environment zone.

In summary, the palaeo-sedimentary environment of the metamorphic protoliths was a low-salinity terrestrial freshwater body in a cold or moderately cold climatic zone. Combined with the geochemical characteristics of REEs, we speculate that the sedimentary environment of the Lazishao graphite deposit was a low-energy static water environment of the fluvial–lagoon facies.

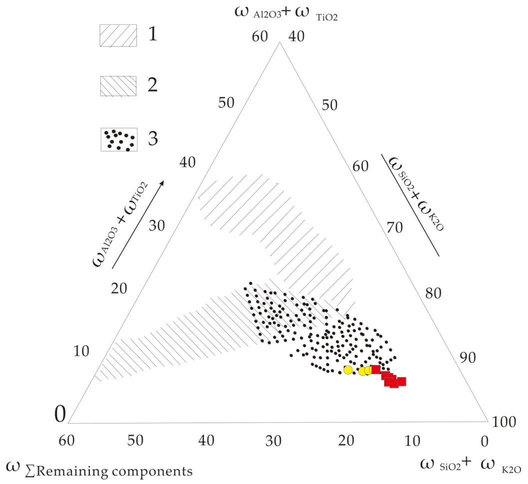

Fig 13 Composition diagram of clay rocks in different climatic zones of Lazishao graphite deposit(Wang Renmin et al., 1986)
1-Terrestrial facies clay compositions in humid and hot climatic zones; 2-Marine facies, lacustrine and lagoon facies clay compositions in dry climatic zones; 3-Terrestrial facies clay compositions in cold or moderately cold climatic zones
（●are mica–quartz schist samples,■ are graphite ore samples）

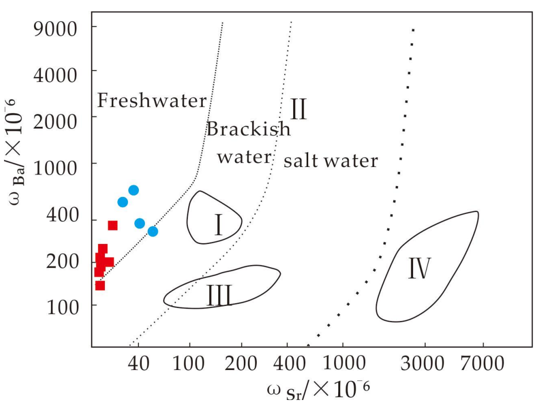

Fig 14 Diagram of Ba-Sr of Lazishao graphite deposit(Wang Renmin et al., 1986)
Ⅰ-Clay in modern deltaic facies brackish water environment; Ⅱ-Pelagic sediments of the Pacific Ocean; Ⅲ-Marine facies carbonate rocks on the Russian platform of different ages; Ⅳ-Modern deposits in a high-salinity waterbody
（●are mica–quartz schist samples,■ are graphite ore samples）

6.3. Provenance based on geochemical properties

Provenance analysis can reveal the location and properties of sediment sources, paths of sediment transport, and characteristics of sedimentation and tectonic evolution of the basin. The clastic components and structure of clastic rocks can also directly reflect the tectonic setting of the provenance area and the sedimentary basin (Liu Baojun et al .,2006)

The Ni–TiO_2 diagram proposed by Floyd et al. (1989) is very accurate in discriminating the provenance of metamorphic protoliths. On this diagram (Fig. 15), all seven graphite ore samples plot in the sandstone zone, two of the four mica–quartz schist samples plot in the argillaceous rock zone, one plots in the felsic rock zone, and one plots between the argillaceous rock and sandstone zones. Together, this suggests that the provenance of the metamorphic rocks and graphite ore in the study area is probably argillaceous rock and sandstone.

