Geochemical Characteristics of Early Permian Pyroclastic Rocks in the Jimunai Basin, West Junggar, Xinjiang (NW China): Implications for Provenance and Tectonic Setting

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Abstract: During the Late Paleozoic, West Junggar (Xinjiang, NW China) experienced a shift in tectonic setting from compression to extension. Ha'erjiao is an important area for investigating collisional structures, post-collisional structures, and magmatic activities. Based on the petrological and geochemical characteristics of pyroclastic and other volcanic rocks in the Permian Kalagang Formation from the borehole ZKH1205 in the Jimunai Basin, the main types of source rock for the pyroclastic rocks deposited in the basin are identified and their implications for the Early Permian tectonic setting examined. The abundance of basalt and andesite lithic fragments in the pyroclastic rocks, together with the REE characteristics and the contents of transition and high field strength elements show that the source rocks were chiefly intermediate–basic volcanic rocks. High ICV values, low CIA values, low Rb/Sr ratios, low Th/U ratios and the mineralogical features suggest weak chemical weathering of the source rocks; the geochemical patterns of the pyroclastic rocks might not only have been impacted by crustal contamination but also might be related to the nature of the magma from the source area. The geochemical properties of the pyroclastic rocks distinguish them from arc-related ones, and such samples plot in the within-plate basalt (WPB) field in some diagrams. This is consistent with the formation background of the Early Permian volcanic rocks in this region.

Key words: pyroclastic rock, provenance, tectonic setting, Kungurian, Central Asian Orogenic Belt

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1 Introduction

Northern Xinjiang, an important part of the Central Asian Orogenic Belt (CAOB), is composed of the most complex accretionary collages on the planet and is responsible for considerable Phanerozoic juvenile crustal growth (e.g., Xiao et al., 2015, 2017; Windley et al., 2007; Wilde, 2015; Huang et al., 2018). This region is situated between the European, Siberian, and Tarim cratons and the Sino-Korean craton (Jahn et al., 2000, 2004; Windley et al., 2007; Safonova et al., 2009, 2011; Xiao et al., 2008, 2010, 2013; Kröner et al., 2013, 2014) and consists mainly of former oceanic islands, seamounts, oceanic plateaus, island arcs, accretionary complexes, ophiolites, and microcontinents resulting from a prolonged subduction-accretion process and multi-stage arc–arc or arc–continent collisions (Khain et al., 2002; Buckman and Aitchison, 2004; Kovalenko et al., 2004; Windley et al., 2007; Xiao et al., 2010; Wilhem et al., 2012; Windley et al., 2007; Kröner et al., 2014; Safonova, 2017), including the Tianshan, Junggar, and Chinese Altay. Thus, this is an ideal region to investigate post-collisional structures and magmatic activities of the CAOB because of the well-

exposed ophiolitic belts (Irtys, Kelameili, and North Tianshan ophiolitic belt in the Late Paleozoic), and volcanic rocks, sedimentary rocks, and juvenile granitoids (Wang and Xu 2006; Xiao et al., 2008; Brookfield, 2000; Windley et al., 2002, 2007; Kang et al., 2019).

Post-collisional geodynamic processes during a significant period of the tectonic evolution in the Late Paleozoic in the Junggar (e.g., Chen and Jahn, 2004; Han et al., 2006; Su et al., 2006; Zhang et al., 2015), and Western Mediterranean, Alpine-Himalayan and Appalachian orogens (e.g., Duggen et al., 2005; Whalen et al., 2006; Conticelli et al., 2009) have been widely discussed, and which were defined by Liegeois (1998) (Fig. 1). Wang and Xu et al. (2006) proposed that the post-collisional period ranged from the Early Carboniferous (Viséan) to the Late Permian. Zhou et al. (2008) investigated that the geochemical characteristics of different types of granite bodies (I-type and A2-type) differ from each other in the two formative stages of the Saur area (337 ± 4 – 302.6 Ma; 297.9 – 290.7 Ma), which indicate a post-collision tectonic environment and reflect the change in tectonic conditions from compression to extension. In addition, the presence of bimodal volcanic rocks, A-type granites and molasse deposits in the Early

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Fig. 1. Diagram showing the evolution of orogeny in northern Xinjiang (After Liegeoi, 1998, and Wang et al., 2006).

Permian also indicate that West Junggar had entered a post-collisional evolutionary stage during the latest Carboniferous–Middle Permian (Han et al., 2006; Su et al., 2006; Zhou et al., 2006, 2008; Chen et al., 2010). Previous studies mainly focused on volcanic rocks (e.g. Cai et al., 2012), including ophiolites (e.g. Safonova et al., 2012), and intrusive rocks (e.g. Zhou et al., 2008; Chen et al., 2010) in this region, where geochronology and geochemical characteristics were used to elucidate the Carboniferous structural style and evolutionary process. To date, few studies have been conducted on Paleozoic strata within the basin (e.g. Zheng et al., 2007; Li et al., 2015), especially the Permian strata, hindering a complete understanding of the tectonic framework of the West Junggar.

In this paper, we report the new whole-rock geochemistry data of the Early Permian pyroclastic rocks from borehole ZKH1205 in the Jimunai Basin. Our aim is to provide new evidence for the tectonic evolution of the northern West Junggar region.

2 Geological Setting

The Jimunai Basin, located in the northern West Junggar basin, is distributed along the Irtysh–Zaysan suture zone (Fig. 2), which marks the terminal stage of the entire evolution of the Irtysh–Zaysan Ocean and the collision between the Siberian and Kazakhstan–Junggar continents or, alternatively, the amalgamation between the Altai and Zharma–Saur terranes (Dobretsov, 2003; Sennikov et al., 2003; Buslov et al., 2001, 2004; Xiao et al., 2009; Li et al., 2015). Faults are widely developed in this region, which mainly include thrusting faults and strike-slip shear faults with an approximately E–W

orientation. The main regional fold structures include the Saur synclinorium and the Halabayi anticlinorium, and the main body of the study area is located on the southern wing of the Saur synclinorium, near its axis (Zhou et al., 2006). Regional faults control the structural framework and stratigraphic distribution of the Saur synclinorium. Volcanic activity in the region occurred during the mid-Devonian to early Permian, which resulted in extensive development of granite intrusions. There are six main felsic and alkali granite intrusions, including I-type granites (the Tasite, Sentasi, Wokensala, and Kaerjia plutons) that were emplaced between 337 ± 4 Ma and 302.6 Ma, and A-type (A2) granites (the Kuoyitasi and Qiaqihai plutons) that were emplaced between 297.9 and 290.7 Ma (Zhou et al., 2008) (Fig. 2c).

