

CHEMICAL CHARACTERIZATION OF VOLCANIC GLASS SHARDS BY ENERGY DISPERSIVE X-RAY SPECTROMETRY WITH EDAX GENESIS APEX2 AND JEOL JSM-6390

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Abstract A chemical characterization of individual volcanic glass shard by electron-beam (E-beam) methods including SEM-EDS is effective for tephra fingerprinting. We installed a new SEM-EDS system composed of EDAX Genesis APEX2 and JEOL JSM-6390. This paper discusses reproducibility, accuracy, and precision of this system based on the analytical data sets of three representative Japanese widespread tephtras and four provided samples by INTAV intercomparison. 710 analyses on homogeneous natural glass shards extracted from a representative Japanese widespread tephtra (Aira-Tn: AT) under the same analytical conditions demonstrate reproducibility of measurements and absence of machine drift. For testing inter-laboratory reproducibility, three representative Japanese widespread tephtras (AT, K-Ah, and Toya) and four natural glasses (rhyolitic Lipari obsidian, phonolitic Sheep Track tephtra, basaltic Laki 1783 A.D. tephtra, rhyolitic Old Crow tephtra) were selected. Results of comparison prove that the new system mostly enabled us to determine the major oxide concentrations comparable with other laboratories. However, in case of lower oxide concentrations less than ca. 0.3 wt% such as TiO₂, MnO, and MgO, similarity and difference in concentrations are not significant because these values are less than the detection limit of SEM-EDS analysis. Also, results of comparison suggest that attention should be paid in determination of glass chemistry with higher content of CaO and Na₂O concentrations for basaltic and phonolitic tephtras such as Laki 1783 A.D. and Sheep Track tephtras.

Key words: tephtra fingerprinting, volcanic glass, glass chemistry, SEM-EDS, inter-laboratory comparison

1. Introduction

Tephrochronology is one of the most powerful tools for correlation and chronology of sediments and geomorphic surfaces, providing reliable and precise datum planes for geomorphology, neotectonics, volcanology, archaeology, and so on. In tephrochronological study, distinction and identification of individual tephtra beds are required, and they are performed by fingerprinting tephtra beds. Many characteristic properties determined by bulk to grain-discrete analyses on mineral grains to individual glass shards have been used for discrimination (Shane

2000; Lowe 2011). Chemical characterization of individual volcanic glass shards by electron-beam (E-beam) methods: electron probe microanalysis (EPMA) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) (e.g. Smith and Westgate 1969; Westgate and Gorton 1981; Shane 2000; Lowe 2011), is broadly employed for tephra fingerprinting. Analysis of individual glass shards is at an advantage compared to analyses of bulk tephra such as neutron activation (INAA), X-ray fluorescence (XRF), and so on because E-beam methods are effective for minimizing the problem of abnormal ranges in chemistry, contamination, and weathering. However, it had been pointed out that the use of published data is complicated by small differences between results produced by different laboratories, proving the requirement of the inter-laboratory reproducibility. In addition, the phenomenon of alkali element migration affecting Na-bearing silicate glasses is focused as the key for obtaining data of sufficient quality (Kuehn *et al.* 2011).

During the last two decades, for determination of the major chemical composition of volcanic glass shards, we had employed several measuring systems of SEM-EDS as follows, that is, a combination of JEOL JED-2001 energy dispersive X-ray micro-analyzer with JEOL JSM-5200 scanning electron microscope (SEM) (Suzuki 1996) from 1991 to 2005 (TMU91-05), and the subsequent combination of JED-2300 energy dispersive X-ray micro-analyzer with JSM-5200/6390 scanning electron microscopes from 2005 to 2013 (TMU05-13). In most Japanese tephrochronology laboratories including our laboratory, as common working standard, glass shards from rhyolitic Aira-Tn tephra (AT, 26-29 ka; Machida 2002) from South Kyushu, Japan are routinely undertaken to check the reproducibility and correct for machine drift. Reproducible analytical work by both measuring systems of TMU91-05 and TMU05-13 has been achieved. Similar analytical results except CaO concentrations have been obtained by six laboratories including our laboratory (Suzuki 1996). It demonstrated that the SEM-EDS analysis of TMU enabled us to determine the major oxide compositions comparable with five laboratories. However, the mean CaO concentrations for AT obtained in those works were slightly lower compared to the concentrations determined in other five laboratories in Japan. Moreover, by an inter-laboratory comparison conducted by the International focus group on Tephrochronology And Volcanism (INTAV) of the International Union for Quaternary Research (INQUA) (Kuehn *et al.* 2011), it was proved that TMU05-13 analytical work has several problems in analysis of the broad range of compositions typically found in tephra glass shards such as rhyolitic, phonolitic, and basaltic compositions. In February 2013, we installed a new SEM-EDS system composed of EDAX Genesis APEX2 energy dispersive X-ray micro-analyzer and JEOL JSM-6390 (Fig. 1). This paper discusses reproducibility, accuracy, and precision of this new system (TMU13) based on the analytical data sets of Japanese representative widespread tephra and four provided samples (collected in Italy, Canada, Iceland, and USA) used for the INTAV intercomparison.

