

CHEMICAL ANALYSIS OF VOLCANIC GLASS BY ENERGY DISPERSIVE X-RAY SPECTROMETRY WITH JEOL JED-2001 AND JSM-5200: ANALYTICAL PROCEDURES AND APPLICATION

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Abstract Analytical procedures of chemical analyses on volcanic glass shards by EDS with JEOL JED-2001 and JEOL JSM-5200 and the results of analyses are described. Moreover, the reliability of analyses are discussed. The results of 760 analyses on glass shards from the AT Tephra, indicating a mean SiO₂ content of 78.1 wt % and a standard deviation of 0.3 %, demonstrate the reproducible analytical work. Comparison of the data with that generated in different laboratories and with different equipment and techniques for the AT Tephra was undertaken. This comparison shows that the analytical accuracy of this measuring system is comparable with WDS and EDS results from other laboratories. This paper also deals with applicative studies of EDS, which are two cases of correlation of tephra. One is the correlation of the Ks 22 Tephra (500—780 ka) within the Kazusa Group in the Boso Peninsula with the KMT distributed in the west area of the Hida Mountains. The other correlation is between Km 1 Tephra within the Shimofusa Group in the Boso Peninsula and the Nuka 4 (*ca.* 300 ka) Tephra of the east foot the Yatsugatake Volcano.

Key words: tephra identification, volcanic glass, EDS, Ks 22 Tephra, Km 1 Tephra

1. Introduction

Chemical analysis on volcanic glass is useful for tephra fingerprinting. Many approaches, such as the electron probe X-ray micro analysis (EPMA), neutron activation (INAA), X-ray fluorescence (XRF) and so on, have been documented (Froggatt, 1983, 1992). Many researchers have often assumed that the EPMA is effective for minimizing the problem of abnormal ranges in chemistry, contamination, and weathering, because the EPMA analyzes individual grains of glass. There are basically two methods of analysis in the EPMA, that is, wavelength dispersive spectrometry (WDS) and energy dispersive spectrometry (EDS). During the last three years, the author has constructed a measuring system which determines the major chemical element of volcanic glass by EDS with JEOL JED-2001 energy dispersive X-ray microanalyzer and JEOL JSM-5200

scanning electron microscope (SEM), and has tested the usefulness of the analysis for Quaternary tephra identification. Results indicate that the analysis with these apparatuses provides a very reliable method for identifying tephra. This paper shows the instrumental techniques including the practical analytical procedures, and discusses the reliability of the analyses. It also presents applicative case studies concerning the correlation of the middle Pleistocene tephtras collected from Central Japan.

2. Analytical Procedures

Sample preparation

Procedures of sample preparation from collecting in field survey to embedding into mount are shown in Fig. 1. In the case of juvenile coarse pumicious clasts, they were crushed and sieved to 0.25–0.063 mm. Using a Frantz isodynamic magnetic separator