The Carboniferous sedimentary infill of the Zaysan–Jimunai Basin can be divided into two stages, which resulted from accretionary processes and were a response to Carboniferous arc-related tectonic evolution (Li et al., 2016). The Lower and Middle Carboniferous sediments that filled the basin are dominated by shallow marine sediments, and then volcanic material entered the basin as the volcanic arc grew northward. With the closure of the Irtysh–Zaysan Ocean in the Late Carboniferous, the sediments of the Early Carboniferous pre-arc basin were buried and uplifted during the collision and combination of the Saur and Altai island arcs (Li, 2016). The sea gradually retreated westward to the Zaysan basin, with the eastern part first transitioning to a terrestrial depositional environment (Li et al., 2016). The ocean closed in the Late Carboniferous, and the whole area was in a tectonic environment of post-collision extension, entering the intracontinental evolutionary stage (Li et al., 2015). Therefore, the period from the Late carboniferous to the

Fig. 2. (a) Simplified tectonic map of the Central Asian Orogenic Belt (Jahn et al., 2004; Windley et al., 2007) with the approximate location of Fig. 1b. (b) Geological map of eastern Kazakhstan to southern Altai area showing the location of the Zaysan–Jimunai Basin (Jimunai Depression). (c) Geologic sketch map in Saur region in west Junggar, Xinjiang (Zhou et al., 2008).

Early Permian is considered to be an important transition in terms of the tectonic background from subduction to collisional accretion in this region (Buslov et al., 2004; Windley et al., 2007; Vladimirov et al., 2008; Yang et al., 2014).

The study area includes outcrops of Devonian, Carboniferous, Permian, and Quaternary strata. The Devonian strata comprise the Hongguleleng, Zhulumute,

Yundukala, and Saurshan groups, which are mainly composed of pyroclastic rocks and mudstones. The Lower Carboniferous strata (Nalinkala, Halabayi and Heishantou groups) are composed mainly of shallow-coastal terrigenous clastic rocks, pyroclastic rocks and intermediate-acid volcanic rocks and the Upper Carboniferous Qiaqihai and Jimunai groups are mainly marine terrigenous clastic rocks with a small amount of

intermediate-acidic volcanic rocks. The Permian strata include the Haerjiawu and Kalagang formations, which consist of intermediate-acidic volcanic rocks, pyroclastic rocks, and normal coal-bearing clastic rocks. The former are mainly distributed near Jimunai, and the latter exposed near Ha'erjiao. The Quaternary strata are composed of unconsolidated sand and gravel beds.

The Kalagang Formation (Fm.) is the main coal-bearing stratum, formed in the Early Permian, as determined by previous studies. Zhou et al. (2006) suggested that the Kalagang Fm. volcanic rocks were formed in the Early Permian by analysing Ar-Ar isotopes giving a date of 282 Ma. Li et al. (2015) found a typical Permian sporopollen assemblage including fern spores in several sets of mudstone or tuff in the Kalagang Fm. The preserved plant fossils also provide biostratigraphic evidence for the formation age (Windley et al., 2002). Based on its coal-bearing conditions and eruption cycles, the Kalagang Fm. is divided into four lithologic sections: the first is the lower coal-bearing section; the second comprises intermediate-acidic rocks and tuff; the third is the upper coal-bearing section; and the fourth is further intermediate rocks and tuff/s (Li et al., 2019). The borehole ZKH1205 is located in the eastern part of Ha'erjiao and passes through the Neogene and into the Lower Permian Kalagang Fm. strata (Fig. 2c). The third lithologic section here is composed of gray tuffaceous sandstone, light gray-black, black tuffaceous rocks, carbonaceous tuffaceous rocks and gray-white volcanic rocks and the fourth lithologic section consists mainly of dark gray, gray and gray-green andesite, amygdaloidal andesite and gray-green, black-green basalt and amygdaloidal basalt.

3 Samples and Analytical Methods

In this study, four volcanic rock samples (H-1-1, H-3-1, H-4, and H-5) and 10 pyroclastic rock samples were collected from the lower coal-bearing section in the Lower Permian Kalagang Fm. from borehole ZKH1205 (Fig. 3). Fresh unweathered samples were collected for petrological and geochemical analysis. Each sample was crushed and milled in a mortar and passed through a 200-mesh sieve for geochemical analyses.

Petrological characteristics analysis was completed at the Key Laboratory of Tectonics and Petroleum Resources at China University of Geosciences (Wuhan). Major oxides were analyzed by a Primus II X-ray fluorescence spectrometer (XRF) at Wuhan Sample Solution Analytical Technology Co., Ltd. In the analysis, 0.6 g dry sample together with 6.0 g of flux ($\text{Li}_2\text{B}_4\text{O}_7$: LiBO_2 : LiF = 9:2:1) and 0.3 g oxidant (NH_4NO_3) were placed in a platinum crucible to fuse in a melting furnace at 1150°C for 14 minutes. Loss on ignition (LOI) was calculated on the dried samples heated up to a temperature of 1000°C.

