Shigeru Kitamura

## I. Introduction

Mineralogical and chemical properties are important for identifying and correlating tephra in remote area as well as in the volcanic area around the origin. The mineral assemblage is generally unique in the same tephra although the proportion is variable to some extent because heavier minerals decrease more quickly with distance. The chemical composition of volcanic glass is principally unchangeable with distance, while it is slightly affected by weathering at the depositional location and the temporal fluctuation of chemistry during the eruption that depends on the vertical structure of original magma.

The Berlín-Chinameca volcanic area is situated in the mountainous inland of the department of Usulután, eastern El Salvador, Central America, where various volcanoes including very active stratovolcano are concentrated and many pumiceous and scoriaceous tephras are accumulated. Middle to large eruptions producing pumiceous tephra has occurred every ten thousand years in average, so that they might have provided many synchronous surfaces in depositonal sequence. If they are traceable to outside of the area, they will become excellent timemarkers.

This study aims at revealing the mineralogical and the chemical properties of the pumiceous tephras observed in the Berlín-Chinameca volcanic area using microscopic observation and X-ray microprobe analysis, and providing a way to trace them to the remote area as a key bed or a time marker .

#### II. Study area

A volcanic chain extends along the pacific coast of Central America from Tacaná Volcano, Guatemala, to Irazú Volcano, Costa Rica, through southern Guatemala and El Salvador, on the E-W tensional field between the Motagua-Polochic transform fault and marine trench on the subduction zone of the Cocos Plate. Five large calderas, called Atitán, Amatitlán, Ayarza, Coatepeque and Ilopango, are located in the northern part of Central America (Fig. 1).

In the mountain of department of Usulután, eastern El Salvador, there is an volcanic area where various volcanoes are concentrated, called the Berlín-Chinameca volcanic area. It comprises several stratovolcanoes, cones and calderas (Fig.2) .

Berlín-Tecapa Volcano is a large volcanic complex composed of basal stratovolcano with large caldera, the diameter of which is ca. 7 km, and several cones formed on the southern rim of the caldera. Tabulete volcano is small stratovolcano situated on the south flank of Berlín-Tecapa Volcano, with a crater of ca. 800 m in diameter. Usulután Volcano is a dissected cone-shaped stratovolcano, located to the southeast of Tabulete Volcano, southernmost of the volcanic area. El Tigre Volcano is a dissected large stratovolcano situated at the center of the volcanic area. Two small cones called Cerro Oromontique

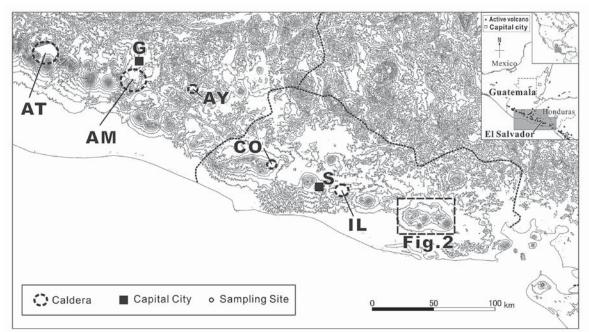


Fig. 1 Index map of southern Guatemala and El Salvador

Contour was created using 7.5-arc-second DEM data from GMTED2000 (Danielson & Gesch, 2011) and GSHHG vector data (Ver.2.3.6; August 19, 2016) distributed by National Oceanic and Atmospheric Administration (NOAA), U. S. Department of Commerce, was used for drawing coastlines. The contour interval is 200 m. Quadrangle delineated by break line exhibits the extent shown in fig. 2. Caldera ; AT: Atitlán, AM: Amatitlán, AY: Ayarza, CO: Coatepeque, IL: Ilopango. Cities; G: Guatemala, S: San Salvador.

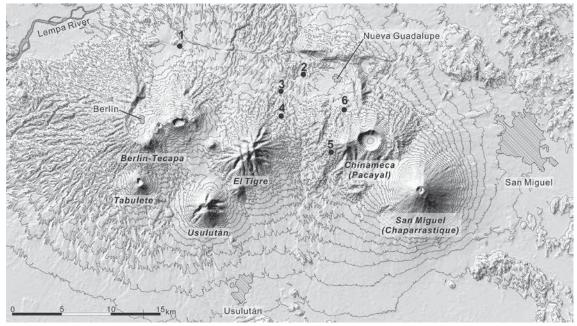


Fig. 2 Location of sampling sites in the Berlín-Chinameca volcanic area.

