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Clinopyroxene and Fe-Ti oxides for correlating the ash from Changbaishan Millennium eruption

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Abstract Volcanic glass compositions and tephra layer age are critical for anchoring their sources and correlating among different sites; however, such work may be imprecise when the tephra has varied compositions. The ash from Changbaishan Millennium eruption (940s AD), a widely distributed tephra layer, has been detected in the far-east areas of Russia, the Korean Peninsula, Japan, and in Greenland ice cores. There are some debates on the presence of this tephra from sedimentary archives to the west of Changbaishan volcano, such as lake and peat sediments in the Longgang volcanic field. In this paper, major element compositions for clinopyroxene and Fe-Ti oxides were performed on proximal tephra from Changbaishan and the Millennium eruption ash record in Lake Sihailongwan. Clinopyroxene and Fe-Ti oxides microlites from Sihailongwan show augite-ferroaugite and titanmagnetite compositions, similar to those from dark pumice in Changbaishan proximal tephra, but different from the light grey pumice, which has ferrohedenbergite and ilmenite microlite compositions. This result implies that the tephra recorded in Sihailongwan was mainly from the trachytic eruptive phase of the Millennium eruption, and the rhyolitic eruptive phase made a relatively small contribution to this area. Analyzing clinopyroxene and Fe-Ti oxides microlites is a new method for correlating tephra layers from Changbaishan Millennium eruption.

Keywords Tephra, Millennium eruption, Changbaishan volcano, Sihailongwan, Clinopyroxene, Fe-Ti oxides

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1. Introduction

Ash from large-scale volcanic eruptions can be deposited across wide areas in a short time. These tephra layers can serve as marker beds for reconstructing volcanic activities and Quaternary climatic changes. Normally, large tephra particles deposit in proximal areas while volcanic glass shards are the predominant in distal regions, and can account for 95% of total ash deposits. Therefore, over the last several decades, major and minor element compositions of glass shards have been widely used to correlate tephra layers among various sites (Shane and Froggatt, 1992; Lee et al., 2004; Lowe, 2011; Tomlinson et al., 2012; Lane et al., 2013; Pearce et al., 2014; Sun et al., 2014a, 2015). Proximal tephra deposits can be destroyed by subsequent eruptions, and records of volcanic activities may be incomplete, but areas farther from the source may yield more detailed records. In addition, correlation of tephra layers among various sites in different directions will reveal the mode of tephra

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dispersal and eruptive processes. Normally, tephra layers from the same volcano or similar geological background share similar glass compositions, and tephra with different glass compositions may be from a single eruption (Smith et al., 2005; Peate et al., 2008; Shane et al., 2008), which makes it difficult to identify their source volcanoes. In some cases, detailed glass compositions with mineral compositions will enable more precise identifications and correlations of tephra layers.

Minerals in tephra usually are more dense than glass shards, and these heavier minerals will be deposited close to volcanic vent. Light minerals and microlites can be transported to more distal sites and these compositions provide a more evidence to correlate tephra layers. For example, the Younger Toba Tuff (YYT) can be traced across the Indian Ocean and Indian subcontinent. Tiny biotite crystals occur in these tephra, and biotite compositions are very effective for discriminating YYT, Middle Toba Tuff (MYT) and Older Toba Tuff (OYT) (Smith et al., 2011). Biotite compositions also have been used successfully in New Zealand and Europe (Shane et al., 2003a, 2003b; Harangi et al., 2005). The Fe-Ti oxides, titanmagnetite and ilmenite, are also widely used to correlate tephra layers based on their chemical compositions and calculated magma temperatures and oxygen fugacities (Cronin et al., 1996a, 1996b; Shane, 1998, 2000; Jensen et al., 2008, 2011; Turner et al., 2011; Preece et al., 2011, 2014; Marcaida et al., 2014). In relatively old strata, glass compositions can not be used to correlate various layers owing to devitrification of volcanic glass shards, but more stable minerals, such as the cummingtonite composition and zircon ages (Matsu'ura et al., 2011, 2012; Coffey et al., 2014). In regions nearer the volcanic vent there are many kinds of minerals in the tephra, such as olivine, pyroxene and apatite, and their compositions also can be used to correlate tephra layers (Cronin et al., 1996a, 1996b; Brauer et al., 2007; Westgate et al., 2008; Sell and Samson 2011). However, these relative heavy and large minerals are very difficult to be transferred to more distal areas.

The Changbaishan Millennium eruption is one of the largest eruptions on Earth in the last 2000 years (Horn and Schmincke, 2000; Wei et al., 2003; Zou et al., 2010). Tephra from this eruption is widely distributed in the Korean peninsula, and Japan, and in Greenland ice cores (Figure 1) (Machida and Arai, 1983; Sun et al., 2014a). In the Longgang volcanic field, upwind of Changbaishan volcano, no visible Millennium eruption ash has been reported and only a cryptotephra layer has been detected, but glass compositions are very different in these reports (Guo et al., 2005; Sun et al., 2015). Recently, four rhyolitic glass shards were reported from the Gushantun peat that are suggested to be from the Millennium eruption or some younger eruptions (Zhao and Hall, 2015; Zhao et al., 2015). Major element compositions of glass shards are widely used to correlate this tephra layer, but glass major element compositions differ among tephras reported from northeastern China, Japan, and Greenland ice cores, making it difficult to correlate this layer precisely in these regions (Sun et al., 2014b). In this wrok, clinopyroxene and Fe-Ti oxides microlite compositions were determined for distal tephra from Lake Sihailongwan and for proximal Changbaishan tephra. This method can be more reliable for correlating this tephra.