Trace element analysis of whole-rock samples was also carried out also at Wuhan Sample Solution Analytical Technology Co., Ltd. using an Agilent 7700e inductively coupled plasma mass spectrometer (ICP-MS), and detailed procedures as described by Liu et al., (2008): (1) 200-mesh samples were dried in an oven at 105°C for 12 hours; (2) 50 mg of powdered sample was accurately

Fig. 3. Comprehensive stratigraphic column of lithology, sampling sites and photographs of Early Permian volcanic rocks and volcanoclastic rocks from borehole ZKH1205.

weighed and placed in a Teflon bomb; (3) 1 ml of high-purity HNO_3 and 1 ml of high-purity HF were slowly added in turn; (4) the Teflon bomb was placed in a steel bushing, then tightened and heated for more than 24 hours in an oven at 190°C; (5) when the Teflon bomb cooled, the cap was opened, and the bomb was steamed on an electric heating plate at 140°C, before adding 1 ml HNO_3 and drying the bomb again; (6) 1 ml high-purity HNO_3 , 1 ml of MQ water and 1 ml of the internal standard element In were added (1 ppm concentration), then the Teflon bomb was placed into the steel bushing again, tightened and heated in the oven at 190°C for over 12 hours; (7) the solution was transferred into a polyethylene material bottle and diluted with 2% HNO_3 to 100 g for ICP-MS testing later.

4 Results

4.1 Petrology

Gray and whitish gray andesite has a bimodal inequigranular texture composed of matrix and phenocrysts (Fig. 4). The phenocrysts (average 70%) are dominated by plagioclase, and the matrix with hyalopilitic texture shows poor orientation of microcrystalline plagioclase and glass (Fig. 4).

Fig. 4. Photomicrographs of andesites from the Kalagang Formation, cross-polarized light.

Fig. 5. Photomicrographs of pyroclastic rocks from the Kalagang Formation, cross-polarized light.
(a) Lithic tuff rocks; (b) carbon-bearing tuffaceous mudstones.

The pyroclastic rocks have high contents of carbon, as evidenced by hand specimens, and are black and gray. Two different types of pyroclastic rock are identified based on petrological characteristics. The first is a deep gray to black lithic tuff which contains predominantly lithic fragments (87–95%, average 91%) and minor contents of feldspar (5–10%, average 8%) and glass (3–6%, average 5%) (Fig. 5a). The lithic fragments are mainly basalt or andesite rocks, and generally have poor sorting, ranging from 100 μ m to 1.5 mm in size, and angular to subangular rounding (Fig. 5a), which indicates

a nearby source and short-distance transport. In addition, some volcanic fragments have vesicular structures. The phenocrysts are mainly plagioclases, with euhedral long prismatic and short and wide planar shapes in some samples (Fig. 5a). The second type is classified as carbon-bearing tuffaceous mudstones, which are located near the coal seams either as the roof or floor (H-7, and H-8-2) and which have relatively low proportions of pyroclastic materials (lithic fragments, crystal clasts, or glass) with a range from 30% to 50% (Fig. 5b). The lithic fragments are mainly composed of andesite rocks with angular shapes

and variable sizes from less than 50 μm to more than 200 μm . In addition, euhedral short prismatic plagioclases occur not only as phenocrysts of the andesite lithic fragments, which have microcrystal plagioclases and a glass matrix but also as individual crystal clasts together with calcite and minor quartz (Fig. 5b).

4.2 Geochemistry

4.2.1 Volcanic rocks

The major oxide and trace element concentrations of volcanic and pyroclastic rock samples from borehole

ZKH1205 are listed in Table 1. LOI ranges from 5.2% to 8.6%, with an average of 6.3%, indicating that the volcanic samples experienced varying degrees of alteration. The major oxides are dominated by SiO_2 , followed by Al_2O_3 and CaO . The sample H-1-1 has a relatively low SiO_2 content, but relatively high Fe_2O_3 , MnO , CaO contents and a low Rittmann Indexes ($\delta = (\text{K}_2\text{O} + \text{Na}_2\text{O})^2 / (\text{SiO}_2 - 43)$; 7.0), which indicate an alkaline pattern. This is further confirmed by the fact that H-1-1 falls within the alkaline field in the SiO_2 - ($\text{K}_2\text{O} + \text{Na}_2\text{O}$) diagram (Le Maitre et al., 1989), whereas the other

Table 1 The concentrations of major (wt%), trace elements (ppm) and their sample parameters from Ha'erjiao

