Identification of multiple widespread tephtras from the volcanic glass shard chemistry of muddy sediments of the Nohbi Formation, central Japan

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Volcanic glass shards in muddy sediments of the late Pleistocene Nohbi Formation of central Japan are considered to be derived from multiple tephtras, although the shards have petrographic properties similar to those of the Aira-Tn tephtra. Hierarchical cluster analysis of concentration data for 58 elements obtained by laser ablation-inductively coupled plasma-mass spectrometry was used to distinguish glass populations in muddy sediment samples from the Nohbi Formation. Cluster analysis of volcanic glass shards from a sample in the lowermost horizon (Nohbi 38-54) of the formation identified the Aira-Tn (44%), Ontake-Pm1 (33%), and Ebisutouge-Fukuda (23%) tephtras. Glass shards from another sample in the middle horizon (Nohbi 60-2) of the formation were identified as being the Aira-Tn (35%) and Ebisutouge-Fukuda (65%) tephtras. The combination of multi-element data and cluster analysis demonstrates that the muddy sediment layers contain several tens of percent of Aira-Tn glass shards, as suggested by previous studies. The Aira-Tn tephtra is the youngest one within the tephtras identified from the Nohbi muddy sediments. As suggested by the previous studies, this evidence indicates that the Nohbi Formation was deposited during and/or after the AT ash fall stage and before the deposition of the Nan'yo Formation.

Keywords : tephtra, volcanic glass shards, muddy sediment, Nohbi Formation, cluster analysis, LA-ICP-MS

I. Introduction

The Nohbi Plain is a typical coastal alluvial plain in the central region of Honshu Island, Japan (Fig. 1). Subsurface geology of the Nohbi Plain consists of the Nan'yo, Nohbi, First Gravel, Atsuta, Second Gravel, Ama, Third Gravel, and Yatomi Formations, in descending order. Depositional process in the Nohbi Plain is controlled by a westward tilting which brings a sedimentary basin (Kuwahara, 1968), and glacial eustasy also influ-

ences the sedimentary facies. The formations of the Nohbi Plain are mainly composed of alternating sand-gravel sediments during regressive intervals and marine muds during transgressive intervals (Sugai *et al.*, 2016). These formations become thicker and deeper toward the west owing to the tilting. The late Pliocene-early Pleistocene Tokai Group (non-marine) underlies these formations (e.g., Kuwahara, 1985; Kuwahara and Makinouchi, 1988).

Among these formations, the Holocene Nan'yo,

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Fig. 1 Locations of the (a) Japan island arc, (b) Nohbi Plain on Honshu Island, Japan, and (c) core drilling sites from which the studied muddy sediment samples of the Nohbi Formation were obtained

The cross-section shown in Fig. 2 is along the Isewangan (the coast of Ise Bay) Expressway. The Nohbi 38-54 and 60-2 muddy sediment samples were obtained from core samples 53-1 and 60-2, respectively. The Aira, Ata, and Kikai calderas, which are regarded as the source volcanoes of AT, Ata-Th, and K-Tz, respectively, were first proposed by Matumoto (1943). The buried Shishimuta caldera, which is regarded as the source volcano of Ss-Pnk (Machida and Arai, 2011), was identified by Kamata (1989). The Kakuto caldera has been considered as the source volcano of Kkt (e.g., Aramaki and Ui, 1976). The presumed source volcanoes of On-Pm1, and Ebs-Fkd and Tky-Ngl (i.e., the Ontake Volcano and the Hida Mountain, respectively) are described in the main text. JS=Japan Sea; YS=Yellow Sea; ECS=East China Sea; OS=Okhotsk Sea; PO=Pacific Ocean; Hida M.=Hida Mountains; Ontake V.=Ontake Volcano; C.=caldera.

Fig. 2 An E-W-oriented cross-section showing the subsurface stratigraphy of the coastal area based on fig. 2 of Makinouchi *et al.* (2001) and Fig. 1 of Makinouchi *et al.* (2013)

The cross-section is along the Isewangan Expressway (fig. 1). The studied muddy sediment samples were obtained from the depths indicated by the boxes in the figure. a.s.l.=above sea level.

late Pleistocene Nohbi, and First Gravel Formations constitute at or near the surface sediments of the Nohbi Plain (Fig. 2), and are regarded as being transgressive- and alluvial-facies formations (e.g., Matsuzawa and Kato, 1954 ; Iseki, 1962 ; Nobi Plain Quaternary Research Group, 1977). The Nohbi Formation (Furukawa, 1972) comprises mainly sand and mud layers, and the sand layers are well compacted ($N \geq 30$; Makinouchi *et al.*, 2001). Volcanic glass shards are scattered throughout the sediment layers (Fig. 3). A detailed overview of the subsurface geology of the Nohbi Plain was given by Makinouchi *et al.* (2001, 2006, 2013). Hori *et al.* (2019) have reviewed in detail the recent research trends of the Nan'yo, Nohbi, and First Gravel Formations.