2. Geological background

The Changbaishan stratovolcano is located on the northeastern margin of the North China Craton, on the border between China and North Korea. It became active in the early Pleistocene, and the most recent eruption was a phreatomagmatic event in 1903 AD (Cui et al., 1995; Fan et al., 2006). It is best known for the Millennium eruption, which produced thick fallout pumice and pyroclastic flows deposits (Horn and Schmincke, 2000; Stone, 2010, 2011, 2013; Liu et al., 2015). Ash from the Millennium eruption has served as a marker layer for reconstructions of the volcanic eruptions, vegetation evolution, event stratigraphy and climatic changes (Nakagawa et al., 2002; Ikehara, 2003; Machida and Arai, 2003; Nanayama et al., 2003; Hughes et al., 2013; Sun et al., 2015). The precise age of this eruption and its climatic impacts are matters of intensive debate. Radiometric ^{14}C dating on charcoals buried in the proximal tephra is the most common method to constrain the tephra age (Liu, 1999), but the age results are different, which makes it more difficult to discuss climatic impacts (Sun et al., 2014b). Discrete glass shards with similar compositions to the ash from Millennium eruption have been detected in Greenland ice cores and the age of this eruption corresponding to the tephra layer was assigned to 940–941 AD (GICC05, 946–947 AD revised age model) or 945 ± 4 AD (GISP2), in addition, there were no substantial climatic impacts resulted from this eruption (Sun et al., 2014a; Sigl et al., 2015).

There are eight maar lakes and various peat bogs in the Longgang volcanic field, 120 km from the Changbaishan volcano (Figure 1). Lake Sihailongwan is one of these maar lakes. A 10–119 m tuff ring around this lake makes it a relatively closed environment; rainfall is the main recharge mode without stream inlets or outlets. Human activities are rare in this region and varves are well developed in this lake (Chu et al., 2014; Stebich et al., 2015).

3. Samples and methods

A drilling core from the deepest part of Sihailongwan was taken in 2008. Samples from 52 cm were first treated with 10% HCl for 12 hours to remove soluble carbonates first and then H_2O_2 was added to the samples to disaggregate

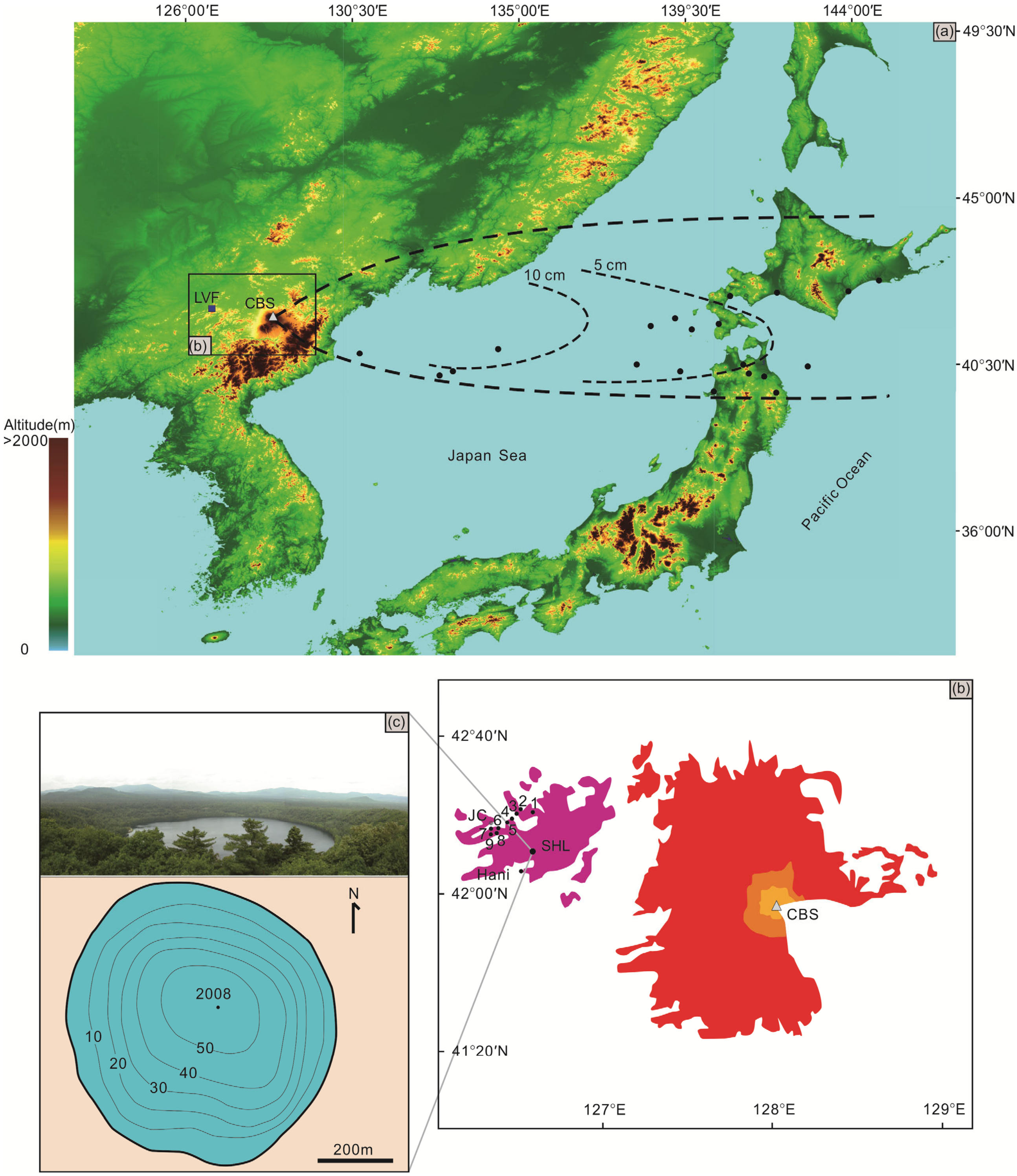

Figure 1 Tephra dispersal of the ash from Changbaishan Millennium eruption and some tephra-detected sites (a), volcanic map of Changbaishan volcano and Longgang volcanic field (b), and photo of Lake Sihailongwan and the coring site (c). (a) is from Machida and Arai (1983) and (c) from Sun et al.(2015). SHL, Lake Sihailongwan; CBS, Changbaishan volcano; Hani, Hani peat. 1, Longquanlongwan; 2, Donglongwan; 3, Nanlongwan; 4, Sanjiaolongwan; 5, Hanlongwan; 6, Dalongwan; 7, Gushantun Peat; 8, Erlongwan; 9, Xiaolongwan.

organic materials. The treated samples were sieved through 30 μm mesh and then mounted on slides. Proximal tephra were sampled from the north slope of Changbaishan volcano, Tianwenfeng peak, where there is a complete modern volcanic sequence. There is a grey pumice layer on thick yellow pumice with age around 4.2 ka (Yang et al., 2014). A dark fallout pumice layer (black and dark grey) is on this light grey layer. Additionally, dark pumice clasts can be found in pyroclastic flows from Jinjiang valley. Both the light and dark layers are attributed to the Millennium eruption (Wei 2013).

