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Quaternary International

journal homepage: www.elsevier.com/locate/quaint

A proposed methodology for analyses of wide-ranged elements in volcanic glass shards in widespread Quaternary tephras

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ARTICLE INFO

Article history:

Available online 7 July 2015

Keywords:

Volcanic glass
Tephra
LA-ICP-MS
Element abundance
Element pattern

ABSTRACT

The abundances of 58 elements from lithium to uranium of volcanic glass shards in 11 Quaternary widespread tephras of Japan and those of 4 tephras of North America have been analyzed using the laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) technique. The analytical values of the major components (SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO, CaO, and K₂O) were systematically lower (<10%) than those of analyzed using electron microanalysis techniques in previous researches, whereas that Na₂O tend to be ~20% higher than those of previous researches using the electron-beam microanalysis technique. The higher values of Na₂O obtained by LA-ICP-MS may result from the absence of the Na-loss phenomenon associated with the electron-beam analytical techniques. Most elements were analyzed with less than 20% of the relative standard deviations (RSDs), whereas some trace elements such as beryllium and some transition metals exhibit higher RSDs (up to ~120%) in 5-repeated analyses on the single glass shard. The LA-ICP-MS technique can be reasonably available for quantitative analyses of the major elements in volcanic glass shards, in addition to the trace elements. The volcanic glass can be clearly distinguished from each other by the patterns of the element abundances. The element abundances and the patterns of the elements of the volcanic glass shards are helpful to more precise identification and correlation of tephra samples.

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1. Introduction

Chemical compositions of volcanic glass shards in the Quaternary widespread tephras have been analyzed using various analytical methods for the purpose of tephra characterization or “fingerprinting” (Westgate and Gorton, 1981; Lowe, 2011). The investigations of chemical compositions of volcanic glass shards in tephras have been mainly based on the major element compositions analyzed by electron probe microanalysis (EPMA) and/or energy-dispersive X-ray spectroscopy (EDX) methods (e.g. Smith and Westgate, 1969; Westgate and Gorton, 1981; Nagahashi et al., 2003; Kuehn et al., 2011; Lowe, 2011). The interrelationships among the compositions of the major elements in volcanic glass shards, such as Na₂O–K₂O–SiO₂ distribution within the single tephra layer, are significantly useful for geochemical discussion about source of volcanoes and compositional heterogeneity of magma system (e.g. Turney et al., 2008;

Smith et al., 2013). Their major compositions are available for identification of tephras preliminarily identified by their stratigraphic distributions and/or ages, and considerably useful for various geochemical discussions.

However, some tephras are compositionally quite similar to others, hence it is sometimes difficult for the major compositions of volcanic glass shards alone to sufficiently work well as “fingerprint” (e.g. Stokes and Lowe, 1988; Brendryen et al., 2010). Therefore, the abundances of the trace elements have been analyzed as stronger geochemical information for identification of tephra samples (e.g. Eastwood et al., 1998, 1999). Instrumental neutron activation analysis (INAA) has been widely used for research on tephras (e.g. Fukuoka et al., 1980; Westgate and Gorton, 1981; Fukuoka, 1991, 1993, 1994). INAA has been used for bulk analysis of volcanic glass shards. In preparation of sample, this method is often needed to remove non-glass grains from samples after routine magnetic separation and/or heavy liquid separation. Tamura et al. (2008) determined the trace elements of volcanic glass shards in the Quaternary tephras in central Japan using the inductively-coupled plasma atomic emission spectrometry (ICP-AES) technique. In the ICP-AES analysis, it is necessary to separate mineral grains from

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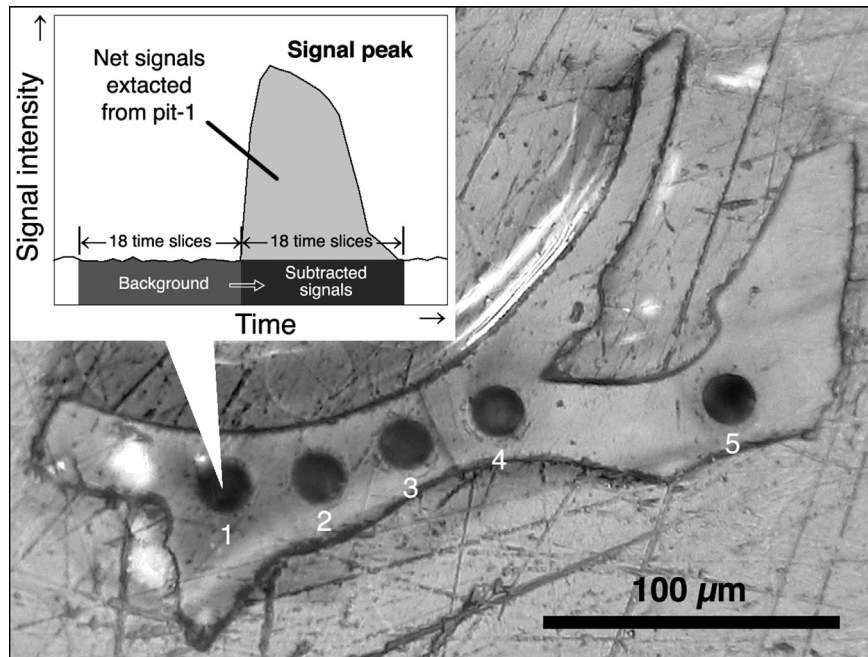