On the basis of the shapes and refractive indices of volcanic glass shards in the Nohbi Formation sediments, Makinouchi *et al.* (2001) argued that those in the middle horizon of the formation could be correlated with the Aira-Tn (AT) widespread marker tephra, which was erupted from

Aira caldera in southern Kyushu Island (Fig. 1-b ; e.g., Machida and Arai, 2011). The eruption age of the AT tephra is currently estimated at $30,078 \pm 96$ cal yr BP, based on ^{14}C dating of drill core samples from Lake Suigetsu (Albert *et al.*, 2018). Makinouchi *et al.* (2001, 2006) estimated the age of the Nohbi Formation to be 20–30 ka, based on the presence of AT volcanic glass shards. However, this estimate is unreliable because of lack of chemical data of the volcanic glass shards.

In this paper, we present major and trace element data for volcanic glass shards in the Nohbi Formation muddy sediments, obtained by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), along with a statistical analysis of these data. Multivariate statistical treatments such as Q-mode factor analysis (QFA) and constrained least-squares (CLS) multiple linear regression techniques have been used for the partitioning of geochemical datasets of bulk sediments and ash layers (e.g., Pisias *et al.*, 2013 ; Scudder *et al.*, 2018). In this study, hierarchical cluster analysis was used to partition the geochemical datasets from two muddy sediment samples from the Nohbi Formation. The cluster analysis successfully identified different tephra units in these samples, including the AT tephra.

II. Samples and analytical methods

1. Samples

The abbreviations for the tephra referred to in this study are based on Machida and Arai (2011). The Nohbi Formation muddy sediment samples (Nohbi 38-54 and 60-2) in the present study correspond to samples 53-1 (54) and 60-2 (46), respectively, described by Makinouchi *et al.* (2001). Samples 38-54 and 60-2 are from the lowermost and middle horizons of the Nohbi Formation, respectively, and have higher volcanic glass contents. These samples were obtained from drill cores for the standard penetration test used to draw a geological cross-section (Isewangan Expressway) of the coastal area of the Nohbi Plain (Figs. 1 and 2 ; Makinouchi *et al.*, 2001). Volcanic glass comprises ~ 1 and ~ 5.5 wt.% of the sieved samples with a grain size of #120–250 (i.e., 0.063–0.125 mm) from the 38-54 and 60-2 samples, respectively. Therefore, the volcanic glass shards actually comprise < 0.01 wt.% of these sediments. The distributions of the refrac-

Fig. 3 Columnar sections of drill cores 60-2 and 53-1 with refractive indices and shapes of volcanic glass shards based on fig. 6 of Makinouchi *et al.* (2001) Classification of the shape of volcanic glass shards is based on Yoshikawa (1976) : bw = bubble wall type, im = intermediate type, and irr = irregularly shaped type.

tive indices of the 38-54 and 60-2 volcanic glass samples are shown in Fig. 3. The refractive indices of these glasses in both samples are 1.498–1.501, and the shard shapes are the bubble wall (Henpei of Yoshikawa, 1976) or intermediate (Chukan of Yoshikawa, 1976) types, with the latter being transitional between the bubble wall and pumiceous (Takoushitsu of Yoshikawa, 1976) types (Fig. 3). The volcanic glass shards have been hydrated almost completely.

