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Key Points:

- A tephra layer from Qixiangzhan eruption was identified in Yuanchi Lake ~30 km east of the Changbaishan volcano
- Qixiangzhan explosive eruption was dated to ~8100 cal yr BP
- Ash from Qixiangzhan eruption can serve as a marker layer around East Asia

Supporting Information:

- Supporting Information S1

Correspondence to:
C. Sun,
suncq@mail.iggcas.ac.cn

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Ash From the Changbaishan Qixiangzhan Eruption: A New Early Holocene Marker Horizon Across East Asia

Chunqing Sun[1,2], **Luo Wang**[1,2], **Gill Plunkett**[3], **Haitao You**[4], **Zeyang Zhu**[1,2,5], **Lei Zhang**[1,2], **Bin Zhang**[1,2,5], **Guoqiang Chu**[1,2], and **Jiaqi Liu**[1,2,4]

[1]Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China, [2]Institutions of Earth Science, Chinese Academy of Sciences, Beijing, China, [3]Archaeology and Palaeoecology, School of Natural and Built Environment, Queen's University Belfast, Belfast, UK, [4]Key Laboratory of Computational Geodynamics of Chinese Academy of Sciences, College of Earth Science, University of Chinese Academy of Sciences, Beijing, China, [5]College of Earth Science, University of Chinese Academy of Sciences, Beijing, China

Abstract Prehistoric Holocene eruptions of Changbaishan volcano in Northeast China are poorly dated, with the exception of the 946 CE Millennium eruption. Poorly refined age estimates for the earlier eruptions present problems for the reconstruction of the eruptive history of the volcano. The Qixiangzhan eruption (QE) is a major controversial event in terms of its eruptive timing (ranging from ~88 to ~4 kyr) and style (effusive or explosive). As a result of the imprecise age estimates for the eruption, a geomagnetic field excursion recorded within the QE comendite has been variably correlated with a number of different excursion events observed elsewhere. In this study, a visible early Holocene tephra was identified in Yuanchi Lake, ~30 km east of the Changbaishan volcanic vent, and was dated to 8831-8100 cal yr BP using Bayesian age modelling. Glass shard compositions enable the correlation of this tephra with the poorly dated QE, as well as with a tephra (SG14-1058) recorded in Lake Suigetsu, in central Japan. These correlations confirm that the QE was explosive and that the ash from the QE can serve as an important early Holocene marker bed across East Asia. In addition, we propose an age of ~8100 cal yr BP for the QE based on the precise date of the Suigetsu SG14-1058 tephra. Our results also confirm that the geomagnetic field excursion recorded in the Qixiangzhan comendite dates to ~8100 cal yr BP.

1. Introduction

Changbaishan volcano (also known as Paektu, or Baitoushan; 128°03′E, 42°00′N), an intraplate stratovolcano on the border between China and North Korea (Figure 1), is known for its Millennium eruption (ME) at 946 CE, which erupted ~100 km^3 of tephra into the atmosphere (Horn & Schmincke, 2000; Oppenheimer et al., 2017; Wei et al., 2003; Xu et al., 2013). Tephra from this eruption is an important marker bed from Northeast China to Japan, and in the Greenland ice sheet (e.g., Chen et al., 2016; Hughes et al., 2013; Machida & Arai, 1983; McLean et al., 2016; Sun, Plunkett, et al., 2014; Sun et al., 2015). Changbaishan volcano experienced several explosive eruptions during the Holocene, in addition to the ME (Sun et al., 2017; Wei et al., 2013; Zou et al., 2010). However, the other explosive eruptions of Changbaishan, such as the controversial Qixiangzhan eruption (QE), are less well studied. The latter eruption produced the Qixiangzhan comendite and derives its name from the weather station (*qixiangzhan* in Chinese) on the northern summit of Changbaishan volcano (Figure S1 in the supporting information).