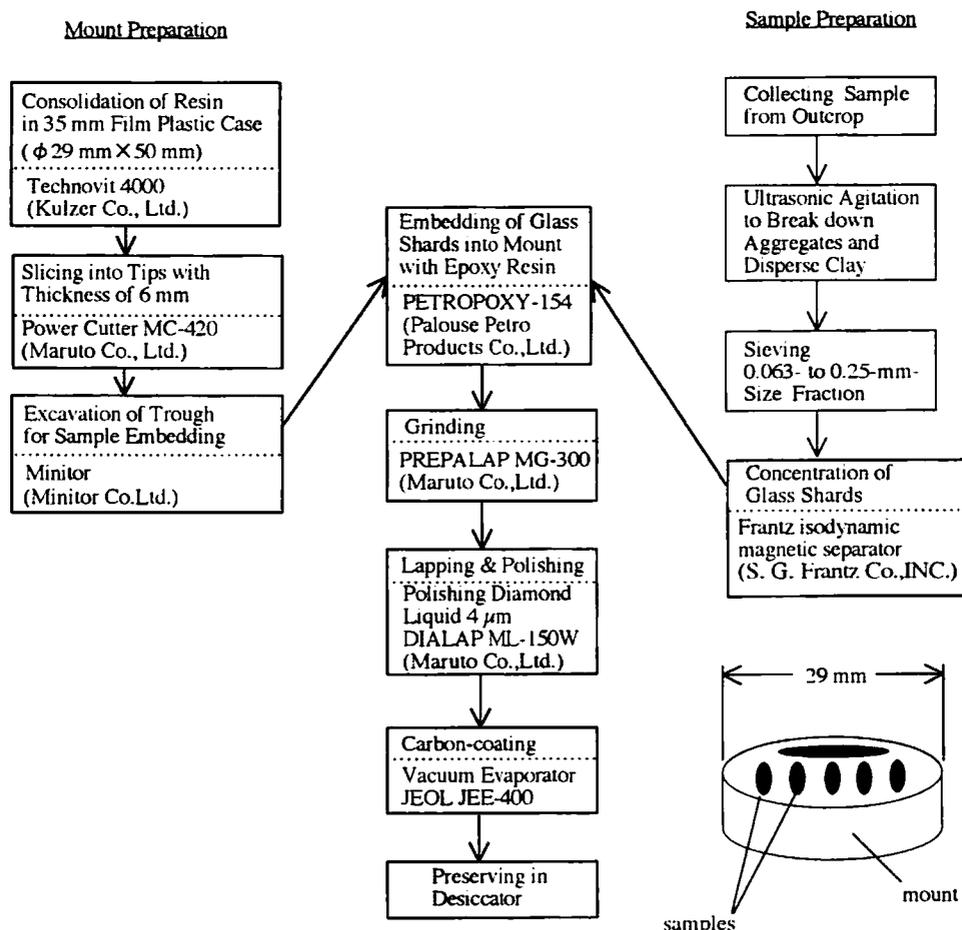


Fig. 1 Procedures of sample preparations

achieves enough concentration of glass shards although high purity separates is not required. Up to 30 glass shards per sample are necessary. Epoxy resin is used for the embedding of the glass shards into a mount. Usually, there are six samples per mount of 29 mm in diameter, including glass shards of the Aira-Tn Tephra (AT) (Machida and Arai, 1992) as common working standard for glass. All EPMA analytical work on volcanic glass should use a freshly exposed (polished) internal surface for analysis (Froggatt, 1992). To adopt this recommendation, the mount is ground until the internal surfaces of the glass are exposed, and then polished with polishing diamond liquid (4 μm). The polished mount should be preserved in a desiccator to keep it dry because if the water is absorbed in the mount, it could possibly result in outgassing which pollutes the electron optical system in the column.

Microprobe analysis

Operating conditions are shown in Table 1. Analyzed shards of glass are selected owing to their shape through the observation of SEM image. Analyses are undertaken under the selected area scanning mode of the beam controller in 1000 \times . Area of scanning

Table 1 Operating Conditions

| | |
|--|----------------------------------|
| Accelerating voltage | 15 kV |
| Tilt of specimen stage (sample surface) | 18° |
| Take of angle of X-ray | 30.41° |
| Working distance | 20 mm |
| Beam current on Faraday cup | 0.3 nanoamps |
| Beam diameter | ca. 10 \times 10 μm |
| Live time | 200 second |
| Magnification | 1000 \times |

Table 2 Standard samples for EDS

| element | material | chemical formula | | wt. % |
|---------|-----------------|------------------------------------|--------------------------------|---------|
| Na | Albite | NaAlSi ₃ O ₈ | Na ₂ O | 11.48 % |
| K | K-Feldspar | KAlSi ₃ O ₈ | K ₂ O | 5.62 % |
| 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 % |

is $10 \times 10 \mu\text{m}$. 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 % of each element. All Fe are calculated as FeO. The characteristic X-rays from samples are detected with a Si(Li) detector, and the spectra are accumulated with a multi-channel analyzer. Quantitative chemical analysis is performed by the "SPRINT III" program which extracts the peak intensities from the obtained raw data with a micro computer wearing a 80286 (10 MHz) CPU in the automated JEOL JED-2001. Correcting methods of the calculation are Background Correcting by top-filtering, Peak Overlap Correcting, and ZAF Correcting. The materials used for obtaining the standard spectrum are listed in Table 2.