Major element analyses were carried out using a JEOL JXA 8100 electron microprobe at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. Nine major elements (Na, Mg, Al, Si, K, Ca, Fe, Ti, Mn) were analyzed with an accelerating voltage of 15 kV, a beam current of 6 nA, and a beam diameter of 5–10 μm according to the size of the glass shards. A 1-μm beam diameter was used to analyze the microlites.

4. Results and discussion

From the dispersal of tephra, west winds prevailed during the Millennium eruption, and tephra was mainly transported to the east of Changbaishan volcano and deposited in northern part of Korean peninsula and Japan (Machida et al., 1990; Horn and Schmincke, 2000). Reports of this tephra west of Changbaishan volcano are rare, especially of fallout pumice, but some pyroclastic flows are found in the Jinjiang valley. Therefore, whether this tephra can be correlated from Japan to areas west of Changbaishan volcano is continually debated. Lake and peat sediments from the Longgang volcanic field are the ideal context to resolve this problem, and also give insights into the mode of tephra dispersal. In addition, this tephra can be linked across continental, marine, and Arctic paleoclimate records.

Glass compositions in a sandy like tephra layer detected in the Xidadianzi and Hani peat sediments illustrate a native eruption, but no felsic tephra layers from Changbaishan volcano were found and assuming that tephra from Changbaishan volcano could not be transported to these upwind sediments (Mao et al., 2002, 2009; Cheng et al., 2008). However, four rhyolitic glass shards were isolated from the Gushantun peat bog with a age of 260 – 420 a cal BP and they were correlated with the Changbaishan Millennium eruption or the younger eruptions based on glass compositions (Zhao and Liu, 2012; Zhao and Hall, 2015; Zhao et al., 2015). A similar cryptotephra layer also can be traced in the Lake Sihailongwan, but those studies show different results. One study found only rhyolitic glass shards in the lake sediments (Guo et al., 2005), while another showed many trachytic glass shards with minor rhyolitic shards similar to compositions of proximal tephra from Changbaishan volcano and distal tephra from Japan and Greenland ice cores (Sun et al., 2015). Therefore, there is no consensus on whether the ash from Changbaishan Millennium eruptions was deposited in the Longgang volcanic field.

Major element compositions of glass shards have been widely used to correlate the Millennium eruption ash in past studies. Glass compositions range from the rhyolitic to trachytic member, corresponding to the Millennium dark and light pumice eruptive phases (Horn and Schmincke, 2000; Nishimoto et al., 2010). In the Japan Sea and on the island of Japan, both rhyolitic and trachytic glass shards (or predominant rhyolitic shards) have been detected (Furuta et al., 1986; Nakagawa et al., 2002; Okuno et al., 2011; Hughes et al., 2013; Nakamura, 2015). Tephra from rhyolitic eruptive phase might be widely distributed in these regions. Ash recorded in the Greenland NGRIP and NEEM-2001-S1 ice cores also shows both rhyolitic and trachytic members (Coulter et al., 2012; Sun et al., 2014a). However, the reported Millennium eruptiosn ash from Longgang volcanic field showed different glass compositions; that is, the rhyolitic glass detected by Guo et al. (2005) and the trachytic glass shards with minor rhyolitc shards reported by Sun et al. (2015). The constrained age of the rhyolitic cryptotephra layer from the Gushantun peat bog shows a large deviation from the age of Millennium eruption (Zhao and Liu, 2012; Zhao and Hall, 2015; Zhao et al., 2015), and we cannot correlate it to any eruptions of Changbaishan volcano. Therefore, whether both rhyolitic and trachytic glass shards were deposited in Longgang volcanic field, or one predominant member was recorded, or there are different glass compositions in different directions is still unresolved.

In the cryptotephra layer from Sihailongwan Lake, there are typically some Fe-Ti oxide and clinopyroxene microlites on the edges or in the cores of glass shards that can be discriminated from the glass shards (Figure 2). The glass shards might affect the compositions of these microlites, especially the Fe-Ti oxides, owing to their relatively small sizes (Table 1, Figure 3), but, in general, these microlites are titanmagnetite. Clinopyroxene microlites are mainly augite and ferroaugite. The Changbaishan proximal dark and light pumices show different mineral assemblages and compositions; many microlites occur in the dark pumice but few in the light pumice (Figure 2). Major element compositions of microlites from proximal tephra illustrate that Fe-Ti oxides are mainly titanmagnetite in the dark pumice and ilmenite in the light pumice. Clinopyroxenes in the dark pumice are augite and ferroaugite, and ferrohedenbergite in the light pumice (Tables 2 and 3, Figure 4). Clinopyroxenes in dark pumice show wider ranges of composition than the microlites from Lake Sihailongwan.

Pyroxene, feldspar, and Fe-Ti oxides are rare in Millennium eruption ash, and it is difficult to understand magmatic processes using these minerals (Zou et al., 2010). However, clinopyroxene and Fe-Ti oxides microlites were detected in the proximal and distal Millennium eruption ash as described in this paper, and such stable mineral compositions can help correlate tephra layers precisely (Shane, 1998, 2000). This paper, for the first time, used such microlites to correlate the Millennium eruption ash. Our result illustrates that tephra recorded in Lake Sihailongwan was mainly from the Millennium trachytic eruptive phase, which resulted from the rare development of such microlites in light pum-

Table 1 Major element compositions (%) for Fe-Ti oxides and clinopyroxene microlites recorded in Sihailongwan