2. Analytical Condition

Sample preparation

Procedures of sample preparation for tephra originated from volcanoes in the Japanese Islands are shown in Suzuki (1996). An unpolished mount containing the four reference glasses distributed by INTAV intercomparison was polished and carbon coated by the same method shown in Suzuki (1996).

In this testing, three representative Japanese widespread tephra were selected, that is, dacitic K-Ah originated from Kikai caldera and rhyolitic AT from the Aira caldera both in Kyushu, and rhyolitic Toya originated from Toya caldera in Hokkaido. Additionally, three homogeneous natural glass shards used in the INTAV intercomparison were selected for inclusion in: (1) rhyolitic obsidian from Lipari Island, Italy, (2) phonolitic Sheep Track tephra from Mt. Edziza, British Columbia, Canada, and (3) basaltic tephra from the 1783 A.D. eruption of Laki volcano in Iceland. An additional sample, Old Crow tephra from Alaska, USA, was also selected.

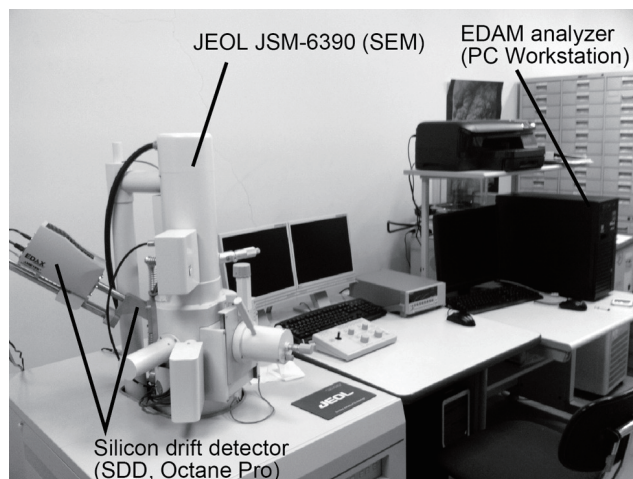


Fig. 1 EDAX SEM-EDS system composed of Genesis APEX2 energy dispersive X-ray micro-analyzer and JEOL JSM-6390 scanning electron microscopes.

Table 1 Operating conditions

Accelerating voltage	15 kV
Tilt of specimen stage (Sample surface)	0°
Take of angle of X-ray	35°
Working distance	10 mm
Beam current on Faraday cup	0.6 nanoamps
Beam diameter	ca. 10 × 10 μm
Live time	200 seconds
Magnification	20,000×

Microprobe analysis

Operating conditions are shown in Table 1. Glass shards are analyzed for nine major elements; Si, Ti, Al, Fe, Mn, Mg, Ca, Na, and K. Results are indicated by the oxide composition in weight % (wt%) of each element. All Fe are calculated as FeO. The characteristic X-rays from samples are detected with a silicon drift detector (SDD, Octane Pro), and the spectra are accumulated with EDAM analyzer (PC Workstation). Quantitative chemical analysis is performed by the "GENESIS SPECTRUM" program which extracts the peak intensities from the obtained raw data in Genesis APEX2. Correcting methods of the calculation is EDAX ZAF Quantification. Reference materials used as primary calibration standards are listed in Table 2. In many laboratories, K-Feldspar or orthoclase is used for K determination as reference material. Although we had also employed K-Feldspar in analyses from TMU91-05 (Suzuki 1996) to TMU05-13, potassium niobate is used for new reference in this study. Preliminary inter-laboratory comparison shows that analyses using potassium niobate are more favorable than those using K-Feldspar. This is probably caused from higher concentration of K₂O (26.14 wt%) in potassium niobate comparing to lower concentration in K-Feldspar (5.62 wt%).