It is well known that the EPMA on glass does not total 100 % in general, and it can be demonstrated that most of this deficiency is due to hydration (Froggatt, 1983, 1992). Consequently, Froggatt (1992) recommended that the EPMA data on glass should be normalized to 100 % to facilitate proper comparison because the degree of hydration for a single tephra can vary with the environment of deposition. In this study, data normalized to 100 % and the original analysis total are determined, and then both are recorded on floppy disks.

3. Reliability of Analysis

Usually, before and after a series of analyses on unknown tephtras, up to 5 analyses of the glass standards from the AT Tephra were undertaken routinely to check the reproducibility and correct for machine drift. In the last three years since August, 1992, 760 analyses on glass shards from of the AT Tephra have been done in 142 measurements in total under the same analytical conditions shown in Table 1. During this period, reproducible analytical work has been achieved with the exception of several measurements such as the October 1993 one. The mean SiO_2 content of 78.1wt % and the standard deviation of 0.3 % calculated from 760 analyses (Fig. 2) demonstrate the reproducibility of measurements and show that machine drift is not a variable that needs to be considered. The coefficient of variation (*C*), which were determined by dividing the standard deviation by the mean, for all elements with a wt % of more than 0.15 % except Mg are less than 0.07. This result means that these analyses do not have as low of accuracy as the WDS analyses by Okumura (1991) whose results indicated the *c* less than 0.05 for the same elements of glass shards from the AT Tephra.

Okumura (1993) pointed out that the KP-IV and Aso-4 Tephtras (Machida and Arai, 1992) are more suitable for the working standard of glass than the AT Tephra because of their ideal compositions of major elements. However, in this study the AT Tephra is used as the working standard although this tephra does not contain enough TiO_2 and MgO . The reasons the AT Tephra was chosen are: 1) glass shards of the AT Tephra, which are chemically homogeneous, have a very narrow range of chemistry, suggestive of no pre-eruptive zonation in the magma chamber, and 2) EPMA dataset obtained by many different laboratories is available for comparison. The latter means that the AT Tephra is an actual standard for comparison of the data generated in different labora-