Characterizing geomagnetic field excursions is crucial for understanding the operation of the geodynamo (Singer et al., 2014). The QE is of substantial interest because it recorded a geomagnetic field excursion within its welded pyroclastic deposits (e.g., Singer et al., 2014; Zhu et al., 2000). Previous age estimates for the QE ranged from ~88 to ~4 kyr (Table 1; Li et al., 1999; Liu & Wang, 1984; Pan, 2016; Singer et al., 2014; Wei et al., 2013; Yang et al., 2014; Yin et al., 1999). However, the precise timing of QE is still unresolved, which has resulted in miscorrelations of this geomagnetic field excursion with excursions recorded elsewhere. For example, Zhu et al. (2000) tried to correlate this excursion to the ~120-kyr Blake event using relatively imprecise K-Ar and $^{40}Ar/^{39}Ar$ dating results. Most recently, Singer et al. (2014) correlated it with the Hilina Pali excursion at around 17 kyr using new $^{40}Ar/^{39}Ar$ dating results directly obtained from the Qixiangzhan comendite and thus reported a new excursion event that they named "Hilina Pali/Tianchi."

There is an ~30-m pyroclastic fall deposit (corresponding to the subunits of lower gray fall NS-1 and upper yellow fall NS-2 described by Sun et al. (2017), hereafter referred to as the pre-ME event) on the northern

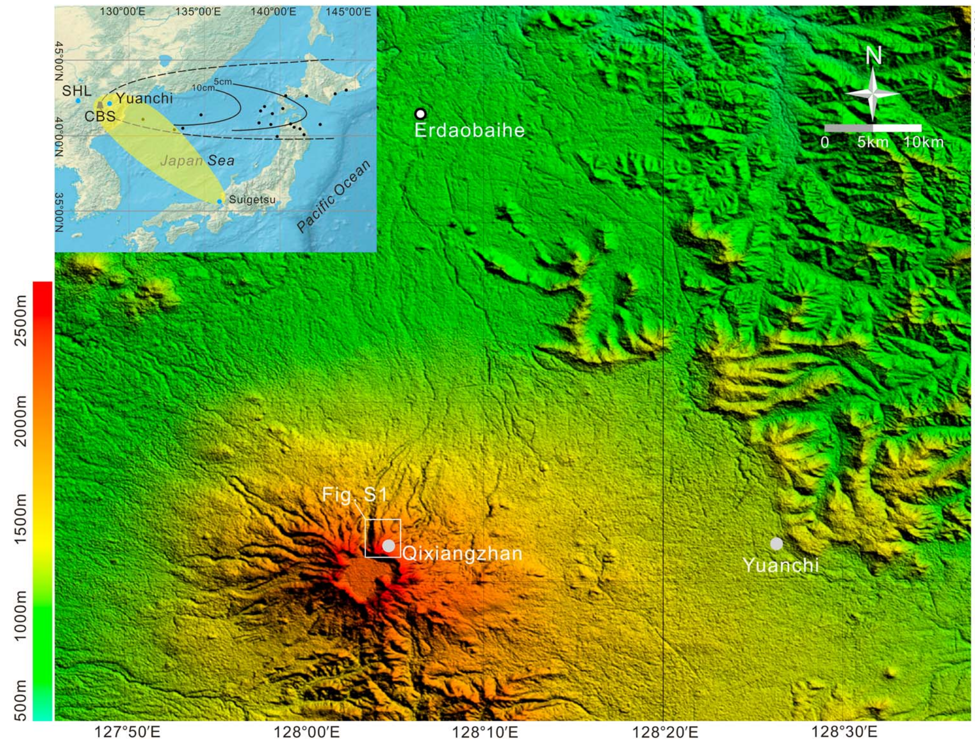

Figure 1. Location and regional topography of Changbaishan volcano (CBS) and Yuanchi Lake shown by a digital elevation model (spatial resolution is ~30 m; data are from www.gscloud.cn). The inset map (base map from http://naturalearthdata.com) shows the known tephra dispersal from the Changbaishan Millennium eruption (dashed line) and Qixiangzhan eruption (yellow shading), as well as the position of Lake Suigetsu and Sihailongwan maar lake (SHL). Black dots represent the locations of major sites from which the B-Tm tephra has been reported (Sun et al., 2017).

summit of Changbaishan volcano, and $^{40}Ar/^{39}Ar$ dating of the fall deposits assigned an age of ~4k yr to this eruption (Yang et al., 2014). However, there is still uncertainty regarding the relationship between the timing of QE and that of the explosive pre-ME eruption due to the unresolved dating of the QE (Table 1). Consequently, precise dating of the QE is crucial, not only for paleomagnetic studies but also for correlations of the Changbaishan proximal field exposures.