Table 2 Standard samples

Element	Material	Chemical formula		wt%
Na	Albite	NaAlSi ₃ O ₈	Na ₂ O	11.48
K	Potassium Niobate	KNbO ₃	K ₂ O	26.14
Ca	Wollastonite	CaSiO ₃	CaO	48.00
Mg	Periclase	MgO	MgO	99.99
Al	Corundum	Al ₂ O ₃	Al ₂ O ₃	99.99
Si	Quartz	SiO ₂	SiO ₂	99.99
Ti	Rutile	TiO ₂	TiO ₂	99.99
Mn	Manganese Oxide	MnO	MnO	99.99
Fe	Hematite	Fe ₂ O ₃	Fe ₂ O ₃	99.99

3. Reliability of Analysis

Reproducibility with no machine drift

Usually, before and after a series of analysis on unknown tephtras, up to six analyses of the glass shards from AT as the working standard were undertaken routinely to check the reproducibility and correct for machine drift (Fig. 2). During the last seven months since May 2013, 710 analyses on AT glass shards have been done in 89 measurements in total under the same analytical conditions except the distance between the specimen and detector. A careless treatment caused the change of this distance less than a few millimeters, resulting in anomalies of analytical total over 100 wt% from September 2013 to November 2013. Despite of this trouble it is concluded that reproducible analytical work has been achieved, judging from stable concentrations of six major elements of which each concentration is > 1 wt% under the recalculation of major element chemistry to 100 wt% on a volatile-free basis (Fig. 2). No systematic drift of the concentrations and the small standard deviation of 0.27 wt% with the mean of 77.87 wt% for SiO₂ calculated from 638 analyses demonstrate the reproducibility of measurement and absence of the machine drift.