	H-1-1(+)	H-1-2	H-2-1	H-2-2	H-3-2	H-3-1(+)	H-4(+)	H-5(+)	H-6	H-7	H-8-1	H-8-2	H-9	H-10
SiO_2	51.29	34.30	39.71	57.45	32.33	63.47	61.81	65.31	44.43	48.15	35.99	21.92	51.63	33.13
TiO_2	0.67	0.57	1.40	0.94	0.73	0.59	0.72	0.66	1.56	0.81	1.69	0.25	1.44	1.11
Al_2O_3	15.18	11.03	17.15	15.89	14.08	13.46	15.04	14.85	15.74	12.06	16.10	6.20	17.89	13.53
Fe_2O_3	6.17	8.73	5.54	4.76	7.06	3.14	4.42	3.98	9.18	3.03	11.16	1.63	6.12	7.81
MnO	0.14	0.26	0.23	0.06	0.32	0.09	0.09	0.07	0.12	0.05	0.18	0.03	0.05	0.31
MgO	2.21	3.21	3.73	2.51	3.94	1.30	1.91	1.20	3.59	1.49	4.83	1.63	2.95	6.62
CaO	6.87	17.48	10.86	2.39	12.63	4.38	3.49	2.08	5.69	3.06	8.01	3.26	3.30	12.42
Na_2O	4.01	1.65	3.48	1.49	0.99	3.17	3.36	4.24	3.29	3.10	1.80	1.71	2.48	2.08
K_2O	3.61	1.33	2.93	3.00	3.85	4.14	3.22	2.29	2.29	1.55	1.12	0.68	2.42	2.01
P_2O_5	0.24	0.34	1.03	0.12	0.15	0.23	0.29	0.24	0.34	0.39	0.36	0.02	0.32	0.63
LOI	8.55	20.72	13.96	10.73	23.11	5.48	5.82	5.20	13.37	26.63	18.42	63.04	10.51	20.01
SUM	98.93	99.62	100.02	99.34	99.18	99.45	100.16	100.09	99.60	100.32	99.66	100.36	99.10	99.64
Li	12.3	20.4	10.9	17.6	22.2	19.2	12.8	4.52	4.54	3.32	32.7	3.39	18.5	13.8
Be	1.26	1.49	2.66	1.93	1.94	1.02	1.70	1.24	1.70	1.04	1.80	0.41	1.41	1.38
Sc	7.40	10.6	20.9	15.6	11.1	6.55	8.35	6.79	22.4	11.8	24.3	4.50	18.0	15.1
V	48.1	73.2	149	126	95.9	42.0	64.2	45.9	194	115	206	33.5	191	156
Cr	42.9	51.4	131	59.5	55.9	47.7	58.6	34.1	39.9	53.6	29.2	42.8	90.3	93.4
Co	8.52	13.3	33.7	14.0	23.3	9.68	9.70	6.59	32.0	16.7	37.2	3.57	30.3	24.3
Ni	32.7	50.6	47.3	48.8	51.6	33.5	41.6	23.6	86.4	42.8	72.7	28.0	69.7	74.7
Cu	25.3	74.0	61.9	35.7	101	57.2	19.6	9.71	63.7	36.9	69.8	9.40	67.0	57.6
Zn	37.6	57.3	89.8	54.9	54.6	26.8	49.0	56.7	86.3	53.2	87.4	24.9	96.8	73.2
Ga	14.5	13.5	18.8	19.5	20.3	11.4	17.6	18.0	19.7	14.0	18.6	7.11	21.4	16.1
Rb	46.5	18.6	55.7	60.3	48.6	52.4	57.3	44.5	36.3	29.0	19.7	19.1	41.0	30.7
Sr	454	705	523	181	459	345	300	227	703	265	590	293	364	553
Y	21.8	18.0	45.7	25.5	16.5	18.3	17.6	18.4	28.2	20.5	30.4	8.34	22.6	19.7
Zr	226	88.1	200	239	148	198	205	225	192	164	198	70.1	203	115
Nb	14.0	6.60	12.1	14.0	9.04	11.9	12.1	14.1	8.20	10.4	8.52	4.55	13.0	8.32
Sn	1.52	2.89	2.08	1.80	6.30	2.01	1.07	1.11	1.60	1.20	1.47	0.90	1.47	1.06
Cs	0.41	0.49	0.74	0.81	0.44	0.38	0.92	0.76	1.14	1.02	0.86	0.50	1.19	0.76
Ba	1116	169	195	263	474	1312	495	109	214	124	150	76.3	198	162
La	25.4	12.5	35.8	20.5	14.6	21.8	24.1	27.4	14.4	20.9	15.2	12.6	21.6	17.2
Ce	51.8	26.5	103	44.8	32.0	45.5	49.1	54.7	34.8	46.2	37.4	24.8	47.9	39.9
Pr	5.94	3.41	12.9	5.21	4.01	5.17	5.54	6.15	4.63	5.62	5.04	2.86	5.90	5.13
Nd	22.1	15.0	60.1	19.7	17.0	19.9	21.5	23.6	20.6	23.2	22.5	10.5	23.9	22.0
Sm	4.35	3.47	14.1	3.82	4.02	4.06	4.14	4.34	5.01	4.59	5.52	1.97	4.99	4.68
Eu	1.09	1.49	3.58	0.91	1.26	1.06	1.18	1.14	1.56	1.12	1.64	0.44	1.29	1.60
Gd	3.69	3.34	12.7	3.43	3.57	3.23	3.39	3.61	4.89	3.91	5.40	1.59	4.14	4.08
Tb	0.60	0.53	1.80	0.64	0.60	0.54	0.52	0.56	0.85	0.60	0.90	0.24	0.66	0.61
Dy	3.72	3.10	9.12	4.06	3.16	3.28	3.06	3.18	4.87	3.45	5.20	1.30	3.94	3.38
Ho	0.74	0.61	1.60	0.89	0.60	0.61	0.60	0.62	0.99	0.71	1.09	0.28	0.79	0.68
Er	2.06	1.57	4.02	2.65	1.48	1.75	1.68	1.77	2.76	2.02	3.05	0.83	2.31	1.86
Tm	0.31	0.24	0.52	0.41	0.20	0.26	0.27	0.27	0.42	0.29	0.43	0.13	0.34	0.26
Yb	2.01	1.46	3.35	2.75	1.31	1.64	1.65	1.75	2.56	1.95	2.68	0.88	2.07	1.62
Lu	0.29	0.22	0.50	0.42	0.18	0.24	0.23	0.27	0.40	0.29	0.42	0.14	0.32	0.25
Hf	5.33	2.26	4.41	5.67	3.48	4.63	4.65	5.03	4.17	3.72	4.31	1.84	4.63	2.88
Ta	0.89	0.36	0.60	0.90	0.52	0.79	0.80	0.91	0.49	0.59	0.54	0.33	0.72	0.45
Tl	0.27	0.085	0.17	0.22	0.18	0.32	0.21	0.17	0.15	0.12	0.075	0.083	0.22	0.15
Pb	7.95	2.82	15.4	5.92	3.68	7.93	6.13	9.89	2.11	5.74	3.31	2.14	10.8	5.42
Th	5.43	1.10	1.53	3.65	1.87	4.71	5.20	5.41	1.29	2.78	1.29	2.86	2.46	1.35
U	2.93	0.41	0.81	1.03	0.55	1.84	2.03	2.02	0.46	0.94	0.46	0.89	0.85	0.41
ΣREE	145.90	91.57	309.39	135.71	100.48	127.36	134.55	147.74	127.05	135.43	136.88	67.02	142.74	123.00
(La/Yb) _{CN}	8.51	5.79	7.20	5.02	7.54	8.98	9.83	10.53	3.80	7.25	3.83	9.70	7.01	7.15
(La/Sm) _{CN}	3.67	2.28	1.60	3.37	2.29	3.38	3.66	3.97	1.82	2.87	1.73	4.02	2.72	2.31
(Gd/Yb) _{CN}	1.48	1.85	3.06	1.01	2.20	1.59	1.65	1.66	1.54	1.62	1.63	1.46	1.61	2.03
Ce/Ce*	1.02	0.98	1.16	1.04	1.01	1.03	1.02	1.02	1.02	1.02	1.03	0.99	1.02	1.02
Eu/Eu*	0.83	1.33	0.82	0.76	1.02	0.89	0.96	0.88	0.96	0.81	0.92	0.75	0.87	1.12

Note: *: volcanic rocks.