The elemental data for the Nohbi Formation samples were compared with some representative marker tephtras whose volcanic glass shards show refractive indices around 1.500. According to fig. 7 of Makinouchi *et al.* (2001), those for the AT, Kikai-Tozurahara (K-Tz), Ata-Toihama (Ata-Th), and Shishimuta-Pink (Ss-Pnk) tephtras from the calderas of Kyushu (Fig. 1-b) were compared. The refractive indices of the volcanic glass shards of these tephtras distribute around 1.500 (e.g., Machida and Arai, 2011). However, the volcanic glass shards of the Amagi-Kawagodaira (Kg) (1.498–1.506 ; Shimada, 2000), Kakuto (Kkt) (1.500–1.502 ; Machida and Arai, 2011) and Seiganji-Toga (Se-Tg) (1.500–1.505 ; Machida and Arai, 2011) tephtras shown in Fig. 7 of Makinouchi *et al.* (2001) were not analyzed in this study. The sampling locations of the samples of the AT, Ata-Th, K-Tz, and Ss-Pnk (Osaka Group Pink ; OGPK) tephtras were described by Maruyama *et al.* (2018).

In addition to these tephtra samples, the elemental data for the samples of the Ebsutouge-Fukuda (Ebs-Fkd), Ontake-Pm1 (On-Pm1), and Takayama-Ngl (Tky-Ngl) tephtras were compared with those for the Nohbi Formation samples. These well-characterized representative marker tephtras are important because the presumed source volcanoes are near the Nohbi Plain, although Makinouchi *et al.* (2001) did not mention Ebs-Fkd. The refractive index of the volcanic glass shards of Ebs-Fkd is 1.500–1.503 (Machida and Arai, 2011), which is similar to those of the Nohbi Formation samples (Fig. 3). The source volcano of the Ebs-Fkd tephtra is presumed to be in the Hida Mountains (Fig. 1-b ; Nagahashi *et al.*, 2000), which is ~160 km NNE of the sampling sites of the studied Nohbi Formation samples. Machida and Arai (2011) proposed that the eruption age of Ebs-Fkd was 1.7 Ma. The Ebs-

Fkd tephtra was distributed widely over Honshu Island, and its estimated thickness on the Nohbi Plain is >50 cm (Machida and Arai, 2011). The eruption age of the Tky-Ngl tephtra, which is presumed to be sourced from the Hida Mountains (Fig. 1-b ; Kajita and Ishihara, 1977 ; Kondo, 1985 ; Mizuno and Kikkawa, 1991), is estimated to be ~0.3 Ma, and the tephtra is distributed from Shikoku to the Kanto district on Honshu Island (Mizuno and Kikkawa, 1991). Ontake volcano to the south of the Hida Mountains (Fig. 1-b) is ~110 km NE of the sampling sites of the studied Nohbi Formation samples. This is regarded to be the source volcano of the On-Pm1 tephtra (e.g., Kobayashi *et al.*, 1967 ; Takemoto *et al.*, 1987). Machida and Arai (2011) proposed an age of 100–95 ka for the On-Pm1 tephtra. The On-Pm1 tephtra is distributed mainly towards the Kanto and Tohoku districts, which is in the opposite direction to the Nohbi Plain. However, this tephtra was supplied to the Nohbi Plain through the Kiso River, and has been found in the Atsuta Formation below the Nohbi Formation (Fig. 2) (Kobayashi *et al.*, 1967). The Kiso River flows down southeast side of Ontake volcano.

The Ontake-Yabuhara (On-Yb) and Ontake-Tatsuno (On-Tt) tephtras (Takemoto *et al.*, 1987) from Ontake volcano were also shown in Fig. 7 of Makinouchi *et al.* (2001) as the tephtras whose volcanic glass shards show the refractive indices around 1.500. However, considering that the refractive index strongly reflects the major element composition of the volcanic glass shard (Nagahashi *et al.*, 2004), the chemical properties of the volcanic glass shards of the On-Yb and On-Tt tephtras may be almost identical to that of the On-Pm1 tephtra. Therefore, the On-Pm1 tephtra is treated as a representative tephtra sample from Ontake Volcano in this study.

The sampling locations of the samples of the Ebs-Fkd tephtra was described by Maruyama *et al.* (2018). The Tky-Ngl tephtra sample was obtained from Kokawadera, Kinokawa City, Wakayama Prefecture. The On-Pm1 tephtra sample was obtained from a cliff around Ina-Toubu Junior High School, Hikage, Ina City, Nagano Prefecture. The refractive indices of the volcanic glass shards of the Nohbi Formation samples (Fig. 3) and the representative marker tephtras (i.e., AT, K-Tz, On-Pm1, Ata-Th,

Tky-Ngl, Ss-Pnk, and Ebs-Fkd) were determined using a refractive index measurement system (RIMS ; Kyoto Fission-Track Co., Ltd. ; Danhara *et al.*, 1992). The petrographic properties of the samples of these representative marker tephra were completely consistent with those briefly described by Machida and Arai (2011).