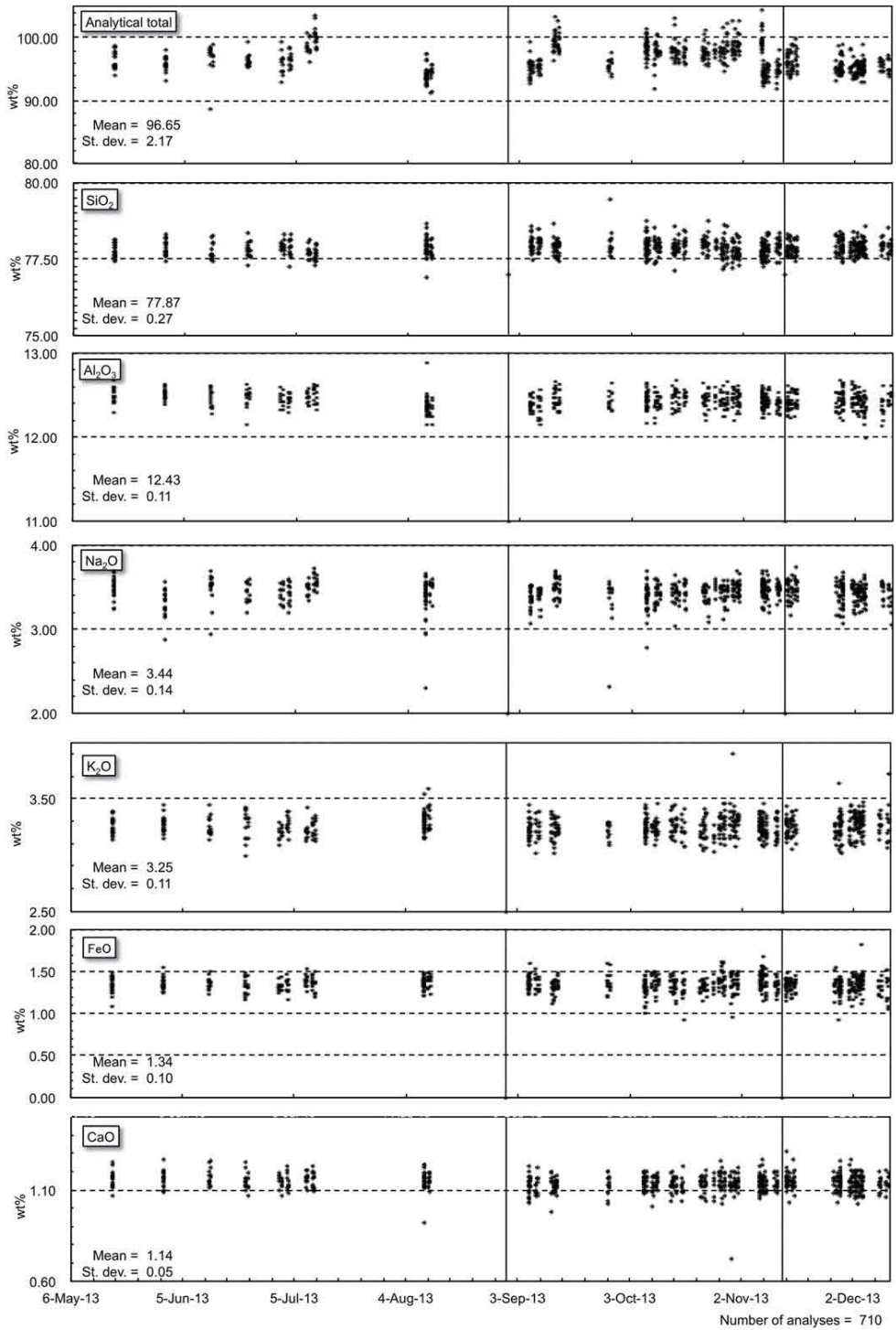


Fig. 2 Results of analyses on glass shards extracted from AT during the last seven months.

4. Inter-laboratory Reproducibility

Japanese widespread tephtras

In this study K-Ah, AT, and Toya are selected for testing inter-laboratory reproducibility. The reasons these tephtras are chosen are: 1) glass shards of AT are chemically homogeneous, having very narrow of chemistry, 2) these glass chemistries ranging from dacite to rhyolite cover those of variation in typical Japanese widespread tephtras, and 3) data sets of E-beam microanalysis of glass shards obtained by many different laboratories are available for comparison. AT is widely treated as the working standard (Fig. 3; *e.g.* Suzuki 1996; Nagahashi *et al.* 2003; Aoki and Machida 2006), indicating effectiveness as an actual standard for comparison of the data sets generated in different laboratories and with different instruments and techniques.