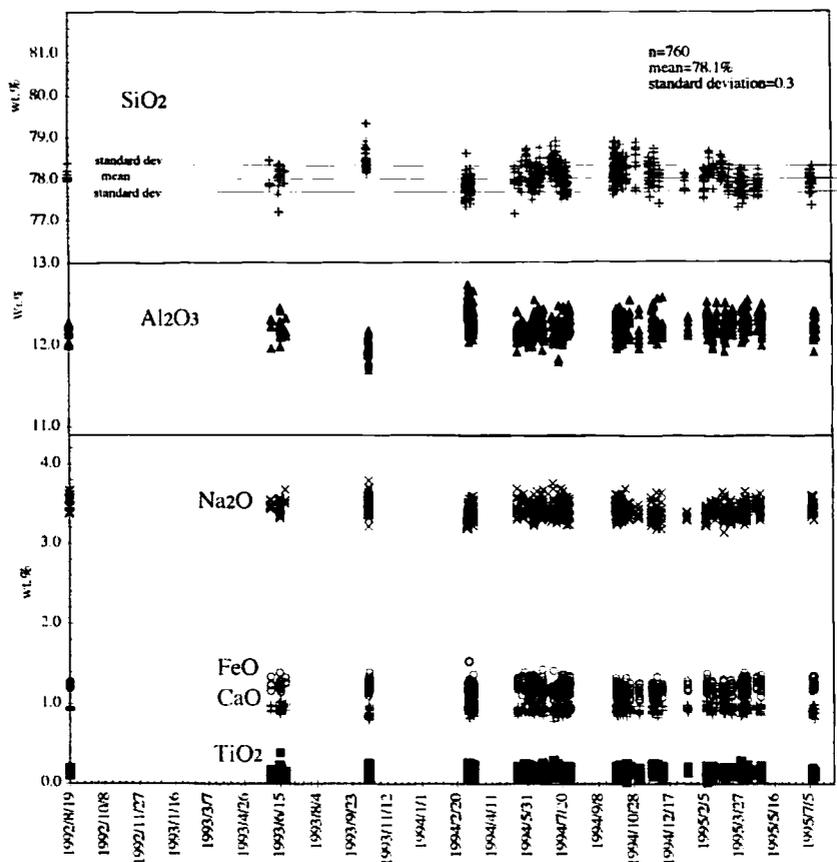
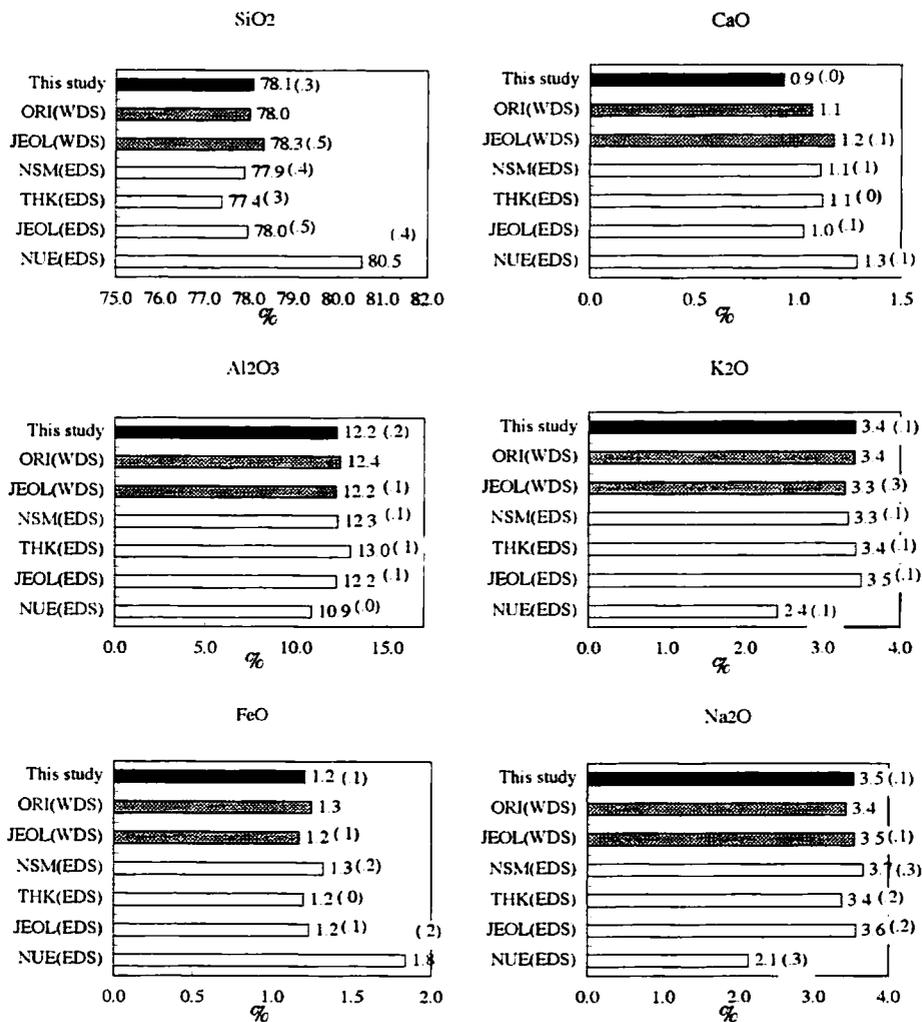