Point No.	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Total
Fe-Ti oxides										
1	2.19	20.63	1.98	67.38	1.03	1.17	0.30	0.18	0.22	95.08
2	2.45	19.74	1.97	67.00	0.95	1.14	0.42	0.33	0.19	94.18
3	1.78	18.85	1.77	68.45	0.99	0.88	0.11	0.26	0.25	93.32
4	1.67	24.92	2.36	64.56	0.64	3.50	0.94	0.02	0.03	98.64
5	2.10	18.82	1.67	70.91	0.90	0.89	0.15	0.25	0.23	95.91
6	2.88	19.32	1.92	70.42	0.96	0.97	0.07	0.20	0.22	96.96
7	1.40	20.04	4.29	66.17	0.51	4.52	0.10	0.12	0.19	97.34
8	1.50	20.61	1.74	67.28	0.91	1.12	0.36	0.10	0.11	93.72
9	1.37	20.18	4.45	67.11	0.50	4.76	0.18	0.10	0.10	98.73
10	1.71	19.31	4.70	66.68	0.49	4.62	0.31	0.25	0.13	98.20
11	1.71	20.66	2.79	66.56	0.76	3.41	0.30	0.24	0.17	96.60
Clinopyroxene										
1	47.90	3.27	4.83	10.31	0.21	11.98	20.81	0.67	0.02	100.00
2	50.42	1.54	3.03	11.63	0.37	11.68	19.76	0.50	0.13	99.05
3	50.26	1.31	2.91	13.83	0.39	10.05	19.61	0.56	0.22	99.14
4	51.69	0.71	1.45	16.18	0.56	9.63	20.09	0.46	0.13	100.89

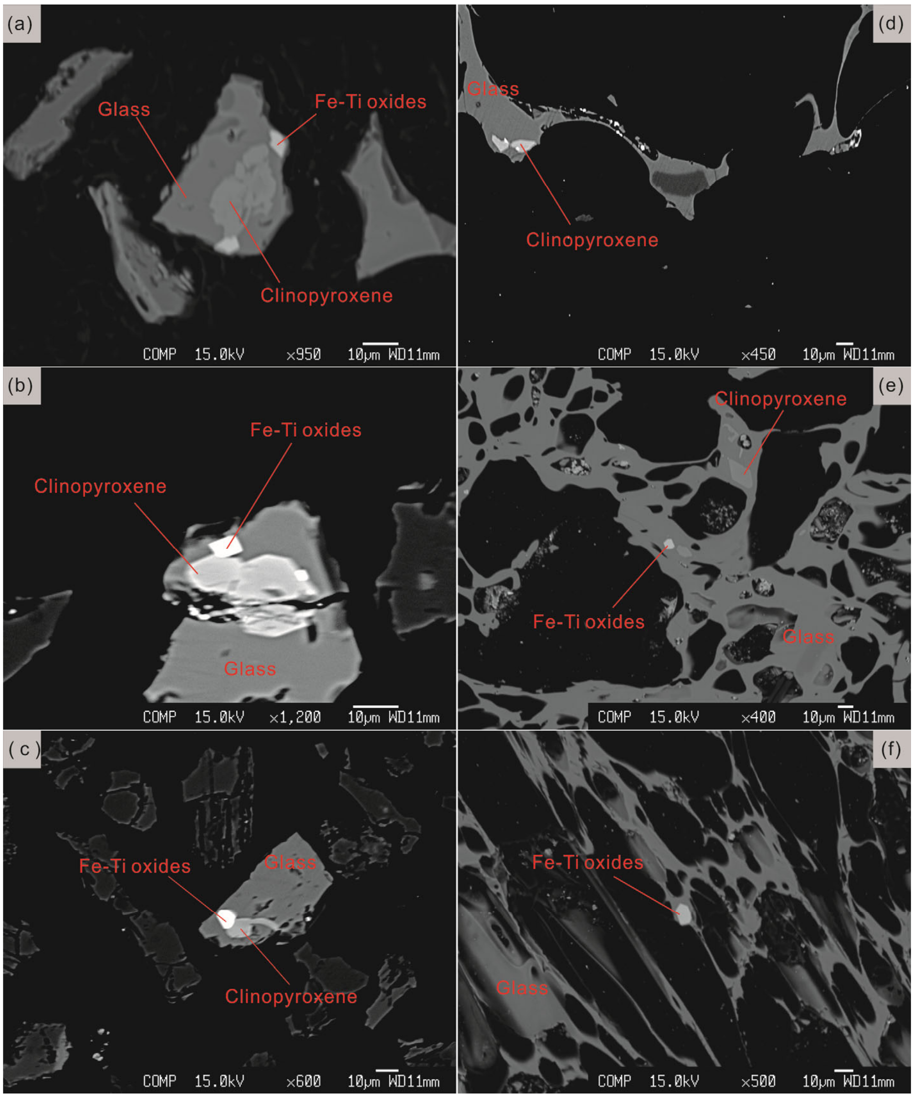

Figure 2 BSE images for the distal tephra from Lake Sihailongwan ((a)–(c)), proximal dark pumice from Changbaishan ((d), (e)), and proximal light pumice from Changbaishan (f). The scale bar is 10 μm.

Table 2 Major element compositions (%) for Fe-Ti oxides and clinopyroxene microlites from Changbaishan Millennium dark pumice