2. LA-ICP-MS analyses

Determination of 58 major and trace elements in the Nohbi Formation volcanic glass shards was undertaken with a Thermo Fisher Scientific iCAP Qc quadrupole ICP-MS instrument coupled to an ESI NWR-193 excimer laser ablation (NWR-exLA) system at Kyoto University, Japan. The wavelength and duration of the laser pulse were 193 nm and 5 ns, respectively. The laser repetition rate and fluence were set to 5 Hz and 3.0–3.2 J/cm², respectively. The beam diameter was 15 μ m and the ablation duration was 20 s for each analysis. Only one analysis was performed on each glass shard.

Volcanic glass shards in the tephra samples whose analytical data were compared with those for the Nohbi Formation samples were analyzed using an iCAP Qc ICP-MS coupled to an ESI NWR-Femto femtosecond LA (NWR-fsLA) system at Kyoto University, Japan. The wavelength and duration of the laser pulse were 260 nm and 600 fs, respectively. The laser repetition rate, fluence, and beam diameter, and duration of analysis, were the same as those of the NWR-exLA analyses. The detailed analytical protocols for the NWR-fsLA and -exLA analyses are described by Maruyama *et al.* (2016a, b, 2017).

Volcanic glass shards from the AT tephra were analyzed by both NWR-fsLA and -exLA techniques. In addition, a single AT volcanic glass shard was analyzed using an iCAP Qc ICP-MS coupled to a Cyber Laser IFRIT femtosecond LA (CL-fsLA) system at the University of Tokyo, Japan, to compare results obtained under different LA conditions. The wavelength and duration of the laser pulse were 260 nm and 190 fs, respectively. The laser repetition rate and fluence were set to 10 Hz and $\sim$ 9.8 J/cm², respectively. Under these conditions, the pit diameter (i.e., beam diameter) was 15–20 μ m. The ablation duration was set to 20 s for each analysis. The other CL-fsLA analytical protocols were essentially the same as those summarized by Maruyama *et*

al. (2016a, b, 2017).

Two synthetic silica-soda-lime glasses distributed by the National Institute of Standards and Technology (NIST ; NIST SRM 610 and 612) were repeatedly analyzed as reference materials. The reference values of these standard glasses reported by Jochum *et al.* (2011) were used for calibration in this study. The analyzed isotope data were obtained by integrating measurement cycles from the beginning to the end of the signal peak. The number of integration cycles was 20 for the NWR-exLA and -fsLA analyses, and 22 for the CL-fsLA analyses. The integrated background signal just before each analysis was subtracted from the analysis signal of each isotope. The number of background integration cycles was the same as that for the signal peaks. The background-corrected data were converted to elemental concentrations using the NIST data, and then internally normalized to measured silicon concentrations. Additional details of the data processing are described by Maruyama *et al.* (2016a, b). The data obtained in this study are summarized in Appendix S1. The data for the K-Tz, Ata-Th, Ss-Pnk (OGPK) tephra, and the AT tephra obtained by NWR-fsLA were published by Maruyama *et al.* (2017) as supplementary material. The optical images of the volcanic glass shards after LA were taken with a Leica DVM5000 HD digital microscope.

3. Hierarchical cluster analysis of elemental data

Hierarchical cluster analysis of the elemental data was used to statistically identify glass populations. Cluster analysis has been previously used for classification of geological materials (e.g., Parks, 1966 ; Rhodes, 1969 ; Till, 1974). In the field of tephrochronology, cluster analysis has been tested and used for the evaluation of tephra relationships (e.g., Kikkawa *et al.*, 1989 ; Baron *et al.*, 2008 ; Tryon *et al.*, 2008 ; Lowe *et al.*, 2017). The cluster analysis was performed using the R software package (R Core Team, 2019). The cluster analyses of the AT, Ebs-Fkd, On-Pml, and Tky-Ngl tephra data were carried out to estimate the range of the maximum heights of pure tephra samples, and compared the maximum heights of the branches of the dendrograms with the results of the cluster analyses for the Nohbi Formation samples. The further neighbor (or

complete linkage) method was used for the hierarchical cluster analysis. Distances or lengths of branches in the dendrograms between the analysis spots are represented as Euclidean distances. The Euclidean distances obtained by the cluster analyses are summarized in Appendix S2.