Fig. 2 Comparison of EPMA results on glass shards of the AT Tephra during the last three years

tories and with different equipments and techniques. Here, comparisons of datasets by the different EPMA analyses are undertaken (Fig. 3). There are seven datasets of the EPMA analyses for the AT Tephra, five generated by using EDS, two by WDS. The mean SiO_2 contents ranging from 77.4 to 78.3wt % were determined by all except for one laboratory, the Nara University of Education (NUE), which determined the mean SiO_2 content of 80.5 %. The standard deviations of SiO_2 content for all laboratories range from 0.3 to 0.5wt %. The mean SiO_2 content of 78.1 wt % with the standard deviation of 0.3 % determined by this study is average among the six laboratories. It is worth noting that the results of this study agree with the two WDS analyses conducted by the Ocean Research Institute (ORI) and JEOL and with two EDS analyses by the National Science Museum and JEOL. Regarding the range of standard deviations (0.3–0.5 %) for these five laboratories, variation of SiO_2 contents ranging from 77.9–78.3wt % indicates an actual chemical variation rather than a difference due to apparatuses. And also, except NUE, mean contents for other elements: Al_2O_3 , FeO, K_2O , and Na_2O are very similar within variation limits. These results mean that the analytical accuracy of this measuring



Number of analyses. This study: 760 ORI: 21 JEOL (WDS): 3 NSM: 8 THK: 10
 JEOL (EDS): 5 NUE: 20-100
 Standard deviation is shown in bracket.

Fig. 3 Comparison of EPMA dataset obtained in the different laboratories for glass shards of the AT Tephra

Abbreviations of laboratories, apparatuses and references are as follows. ORI: Ocean Research Institute, University of Tokyo, JEOL JCSA-733, Machida and Arai (1992); JEOL: JEOL Co., LTD., apparatuses of WDS and EDS are unknown, unpublished data; NSM: National Science Museum, JEOL T200 and EDS LINK SYSTEM, Y. Tokui personal communication; THK: Tohoku University, HITACHI X-560S and Kevex-Quantex7000, Yagi and Soda (1989); NUE: Nara University of Education, HITACHI X-650 SEM and Kevex μ X7000Q EDAX, Nishida (1983)

system is comparable with the WDS and EDS results from other laboratories. However, the mean CaO content of 0.9wt % obtained in this study is slightly smaller compared to the contents determined in other laboratories, that is 80 % of that determined by WDS analysis by JEOL. As the cause of this decrease in CaO content has not yet been clarified, it is necessary to note this characteristic of this apparatus, and comparison with data in other studies should be undertaken with caution. Although this problem remains, similar results, with the exception of CaO content, have been obtained by six laboratories including this study. This demonstrates that the EDS analysis with JEOL JED-2001 and JSM-5200 enabled us to determine the major oxide compositions comparable with five laboratories and with different methods.

4. Application for Tephra Correlation

Applicative study for correlation of tephra by using the measuring system shown above have been documented (*e.g.*, Suzuki and Soda, 1994). Correlation of the unknown early to middle Pleistocene tephra to the established tephrostratigraphy of the Kazusa and Shimofusa Groups distributed around the Boso Peninsula, 30-60 km southwest of Tokyo, in Central Japan, has been attempted by checking the similarity of glass chemistry. As a result, two correlations of tephra were undertaken. These tephra will play an important role in compiling the middle Pleistocene chronology of Central Japan as two marker horizons of 500–780 ka and *ca.* 300 ka. The results are given as follows.