Point No.	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Total
Fe-Ti oxides										
1	1.90	20.71	2.24	65.15	0.72	2.39	0.13	0.34	0.25	93.82
2	0.23	26.00	1.28	68.55	1.19	0.71	0.04	0.09	0.03	98.10
3	0.08	25.63	1.10	69.10	1.01	0.67	0.11	0.08	0	97.77
4	1.19	21.64	2.28	63.79	0.60	1.95	0.32	0.23	0.09	92.08
5	0.18	25.67	1.16	68.00	1.08	0.64	0.02	0.03	0.02	96.40
6	1.53	18.70	3.14	67.28	0.55	2.32	0.12	0.21	0.15	93.99
7	0.31	24.96	1.10	68.57	1.10	0.63	0.08	0.10	0.05	96.90
8	0.18	25.29	0.94	69.59	1.13	0.42	0.03	0.03	0.02	97.61
9	1.39	18.17	2.41	71.39	0.66	1.32	0.02	0.16	0.17	95.68
10	0.13	26.20	1.29	68.43	1.04	0.73	0.07	0.04	0	97.92
11	0.16	26.65	1.29	68.08	0.99	0.79	0.04	0.05	0.01	98.05
12	0.39	26.05	1.23	68.49	1.03	0.82	0.10	0.02	0.02	98.14
13	1.84	24.43	2.38	62.99	0.66	2.98	0.20	0.25	0.19	95.90
14	1.60	23.16	2.27	64.93	0.72	2.10	0.12	0.18	0.17	95.22
15	2.32	22.15	2.47	64.51	0.69	2.39	0.11	0.30	0.24	95.19
16	2.13	23.13	2.27	63.41	0.72	2.14	0.08	0.29	0.23	94.41
17	0.45	24.61	1.56	68.03	0.88	1.69	0.02	0.02	0.04	97.3
18	1.83	20.66	1.95	68.12	0.92	1.04	0.06	0.18	0.24	94.98
19	2.14	22.20	1.70	67.62	0.93	0.76	0.13	0.37	0.22	96.07
20	0.20	25.92	1.30	69.13	1.04	0.72	0.07	0.02	0	98.40
Clinopyroxene										
1	49.63	0.53	0.71	22.11	0.82	6.00	20.34	0.46	0.02	100.62
2	49.56	0.56	0.76	20.32	0.81	6.80	20.42	0.40	0.02	99.64
3	52.45	0.54	0.82	18.37	0.49	8.34	20.17	0.54	0.09	101.81
4	51.51	0.50	0.95	18.71	0.62	8.27	19.66	0.49	0.08	100.79
5	47.99	2.93	5.73	12.47	0.34	10.67	18.52	0.99	0.28	99.92
6	48.60	2.87	5.22	11.22	0.25	11.42	20.22	0.64	0.17	100.60
7	46.26	3.87	6.01	12.54	0.24	9.91	19.84	0.74	0.25	99.64
8	46.36	3.49	6.28	12.30	0.26	9.90	20.22	0.74	0.14	99.68
9	47.49	3.31	5.14	11.28	0.21	11.17	19.66	0.60	0.19	99.04
10	49.95	2.13	3.98	10.73	0.29	12.58	19.30	0.58	0.16	99.69
11	51.51	1.24	2.13	10.08	0.29	14.30	19.29	0.37	0.12	99.32
12	48.15	2.89	5.02	11.70	0.27	11.23	20.36	0.70	0.18	100.50
13	49.44	2.41	4.92	10.87	0.28	11.65	19.97	0.69	0.30	100.52
14	50.45	1.72	3.73	11.68	0.30	12.13	20.01	0.58	0.17	100.78
15	48.68	2.42	4.86	11.77	0.25	11.35	20.04	0.57	0.21	100.14
16	48.63	2.29	5.19	11.06	0.23	11.33	20.78	0.65	0.10	100.26
17	47.65	3.03	5.23	11.73	0.24	10.85	19.70	0.67	0.11	99.22
18	45.67	3.55	6.57	11.90	0.25	10.71	20.31	0.62	0.09	99.65
19	49.12	2.52	4.88	12.13	0.27	10.46	20.04	0.69	0.28	100.40

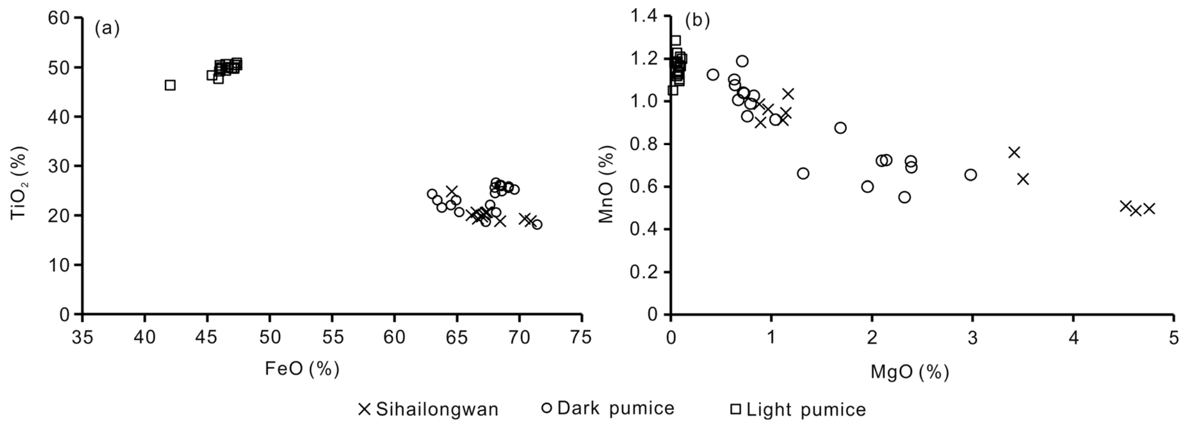

Figure 3 Fe-Ti oxides compositions for proximal tephra from Changbaishan volcano and distal tephra recorded in Lake Sihailongwan.

Table 3 Major element compositions (%) for Fe-Ti oxides and clinopyroxene microlites from Changbaishan Millennium light pumice

Point No.	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Total
Fe-Ti oxides										
1	1.50	47.64	0.22	45.89	1.23	0.06	0.02	0.19	0.16	96.91
2	1.05	48.38	0.15	45.40	1.13	0.08	0.05	0.12	0.1	96.46
3	0.39	46.32	0.00	42.04	1.05	0.02	3.35	0.05	0	93.91
4	0.44	49.59	0.09	46.04	1.19	0.07	0.07	0.03	0.04	97.56
5	0.13	49.37	0	46.48	1.21	0.09	0.05	0.01	0	97.34
6	0.17	50.36	0.05	46.00	1.29	0.05	0.06	0.02	0.03	98.03
7	0.21	49.16	0	45.95	1.20	0.11	0.03	0	0.01	96.66
8	0.34	49.90	0.05	46.97	1.18	0.04	0.04	0.07	0.03	98.62
9	0.65	50.07	0.13	46.67	1.10	0.09	0.11	0.08	0.07	98.96
10	0.32	50.51	0.04	47.38	1.17	0.10	0.03	0.11	0.04	99.68
11	0.24	49.91	0.05	47.17	1.14	0.08	0.05	0.01	0.02	98.67
12	0.67	49.91	0.11	46.16	1.12	0.06	0.07	0.10	0.08	98.28
13	0.62	50.51	0.09	47.23	1.18	0.06	0.04	0.04	0.04	99.82
14	0.13	50.67	0.00	46.46	1.09	0.08	0.12	0.06	0.01	98.63
15	0.28	49.79	0.02	47.15	1.19	0.05	0.02	0.03	0.03	98.56
16	0.16	50.92	0.03	47.35	1.14	0.07	0.07	0.01	0.02	99.76
17	0.17	50.68	0.03	46.70	1.17	0.09	0	0.02	0.02	98.87
Clinopyroxene										
1	48.72	0.33	0.29	33.37	1.59	1.28	11.95	1.25	0.15	98.98
2	49.73	0.29	0.75	29.66	1.35	1.33	14.66	1.52	0.22	99.51
3	49.30	0.70	0.17	28.25	0.86	1.47	17.93	1.57	0	100.25
4	48.93	0.20	0.12	28.28	0.90	1.57	17.72	1.46	0	99.19
5	49.39	0.25	0.15	28.80	0.79	1.08	16.98	1.99	0	99.45
6	49.60	0.19	0.15	28.68	0.71	0.94	17.29	2.26	0	99.77
7	49.65	0.30	0.17	29.10	0.9	1.08	18.75	1.13	0.02	101.10
8	48.81	0.24	0.18	28.56	0.84	1.38	17.81	1.62	0.01	99.44
9	48.63	0.27	0.14	29.03	0.82	1.18	17.85	1.64	0.00	99.55
10	48.81	0.24	0.13	28.90	0.84	1.34	18.17	1.76	0.04	100.23
11	49.50	0.26	0.18	28.83	0.79	1.21	18.24	1.64	0.02	100.67
12	49.13	0.27	0.12	29.01	0.74	0.10	17.17	2.31	0	99.73
13	49.12	0.23	0.14	29.27	0.90	1.3	17.55	1.82	0.00	100.33