A combination of the wt.% values for nine major elements and $\mu\text{g/g}$ values for 49 trace elements were used for the cluster analysis. In preliminary tests, a dataset of element concentrations normalized relative to crustal abundances was used. However, the results of these tests were not as good as simply using measured concentration data.

In other preliminary tests, data for some elements (e.g., Be, Ni, Mo, Ag, Cd, In, and Sn), whose analytical values are relatively low and/or slightly scattered, had a negligible effect on the cluster analysis results. However, the data for these elements were included in the final cluster analyses in order to utilize as many discriminating factors as possible.

III. Results and discussion

1. Difficulties in glass identification

The distribution of volcanic glass refractive indices in the Nohbi Formation samples (Makinouchi *et al.*, 2001) can constrain the tephtras that might be present in these samples. The glass refractive indices in the 60-2 sample have two peaks at around 1.500 (Fig. 3 ; Makinouchi *et al.*, 2001). The lower (1.499) and higher (1.501) peaks (Fig. 3) correspond to those in the AT (1.498–1.501) and Ebs-Fkd (1.500–1.503) tephtras (Machida and Arai, 2011), respectively. Moreover, the mode of the refractive indices and the shapes of the glass shards in the sample 38-54 (Fig. 3 ; Makinouchi *et al.*, 2001) suggest that the AT tephtra (mode = 1.499–1.500 ; Machida and Arai, 2011) is a dominant component in this sample. The refractive indices of volcanic glass shards in the On-Pm1 tephtra are identical to those of the Ebs-Fkd tephtra (1.500–1.503 ; Machida and Arai, 2011), and those of the Tky-Ngl tephtra are similar to those of the AT tephtra (1.498–1.500 ; Machida and Arai, 2011). Therefore, these tephtras, which were erupted in and/or near the Hida Mountains, should be considered candidates for correlation with the Nohbi Formation samples.

The Ebs-Fkd, On-Pm1, and Tky-Ngl tephtras are only candidates whose source volcanoes are near the Nohbi Plain from the similarity of the refractive indices of the volcanic glass shards.

In some previous studies, major and some trace elements (e.g., Sr, Y, Ba, and La) in volcanic glass shards obtained by ICP emission analysis have been used for tephtra correlation and identification (e.g., Kikkawa *et al.*, 1989 ; Kikkawa, 1990 ; Tamura *et al.*, 2005, 2008). These relatively abundant trace elements (normally several tens to hundreds of $\mu\text{g/g}$ in rhyolitic glass shards ; e.g., Maruyama *et al.*, 2016a, 2017) can be used to robustly identify and correlate individual tephtras (e.g., Nogami *et al.*, 2018). Based on the glass refractive index data, we compared the chemical compositions of the volcanic glass shards from the Nohbi Formation samples and some representative marker tephtras described above. Figure 4 shows a plot of Ba/La versus La/Y for the volcanic glass shards of the Nohbi Formation samples, along with data for eight tephtras whose volcanic glass shards show similar refractive indices to those of AT for comparison. Although the Kkt sample has not been analyzed in this study, the analysis data obtained by Kimura *et al.* (2015) are available for this comparison. Figure 4 clearly shows that the K-Tz, Tky-Ngl, and Kkt tephtras are absent in the Nohbi Formation samples. The data for sample 38-54 mainly overlap with those of AT, On-Pm1, and Ss-Pnk, although some data are slightly scattered (Fig. 4-a). Figure 4-a shows that the volcanic glass shards in sample 38-54 contain the AT and On-Pm1 tephtras, but the presence of Ata-Th, Ss-Pnk, and Ebs-Fkd is equivocal. On the other hand, data for sample 60-2 almost overlap with those of AT, Ata-Th, and Ebs-Fkd (Fig. 4-b), but On-Pm1 and Ss-Pnk are not present.

There are still some ambiguities in distinguishing glass populations from these trace elements, given the slightly scattered data for sample 38-54 (Fig. 4-a). In particular, the data for analytical spots A-M and A-AF in sample 38-54 make partitioning of the dataset more complex. This means that it is necessary to make further comparison(s) using other major and/or trace element data. Moreover, this type of comparison is somewhat subjective, because it is based on visual evaluation of chemical data on a

Fig. 4 Plots of La/Y vs Ba/La ($\mu\text{g/g}$) for volcanic glass shards in the Nohbi samples

The AT data obtained by NWR-fsLA are plotted on this figure. "A-M" and "A-AF" in (a) indicate analysis spots M and AF on mount A of the Nohbi 38-54 sample. "A-D" in (b) indicates analysis spot D on mount A of the Nohbi 60-2 sample. The ratios for Kkt were calculated from the data determined by Kimura *et al.* (2015).

bivariate plot, although some mathematical techniques such as linear discriminant analysis are sometimes used for such evaluations (e.g., Nogami *et al.*, 2018).