Tephra from explosive eruptions can be deposited over a large area, forming widely distributed marker beds, which are important chronological tools for paleoenvironmental, geological, and archeological studies (e.g., Cook et al., 2018; Lane et al., 2013, 2017; Lowe, 2011; van der Bilt et al., 2017). Whether the QE produced extensive pyroclastic deposits or merely effusive lava flows has been debated for several decades (Fan et al., 1999; Li et al., 1999; Liu et al., 1998, 2007; Pan et al., 2013). Tephra from the Holocene explosive eruptions of Changbaishan may have been transported and deposited several kilometers away from the volcanic vent (Sun et al., 2017). Therefore, characterizing the eruptive style of the QE is also important for tephrochronological research during the early Holocene.

Table 1
Published Dating Results of the Qixiangzhan Eruption

Dating results	Dating methods	Sources
~8100 cal yr BP	Tephrochronology	This study
7.6 ± 0.2 to 10.5 ± 0.5 kyr	$^{40}Ar/^{39}Ar$	Heizler et al. (2015)
17 kyr	$^{40}Ar/^{39}Ar$	Singer et al. (2014)
11, 16, 19 kyr	$^{40}Ar/^{39}Ar$	Yang et al. (2014)
11 ± 0.5 kyr	$^{40}Ar/^{39}Ar$	Pan (2016)
<19 kyr	K-Ar	Wei et al. (2013)
<88 kyr	K-Ar	Liu and Wang (1984)
12.2 kyr	^{238}U-^{230}Th	Zou et al. (2014)
3930 yr BP	Electron spin resonance	Yin et al. (1999)
<4 kyr	Stratigraphy sequence	Li et al. (1999)

A Changbaishan sourced tephra layer (SG14-1058) dated to around 8166–8099 cal yr BP (95% confidence) has been detected in Lake Suigetsu, central Japan (McLean et al., 2018). However, it is still not clear which eruption of Changbaishan volcano can be correlated with this tephra layer. The age of this tephra layer is near the abrupt cooling transition that occurred at around 8.2 kyr BP (i.e., the north hemispheric "8.2 event," the duration of which is about 300 yr; Alley et al., 1997). Regional and global correlations of this event in paleoenvironmental records is useful for understanding its causes, timing, and mechanisms. Therefore, characterizing this Changbaishan-sourced tephra layer is

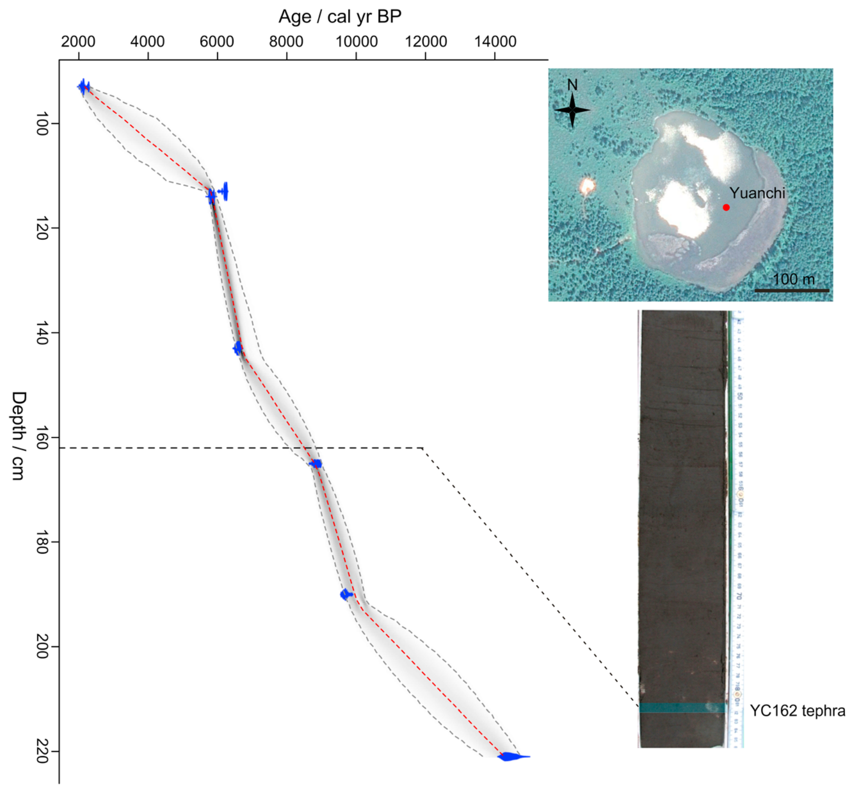

Figure 2. Bayesian age-depth model for the sediment core from Yuanchi Lake. Dashed line represents the position of the YC162 tephra attributed to the Qixiangzhan eruption of Changbaishan volcano. Inset images show Yuanchi Lake, (top) the position of the coring site, and (bottom) the YC162 tephra in the lake sediment.