Fig. 1. Optical micrograph of the volcanic glass shard of AT tephra after the laser ablation taken by the Leica DVM5000 HD digital microscope. The white numbers indicate the pits produced by the laser ablation. Aerosol extracted from each pit was introduced into the ICP-MS, and then the signals of 58 elements were measured at 2 s intervals. The schematic diagram of the method for obtaining the sample signals extracted from the pit is also embedded in this figure.

glass shards, and to prepare huge amounts of sample (~0.5 g) for each analysis. Similarly, solution-nebulization ICP mass spectrometry (ICP-MS) technique requires 0.1–0.5 g of purified samples to be digested in acid (Pearce et al., 1999).

The laser ablation ICP-MS (LA-ICP-MS) technique has an advantage of analysis on the individual glass shard without unfavorable incorporation of coexisting mineral grains. In order to derive further detailed geochemical information from volcanic glass shards, incompatible elements including mainly the rare earth elements (REEs) and some other trace elements such as Rb, Zr, Th, and U in volcanic glass shards have been analyzed using LA-ICP-MS (e.g. Pearce et al., 2008, 2011; Westgate et al., 2008, 2011). Ion beam analysis (IBA) technique is also now employed on analyses of volcanic glass shards (e.g. Begét and Keskinen, 2003; Charlier and Wilson, 2010). The spatial resolution of LA-ICP-MS is lower (practically >10 μm in size) than that of IBS which is normally 5–10 μm in size (Lowe, 2011), whereas LA-ICP-MS has advantages of rapid and relatively simple analytical processes in comparison with IBA. At present, the combination of EPMA/EDX for the major element analysis and LA-ICP-MS for the trace element analysis seems to be widely regarded as one of the best choice for geochemical research of volcanic glass shards.

However, in the case that tiny silicate grains such as plagioclase exist within a volcanic glass shard, it is more advantageous to measure the major elements together with the trace element abundances in order to distinguish the analytical result of the sample in which silicate minerals are incorporated. In this view, it is more preferable to analyze the major elements together with the trace elements in volcanic glass shards at a time.

In this paper, we present the element abundances of a total of 58 elements including the major elements commonly analyzed by EPMA/EDX, and their patterns of the Quaternary volcanic glass shards in the tephra in Japan and those derived from the volcanoes in North America analyzed by the LA-ICP-MS technique.

2. Samples and analytical procedures

2.1. Samples

In this study, the volcanic glass shards in 11 tephra samples of Japan and 4 tephra samples of North America were investigated. The names and the abbreviations of the tephra used in this study are listed in Table 1. The sizes of the volcanic glass shards in the tephra samples typically range from 60 to 250 μm , and most of them are bubble-wall shards or junctions of bubble-wall (e.g. Fig. 1). The volcanic glass shards in the tephra samples coexist with coarse and euhedral/subhedral mineral grains such as alkali-feldspar, plagioclase, orthopyroxene, clinopyroxene, and quartz.

Table 1
List of tephra samples.

	Name of tephra	Abbreviation ^a	Source volcano ^b
Japan	Shikotsu-daiichi Ignimbrite	Spfl	(a) 1
	Toya	Toya	(a) 2
	Towada-Hachinohe	To-H	(a) 3
	Takayama-Ng1	Tky-Ng1	(a) 4
	Ontake-Daiichi Pumice	On-Pm1	(a) 5
	Sambe Kisuki	SK	(a) 6
	Osaka Group Pink (OGPK)	Ss-Pnk	(a) 7
	Aso-4	Aso-4	(a) 8
	Aira-Tanzawa	AT	(a) 9
	Kikai-Tozurahara	K-Tz	(a) 10
Kikai-Akahoya	K-Ah	(a) 10	
North America	Lava Creek Tuff A	LCTA	(b) 1
	Lava Creek Tuff B	LCTB	(b) 1
	Mesa Fall Tuff	MFT	(b) 1
	Bishop Tuff	BT	(b) 2

^a Names and abbreviations of tephra in Japan are based on Machida and Arai (2003).

^b Number of a source volcano shown in Fig. 2. (a) and (b) mean Fig. 2(a) and (b), respectively.

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