The concentrations and/or ratios of some relatively abundant trace elements are useful for the grouping and identification of tephras (Fig. 4). However, using this method, it is difficult to evaluate and quantify in detail the relationships amongst the individual spot/shard analyses. Therefore, hierarchical cluster analysis was used in this study to distinguish glass chemistry populations with less subjectivity.

2. Cluster analysis

Firstly, potential differences due to the three different LA instruments used in this study were evaluated. In addition, the ranges of the branches (Euclidean distances) of each pure tephra sample were estimated to partition the volcanic glass shards of the Nohbi Formation samples into individual tephra components. The

analytical data belonging to the same branch with a maximum height equivalent to that of the pure tephra can be used to identify the specific tephra.

Figure 5 compares the dendrograms of the pure AT tephra sample obtained by NWR-fsLA on six AT glass shards, NWR-exLA on five AT glass shards, and CL-fsLA on one AT glass shard. The maximum heights (distances) of the NWR-fsLA, NWR-exLA, and CL-fsLA data are 281.6, 239.2, and 256.7, respectively (Fig. 5). There is no significant difference between the fsLA and exLA data (Fig. 5-a and b). Moreover, the maximum height obtained from 20 analyses of the single AT glass shard is intermediate between those of the NWR-fsLA and NWR-exLA data on numerous AT glass shards (Fig. 5-a and b). These results suggest that the cluster analysis is not affected by the different instruments and LA conditions. Figure 6 shows the dendrograms obtained from the Ebs-Fkd, On-

Fig. 5 Dendrograms for AT volcanic glass shards analyzed by (a) NWR-fsLA, (b) NWR-exLA, and (c) CL-fsLA. The total numbers of analyzed shards and spots for each LA analysis are shown at lower left in each dendrogram. The lettering and numbering of each analysis represent the glass shard name and analysis number of the glass shard, respectively. For example, "AF-03" in (a) represents the third analysis of the AF glass shard.

Pm1, and Tky-Ng1 tephra data. The maximum heights of the branches of Ebs-Fkd, On-Pm1, and Tky-Ng1 are 286.3, 333.5, and 261.0, respectively. These values are generally equivalent to those obtained from the AT data (Fig. 5). The maximum height of the branches obtained from the cluster analysis of pure tephra samples was 240–340.

Figure 7 shows the dendrograms obtained from the Nohbi Formation sample data. Figures 8 and 9 show the elemental patterns of each separated tephra relative to crustal abundances (Taylor and McLennan, 1985 ; Rudnick and Fountain, 1995 ; McLennan and Taylor, 1996 ; McLennan, 2001) based on the results of the cluster analysis shown in Fig. 7. The data for sample 38-54 are divided into Groups A (A-AP–A-AQ) and B (A-B–A-AK) in the first branching

(Fig. 7-a). The elemental pattern obtained from Group A is similar to that of the AT tephra (Fig. 8-a), and can be classified as AT glass shards. Group B is subdivided into Groups C (A-B–A-AN) and D (A-AW–A-AK) (Fig. 7-a). The elemental patterns of Groups C and D are generally similar to those of the Ebs-Fkd and On-Pm1 tephras, respectively (Fig. 8-b). In particular, the pattern of Group D exhibits an obvious Y-depletion, which is a characteristic of the On-Pm1 tephra. The patterns of Groups C and D are distinguishable from those of the Ata-Th and Ss-Pnk tephras (Fig. 8-b). The analyses of shards A-M and A-AF, which deviate from the other data in Fig. 4-a, are identified as the AT (Group A) and On-Pm1 (Group D) tephras, respectively. The maximum heights of the branches of Groups A (217.1), C (269.6), and D (340.3) are slightly below or

Fig. 6 Dendrograms for volcanic glass shards in the (a) Ebs-Fkd, (b) On-Pm1, and (c) Tky-Ng1 tephra, and optical images of volcanic glass shards of (d) Ebs-Fkd, (e) On-Pm1, and (f) Tky-Ng1 tephra after laser ablation. The notation for the analysis spots is the same as for Fig. 5. In (d), (e), and (f), the analysis numbers are shown on the LA pits on the volcanic glass shards. The shapes of the volcanic glass shards shown in (d), (e), and (f) can be classified into a pumiceous type.