Kasamori 22 (Ks 22) Tephra and Kaisho-Kamitakara Pyroclastic Flow Deposit (KMT)

The Ks 22 Tephra occurs as a thin (5 cm), white-gray, vitric ash layer in marine sediments of the Kasamori Formation of Kazusa Group. The Ks 22 Tephra is mainly composed of pumice type of glass shards and biotite crystal. Fission track dating of

Table 3 Chemical composition of glass shards from the Ks 22, KMTR, Km 1 and Nuka 4 Tephra

| Tephra (locality) | | SiO ₂ | TiO ₂ | Al ₂ O ₃ | FeO | MnO | MgO | CaO | K ₂ O | Na ₂ O | Total | n |
|---|----------|------------------|------------------|--------------------------------|-----|-----|-----|-----|------------------|-------------------|-------|----|
| Km 1 (Negishi, Kimitsu, Chiba) | mean | 68.8 | 0.6 | 15.1 | 3.2 | 0.1 | 0.9 | 1.8 | 5.4 | 4.1 | 100.0 | 13 |
| | st. dev. | 0.1 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.1 | 0.1 | 0.1 | | |
| Nuka 4 (Kawadaira, Minami-maki, Nagano) | mean | 68.8 | 0.6 | 15.1 | 3.2 | 0.1 | 0.9 | 1.8 | 5.4 | 3.9 | 100.0 | 12 |
| | st. dev. | 0.2 | 0.0 | 0.1 | 0.1 | 0.0 | 0.1 | 0.1 | 0.1 | 0.2 | | |
| Ks 22 upper (Senda, Chonan, Chiba) | mean | 77.1 | 0.1 | 12.6 | 0.9 | 0.1 | 0.2 | 0.5 | 5.3 | 3.3 | 100.0 | 12 |
| | st. dev. | 0.1 | 0.0 | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | 0.1 | 0.1 | | |
| Ks 22 middle (Senda, Chonan, Chiba) | mean | 77.1 | 0.1 | 12.6 | 0.9 | 0.1 | 0.3 | 0.5 | 5.2 | 3.3 | 100.0 | 13 |
| | st. dev. | 0.2 | 0.0 | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | 0.1 | 0.1 | | |
| Kamitakara pfl. middle (Nyukawa, Gifu) | mean | 77.0 | 0.1 | 12.7 | 0.8 | 0.1 | 0.3 | 0.6 | 5.2 | 3.2 | 100.0 | 13 |
| | st. dev. | 0.2 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.1 | 0.1 | | |
| Kamitakara pfl. lower (Nyukawa, Gifu) | mean | 77.2 | 0.1 | 12.7 | 0.9 | 0.1 | 0.2 | 0.6 | 5.0 | 3.2 | 100.0 | 7 |
| | st. dev. | 0.1 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.0 | 0.1 | 0.2 | | |

Analyses recalculated to 100% on a water-free basis and presented as a mean and standard deviation on *n* analyses. Apparatus used and operating conditions are shown in text.

530 ± 40 ka (Tokuhashi and Endo, 1984) and the stratigraphic position above the Brunhes-Matsuyama Paleomagnetic boundary (780 ka: Cande and Kent, 1992) show that the Ks 22 Tephra deposited in the middle Pleistocene. The major oxide compositions of glass shards were determined for upper and middle units of the Ks 22 Tephra (Table 3). The mean SiO₂ contents of about 77.1wt % and a total alkali content of about 8.5wt % (K₂O: 5.2–5.5wt %) indicate a calc-alkaline rhyolite. The mean compositions from each unit are similar within variation limits. Features of the Ks 22 Tephra characterized by higher K₂O content and the presence of biotite crystal suggest that this tephra was possibly erupted from a volcano distant from the volcanic front in Central Japan.