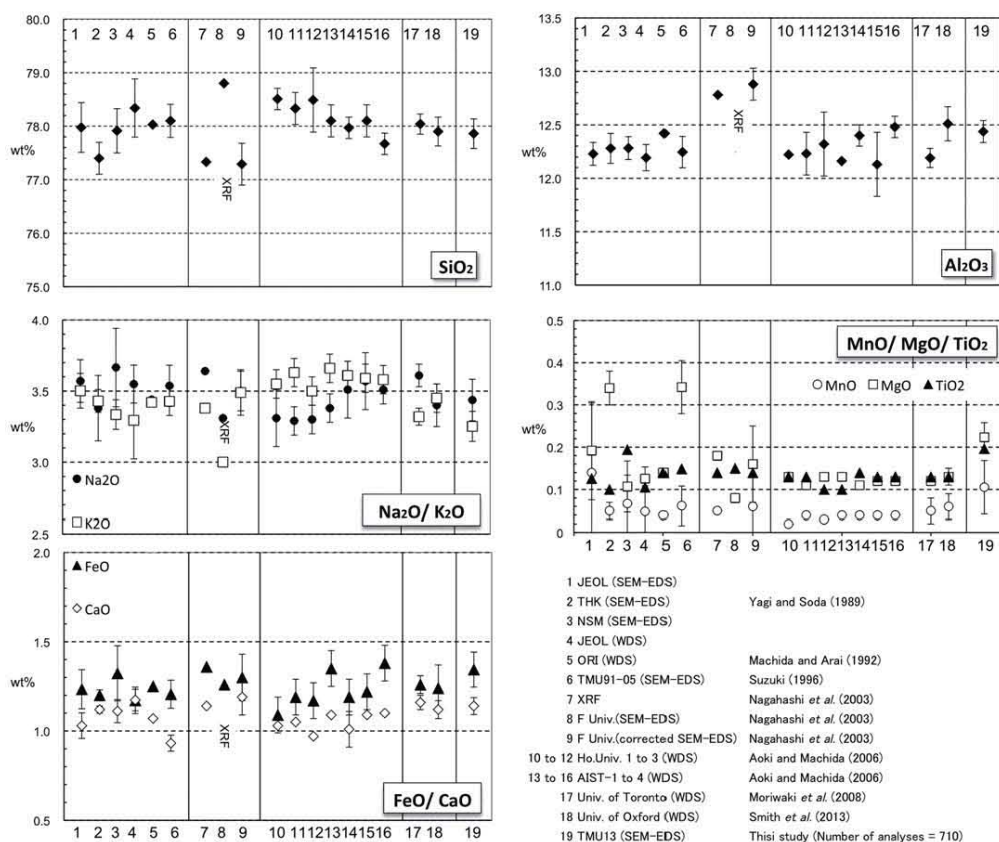


Fig. 3 Inter-laboratory comparison for AT. Symbol and error bar indicate mean and its ± 1 standard deviation, respectively.

There are twelve data sets of the E-beam microanalyses for AT, six generated by SEM-EDS including this study, six by WDS (Fig. 3). In addition, one data set determined by XRF and the SEM-EDS results corrected by this XRF analysis (Nagahashi *et al.* 2003) are available for the

comparison. The mean SiO₂ concentrations determined under the recalculation of major element chemistry to 100 wt% on a volatile-free basis ranges from 77.3 (No.8) to 78.8 (No.9) wt% by all laboratories. The standard deviations of SiO₂ concentration for all laboratories range less than 0.6 wt %. The mean SiO₂ concentration of 77.87 wt% with the standard deviation of 0.27 wt% by this study is average among other laboratories. Also, mean concentrations of Al₂O₃, FeO, CaO, K₂O, and Na₂O are positioning between the highest and lowest ones for each value determined by other laboratories. Mean concentrations of MnO and MgO are also between the highest and lowest ones, and TiO₂ content obtained in this study are slightly higher compared to those by other laboratories. However, similarity of MnO and MgO contents and difference in TiO₂ concentration are not significant. Lower concentrations of these elements less than 0.3 wt% means that these values are less than the measurement accuracy as SEM-EDS, as detection limit of SEM-EDS analysis is about 0.1 wt% (Reed 2005). This demonstrates that the SEM-EDS analysis with EDAX Genesis APEX2 and JEOL JSM-6390 enabled us to determine the major oxide concentrations comparable with nine laboratories and with different methods.

Other tests of inter-laboratory reproducibility by Japanese widespread tephtras are carried out using dacitic K-Ah and rhyolitic Toya tephtras. Published data sets of mean concentrations of SiO₂, FeO, CaO, K₂O, Na₂O, Al₂O₃ for K-Ah (Yagi and Soda 1989; Machida and Arai 2003; Aoki and Machida 2006; Moriwaki *et al.* 2008; Smith *et al.* 2013) and those for Toya (Machida *et al.* 1987; Yagi and Soda 1989; Shirai *et al.* 1997; Aoki and Machida 2006) are shown by open symbols with the same data sets in this study by closed symbols (Fig. 4). These data sets show close agreement between results by this study and other laboratories.