almost identical to those of the pure tephra samples. Therefore, sample 38-54 can be shown by cluster analysis to contain three tephra, in the following proportions : AT = 44%, Ebs-Fkd = 23%, and On-Pm1 = 33%. There are some slight deviations in elements such as Li, Er, Tm, and W in the mean values for Groups C and D (Fig. 8-b). These deviations appear to be due to the smaller number of analyses used for calculation

of the mean values, rather than the effect of secondary alteration or the incorporation of other unknown tephra(s).

Sample 60-2 can be divided into two groups (Fig. 7-b). Group A (B-K-A-I) corresponds to the AT tephra and Group B (A-L-B-F) corresponds to the Ebs-Fkd tephra. The maximum heights of the branches of Groups A (213.3) and B (269.0) are slightly lower than those of the pure tephra

Fig. 7 Dendrograms for volcanic glass shards in the Nohbi (a) 38-54 and (b) 60-2 samples, and optical images of volcanic glass shards in the Nohbi (c) 38-54 and (d) 60-2 samples after laser ablation

The volcanic glass shards in sample Nohbi 38-54 can be divided into the AT, Ebs-Fkd, and On-Pm1 tephtras. Those in sample Nohbi 60-2 can be divided into the AT and Ebs-Fkd tephtras. The letter labeling of each analysis spot refers to the resin mount and glass shard. For example, "A-AP" in (a) represents the glass shard AP in mount A. "LA" on the optical images (c) and (d) represent the LA pits. The glass shards classified as AT have an appearance of the bubble wall type. The shapes of those classified as Ebs-Fkd and On-Pm1 are pumiceous/intermediate types.

Fig. 8 Mean elemental patterns for the glass shards in (a) Groups A and B, and (b) Groups C and D from the Nohbi 38-54 sample (Fig. 7)

All errors are $1\sigma_{\text{mean}}$.

samples. The shard analysis A-D that deviates from the distribution of the AT, Ebs-Fkd, and Ss-Pnk tephra in Fig. 4-b is identified as the Ebs-Fkd tephra (Group B). As for sample 38-54, the mean data values for each group show slight deviations (e.g., heavy rare earth elements and Hf for Group A; Fig. 9). Nevertheless, the major elements (e.g., Mg), Y-Nb, and light rare earth elements successfully identify the AT and Ebs-Fkd tephra in sample 60-2. The analysis data for some shards overlap with the distribution of Ata-Th in Fig. 4-b. However, the patterns of Groups A and B are obviously different from

that of the Ata-Th tephra (Fig. 9). The cluster analysis indicates that the proportions of the AT and Ebs-Fkd tephra in sample 60-2 are 35% and 65%, respectively.

The shapes of the volcanic glass shards in the Nohbi Formation samples can be classified into bubble wall type, or an intermediate type between bubble wall and pumiceous (Takoushitsu of Yoshikawa, 1976) types (Makinouchi *et al.*, 2001) (Fig. 7-c and d). As with the volcanic glass shards of Ebs-Fkd (Fig. 6-d) and Tky-Ngl (Fig. 6-f), those of On-Pm1 are typically pumiceous (Kobayashi *et al.*, 1967; Takemoto *et al.*, 1987)

Fig. 9 Mean elemental patterns for the glass shards in Groups A and B from the Nohbi 60-2 sample (Fig. 7)
All errors are $1\sigma_{\text{mean}}$.

(Fig. 6-e). However, some crushed pumice can produce shards with an appearance similar to the bubble wall type. The glass shards of On-Pm1 with bubble wall or intermediate type shapes (i.e., lower porosity types; Fig. 7-c) may have been deposited on the Nohbi Plain with little water transport. The catchment area of the Kiso River includes Ontake volcano, and the upper reaches of the Kiso River run through eastern Ontake volcano (e.g., Ministry of Land, Infrastructure and Transport, 2008). Therefore, the Kiso River may have transported the On-Pm1 pumice grains to the Nohbi Plain from the area where the On-Pm1 tephra fallout occurred (Kobayashi *et al.*, 1967).