The solid circle with number exhibits location of exposure and the number corresponds to the column number in fig. 3. Shaded map was created using 30-arc-second DEM data from SRTM provided by National Aeronautics and Space Administration, NASA, U.S., and shown with superimposed contour map (contour interval:50m) originating from Arc/Info vectors of topographic map of El Salvador with the scale of 1:25,000, offered by Patrimonio del Cultura de El Salvador.

and Cerro la Manita are observed to be formed on the west and the south flank of the El Tigre Volcano. Chinameca-Pacayal Volcano is stratovolcano that occupies the northeastern part of the Berlín-Chinameca volcanic area, on the top of which a 2-km-wide crater called "Laguna Seca El Pacayal" is observed to be formed. A parasitic cone, Cerro El Limbo, is located on the west of the crater. San Miguel Volcano, another name "Chaparrastique", is the most active volcano in the present in the volcanic area. At the 700-m-wide crater on th top of the volcano, small eruptive plume has been frequently observed since 2013.

#### III. Tephra stratigraphy in the Berlín-Chinameca volcanic area

CEL (1995) reported many pumice layers and prominent scoria in and around the Berlín-Chinameca volcanic area, and proposed their stratigraphy. Kitamura (2018) confirmed the existence of four more pumice layer that were mentioned as nameless "pumice" in columnar section in the CEL report, and demonstrated the stratigraphic position of three wide-spread tephra in the tephra sequence in the area.

According to the two documents, pumice layers are called as follows, from the lower to the upper; Blanca Rosa, Jucuapa 1, Jucuapa 2, Jucuapa 3, Twin/Las Gemeras, Unit/Unidad-A, Jucuapa 4, Pacayal 1, Volcan/Pacayal 2, Pacayal 3 and Pacayal 4 (Fig. 3). They are overlain by a well-sorted stratified dark grey scoria-fall deposit called the Triunfo scoria and slightly poorly sorted scoria-fall deposit with breadcrust bomb called the Mercedes scoria.

The Blanca Rosa pumice is composed of white and pink pumice lapilli, comprising multiple units of well-sorted pumice lapilli intercalating poorly-sorted pumice with volcanic ash. Jucuapa 1, 2 and 3 pumice layers contain pale-grey yellow to light-grey pumice lapilli and pale-pink to dull-reddish pumice lapilli. While the Jucuapa 1 pumice is rather massive, the Jucapa 2 pumice is partly rich in grey scoria grain at the basal unit. The Jucuapa 3 pumice is rather rich in lithic fragment. Two white vitric ash laminas are found under the Jucuapa 1 pumice and the Jucuapa 2 pumice at the close levels, the former is the Chinameca 2 ash presumably derived from Ilopango Caldera and the latter is correlated to the Los Chocoyos tephra from Atitlán Caldera dated 84 ka (Fig.1; Kitamura, 2018) .

The Twin/Las Gemelas pumice is thickly deposited pumice-fall deposit comprising two major units. Another pumice-fall deposit named "Unit-A" or "Unidad-A" is observed above the Twin/Las Gemelas pumice intercalating thinly bedded volcanic ash soil or "tephric loess". In spite that Kutterolf *et al.* (2008) identified the Twin/Las Gemelas tephra to be combined with the Unit/Unidad-A tephra as a single layer in marine cores and called it "TT/AT", inland a short interval is identifiable between them in the sequence by the existence of tephric loess. The Jucuapa 4 pumice comprises several units, such as fall-out pumice, dark reddish brown ash, and pumice flow. The fall-out pumice unit is composed of light yellow to pale-grey yellow pumice and pink pumice containing abundant lithic fragment and a small amount of banded pumice also can be found.

The Pacayal 1 pumice is thickly deposited pumice-fall deposit composed of well-sorted "pure" white pumice and pink block, and overlying pumice-flow deposit that buries topographical depression. It is underlain by a thin layer of white vitric ash that is correlated to the either of the Conacaste tephra or the Congo tephra from Coatepeque Caldera. The Volcan/Pacayal 2 pumice is composed of multiple layers of pumice, scoria and volcanic sand. Although it is named "Volcan" in CEL (1995), it is called "the Volcan/