Fig. 6. All analyzed samples in TAS (total alkalis vs. silica; Le Bas et al., 1986) diagram. Alkaline versus subalkaline fields separated by the Macdonald and Katsura (1964) dashed line, and Zr/TiO₂-Nb/Y discrimination plot of volcanic rocks and pyroclastic rocks (after Winchester and Floyd, 1977).

samples fall in the calc-alkaline field. However, all samples fall in the calc-alkaline dacite/rhyolite field in the Th-Co diagram, possibly because the major elements can be influenced by hydrothermal alteration, as reported by Hastie et al. (2007). A similar conclusion can be drawn by other diagrams, such as Yb vs La, Zr vs Y, and Th vs Yb. In the Zr/TiO₂-Nb/Y diagram (Floyd and Winchester, 1978), all volcanic samples are classified as trachyandesite close to the dacite field (Fig. 6). Based on the results from the TAS diagram, the total contents of alkali elements have probably not changed greatly, indicating that major elements were affected more strongly than the trace elements (Hu et al., 2010).

The volcanic rocks show strong positive anomalies in Rb, K, and U, moderate to weak positive anomalies in Nd and Zr, strong negative anomalies in Nb, Ta, and Ti, and moderate to weak negative anomalies in Sr and P on a primitive mantle normalized spider diagram, which is consistent with the intermediate-basic volcanic rock patterns of the Kalagang Fm. in Saur (Tan et al., 2006) and the Tuoli region (Gao et al., 2014) (Fig. 7). The total Rare Earth Element (REE) content ranges from 127.3 to 147.7 ppm, with an average of 138.8 ppm. The chondrite-normalized REE distribution pattern (Fig. 8) shows a rightward slope of the Light REEs (LREEs) distributive curve and a flat Heavy REEs (HREEs) distributive curve, with weak Eu anomalies (Eu/Eu*: 0.8–0.9, average 0.8) and no Ce anomalies (1.0–1.03, 1.02 on average). The value of (La/Yb)_{CN} (CN = Chondrite Normalized) varies between 8.5 and 10.5 (9.5 on average), indicating that the samples are relatively enriched in LREEs.

4.2.2 Pyroclastic rocks

The pyroclastic rocks have relatively high LOI ranging from 10.5 to 63.0 wt% (22.1 wt% on average), especially H-8-2 with the highest (63.0 wt%), likely because of the higher contents of organic matter, as indicated by petrologic results (Fig. 5). The pyroclastic rocks are also characterized by distinctly variable SiO₂ contents ranging from 33.1 to 57.5% (average 42.4%). Samples H-2-2 and

Fig. 7. Primitive mantle-normalized trace elements spider diagrams of Kalagang Formation.

Patterns for oceanic island basalts (OIB) are from Sun and McDonough (1989); The light yellow area shows the range of Permian intermediate-basic volcanics in Saur and Tuoli area (Kalagang Formation), data from Gao et al. (2014) and Tan et al. (2007); The light grey area shows the range of subduction zone basalts, with the lower and upper limits being defined by “average” low-K and high-K basalts, respectively (Tatsumi and Eggins, 1995); The deep grey area shows the range of Late Permian contaminated continental basaltic lava from the Emeishan large igneous province (Xia, 2014).

H-9 have relatively higher SiO₂ (57.5 and 51.4 wt%) and CaO contents (2.4 and 3.3 wt%), respectively, which may be attributed to the high proportions of quartz and calcite, which is consistent with the abundant calcite veins commonly observed by petrological analysis (Fig. 3). The Al₂O₃ content in these samples ranges from 11.0–17.9 wt% (15.3%, average), and the TiO₂ content ranges from 0.6 to 1.7 wt%.

In the primitive mantle normalized trace element spider diagram, the samples show strong positive anomalies in Large Ion Lithophile Elements (LILEs) (e.g., Rb, K, and Pb) and strong negative anomalies in High Field Strength Elements (HFSEs) (e.g., Nb, Ta, Ti). In addition, P has slightly positive and negative anomalies (Fig. 7). The

Fig. 8. Chondrite normalized trace element spider diagrams for the Kalagan Formation.

Data of Permian intermediate-basic volcanics in Saur and Tuoli aera (Kalagan Formation) are plotted for comparison (Gao et al., 2014; Tan et al., 2007).

samples display highly variable Σ REE contents, from 67.0 to 309.4 ppm (average 74.8 ppm), among which H-8-2 (67.0 ppm) shows a remarkable depletion, whereas H-2-1 (309.4 ppm) shows a strong enrichment. The chondrite-normalized REE distribution patterns are characterized by slight LREEs enrichment and a relatively weak fractionated flat pattern of HREEs. The samples have no Eu and Ce anomalies (Eu/Eu^* , average 0.9; Ce/Ce^* : 1.0–1.2, average 1.0), except for sample H-8-2 with a negative anomaly ($\text{Eu}/\text{Eu}^* = 0.8$) and sample H-1-2 with a slightly positive anomaly ($\text{Eu}/\text{Eu}^* = 1.3$) (Fig. 8).

5 Discussion

5.1 Weathering and alteration effects

In the present study, all the samples have higher LOI contents, which might be caused by alteration effects (in volcanic rocks) or higher content of organic matter content (in pyroclastic rocks). In accordance with the petrological research, plagioclase was the most easily altered to smectites, carbonate, and clay minerals in volcanic rocks (Fig. 4). The pyroclastic rocks generally tend to contain higher contents of organic matter, causing elevated LOI values. Generally, some major elements (e.g., Ti, P, Fe, and Mn), the HFSEs, REEs, Th, and transition elements are not readily transported by hydrothermal alteration, and thus, those elements may exhibit no obvious correlation with LOI (Zhou, 1999; Wang et al., 2006; Liu et al., 2018), whereas the Al_2O_3 , SiO_2 , and Rb contents clearly decrease with increasing LOI, implying that their original contents were modified by alteration.