important not only for its chronological marker significance for synchronizing the 8.2 event across regions but also for better understanding the eruptive sequence of the less studied Changbaishan volcano.

In this study, we use the tephrochronological method (from proximal Changbaishan exposures to distal lacustrine tephra records) to constrain the eruptive timing and style of the QE. We find that Changbaishan volcano experienced an explosive eruption at ~8100 cal yr BP, that is, the QE. In addition, the ash from Qixiangzhan eruption (QEA) is confirmed as forming another important time-equivalent marker bed across East Asia through its correlation with the tephra record in central Japan. Our results also confirm that tephrochronology is important for dating the explosive eruptions of this less well studied volcano.

2. Material and Methods

2.1. Proximal Qixiangzhan Comendite

At the Tianwenfeng Peak on the northern summit of Changbaishan volcano, there is a conspicuous "lava flow"-like landform: the Qixiangzhan comendite (Figure S1). The feature extends to about 5 km in length, about 400–800 m in width, and about 50–150 m in thickness (Pan et al., 2013; Yang et al., 2014). It consists of welded gray pyroclastic deposits, which were sampled in this study to characterize the major element geochemistry of its glass component (Figure S1; Pan et al., 2013).

2.2. Yuanchi Lake

Yuanchi Lake (42°01′55″N, 128°26′07″E 1270 m a.s.l.; Figure 1), ~30 km east of the Changbaishan volcanic vent, is a shallow lake, ~200 m in diameter with a maximum water depth of ~1 m (Figure 2). The lake is mainly supplied by rainwater and groundwater, and there are no inflowing or outflowing streams. Previous studies ascribed the formation of Yuanchi Lake to a phreatomagmatic eruption given its circular shape, and thus, it is designated a maar lake (Jin & Zhang, 1994). However, there are no phreatomagmatism-related tuff rings around the lake and its origin needs to be studied in more detail in the future.

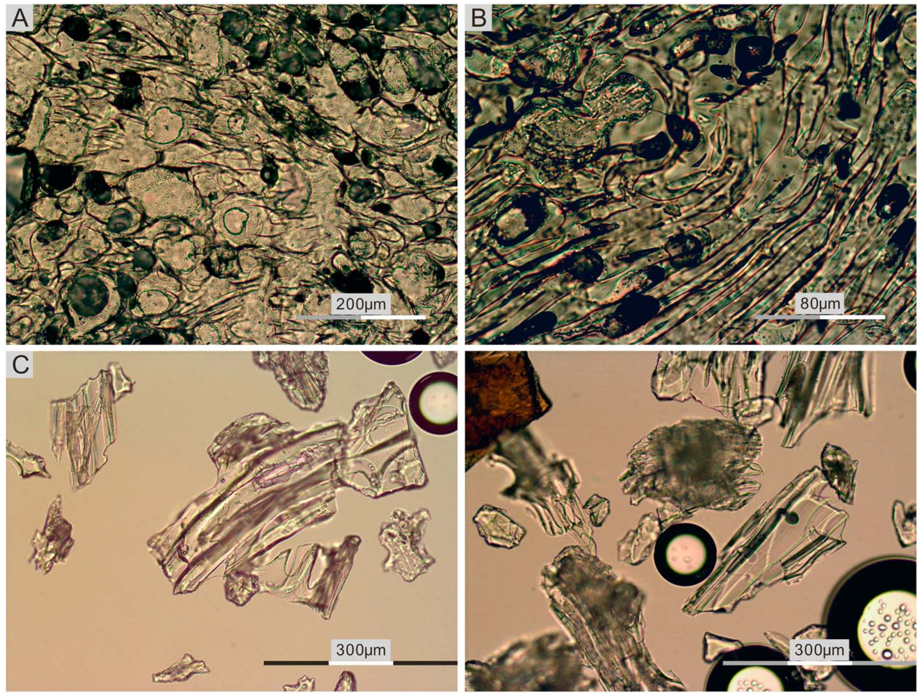

Figure 3. Photos of (a, b) the comendite from Qixiangzhan, north summit of Changbaishan volcano, and (c, d) the tephra recorded in Yuanchi Lake.