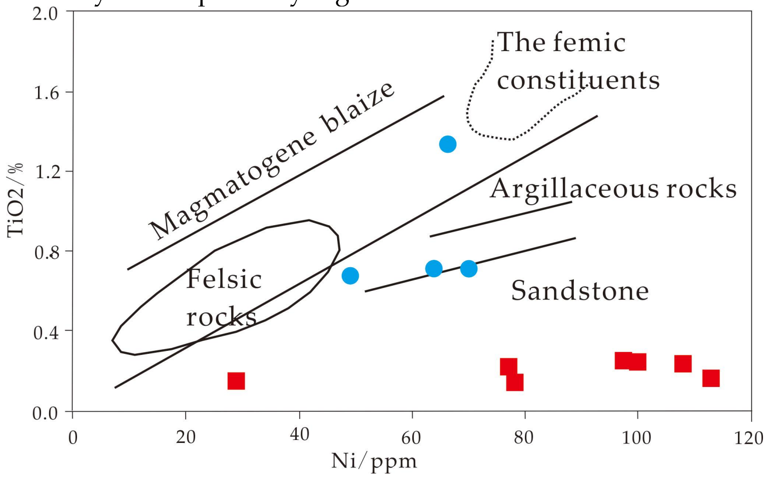

Fig 15　Diagram of Ni-TiO_2 of Lazishao graphite deposit

（●are mica–quartz schist samples,■ are graphite ore samples）

The La/Th–Hf diagram (Fig. 16) proposed by Floyd and Leveridge (1987) was adopted to further verify the provenance of the graphite-bearing metamorphic rocks. All 11 samples plot within the mixed felsic–intermediate source zone. On the Th–Hf–Co ternary diagram proposed by Taylor and McLennan (1985) (Fig. 17), all 11 samples plot within the upper crust region.

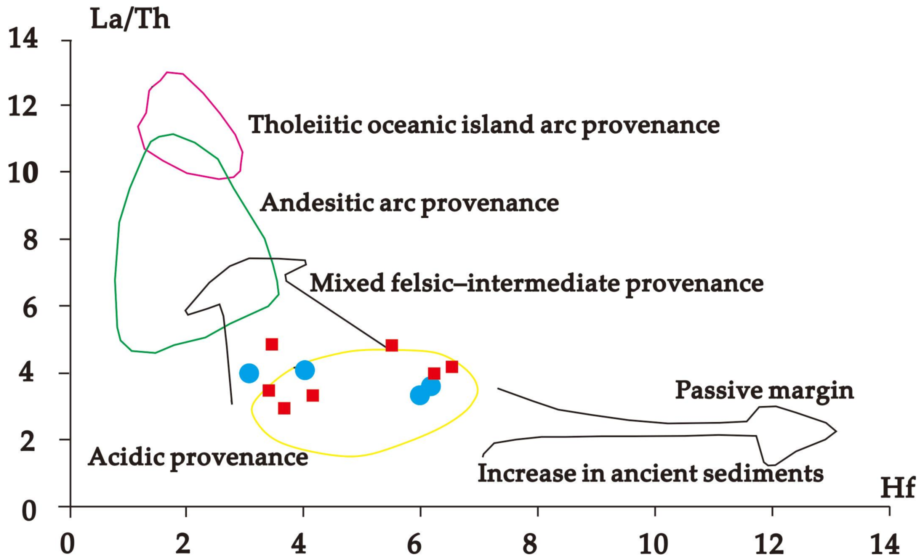

Fig 16　Diagram of La/Th-Hf of Lazishao graphite deposit

（●are mica–quartz schist samples,■ are graphite ore samples）

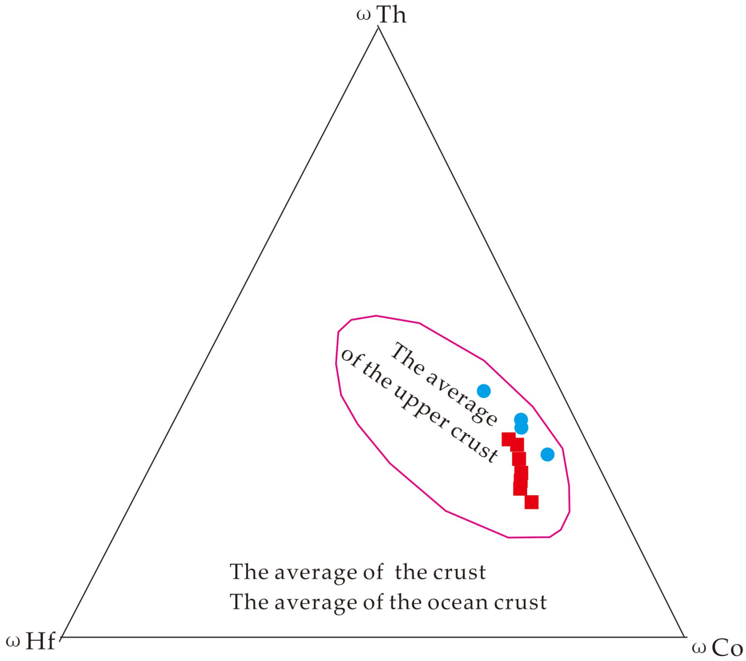

Fig 17 Diagram of Th-Hf-Co of Lazishao graphite deposit

（●are mica–quartz schist samples,■ are graphite ore samples）

In summary, the Lazishao graphite deposit originated from the upper crust, with the main components being argillaceous rock and sandstone from a felsic–intermediate source area.