The AT tephra (30 ka ; Albert *et al.*, 2018) and the tephtras which are older than AT were detected from the Nohbi muddy sediments by the cluster analysis. Therefore, the depositional age of the Nohbi Formation cannot be backdated before the AT eruption age. However, it is difficult to identify the AT ash fall horizon in the Nohbi Formation, because samples 38-54 and 60-2 contain the AT volcanic glass shards. The presence of the AT volcanic glass shards implies that the Nohbi Formation was deposited during and/or after the AT ash fall. The more precise

dating of the deposition of the Nohbi Formation is further problem.

Combined cluster analysis of major and various trace elements may be advantageous, in terms of the number of “decision factors” available for statistical analysis. However, considering the preliminary tests conducted in this study, there are still some subjective decisions that can control the results of cluster analysis. For example, some low-concentration elements have little effect on the results of cluster analysis. In contrast, relatively abundant trace elements are essential for the statistical analysis. Nogami *et al.* (2018) suggested that the trace elements Rb, Sr, Y, Zr, La, and Ce are suitable for tephra identification. In addition to these elements, Ba (e.g., Tamura *et al.*, 2005, 2008) should also be included in the statistical analysis, given the high abundance of Ba in rhyolitic glass shards and the comparison shown in Fig. 4. However, it may be unnecessary to select specific elements for statistical analysis, given the fact that principal component analysis can rapidly identify components in datasets. As such, it may better to undertake the statistical analysis on the full suite of analyzed elements.

IV. Conclusions

To identify the presence of the AT tephra in the Nohbi Formation, the concentrations of 58 major and trace elements in volcanic glass shards were determined by LA-ICP-MS. The relationship between the Ba/La and La/Y ratios of the volcanic glass shards from sample 38-54 suggested that it contains the AT and On-Pm1 tephra, although the presence of Ebs-Fkd is equivocal. On the other hand, that of the volcanic glass shards from sample 60-2 suggested that it contains the AT and Ebs-Fkd tephra.

Hierarchical cluster analysis was applied to the elemental concentration data for the Nohbi Formation samples. From the cluster analysis results, the volcanic glass shards in sample 38-54 were identified as being the AT (44%), Ebs-Fkd (23%), and On-Pm1 (33%) tephra, and those in sample 60-2 were identified as the AT (35%) and Ebs-Fkd (65%) tephra. Our results confirm those of Makinouchi *et al.* (2001), in that the Nohbi Formation contains AT volcanic glass shards. This result indicates that the Nohbi Formation was deposited during and/or after the AT ash fall stage.

The results of this study demonstrate that a combination of LA-ICP-MS multi-element data and cluster analysis can rapidly and objectively identify different glass populations in sediments.

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* Title etc. translated by T.M.
- The following appendixes are published as electronic appendixes on the website of The Quaternary Research (Daiyonki-kenkyu).
<<http://quaternary.jp/journals/data.html>>
- Appendix S1** Analytical results of volcanic glass shards
- Appendix S2** Euclidean distances among analysis data for the individual tephra samples

火山ガラスの化学組成に基づく濃尾層泥質堆積物中の 広域テフラの識別

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[要 旨]

後期更新世の濃尾層に含まれる泥質堆積物中の火山ガラスは、複数のテフラに由来するものと考えられる。濃尾層泥質堆積物の火山ガラスをグループ分けするために、LA-ICP-MSを用いて測定された、火山ガラスの58種の元素濃度データの階層的クラスター分析を適用した。クラスター分析の結果から、濃尾層基底の試料(Nohbi 38-54)に含まれる火山ガラスは、始良 Tn (44%)、御岳第1 (33%)、恵比寿峠福田 (23%) に分けられた。また、濃尾層中部の試料(Nohbi 60-2)に含まれる火山ガラスは、始良 Tn (35%) と恵比寿峠福田 (65%) に分けられ

た。LA-ICP-MSを用いて測定された多元素同時分析と測定データのクラスター分析によって、先行研究で示唆された通り、濃尾層の泥質堆積物中に数十%の始良 Tn の火山ガラスが存在している証拠が得られた。濃尾層に多量の始良 Tn テフラ成分が存在し、始良 Tn テフラが最も新しいテフラ成分であることは、濃尾層の堆積年代に制約を与えるものである。この結果に基づけば、濃尾層は始良 Tn テフラの降灰期間中、あるいは降灰後に堆積したと考えられる。

キーワード：テフラ、火山ガラス、泥質堆積物、濃尾層、クラスター分析、LA-ICP-MS

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