The Kamitakara Pyroclastic Flow Deposit (KMT) (Harayama, 1990), distributed in the west area of the Hida Mountains in Central Japan, is a large ignimbrite erupted from the Kaisho Source Vent located about 80 km west of the volcanic front. This ignimbrite is made of biotite rhyolite, and is assumed to be more than 40 km³ in volume (Harayama, 1990). Glass analyses for middle and lower horizons of the KMT indicate that the mean SiO₂ and K₂O contents of 77.0–77.2wt %, 5.0–5.2wt % shows a calc-alkaline rhyolite. These chemical compositions of the KMT are very similar to those of the Ks 22 Tephra. To effect numerical comparison of analyses, the similarity coefficient (SC) is calculated by averaging the ratio (<1) obtained by dividing pairs of analyses, element by element (the lesser is the numerator) (Borchardt *et al.*, 1972). Values close to unity denote chemical similarity, with SC > 0.92 (Froggatt, 1992) generally being consistent with correlation. The results calculated for each unit of the Ks 22 Tephra and KMT produce SC values from 0.93 to 0.96 (Table 4). Consequently, this shows that the KMT can be correlated with the Ks 22 Tephra. Harayama (1990) estimated that the KMT was erupted in the Jaramillo event (984-1049 ka: Cande and Kent, 1992) or in early of middle Pleistocene judging from two radiometric ages, 920 ± 110 ka by the K-Ar method and 650 ± 250 ka by the fission track method. On the other hand, the Ks 22 Tephra is found above the Brunhes-Matsuyama Paleomagnetic boundary. These results show that the KMT correlative to the Ks 22 Tephra was occurred between 500–780 ka.

Table 4 Correlation matrix of similarity coefficients comparing the major element chemistry of glass shards presented in Table 3

| | 1 | 2 | 3 | 4 | 5 | 6 |
|----------------|-------------|------|-------------|-------------|------|---|
| 1 Km 1 | X | | | | | |
| 2 Nuka 4 | 0.98 | X | | | | |
| 3 Ks 22 upper | 0.55 | 0.55 | X | | | |
| 4 Ks 22 middle | 0.55 | 0.55 | 0.96 | X | | |
| 5 KMT middle | 0.55 | 0.55 | 0.93 | 0.95 | X | |
| 6 KMT lower | 0.56 | 0.56 | 0.94 | 0.93 | 0.91 | X |

Figures in bold are SC > 0.92 as the lower limit of acceptance of correlation.

Kami-izumi 1 (Km 1) Tephra and Yatsugatake Nuka 4 Tephra

Approximately 5 cm of a fine vitric ash layer is exposed in a small outcrop at Negishi near the Obitsu River within the middle Pleistocene Kami-izumi Formation of the Shimofusa Group, and has been referred to as the Kami-izumi 1 (Km 1) Tephra (Tokuhashi and Endo, 1984). Examination by microscope indicates that separates are mainly both bubble-wall and pumice types of volcanic glass shards. The refractive index of shards ranging from 1.520—1.522 was determined. A vitric ash layer, which occurs in the similar stratigraphic position and contains the glass shards with similar grain-size and shape distribution and identical refractive index, has been described by Suzuki and Hayakawa (1990) in the east foot of the Yatsugatake Volcano located 120 km west of Tokyo. Chemical compositions of volcanic glass are compared. From Table 3 it is clear that the Km 1 Tephra is chemically similar to the Nuka 4 Tephra ($SC=0.98$), showing that they are correlated.

The source of the Km 1 Tephra and the Nuka 4 Tephra has not yet been identified, but Kikkawa (1990) suggested that the Nuka 4 Tephra is correlated to the Aso-1, which is an extensive ignimbrite surrounding the Aso Caldera in Central Kyushu about 800 km distant from Central Japan. The Nuka 4 Tephra is intercalated between the Omachi APm Tephra Beds (300—350 ka) and the BBP Tephra (250—300 ka) (Suzuki, 1992). This stratigraphic position shows that the age of the Nuka 4 Tephra is around 300 ka.

Acknowledgments

I thank Mr. Naoto Saito for providing reference samples of the Kamitakara Pyroclastic Flow Deposit, and Instruction Center of JEOL Co., Ltd. for providing technical information and EDS and WDS data. I wish to dedicate this paper to Professor Hiroshi Machida in commemoration of his retirement from Tokyo Metropolitan University, who led the author to study Quaternary research and Tephra study. I am grateful to him for his hearty advice, encouragement and constructive criticism.

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