6.4 Tectonic environment

The discrimination formula $Al_2O_3/(Al_2O_3+Fe_2O_3)$ of Jewell and Stallard (1991) is commonly used to determine geotectonic setting during the deposition of sedimentary rocks. An $Al_2O_3/(Al_2O_3+Fe_2O_3)$ ratio between 0.6 and 0.9 indicates a continental margin environment, a ratio between 0.4 and 0.7 indicates a pelagic environment, and a ratio between 0.1 and 0.4 indicates a mid-ocean ridge environment. The $Al_2O_3/(Al_2O_3+Fe_2O_3)$ ratios of the samples from the Lazishao graphite deposit range from 0.69 to 0.82, with an average of 0.76 (Table 5), indicating a continental margin environment, which is consistent our other results. Similarly, on a K_2O/Na_2O–SiO_2 diagram [37] (Fig. 18), all seven graphite ore samples and plot in the passive continental margin region, three of the four mica–quartz schist samples plot in the active continental margin region, and one of the four mica–quartz schist samples plots in the island arc region.

Table 5 Al_2O_3/（$Al_2O_3+Fe_2O_3$） of Lazishao graphite deposit

sample number	LZS-BZY-01	LZS-BZY-02	LZS-SMK-01	LZS-SMK-02	LZS-SMK-03	LZS-SMK-04	LZS-SMK-05	LZS-SMK-06	LZS-SMK-07	LZS-BZY-03	LZS-BZY-04
sample type	mica–quartz schist sample	mica–quartz schist sample	graphite ore sample	graphite ore sample	graphite ore sample	graphite ore sample	graphite ore sample	graphite ore sample	graphite ore sample	mica–quartz schist sample	mica–quartz schist sample
Al2O3/Al2O3+Fe2O3	0.82	0.77	0.75	0.72	0.73	0.69	0.77	0.71	0.76	0.82	0.80

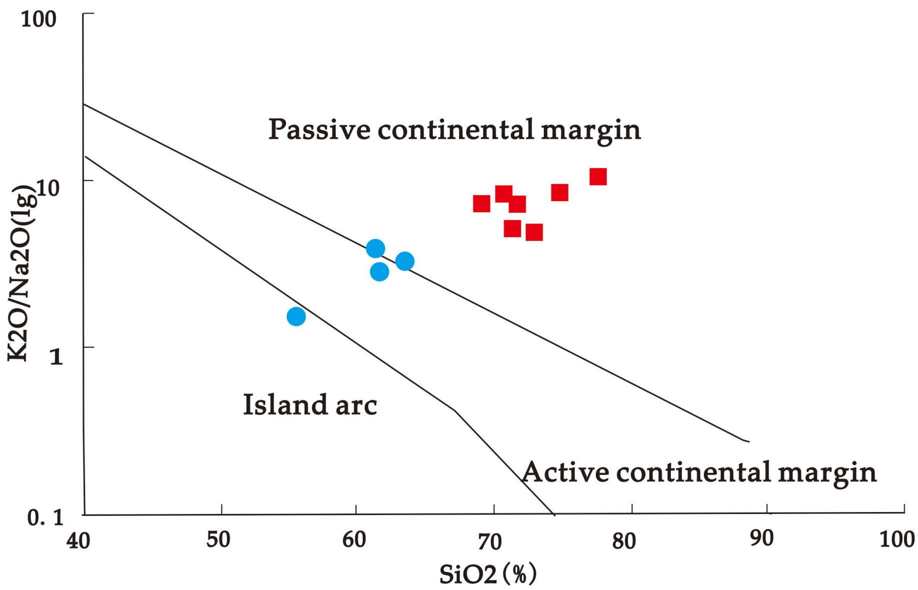

Fig 18 Diagram of K_2O/Na_2O–SiO_2 of Lazishao graphite deposit

（● are mica–quartz schist samples, ■ are graphite ore samples）

In summary, protoliths of the metamorphic rocks were deposited along a passive continental margin that remained stable for a sufficient period to form a low-energy freshwater environment in which organic-rich claystone and greywacke were deposited. These deposits were then subjected to regional metamorphism, during which organic carbon was recrystallised into graphite.