The chemical index of alteration ($\text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100$, where CaO^* represents the CaO only incorporated into silicate minerals) is considered to be a useful parameter in inferring the weathering degree of source rocks (Nesbitt and Young, 1982). However, the source rocks can be affected by recycling, which will influence CIA values. Cox et al. (1995) proposed the index of compositional variability ($\text{ICV} = (\text{Fe}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{MnO} + \text{TiO}_2) / \text{Al}_2\text{O}_3$) to

determine whether the source rocks have been recycled or not. In this study, the ICV values (1.3–4.6, average 2.6) show that the source rocks have not been recycled. When plotted in the A-CN-K ($\text{Al}_2\text{O}_3 - (\text{CaO}^* + \text{Na}_2\text{O}) - \text{K}_2\text{O}$) ternary diagram (Fig. 9), the sediments exhibit positions commensurate with low CIA values (49.3–69.3, average 59.3), and most of the samples yield a series of CIA values distributed along a straight line (ideal weathering trend) parallel to the A-CN sideline (Nesbitt and Young, 1982; McLennan, 1993). However, some data points plot on a line deviating from the theoretical trend, suggesting K_2O addition as a result of diagenetic K-metasomatism (conversion of kaolinite to illite), so it is necessary to make corrections for this (Fedot et al., 1997; Rieu et al., 2007; Yan et al., 2010) (Fig. 9). The corrected CIA values show the same weathering intensity (Nesbitt and Young, 1989). The mineralogical variation can also provide some evidence for the weathering intensity. There is abundant plagioclase and little to no clay minerals in the pyroclastic rocks, especially in the carbon-bearing tuffaceous mudstone, which also indicates a low to moderate degree of chemical weathering, consistent with the CIA values (Fig. 5).

During the process of weathering or recycling, U is more likely to migrate than Th, resulting in an increase in the Th/U ratio. McLennan et al. (1993) proposed that a Th/U-Th diagram can be used to discriminate the degree of sediment recycling and heavy-mineral sorting. The ratios of the pyroclastic rocks range from 1.89 to 3.54 with an average of 2.95, which is lower than that of the UCC [Upper Continental Crust] (3.8, Taylor and McLennan, 1985). In the Th/U-Th diagram (Fig. 10), however, the points do not follow the normal weathering trend and almost all samples plot close to the field of depleted mantle source,

Fig. 9. Chemical compositional variations in Kalagan Formation in ternary A-CN-K plot and associated chemical index of alteration (CIA) variations. Correction for K-metasomatism is made by projecting data points back to the ideal weathering pathway from K-apex (dashed arrows).

Ka, kaolinite; Chl, chlorite; Gi, Gibbsite; Sm, smectite; Ms, muscovite; Pl, plagioclase; Kfs, K-feldspar (after Nesbitt and Young, 1984; Cox et al., 1995).

indicating that these sediments were derived from source rocks with a low degree of weathering or from sediment with very little recycling (Meinhold et al., 2007; Xiang et al., 2015). The Th/Sc ratio characterizes the average provenance, whereas an increase in the Zr/Sc ratio alone indicates significant sediment reworking, consistent with zircon enrichment (McLennan, 1993). The Th/Sc and Zr/Sc of pyroclastic rocks have a significant positive correlation in the study area ($R^2 = 0.88$, Fig. 11), revealing that the geochemical changes are determined by the sediment-region rocks rather than by sedimentary recycling (Cullers, 1994; Li et al., 2015).

5.2 Crustal contamination, and partial melting

The samples, including volcanic and pyroclastic rocks, have relatively low contents of MgO (average 1.65 wt% and 3.45 wt%) and compatible elements, including Ni (average 32.0 and 57.3 ppm) and Cr (average 45.8 and 64.7 ppm), respectively, possibly suggesting that the samples represent evolved magmas rather than primitive magmas directly generated by partial melting of mantle sources (He et al., 2015). The positive correlation between SiO_2 and Th/La ($R^2 = 0.40$) and U/Nb ($R^2 = 0.36$) indicates extensive crustal contamination (Wang et al., 2011; Tang et al., 2013; Ma et al., 2015). In addition, the volcanic and pyroclastic samples are characterized by elevated contents of LILEs (Rb and Pb) and LREEs, strong negative

anomalies in HFSEs (Nb, Ta, and Ti), slightly or no negative Eu anomalies and Nb/La ratio < 1 (average 0.53 and 0.52, respectively), which appear to indicate crustal contamination (Condie, 2001; Kieffer et al., 2004). However, these abovementioned geochemical features might also have been affected by the tectonic environment. For example, the enrichment of LILEs and LREEs in the volcanic rocks might also have been caused during the subduction process by low-temperature partial melting in the source area (Pearce et al., 1990; Kürüm et al., 2017); low contents of Nb, Ta and Ti are also characteristic of island arc and active continental margin basalts (Pearce, 1982; Keppler, 1996; You et al., 1996; Xia, 2014; Xia and Li, 2019).

The ratios of Nb/U, Ta/U and Ce/Pb are sensitive indicators for identifying contamination and tectonic environments (Hofmann et al., 1986; Hofmann, 1997; Jahn et al., 1999; Jiang et al., 2006; Sun et al., 2008; Tang et al., 2012, 2017). All samples show lower ratios of Nb/U (average 6.05 and 14.89, respectively), Ta/U (average 0.39 and 0.86, respectively), and Ce/Pb (average 6.45 and 9.16, respectively) than MORB, OIB and the mean value of crust, and these ratios cannot be caused easily by crustal contamination (Shu et al., 2017). On the Nb/Th, Ta/Th and Th/Yb primitive mantle-normalized ratio plots (Fig. 12), the samples are controlled by the N-MORB, upper crust (UC) and lower crust (LC) mixing trend lines. The volcanic rocks and sample H-8-2 are more closely related to the UC trend line, whereas the pyroclastic rocks are more similar to the LC trend line (Tang et al., 2017). This also cannot be explained simply by crustal contamination and that may be inherited from their magma sources. Zhou et al. (2006) also confirmed that the Permian volcanic rocks in the Saur area did not originate from the residual melt of mantle-derived basalt magma after the differentiation of basic plagioclase, but from crust–mantle mixed source magma.