In March 2017, three parallel sediment cores with a composite length of 4.45 m were obtained from the center of Yuanchi Lake. The cores were transported to the laboratory in Beijing, split, described, and sampled. The core can be divided into five lithological units: Unit 1 (4.45–4.15 m) consists of yellow coarse sand; Unit 2 (4.15–2.01 m) consists of silty mud containing occasional volcanic breccias; Unit 3 (2.01–0.91 m) consists of dark organic mud with a visible patchy tephra layer at around 162 cm; Unit 4 (0.91–0.41 m) is the Millennium light gray pyroclastic fall deposit consisting of well-sorted pumice lapilli; and Unit 5 (0.41–0 m) consists of silty clay interbedded with pyroclastic deposits.

2.3. Tephra Separation

A visible patchy gray tephra layer was identified at 1.62-m depth (YC162) in Yuanchi Lake sediment. It consisted of a discontinuous tephra layer, with tephra patches extending up to 1.58 m. Usually, such an irregular distribution of a tephra bed in sedimentary sequences signifies postdepositional processes, for example, the fallout of tephra on snow cover (Housley & Gamble, 2015). Tephra samples were picked from the core and then were treated with 10% HCl to remove carbonates and with 30% H_2O_2 to remove organic material. Chemically treated samples were sieved, and particles between 30 and 80 μm were retained and then mounted and polished for electron microprobe analysis (EPMA).

2.4. Chronology

For the uppermost 221 cm of Yuanchi sediment, a total of seven plant macrofossil samples were selected and dated by accelerator mass spectrometry at the Beta Analytic Radiocarbon Laboratory, Florida, USA (Table S1 and Figure 2). Radiocarbon ages were calibrated using the IntCal13 curve, and the calibrated ranges are reported as two standard deviations (Reimer et al., 2013).

2.5. Geochemical Analysis

The major element composition of glass shards of proximal Qixiangzhan comendite and tephra recorded in Yuanchi Lake was measured using a JEOL JXA 8100 electron probe microanalyzer (EPMA, with a wavelength-dispersive spectrometer) at the State Key Laboratory of Lithospheric Evolution of the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing. Ten major and minor elements (Na, Mg, Al, Si, K, Ca, Fe, Ti, Mn, and P) were analyzed with an accelerating voltage of 15 kV, a beam current of 6 nA, and a beam diameter

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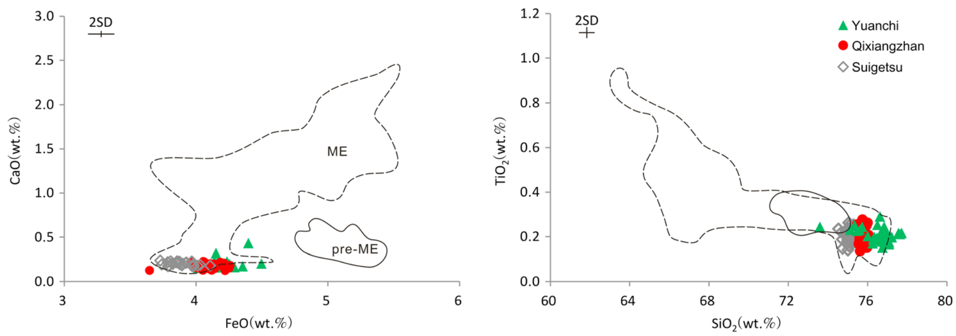

Figure 4. Biplots of glass shards showing comparisons of the Qixiangzhan comendite from proximal Changbaishan volcano, Yuanchi Lake, and Lake Suigetsu from Japan. Envelopes represent the geochemical range of glass shards from the Changbaishan Millennium eruption (ME), and the pre-Millennium eruption (pre-ME, that is, the fall deposit of subunits NS-1 and NS-2) is included. Glass data sources: ME is from Chen et al. (2016), Hughes et al. (2013), and Sun et al. (2015, 2017); pre-ME is from Sun et al. (2017); and Suigetsu is from McLean et al. (2018). Representative error bars for the Yuanchi and Qixiangzhan tephras (two standard deviations [2 SD]) were calculated from secondary glass standard analyses.

of 10 μm. Peak counting times used were 20 s for all elements except for Na (10 s), and the Na content was determined at the start of the analysis. Secondary standard glass from the MPI-DING fused glass, ATHO-G rhyolitic in composition, was used to check the precision and accuracy of the data (Jochum et al., 2006).