7. Conclusions

1. The metamorphic rocks of the Lazishao graphite deposit mainly belong to the second member of the Lengzhuguan Formation of the Kangding Group; their lithology is mainly sericite (muscovite)–quartz schist and two-mica–quartz schist.
2. SiO_2 in the Lazishao metamorphic rocks is generally high, ranging from 55.60% to 77.94%; $K_2O > Na_2O$, and $K_2O/Na_2O+K_2O > 0.5$; fractionation of LREEs > fractionation of HREEs; there are moderate negative Eu anomalies; ionic lithophile elements (Rb, Ba, and K) are relatively enriched, but Sr is prominently depleted.
3. Lithogeochemical analysis shows that the metamorphic protoliths of the graphite deposit were sedimentary rocks whose lithology was dominated by carbonaceous claystone and greywacke.
4. The palaeo-sedimentary environment was a low-salinity terrestrial freshwater body in a cold or moderately cold climatic zone. Sediments were sourced from the upper crust, and the main provenance components were argillaceous rock and sandstone from a felsic–intermediate source area.
5. Tectonic discrimination diagrams suggest that protoliths of the metamorphic rocks in the study area were probably deposited in an organic-rich fluvial–lagoon facies environment on a continental margin; organic-rich claystone and greywacke were deposited over a long period and then subjected to regional metamorphism during which organic carbon was recrystallised into graphite.

References

Allgre C T. 1978. Quantitative models of trace elements. Earth Plant Sci Lett, 38: 1-25.

B.E.Leake. 1969. The discrimination of ortho and paracharnockitic rocks, anotthosites and amphibolites.The Indian Mineralogist，vol.10,pp.89-104.

Boynton W V. 1984. Geochemistry of the Rare Earth Elements: meteorite Studies. In: Henderson, p. (Ed),Rare Earth Element Geochemistry[M]. Amsterdam:Elsevier Sci. Publ. Co. , 63-114.

Department of Natural Resources of Sichuan Province. 2017. Overall Plan of Mineral Resources of Sichuan Province (2016-2020)[R].

Deng Shaojun. 2020. Study on Geological and Geochemical Characteristics and Genesis of Nanjiang Pinghe Graphite Deposit, Sichuan Province[D].Southwest University of Science and technology.

Deng Shaojun, Zhu Yuyin, Li Hujie. 2020. Protolith Recovery and Discussion on Paleosedimentary Environment of Pinghe Graphite Metamorphic Rocks in Nanjiang[J]. Journal of Southwest University of Science and Technology, 35(01): 25-29.

Feng Wei. 2019. Geochemistry and Metallogeny of the Daliangzikou graphite deposit in Laiyang Country,Shandong province[D]. Chang'an University.

Floyd P A, Winchester JA, Park RG .1989. Geochemistry and tectonic setting of Lewisian clastic metasediments from the Early Proterozoic Loch Maree Group of Gairloch, NW Scotland. Precambrian Res 45:203-214.

Floyd P A, Leveridge B E. 1987. Tectonic environment of the Devonian Gramscatho basin, south Cornwall: framework mode and geochemical evidence from turbiditic sandstones[J].Journal of the Geological Society, 144(4): 531-542.

Goldstein S J and Jacobsen S B. 1988. Rare earth elements in river waters [J]. Earth and Planetary Science Letters, 89:35-47.

He Tongxing, Lu Liangzhao, Li Shuxun, et al.1980. Petrology of metamorphic rocks [M]. Beijing: Geological Publishing House.

Haskin L A, Haskin M A, Frey F A, et al. 1968. Relative and absolute terrestrial abundances of the rare earths Relative and absolute terrestrial abundances of the rare earths, Origin and Distribution of the Elements[C]//Ahrens, L. H (Ed.), Origin and Distribution of the Elements. Oxford: Pergamon, 889-911.

Jiang Guangming. 2016. Geological characteristics and economic and technical evaluation of Nanjiang Graphite deposit in Sichuan Province[J].New Technology & New Products of China08:130-138.

Jewell P W. Stallard R F. 1991. Geochemistry and paleoceanographic setting ofcentral Nevadabedded barites[J]. The Journal of Geology. 151-170.