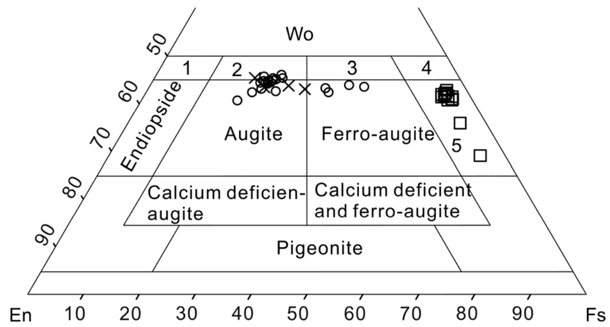

Figure 4 Pyroxene compositions for the proximal tephra from Changbaishan volcano and distal tephra recorded in Lake Sihailongwan. Data symbols are the same as those in Figure 3. 1, Diopside; 2, sahlite; 3, ferro-sahlite; 4, herdenbergite; 5, ferro-herdenbergite.

ice, or dark pumice might make a more important contribution to Longgang volcanic field than light pumice. Additionally, major element compositions for clinopyroxene and Fe-Ti oxides microlites provide another method to correlate and discriminate those modern eruptive sequences.

5. Conclusions

Both light and dark pumice occur in the Millennium eruptions ash, and different minerals are found in these pumices. Augite-ferroaugite and titanmagnetite microlites occur in the dark pumice, while ferrohedenbergite and ilmenite are found in the light pumice. There are also some microlites on the glass shards in the tephra recorded in Lake Sihailongwan, which exhibit similar compositions to the dark pumice with trachytic glass compositions and are different from those in the light pumice. Mineral and glass compositions show that the tephra recovered from west of the Changbaishan volcano has different compositions from those east of volcano, and that the Millennium trachytic eruptive phase had more significant impacts than the rhyolitic phase. Therefore, in future studies in this area, both trachytic and rhyolitic (or the predominant trachytic) glass shards should be detected when trying to correlate tephra layers to the Millennium eruption. Additionally, clinopyroxene and Fe-Ti oxides microlites offer a new method to correlate this tephra.

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References

Brauer A, Wulf S, Mangili C, Moscariello A. 2007. Tephrochronological dating of varved interglacial lake deposits from Piànico-Sèllere (Southern Alps, Italy) to around 400 ka. J Quat Sci, 22: 85–96

Cheng S, Mao X, Wang F, Hong Y, Zhu Y, An Q. 2008. Tephra discovered in high resolution peat sediment and its indication to climatic event. J China Univ Geosci, 19: 174–183

Chu G, Sun Q, Xie M, Lin Y, Shang W, Zhu Q, Shan Y, Xu D, Rioual P, Wang L, Liu J. 2014. Holocene cyclic climatic variations and the role of the Pacific Ocean as recorded in varved sediments from northeastern China. Quat Sci Rev, 102: 85–95

Coffey K T, Schmitt A K, Ford A, Spera F J, Christensen C, Garrison J. 2014. Volcanic ash provenance from zircon dust with an application to Maya pottery. Geology, 42: 595–598

Coulter S E, Pilcher J R, Plunkett G, Baillie M, Hall V A, Steffensen J P, Vinther B M, Clausen H B, Johnsen S J. 2012. Holocene tephras highlight complexity of volcanic signals in Greenland ice cores. J Geophys Res, 117: D21303

Cronin S J, Neall V E, Stewart R B, Palmer A S. 1996a. A multiple-parameter approach to andesitic tephra correlation, Ruapehu volcano, New Zealand. J Volcanol Geotherm Res, 72: 199–215

Cronin S J, Wallace R C, Neall V E. 1996b. Sourcing and identifying andesitic tephras using major oxide titanomagnetite and hornblende chemistry, Egmont volcano and Tongariro Volcanic Centre, New Zealand. Bull Volcanol, 58: 33–40

Cui Z X, Wei H Q, Liu R X. 1995. Historical documentation research of eruptions of the Tianchi Volcano, Changbaishan (in Chinese with English abstract). In: Liu R X, ed. Volcanism and Human Environment. Beijing: Seismological Press. 36–39

Fan Q, Sui J, Wang T, Li N, Sun Q. 2006. Eruption history and magma evolution of the trachybasalt in the Tianchi volcano, Changbaishan (in Chinese with English abstract). Acta Petrol Sin, 22: 1449–1457

Furuta T, Fujioka K, Arai F. 1986. Widespread submarine tephras around Japan—Petrographic and chemical properties. Mar Geol, 72: 125–142

Guo Z, Liu J, Fan Q, He H, Sui S, Chu G, Liu Q, Negendank J F W. 2005. Source of volcanic ash in the sediments of Sihailongwan Maar, NE China, and its significance(in Chinese with English abstract). Acta Petrol Sin, 21: 251–255