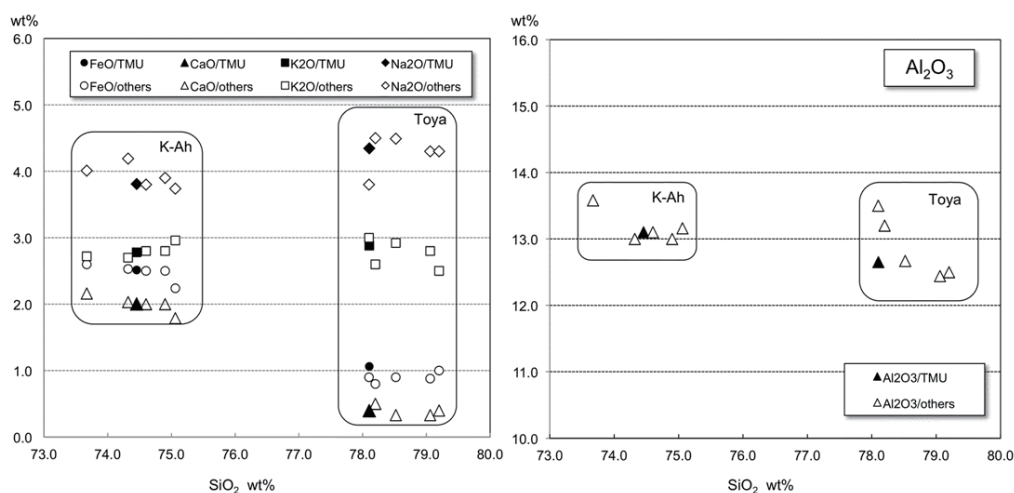


Fig. 4 Inter-laboratory comparison for representative Japanese widespread tephtras, K-Ah and Toya. Values by other laboratories for K-Ah are after Yagi and Soda (1989), Machida and Arai (2003), Aoki and Machida (2006), and Moriwaki *et al.* (2008), and Smith *et al.* (2013), and those for Toya after Machida *et al.* (1987), Yagi and Soda (1989), Shirai *et al.* (1997), and Aoki and Machida (2006).

Glasses used in the INTAV intercomparison

In the INTAV intercomparison, three homogeneous natural glasses were selected for inclusion in: (1) rhyolitic obsidian from Lipari Island, Italy, (2) phonolitic Sheep Track tephra from Mt. Edziza, British Columbia, Canada, and (3) basaltic tephra from the 1783 A.D. eruption of Laki volcano in Iceland. An additional sample, Old Crow tephra from Alaska, USA, was also selected. Data we analyzed on these glass shards are shown in Table 3 and Fig. 4 together with the preferred medians along with standard deviations recommended by Kuehn *et al.* (2011).

Table 3 Comparison of data sets for four glasses used in the INTAV intercomparison. See text for the explanation of broken-line, thin lined, and thick lined boxes.

Sample name	Number of analysis for each sample = 20.														Analytical total	
	SiO ₂	TiO ₂	ZnO ₂	Al ₂ O ₃	FeO	BaO	MnO	MgO	CaO	K ₂ O	Na ₂ O	P ₂ O ₅	Cl	F		SO ₂
Lipari obsidian																
Mean in this study	74.49	0.12	—	13.24	1.61	—	0.13	0.14	0.75	5.02	3.84	—	—	—	—	99.35
st. dev.	0.29	0.04	—	0.08	0.08	—	0.06	0.04	0.03	0.04	0.05	—	—	—	—	0.39
E-beam preferred median	74.60	0.07	0.02	13.10	1.55	0.04	0.07	0.04	0.73	5.13	4.07	0.01	0.34	0.15	0.01	99.55
st. dev.	0.60	0.01	—	0.20	0.03	0.02	0.02	0.09	0.03	0.13	0.11	0.02	0.02	0.02	—	0.79
Mt. Edziza Sheep Track																
Mean in this study	62.01	0.32	—	17.65	4.43	—	0.22	0.21	1.10	5.13	7.39	—	—	—	—	98.47
st. dev.	0.55	0.04	—	0.18	0.19	—	0.07	0.05	0.13	0.18	0.13	—	—	—	—	0.70
E-beam preferred median	61.90	0.24	0.16	18.00	4.54	0.03	0.14	0.12	1.10	5.34	8.09	0.04	0.21	0.21	0.02	99.31
st. dev.	0.60	0.01	—	0.40	0.14	0.02	0.01	0.01	0.06	0.19	0.37	0.02	0.02	0.02	0.01	0.78
Laki 1783 A.D.																
Mean in this study	49.89	3.03	—	12.85	13.66	—	0.24	5.40	9.94	0.50	2.76	—	—	—	—	98.28
st. dev.	0.19	0.10	—	0.11	0.13	—	0.08	0.07	0.08	0.04	0.06	—	—	—	—	0.42
E-beam preferred median	49.70	3.08	—	13.00	14.10	0.05	0.23	5.39	9.70	0.46	2.85	0.35	0.02	0.11	0.09	98.71
st. dev.	0.40	0.11	—	0.30	0.30	0.02	0.05	0.12	0.02	0.02	0.12	0.02	0.01	0.06	0.02	0.78
Old Crow																
Mean in this study	72.59	0.36	—	12.66	1.66	—	0.11	0.38	1.44	3.53	3.55	—	—	—	—	96.28
st. dev.	0.53	0.05	—	0.09	0.09	—	0.06	0.04	0.04	0.08	0.08	—	—	—	—	0.64
E-beam preferred median	72.50	0.30	—	12.40	1.60	—	0.05	0.27	1.43	3.56	3.68	0.04	0.27	0.19	0.01	95.83
st. dev.	0.80	0.03	—	0.20	0.04	—	0.02	0.01	0.03	0.14	0.18	0.03	0.02	0.02	—	1.15

All value is in wt%.