Li Chao, Wang Denghong, Zhao Hong, et al. 2015. Minerogenetic regularity of graphite deposits in China[J].Mineral Deposits, 34(06):1223-1236.

Long Tao.2016.The geochemical characteristics and deposit genesis analysis of Liu Mao graphite deposit in Ji Xi County of Hei Long jiang Province[D].China University of Geosciences (Beijing).

Liu Xinxin. 2015. Chronology,Geochemical characteristics and Genesis of the Xiaodouling graphite deposit in Xichuan county, Henan province[D]. China University of Geosciences (Beijing).

Liang Shuai. 2015. Genisis Studies of typical crystalline Graphite deposits, In The North China[D]. Liaoning Technical University.

Liu Baojun,Han Zuozhen,Yang Renchao. 2006. Progress prediction and consideration of the research of modern sedi mentology.Special Oil and Gas Reservoirs：13(5):1-9.

Murray R W, Brink M R and Brumsack H J, et al. 1991. REE in Japen Sea sediments and diagenetic behavior of Ce/Ce*:Results from ODP Log 127 [J]. Geochim Cosmochim Acta, 55: 2453-2466.

Meng Hui.2015. The geochemical characteristics and deposit genesis analysis of Liu gezhuang graphite deposit in Pingdu County of Shandong Province[D].China University of Geosciences (Beijing).

Melezhik and Predovsky. 1982, Geochemistry of early Proterozoic lithogenesis [M].

Piper D Z. 1985. Rare earth elements in the sedimentary cycle:a summary [J]. Chem Geol, 14:285-304.

Sun S S, Mc Donough W F. 1989. Chemical and isotopic systematic of oceanic basalts: Implications for mantle composition and processes[A]. In:Sanrder A D and Norry M J, eds.

Magmatism in the ocean basins[C]. Geological Society of London Special Publication. 42:313-345.
Simonen A. 1953. Stratigraphy and Sedimentation of the Sveco fennidic, early Archean Supracrustal Rocks in Southwestern Finland.Bull.Comm [J]. Geol.Finlande, No160, p. 1-64.
Sholkovitz E R, Jacobson S B. 1994. Ocean particle chemistry:the fractionation of REE between suspend-ed paricles and sea water [J]. Geochim Cosmochim Acta. 58:1567-1579.
Taylor S R, Mc Lennan Evolution.1985.. Oxford: S M. The Continental Crust: Its Composition and Blackwell[M]. 1-312.
Wildman T R and Haskin L A. 1973. Rare Earth in Precambrian Sediments [J]. Geochim. CosmochimActa, Vol.37, No.3, pp.419-438.
Winchester J A Park R G etal. 1980. The geochemistry of Lewisian semipelitic schists from the Gairloch District, wester Ross [J]. Scottish Journal of Geology, 16(2):165-179.
Wang Renmin, He Gaopin, Chen Zhenzhen, et al.1986. Graphical discriminant method for protolith of metamorphic rocks [M]. Beijing: Geological Publishing House.
Wang Li, Fan Junlei, Feng Yangwei. 2017.Graphite Resources Status Quo and Distribution of Graphite Deposits in China[J].Coal Geology Of China, 29(07): 5-9.
Wang Xue. 2014. Geological Characteristics and Prospecting Directions of TheJinsuoqiao Iron Gold Deposit in Huidong,Sichuan[D]．Chengdu University of Technology.
Yu Haijun ,Li Fan, Xiang Hui, et al. 2017. Research Report on Comprehensive Zoning and Planning Zoning of Mineral Resources Development and Utilization in Sichuan Province[R].Chengdu:Mine bureau of sichuan province，106 geological team
Yu Haijun, Wang Xue, Bai Jiaquan. 2020. Main Ore-controlling Structural Characteristics and Prospecting Model of Panzhihua Graphite Deposit[J]. SiChuan Nonferrous Metal. 04:33-35.
Zhang Tengfei. 2015 .The geochemical characteristics and deposit genesis analysis of Xiao chagou graphite depositin Zhenping County of Henan Province[D].China University of Geosciences (Beijing).
Zhang Lingyan, Wang Hao ,Guan Junfang, et al. 2013 . Study on process mineralogy of the graphite innanjiang county sichuan province[J].Mining & Metallurgy, 95-100.
Zhao Zhenhua. 1997. Principle of Trace Elements Geochemistry [M]. Beijing: Science Press.