3. Results

Proximal Qixiangzhan comendite from Changbaishan volcano contains colorless glass (Figures 3a and 3b). The tephra layer (YC162) consists predominantly of colorless cuspate and pumiceous glass shards with a maximum length of 300 μm (Figures 3c and 3d). For the YC162 tephra, SiO_2 varies from 73.60 to 77.73 wt%, CaO from 0.16 to 0.32 wt%, and FeO from 4.02 to 4.50 wt% (Figure 4 and Table S2). Volcanic glass compositions from the Qixiangzhan comendite range from 75.49 to 76.16 wt% SiO_2, 0.12 to 0.23 wt% CaO, and 3.65 to 4.26 wt% FeO (Figure 4 and Table S2).

When considering the evidently patchy distribution of the YC162 tephra, the first appearance of the tephra should represent the timing of volcanic eruption. In this study, we established a Bayesian-based chronology using the age-depth modeling software Bacon v2.2 (Blaauw & Christen, 2011), and an age of 8831–8100 cal yr BP (95% confidence; Figure 2) was assigned to the YC162 tephra.

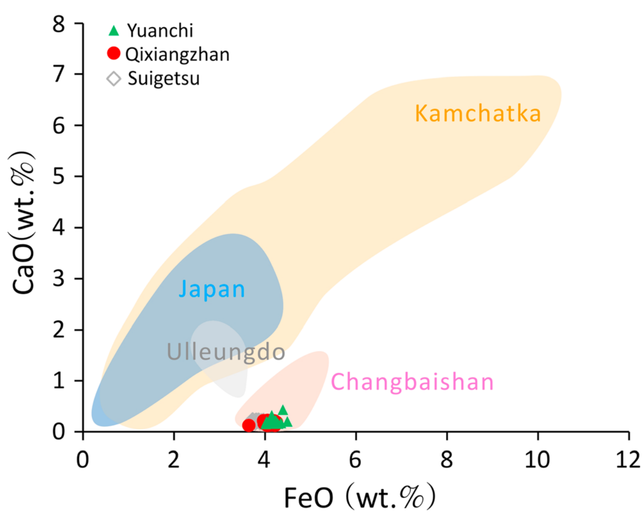

Figure 5. FeO-CaO biplot differentiating tephra from Changbaishan from other adjacent volcanic regions. Glass data sources: Kamchatka is from Hasegawa et al. (2011), Kyle et al. (2011), and Ponomareva et al. (2015, 2017); Japan is from Aoki and Machida (2006); Ulleungdo is from Machida et al. (1984) and Smith et al. (2011); and Changbaishan is from Chen et al. (2016) and Sun et al. (2017, 2015).

4. Discussion

4.1. Source of the YC162 Tephra and Eruption Timing of the QE

The ratio of FeO to CaO of the glass component of tephras from Changbaishan enables tephra from this source to be easily separated from those from the neighboring volcanic regions of Japan, Kamchatka, and Ulleungdo (Figure 5; Sun, You, et al., 2014). YC162 tephra falls in the field of Changbaishan volcano, illustrating that this tephra most likely derives from Changbaishan.

During the Holocene, Changbaishan volcano experienced historical eruptions at around 1403 CE, 1668 CE, 1702 CE, and 1903 CE, the ME at 946 CE, and the pre-ME event at ~4 kyr (Oppenheimer et al., 2017; Sun et al., 2017; Wei et al., 2003; Yang et al., 2014). When considering the previous dating results for the Qixiangzhan comendite (Table 1), the controversial QE also might be considered as a Holocene eruption.