Harangi S, Mason P R D, Lukács R. 2005. Correlation and petrogenesis of silicic pyroclastic rocks in the Northern Pannonian Basin, Eastern-Central Europe: *In situ* trace element data of glass shards and mineral chemical constraints. J Volcanol Geotherm Res, 143: 237–257

Horn S, Schmincke H-U. 2000. Volatile emission during the eruption of Baitoushan Volcano (China/North Korea) ca. 969 AD. Bull Volcanol, 61: 537–555

Hughes P D M, Mallon G, Brown A, Essex H J, Stanford J D, Hotes S. 2013. The impact of high tephra loading on late-Holocene carbon accumulation and vegetation succession in peatland communities. Quat Sci Rev, 67: 160–175

Ikehara K. 2003. Late Quaternary Seasonal Sea-Ice History of the Northeastern Japan Sea. J Oceanogr, 59: 585–593

Jensen B J L, Froese D G , Preece S J, Westgate J A, Stachel T. 2008. An extensive middle to late Pleistocene tephrochronologic record from east-central Alaska. Quat Sci Rev, 27: 411–427

Jensen B J L, Preece S J, Lamothe M, Pearce N J G, Froese D G, Westgate J A, Schaefer J, Begét J. 2011. The variegated (VT) tephra: A new regional marker for middle to late marine isotope stage 5 across Yukon and Alaska. Quat Int, 246: 312–323

Lane C S, Chorn B T, Johnson T C. 2013. Ash from the Toba supereruption in Lake Malawi shows no volcanic winter in East Africa at 75 ka. Proc Natl Acad Sci USA, 110: 8025–8029

Lee M Y, Chen C H, Wei K Y, Iizuka Y, Carey S. 2004. First Toba supereruption revival. Geology, 32: 61–64

Liu J Q, Chen S S, Guo Z F, Guo W, He H Y, You H T, Kim M H, Sung G H, Kim H. 2015. Geological background and geodynamic mechanism of Mt. Changbai volcanoes on the China-Korea border. Lithos, 236-237: 46–73

Liu J Q, 1999. Volcanoes in China. Beijing: Science Press

Lowe D J. 2011. Tephrochronology and its application: A review. Quat Geochronol, 6: 107–153

Machida H, Arai F. 1983. Extensive ash falls in and around the sea of Japan from large late quaternary eruptions. J Volcanol Geotherm Res, 18: 151–164

Machida H, Arai F. 2003. Atlas of Tephra In and Aroud Japan. Tokyo: University of Tokyo Press

Machida H, Moriwaki H, Zhao D C. 1990. The recent major eruption of changbai volcano and its environmental effects. Geogr Rep Tokyo Metrop Univ, 25: 1–20

Mao X, Hong Y, Zhu Y, Wang H. 2002. Discovery of volcanic explosion-derived materials in Jinchuan peat and its significance (in Chinese with English abstract). Acta Mineral Sin, 22: 9–14

Mao X, Cheng S, Hong Y, Zhu Y, Wang F. 2009. The influence of volcanism on paleoclimate in the northeast of China: Insights from Jinchuan peat, Jilin Province, China. Chin J Geochem, 28: 212–219

Marcaida M, Mangan M T, Vazquez J A, Bursik M, Lidzbarski M I. 2014. Geochemical fingerprinting of Wilson Creek formation tephra layers (Mono Basin, California) using titanomagnetite compositions. J Volcanol Geotherm Res, 273: 1–14

Matsu'ura T, Miyagi I, Furusawa A. 2011. Late Quaternary cryptotephra detection and correlation in loess in northeastern Japan using cummingtonite geochemistry. Quat Res, 75: 624–635

Matsu'ura T, Furusawa A, Yanagida M. 2012. Detection and correlation of widespread cryptotephras in middle Pleistocene loess in NE Japan using cummingtonite geochemistry. J Asian Earth Sci, 60: 49–67

Nakagawa M, Ishizuka Y, Kudo T, Yoshimoto M, Hirose W, Ishizaki Y, Gouchi N, Katsui Y, Solovyow A W, Steinberg G S, Abdurakhmanov A I. 2002. Tyatya Volcano, southwestern Kuril arc: Recent eruptive activity inferred from widespread tephra. Isl Arc, 11: 236–254

Nakamura Y. 2015. Stratigraphy, distribution, and petrographic properties of Holocene tephras in Hokkaido, northern Japan. Quat Int, 397: 52–62

Nanayama F, Satake K, Furukawa R, Shinokawa K, Atwater B F, Shigeno K, Yamaki S. 2003. Unusually large earthquakes inferred from tsunami deposits along the Kuril trench. Nature, 424: 660–663

Nishimoto J, Nakagawa M, Miyamoto T, Taniguchi H. 2010. Magma system of 10th century eruption of Baitoushan volcano: Inferred from petrogical and geochemical characteristics (in Japanese with English abstract). In: Taniguchi H, ed. Earth Science of Baitoushan Volcano and Its Adjacent Area, Northeast China, Center for Northeast Asian Studies. Sendai: Tohoku University Monograph Series. 71–94

Okuno M, Torii M, Yamada K, Shinozuka Y, Danhara T, Gotanda K, Yonenobu H, Yasuda Y. 2011. Widespread tephras in sediments from lake Ichi-no-Megata in northern Japan: Their description, correlation and significance. Quat Int, 246: 270–277

Pearce N J G Westgate J A, Gatti E, Pattan J N, Parthiban G, Achyuthan H. 2014. Individual glass shard trace element analyses confirm that all known Toba tephra reported from India is from the c. 75-ka Youngest Toba eruption. J Quat Sci, 29: 729–734

Peate I U, Kent A J R, Baker J A, Menzies M A. 2008. Extreme geochemical heterogeneity in Afro-Arabian Oligocene tephras: Preserving fractional crystallization and mafic recharge processes in silicic magma chambers. Lithos, 102: 260–278

Preece S J, McGimsey R G, Westgate J A, Pearce N J G, Perkins W T. 2014. Chemical complexity and source of the White River Ash, Alaska and Yukon. Geosphere, 10: 1020–1042