Among forty comparisons for data set of both individual nine oxide and analytical total for four samples, nineteen mean oxide concentrations and three analytical totals by this study are within each range of the preferred medians and its ± 1 standard deviation (Table 3; Fig. 5). All four obtained SiO₂ concentrations ranging from basaltic tephra (49.89 ± 0.19 wt%, Laki 1783 A.D.) to rhyolitic obsidian (74.49 ± 0.29 wt%, Lipari obsidian) are very similar to those of the preferred values recommended. As for higher concentration oxide of Al₂O₃, a mean (12.66 ± 0.09 wt%) of Old Crow tephra by this study is slightly higher than its preferred median and ± 1 standard deviation (12.40 ± 0.20 wt%), positioning out of the range. However, these ranges of mean with its standard deviation determined by this study and the preferred values are overlapping, therefore it can be concluded that this difference is negligible.

There are ten cases where E-beam preferred median is less than ca. 0.3 wt% (about a few times of the detection limit of SEM-EDS analysis), they are TiO₂, MnO, and MgO concentrations as shown in broken-line boxes in Table 3. Indeed, in all these cases except MnO value of Laki 1783 A.D., mean oxide concentration by this study is not within its range of the preferred medians and

its ± 1 standard deviation. As discussed in AT case, these differences are not significant, considering the detection limit and accuracy of SEM-EDS analysis.

In sixteen determinations of other FeO, CaO, K₂O, and Na₂O concentrations, useful oxides for fingerprinting tephra, one-half of the data sets closely agree with recommended data sets. In four cases, as the same as Al₂O₃ concentrations of Old Crow tephra case, ranges of mean with its standard deviation determined by this study and the preferred range are overlapping. These cases are shown in thin lined boxes in Table 3, and they are not significant disagreement. In other four cases (thick lined boxes), the obtained range and the preferred range do not overlap.

However, difference in FeO concentration of Laki 1783 A.D. is negligible because these ranges are very close, that is, the former 13.66 ± 0.13 wt% and the latter 14.10 ± 0.30 wt%. A 9.94 ± 0.08 wt% CaO concentration for Laki 1783 A.D. by this study is slightly higher than the preferred value of 9.70 ± 0.02 wt%, although the apparent high level of agreement between data sets for CaO among laboratories where CaO concentration is less than 3 wt% in not only INTAV comparison but also Japanese widespread tephra comparison. The discrepancy (0.98 %) between these results also seems to be within the measurement error range, but this suggests that attention should be paid in determination of glass chemistry with higher content of CaO.

Na₂O concentrations obtained in this study tend to be lower. This problem does appear to be present among the measurements of Lipari obsidian and Sheep Track tephra with Na₂O concentrations more than 4 wt% of the preferred median. The higher of actual Na₂O concentrations, the larger of decrease in the obtained concentrations, that is, 94% for the preferred value of 4.07 ± 0.11 wt% and 91 % for that of 8.09 ± 0.37 wt%. Although Na₂O concentrations are less than 4 wt% where the mean value by this study is within the range of the preferred values, this tendency is also recognized in those of Laki 1783 A.D. and Old Crow tephra (Table 3). Such systematical effects of alkali element migration in E-beam methods are well known (Kuehn *et al.* 2011). Attention is also needed in determination of glass chemistry with higher content of Na₂O concentration. Obtaining accurate Na₂O concentrations for the phonolitic tephra such as Sheep Track tephra proved to be a challenge for the apparatus treated in this study.

5. Conclusions

In this paper, we report electron-beam microanalytical data sets for five types of volcanic glass shards obtained by a new SEM-EDS system, and discuss its reproducibility, accuracy, and precision. Results of analyses for glass shards from working standard tephra under the same analytical conditions prove reproducibility of measurements and absence of machine drift. In general, there is close agreement of analytical data sets between this study and other laboratories for major oxide concentrations. However, in determination of lower concentrations less than ca. 0.3 wt% such as TiO₂, MnO, and MgO, similarity and difference in concentrations are not significant because of the detection limit of SEM-EDS analysis. Also, there are not enough agreements in determination of glass chemistry with higher content of CaO and Na₂O concentrations, meaning in analyses on basaltic and phonolitic tephra careful treatment of data set is needed.