The stratigraphic relationships between the Qixiangzhan comendite and the pre-ME fall deposits on the northern summit are unclear because of the incomplete preservation of the proximal eruptive

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sequences caused by subsequent eruptions. Unfortunately, the previously poorly resolved dating (Table 1) of the Qixiangzhan comendite has resulted in the ages of these eruptives becoming increasingly unclear. However, the glass geochemical composition of the Qixiangzhan comendite and YC162 tephra are evidently distinct from the pre-ME fall deposits, which have a substantially higher FeO content (Figure 4). Consequently, regardless of the ages of these two events, it is clear that the YC162 tephra in Yuanchi Lake is not from the eruption corresponding to the ~ 4-kyr pre-ME.

Ash geochemistry from the Changbaishan ME has been relatively well characterized over the past few decades based on extensive proximal sampling and distal tephra records (Chen et al., 2016; Hughes et al., 2013; McLean et al., 2016; Sun, Plunkett, et al., 2014; Sun, You, et al., 2014; Sun et al., 2015, 2017). The Qixiangzhan comendite has a glass composition that cannot be separated from the rhyolitic member of the ME (Figure 4). However, ash from the ME usually has light brown shards (Sun et al., 2015), which are absent in the QEA (Figure 3), and typically, the Changbaishan ME has glass compositions ranging from rhyolite to trachyte. In addition, the field exposures near Yuanchi Lake show that the ME ash also contains glass shards ranging in composition from trachytic to rhyolitic (Sun et al., 2017). Therefore, the YC162 tephra cannot be from the rhyolitic member of the ME.

The field-observed vesicular Qixiangzhan comendite and the vesicular structure of the glass shards (Figure 3) demonstrate that the QE was an explosive eruption (e.g., Pan et al., 2013). The YC162 tephra has a glass composition consistent with that of the Qixiangzhan comendite (Figure 4), implying that this tephra is from the QE. The Bayesian-modeled age for the YC162 (8831–8100 cal yr BP, 95% confidence) falls in the age range of the QE (Table 1), which also supports our contention that the YC162 tephra is from the QE. The QEA detected in the Yuanchi Lake ~30 km away from the Changbaishan volcanic vent strongly supports that the QE being an explosive eruption.

The most recent tephrochronological studies from Lake Suigetsu revealed a tephra layer (SG14-1058) dated to around 8166–8099 cal yr BP (95% confidence; McLean et al., 2018). The authors correlated it with Changbaishan given that the same volcano usually produced similar products; however, it is difficult to constrain the tephra to a specific eruption because of the lack of proximal sequences with which to compare it. The modeled age range of YC162 tephra from Yuanchi Lake also overlaps with that of the Suigetsu SG14-1058 tephra (8166–8099 cal yr BP) at the 95% confidence interval, and we propose that the two tephras were erupted by the same event.

The SG14-1058 tephra exhibits similar glass major element compositions to those from YC162 tephra and Qixiangzhan comendite within the range of uncertainty (Figures 4 and 5). Minor alkaline (i.e., Na_2O and K_2O) and SiO_2 offsets between YC162, Qixiangzhan, and the published SG14-1058 tephra may be explained by slight differences in instrumental precision, as revealed by the secondary glass (ATHO-G) standard data reported here and by McLean et al. (2018) and with respect to accepted values for this standard (Jochum et al., 2006). Therefore, we propose that both the SG14-1058 tephra recorded in Lake Suigetsu and the YC162 tephra can be correlated with the Qixiangzhan comendite, and thus, we assign an age of ~8100 cal yr BP to the eruption timing of QE using the more refined date of the SG14-1058 tephra from Lake Suigetsu.

4.2. Geochronological Implications

Previous age estimates of the QE are typically older than 10 kyr (Table 1). Tephrochronological constraints by Bayesian age modeling from Yuanchi and Suigetsu Lakes assign an age of ~8100 cal yr BP to the QE, which is younger than most $^{40}Ar/^{39}Ar$-derived age estimates. Only the $^{40}Ar/^{39}Ar$ age estimate of Heizler et al. (2015) is similar to our modeled age for QE. Older-age estimates obtained by $^{40}Ar/^{39}Ar$ dating may have resulted from excess argon in melt inclusions and xenocrysts or phenocrysts (Heizler et al., 2015; Ramos et al., 2016). Tephra layers recorded in the lake and peat sediments around the volcano therefore offer an important means to resolve problems relating to the eruption timing and to reconstruct the eruptive sequence of an active volcano, such as the less studied Changbaishan volcano. In addition, our modeled age for the QE also implies that a geomagnetic field excursion younger than the 17-kyr Hilina Pali excursion was recorded in the Changbaishan Qixiangzhan comendite (e.g., Singer et al., 2014; Zhu et al., 2000).