Preece S J, Pearce N J G, Westgate J A, Froese D G, Jensen B J L, Perkins W T. 2011. Old Crow tephra across eastern Beringia: A single cataclysmic eruption at the close of Marine Isotope Stage 6. Quat Sci Rev, 30: 2069–2090

Sell B K, Samson S D. 2011. A tephrochronologic method based on apatite trace-element chemistry. Quat Res 76: 157–166

Shane P A R. 1998. Correlation of rhyolitic pyroclastic eruptive units from the Taupo volcanic zone by Fe-Ti oxide compositional data. Bull Volcanol, 60: 224–238

Shane P A R. 2000. Tephrochronology: A New Zealand case study. Earth-Sci Rev, 49: 223–259

Shane P A R, Nairn I A, Martin S B, Smith V C. 2008. Compositional heterogeneity in tephra deposits resulting from the eruption of multiple magma bodies: Implications for tephrochronology. Quat Int, 178: 44–53

Shane P A R, Smith V C, Nairn I. 2003a. Biotite composition as a tool for the identification of Quaternary tephra beds. Quat Res, 59: 262–270

Shane P A R, Smith V C, Lowe D J, Nairn I. 2003b. Re-identification of c.15 700 cal yr BP tephra bed at Kaipo Bog, eastern North Island: Implications for dispersal of Rotorua and Puketarata tephra beds. New Zealand J Geol Geophys, 46: 591–596

Shane P A R, Froggatt P C. 1992. Composition of widespread volcanic glass in deep-sea sediments of the Southern Pacific-Ocean—An Antarctic source inferred. Bull Volcanol, 54: 595–601

Sigl M, Winstrup M, McConnell J R, Welten K C, Plunkett G, Ludlow F, Büntgen U, Caffee M, Chellman N, Dahl-Jensen D, Fischer H, Kipfstuhl S, Kostick C, Maselli O J, Mekhaldi F, Mulvaney R, Muscheler R, Pasteris D R, Pilcher J R, Salzer M, Schüpbach S, Steffensen J P,Vinther B M, Woodruff T E. 2015. Timing and climate forcing of volcanic eruptions for the past 2500 years. Nature, 523: 543–549

Smith V C, Pearce N J G, Matthews N E, Westgate J A, Petraglia M D, Haslam M, Lane C S, Korisettar R, Pal J N. 2011. Geochemical fingerprinting of the widespread Toba tephra using biotite compositions. Quat Int, 246: 97–104

Smith V C, Shane P A R, Nairn I A. 2005. Trends in rhyolite geochemistry, mineralogy, and magma storage during the last 50 kyr at Okataina and Taupo volcanic centres, Taupo Volcanic Zone, New Zealand. J Volcanol Geotherm Res, 148: 372–406

Stebich M, Rehfeld K, Schlutz F, Tarasov P E, Liu J, Mingram J. 2015. Holocene vegetation and climate dynamics of NE China based on the pollen record from Sihailongwan Maar Lake. Quat Sci Rev, 124: 275–289

Stone R. 2010. Is China's riskiest volcano stirring or merely biding its time ? Science, 329: 498–499

Stone R. 2011. Vigil at North Korea's Mount doom. Science, 334: 584–588

Stone R. 2013. Sizing up a slumbering giant. Science, 341: 1060–1061

Sun C, Plunkett G, Liu J, Zhao H, Sigl M, McConnell J R, Pilcher J R, Vinther B, Steffensen J P, Hall V. 2014a. Ash from Changbaishan Millennium eruption recorded in Greenland ice: Implications for determining the eruption's timing and impact. Geophys Res Lett, 41: 694–701

Sun C, You H, Liu J, Li X, Gao J, Chen S. 2014b. Distribution, geochemistry and age of the Millennium eruptives of Changbaishan volcano, Northeast China — A review. Front Earth Sci, 8: 216–230

Sun C, You H, He H, Zhang L, Gao J, Guo W, Chen S, Mao Q, Liu Q, Chu G, Liu J. 2015. New evidence for the presence of Changbaishan Millennium eruption ash in the Longgang volcanic field, Northeast China. Gondwana Res, 28: 52–60

Tomlinson E L, Kinvig H S, Smith V C, Blundy J D, Gottsmann J, Muller W, Menzies M A. 2012. The Upper and Lower Nisyros Pumices: Revisions to the Mediterranean tephrostratigraphic record based on micron-beam glass geochemistry. J Volcanol Geotherm Res, 243-244: 69–80

Turner M B, Cronin S J, Bebbington M S, Smith I E M, Stewart R B. 2011. Integrating records of explosive and effusive activity from proximal and distal sequences: Mt. Taranaki, New Zealand. Quat Int, 246: 364–373

Wei H, Sparks R S J, Liu R, Fan Q, Wang Y, Hong H, Zhang H, Chen H, Jiang C, Dong C, Zheng Y, Pan Y. 2003. Three active volcanoes in China and their hazards. J Asian Earth Sci, 21: 515–526

Wei H, 2013. Changbaishan Tianchi Volcano. Beijing: Seismological Press

Westgate J A, Preece S J, Froese D G, Pearce N J G, Roberts R G, Demuro M, Hart W K, Perkins W. 2008. Changing ideas on the identity and stratigraphic significance of the Sheep Creek tephra beds in Alaska and the Yukon Territory, northwestern North America. Quat Int, 178: 183–209

Yang L, Wang F, Feng H, Wu L, Shi W. 2014. $^{40}Ar/^{39}Ar$ geochronology of Holocene volcanic activity at Changbaishan Tianchi volcano, Northeast China. Quat Geochronol, 21: 106–114

Zhao H, Hall V A. 2015. Assessing the potential for cryptotephra studies in Northeastern China. Holocene, 25: 772–783

Zhao H, Liu J. 2012. Cryptotephra discovered in Gushantun peat of NE China and its significance (in Chinese with English abstract). Seismol Geol, 34: 516–530

Zhao H, Li X, Hall V. 2015. Holocene vegetation change in relation to fire and volcanic events in Jilin, Northeastern China. Sci China Earth Sci, 58: 1404–1419

Zou H, Fan Q, Zhang H. 2010. Rapid development of the great Millennium eruption of Changbaishan (Tianchi) Volcano, China-North Korea: Evidence from U-Th zircon dating. Lithos, 119: 289–296