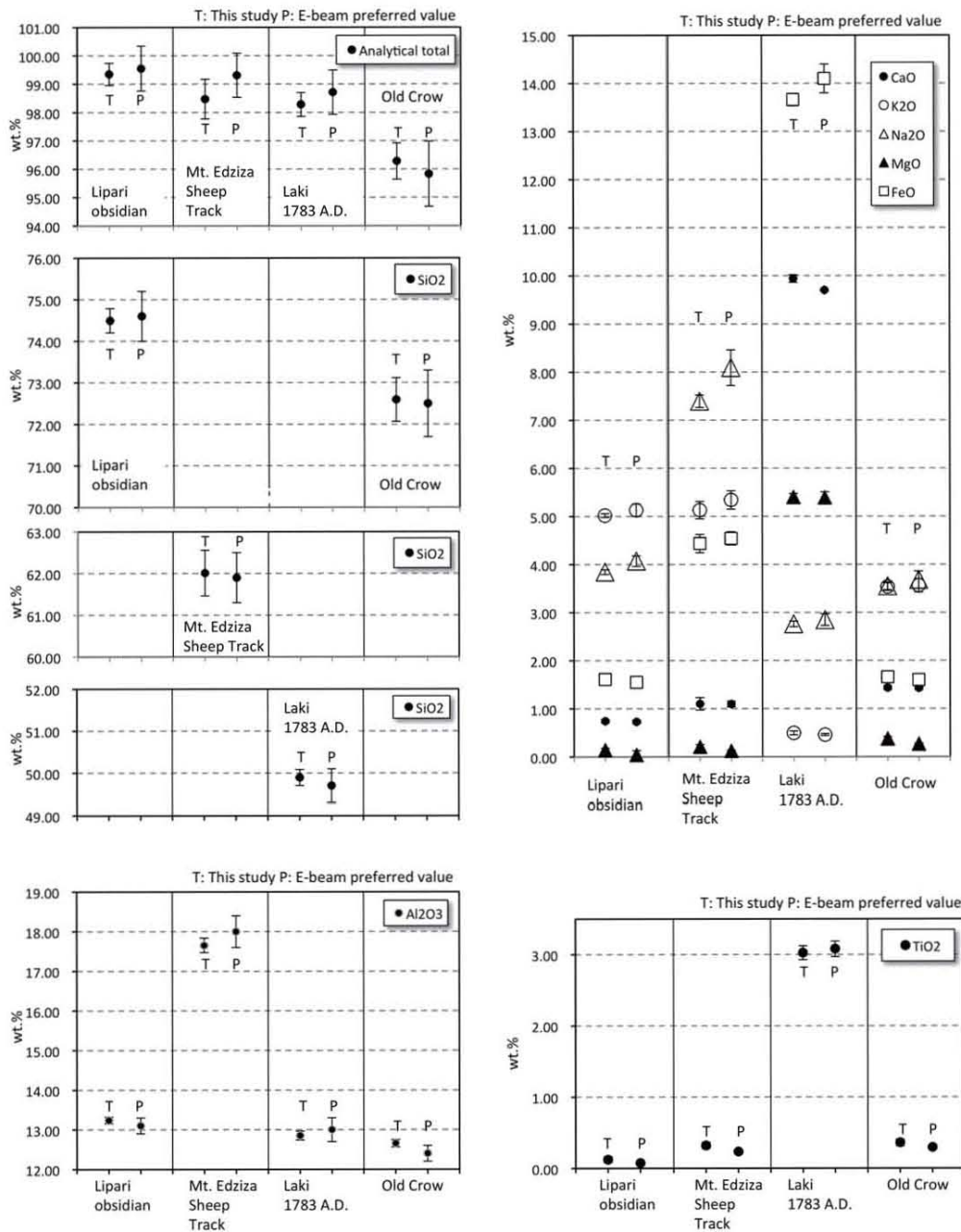


Fig. 5 Inter-laboratory comparison for four glasses used in the INTAV intercomparison. Symbol and error bar of this study indicate mean and its ± 1 standard deviation, respectively, and those of E-beam preferred values indicate medians and its ± 1 standard deviation.

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