^{238}U-^{230}Th dating yielded an age of about 12 kyr for the QE (Wang et al., 2001; Zou et al., 2014), and this zircon age is also older than the tephrochronological age estimate obtained in the Yuanchi and Lake Suigetsu records. Combining the zircon ages with tephrochronologically constrained eruption timing implies that the magma residence time for the QE was about 4 kyr. Zircon age and Ra/Th isotopes suggest that the ME magma residence time is about 6–10 kyr (Ramos et al., 2016; Zou et al., 2010, 2014). Such a residence time of ME magma is similar to the age of QE assigned by this study (i.e., ~8100 cal yr BP). In addition, temperature estimated from alkali feldspar-glass geothermometry assigned a temperature of ~740 °C to the Millennium comenditic magma, and ~710 °C to the Qixiangzhan comenditic magma (Zou et al., 2010, 2014). Therefore, it is highly plausible that the comenditic magma existed beneath the Changbaishan volcano for a long time, and the QE was a precursor for the ME.

4.3. A New Marker Horizon Across East Asia

Correlations of the YC162 tephra and SG14-1058 tephra recorded in Lake Suigetsu firmly establishes the QEA as another important Changbaishan-sourced marker horizon from central Japan to Northeast China (Figure 1). The timing of the QE eruption is near the 8.2 event, which is an important rapid cooling event that occurred at around 8.2 kyr BP (Alley et al., 1997), and this event also can be detected in the Hani peat bog from Longgang volcanic field, ~120 km west of Changbaishan (Hong, Liu, et al., 2009; Hong, Hong, et al., 2009). When considering the occurrence of the QEA in central Japan, and the relative short distance from Changbaishan to Hani peat, the widespread QEA has the potential to serve as an important marker bed for synchronizing paleoenvironmental records around the time of the 8.2 event from Japan to Northeast China.

Ash clouds from Changbaishan eruptions were predominantly transported to the east of this volcano, such as the eastern tephra dispersal of the ME and several visible tephra layers recorded in the Japan Sea, while only the cryptotephra from ME was identified in Lake Sihailongwan to the west of Changbaishan (Figure 1; Ikehara, 2015; Sun et al., 2015). Ash from the Changbaishan ME has been identified in sediments from Northeast China to the Japan Sea, Japan Island, and even Greenland ice cores and thus forms an important north hemispheric marker horizon (Chen et al., 2016; Hughes et al., 2013; Machida & Arai, 1983; McLean et al., 2016; Sun et al., 2015; Sun, Plunkett, et al., 2014). The correlations of the Qixiangzhan comendite, YC162 tephra, and SG14-1058 in Lake Suigetsu at least implies that the QEA was mainly transported to the southeast of Changbaishan volcano (Figure 1). The similarity in the distribution of the ME and QE tephras may indicate that the QEA was also predominantly transported to the east of Changbaishan volcano, and the eruption season of QE may be in line with that of ME (autumn to winter), assuming a similar early Holocene weather pattern (i.e., wind direction) with that today (Oppenheimer et al., 2017). The high concentration of QEA glass recorded in Lake Suigetsu (>5,000 shards per gram of sediment; McLean et al., 2018) strongly suggests that the QEA may be dispersed in a wider area than the present modest estimated distribution of this study (Figure 1). Thus, this tephra layer potentially offers an important early Holocene marker horizon around East Asia that has not before been recorded because of the limited application of cryptotephra studies in this region. This study implies that searching for cryptotephra in the sedimentary archives beyond the volcanic regions of East Asia would be of immense value to paleoclimate and volcanological studies.

5. Conclusions

The ash from QEA was identified in Yuanchi Lake ~30 km east of Changbaishan volcano. The visible YC162 tephra and distal tephra (SG14-1058) layers recorded in Lake Suigetsu, Japan (McLean et al., 2018), demonstrate that the QE was explosive and that the resulting QEA can serve as a marker bed from central Japan to Northeast China. This study assigned a date of ~8100 cal yr BP to the QE. This age estimate for the QE confirms that a geomagnetic field excursion younger than the 17-kyr Hilina Pali excursion was recorded in the Changbaishan Qixiangzhan comendite (Singer et al., 2014).

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