In the diagram of La vs. La/Sm (Treuil and Varet, 1973), the La/Sm ratio increased with the increasing La content ($R^2 = 0.6$). Therefore, the compositional variations of the pyroclastic rocks are likely to have resulted from partial melting (Fig. 13). Correspondingly, Tan et al. (2006) analyzed the trace elements of the Permian volcanic rocks in the Saur area, and concluded that the mechanism of formation of the basic and intermediate volcanic rocks was mainly equilibrium partial melting, and that magmatic fractional crystallization was not significant, whereas the rock-forming processes of intermediate-acidic volcanic rocks were influenced by both partial melting and fractional crystallization. Ratios such as Zr/Y and Zr/Nb are used to determine the degree of partial melting or the effects of partial melting (Fitton et al., 1988). Our samples have low Zr/Y and medium-high Zr/Nb ratios, indicating moderate degree partial melting.

5.3 Provenance

Volcanic material (volcanic lithic fragments, crystal clast, and glass) represents a high proportion of the pyroclastic rocks, indicating a primary volcanic rock source. The lithic tuff contains abundant basalt and andesite lithic fragments. Also, the majority of these lithic

Fig. 10. Th/U vs. Th bivariate plot of Kalagang Formation pyroclastic rocks (McLennan et al., 1993).

Fig. 11. Th/Sc-Zr/Sc diagram after McLennan et al. (1993). Data of tonalite, granodiorite, rhyolite and andesite are from Condie (1993), data of basalt and dacite are from Roser et al. (2002) and Xiang et al. (2015).

Fig. 12. Trace element ratio diagrams of Kalagang Formation pyroclastic rocks and volcanic rocks after Dongmei Tang (2017). The primitive mantle, N-MORB, E-MORB and OIB values are from Sun and McDonough (1989), and trace element values of the upper crust (UC) and lower crust (LC) are from Rudnick and Gao (2003).

Fig. 13. Discrimination plots of Th/Yb versus Ta/Yb (after Gorton and Schandl, 2000) and Th/Hf versus Ta/Hf (after Schandl and Gorton, 2002) for tectonic settings.

fragments appear angular to subangular in shape. All the petrological features reflect short-distance transport of basaltic and andesite materials from the sediment-source region. In addition, some elements, such as REEs, HFEEs and transition metal elements (e.g. Co, Ni, V, Cr, Sc), are considered immobile during weathering, sedimentary transport, deposition, diagenesis, and most intense hydrothermal alteration (Cullers et al., 1988; Taylor and McLennan, 1985; McLennan et al., 1993; Condie, 1993; Zhou, 1999; Hawkesworth et al., 1997; Wang and Xu 2006; Xiang et al., 2015). Therefore, these elements are particularly useful in discriminating the nature of the

parent rock for clastic sedimentary rocks.

Transition metal element contents are higher in mafic and ultramafic rocks and lower in felsic rocks, while HFSEs (e.g. Zr, Th, La, Y, Nb) are abundant in felsic rocks (Asiedu et al., 2017). The pyroclastic rocks have relatively high contents of Cr (29.2–130.6 ppm, average 64.7 ppm), Ni (28.0–86.4 ppm, average 57.3 ppm), and low Cr/Ni ratio (< 1.3), indicating input of mafic volcanic rocks rather than ultramafic rocks from the source area. The Ti/Nb ratio of the source rock generally does not change during weathering and transport and thus can be used to indicate the type of source rocks, with a Ti/Nb ratio greater than 300 indicative of the input of basic volcanic rocks and less than 300 indicative of the input of acidic volcanic rocks (Jenchen and Rosenfeld, 2002). The ratio of Ti/Nb in the pyroclastic rocks is higher than 300, with an average of 669, indicating the input of basic compositions. In addition, the ratios of Th/Sc, Th/Co, Th/Cr and La/Co are significantly different between mafic and felsic source rocks (Cullers, 2000; Zaid, 2015; Asiedu et al., 2017) and can be used to determine the provenance of rocks (Armstrong-Altrin et al., 2013). The source rocks of the pyroclastic rocks in the study area are similar to mafic volcanic rocks, except for sample H-8-2, which is similar to felsic rocks (Table 2). Classification diagrams, such as Zr/TiO₂-Nb/Y, have been widely used to identify source rock types. In this diagram, only sample H-8-2 falls into the rhyodacite/dacite area, whereas the other samples fall into the andesite and sub-alkaline basalt area (Fig. 6).

The REE content, distribution pattern and Eu anomaly can be used as important indicators for the identification of sedimentary source rocks (Taylor and McLennan, 1985; Xiang et al., 2015; Asiedu et al., 2017). Felsic volcanic rocks have a high ratio of LREE/HREE and a strong negative Eu anomaly, whereas mafic volcanic rocks have a low LREE/HREE ratio and no negative Eu anomalies (Cullers, 1994, 2000; Yan et al., 2012). The REE distribution pattern of pyroclastic rocks in Harjiao and the adjacent region is similar to that of intermediate-basic volcanic rocks, with low LREE/HREE ratios (1.79–3.63, average 2.57) and weak Eu anomalies (Eu/Eu*: 0.75–

Table 2 Element ratio ranges of pyroclastic rocks compared to the ratios of sedimentary rocks derived from felsic rocks and mafic rocks

	H-1-2	H-2-1	H-2-2	H-3-2	H-6	H-7	H-8-1	H-8-2	H-9	H-10	Range of sediments from felsic sources	Range of sediments from mafic sources	Average UCC
Th/Sc	0.10	0.07	0.23	0.17	0.06	0.24	0.05	0.64	0.14	0.09	0.84–20.5	0.55–0.22	0.79
Th/Co	0.08	0.05	0.26	0.08	0.04	0.17	0.03	0.80	0.08	0.06	0.67–19.4	0.04–1.40	0.63
Th/Cr	0.02	0.01	0.06	0.03	0.03	0.05	0.04	0.07	0.03	0.01	0.13–2.70	0.02–0.05	0.13
Eu/Eu*	1.33	0.81	0.76	1.01	0.96	0.80	0.92	0.75	0.86	1.12	0.32–0.94	0.7–1.2	0.63
(La/Lu) _{CN}	5.95	7.51	5.05	8.60	3.78	7.61	3.80	9.68	6.99	7.26	3.0–27.0	1.1–7.0	9.73
La/Co	0.94	1.06	1.46	0.63	0.45	1.26	0.41	3.53	0.71	0.71	1.4–22.4	0.14–0.38	1.76

Data from Cullers et al. (2000); Asiedu et al. (2017); Zaid et al. (2015).

1.33), except for sample H-8-2 with the highest LREE/HREE ratio (3.63) and the lowest Eu/Eu* value (0.73), indicative of intermediate-acidic volcanic rocks. In addition, sample H-8-2, from the roof of a coal seam, has the highest value of LOI (63 wt%), and its geochemical characteristics resemble the underlying coal seam, indicating that they most likely have the same source rock.

5.4 Tectonic setting and implications

The elevated concentrations of LILEs and LREEs, along with the negative anomalies of HFSEs (e.g. Nb and Ta), as well as the absence of significant Eu and Ce anomalies, most likely indicate an intraplate affinity, which is similar to the post-collisional volcanic rocks in the West and East Junggar (Tan et al., 2006; Li et al., 2014, 2015; Su et al., 2012; Xu et al., 2013). In some discriminant diagrams, such as Th/Yb-Ta/Yb and Th/Hf-Ta/Hf (Gorton and Schandl, 2000), which are widely used to distinguish the tectonic setting of intermediate rocks, all the pyroclastic rocks fall in the within-plate volcanic zones (WPVZ), whereas the volcanic rocks fall in the boundary between within-plate volcanic zones and active continental margin (ACM) (Fig. 14). The similarity is that in the Zr/Y-Zr diagram (Pearce and Norry, 1979), all samples fall into or near the within-plate basaltic (WPB) field (Fig. 15), however, they plot in the arc-related field in other discriminant diagrams using Nb, Ta, Ti or Th as discriminating factors. These anomalous geochemical patterns may be explained by crustal contamination or variable degree of fractional crystallization and melting rather than by tectonic setting. For example, contamination by continental crust or lithosphere can impart subduction-like signatures and lead to the misidentification of contaminated continental intraplate basalts as arc-related ones (Xia et al., 2008, 2014; Ernst et al., 2005; Jourdan et al., 2007; Neumann et al., 2011). Xia et al. (2016, 2019) proposed that contaminated continental intraplate basalts are characterized by pronounced negative Nb, Ta, and Ti anomalies, but the concentrations of incompatible trace elements are conspicuously higher than those of subduction-zone basalts. Therefore, for basalts contaminated by the crust or lithosphere, diagrams often fail to indicate accurately the corresponding tectonic setting (Xia et al., 2014). Our samples show distinct negative Nb and Ta, whereas the incompatible elements are significantly higher in the samples than in subduction zone basalts (Fig. 7), which is similar to the distribution pattern of contaminated basalts in the Emeishan large igneous province (Xia et al., 2014).

Fig. 14. Zr/Y-Zr diagram after Pearce and Norry (1979), the continental and oceanic arc fields defined by Pearce (1982 or 1983).

Vertically from bottom to top, the borehole ZKH1205 records two phases of volcanism according to the petrological features during the early Permian. The major source rocks might have been derived from periodic eruptions of volcanic rocks (basalt and andesite). The adjacent region also features a contemporary basalt that was generated in the extensional stage of the post-collisional setting with significant bimodal features. Furthermore, the widely generated contemporary A-type granites provide additional evidence for the extensional regime (Zhou et al., 2008). As noted above, the Irtysh-Zaysan suture zone formed in the Late Carboniferous (Chen et al., 2010), indicating the termination of collision. In fact, the plutons in West Junggar, East Junggar, southern Chinese Altai, and the Chinese Western Tianshan that formed in the latest Late Carboniferous to Middle Permian, were all generated in a post-collisional setting (Chen et al., 2010). Therefore, with the closure of the Irtysh-Zaysan Ocean and the collision between the Siberian and Kazakhstan-Junggar continents or because of the amalgamation between the Altai and Zharmasaur terranes, the Ha'erjiao region entered a post-collisional extensional stage in the Early Permian.

6 Conclusions

Based on the results and the reported data of our study,

we estimate the provenance and tectonic setting of the Lower Permian Kalagang Formation rocks in the Jimunai Basin and provide new evidence for the tectonic evolution of the northern West Junggar region.

The pyroclastic rocks studied have high contents of loss on ignition (LOI), which might be caused by high contents of organic matter. The petrological characteristics, abundant presence of plagioclase and absence of clay minerals, together with geochemical parameters such as a low value of the chemical index of alteration (CIA) and the ratio of Rb/Sr, indicate a relatively weak chemical weathering intensity. The Th/Sc and Zr/Sc ratios of the pyroclastic rocks have a strong positive correlation ($R^2 = 0.88$), indicating that geochemical variation was dominated by the composition of the source materials and not by sediment recycling.

The pyroclastic rocks also show that there are two types of source rocks: (1) intermediate-basic volcanic rock with high Ti/Nb ratios, low Th/Sc and light (LREE)/heavy (HREE) rare earth element ratios, and weak Eu anomalies (Eu/Eu*: 0.75–1.33); and (2) felsic volcanic rocks based on one sample (H-2), which is completely different from others but similar to the underlying coals, with the highest LREE/HREE ratio and lowest Eu/Eu* value, and falls into the rhyodacite/dacite area on the Zr/TiO₂-Nb/Y diagram.

The samples analyzed in this study are enriched in LILEs and LREEs, have negative anomalies in some HFSEs (e.g., Nb and Ta) and no significant Eu and Ce anomalies, indicating an intraplate affinity, which is similar to those of the post-collisional volcanic rocks reported from the West and East Junggar terranes. Because of crustal contamination, all the pyroclastic rocks fall in or near the within-plate volcanic zones (WPVZ) or within-plate basaltic (WPB) in the discriminant diagrams used, which do not use Nb, Ta and Ti as discriminating factors. This geochemical pattern is similar to that of the latest Upper Carboniferous–Middle Permian basalts in the adjacent region, which were generated in a post-collisional setting.

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