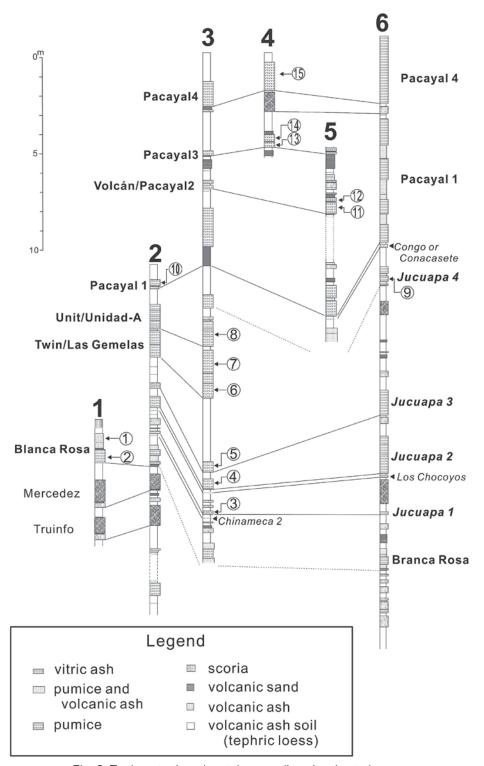


Fig. 3 Tephra stratigraphy at the sampling sites in study area

Number above the column corresponds to exposure number shown in fig. 2. Number with circle at the side of the column shows the number of sample collected at the level, corresponding the number shown in table 1.

Pacayal 2 pumice" in the article according to Kitamura (2018). The Pacayal 3 pumice contains pale grey and light grey pumice, comprises pyroclastic-flow and pumice-fall deposit. The Pacayal 4 pumice, which contains light-grey pumice, pale-grey pumice and pink pumice, comprises pyroclastic-flow deposit and pumice-fall deposit (CEL, 1995).

Sample	Tephra	Mineral assemblage	Chemistry	SiO2	TiO2	AI2O3	FeO	MnO	MgO	CaO	K2O	Na2O	Total
No.				(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
1	Blanca Rosa	opx >> cpx;	Average	69.2	0.5	15.3	3.3	0.2	0.7	2.4	2.9	5.5	100.0
	(lower pumice)	tr. bi; opq	St. Dev.	0.8	0.1	0.3	0.3	0.1	0.1	0.3	0.2	0.3	(28)
2	Blanca Rosa	opx >> cpx; al,	Average	69.4	0.4	15.4	3.1	0.1	0.7	2.6	3.0	5.2	100.0
	(upper ash)	<i>tr</i> . bi; opq	St. Dev.	0.8	0.1	0.7	0.3	0.1	0.1	0.4	0.2	0.3	(34)
3	Jucuapa 1	opx > cpx; <i>tr</i> . opq	Average	66.7	0.8	15.1	5.1	0.1	1.2	3.9	2.5	4.7	100.0
			St. Dev.	0.8	0.1	0.7	0.5	0.1	0.3	0.4	0.2	0.4	(33)
4	Jucuapa 2	opx > cpx; <i>tr</i> . opq	Average	65.6	0.6	16.5	4.5	0.1	1.2	4.4	1.9	5.2	100.0
			St. Dev.	1.8	0.1	2.0	0.9	0.1	0.3	1.1	0.3	0.3	(37)
5	Jucuapa 3	opx > cpx; <i>tr</i> . opq	Average	65.7	0.7	15.8	5.0	0.1	1.3	4.3	2.0	5.1	100.0
			St. Dev.	1.0	0.1	0.8	0.9	0.1	0.3	0.4	0.2	0.3	(35)
6	Twins-Las Gemelas	opx > cpx; opq	Average	69.2	0.6	14.9	3.7	0.1	0.9	3.2	2.6	4.8	100.0
	(lower)		St. Dev.	0.4	0.1	0.2	0.3	0.1	0.1	0.1	0.1	0.3	(24)
7	Twins-Las Gemelas	opx >> cpx; opq	Average	69.0	0.6	14.7	3.8	0.2	0.9	3.1	2.7	5.0	100.0
	(upper)		St. Dev.	0.8	0.1	0.5	0.2	0.1	0.2	0.3	0.1	0.3	(10)
8	Unit/Unidad-A	opx > cpx; opq	Average	68.9	0.6	14.8	3.8	0.2	1.1	3.4	2.4	4.8	100.0
			St. Dev.	0.6	0.0	0.3	0.1	0.1	0.2	0.4	0.2	0.7	(6)
9	Jucuapa 4	opx >> cpx; al;	Average	69.2	0.5	15.3	3.3	0.1	0.7	2.6	3.0	5.3	100.0
		opq	St. Dev.	0.5	0.1	0.4	0.3	0.1	0.1	0.2	0.2	0.2	(30)
10	Pacayal 1	opx >> cpx; opq	Average	74.1	0.4	13.5	2.0	0.1	0.4	1.9	3.1	4.5	100.0
			St. Dev.	0.3	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.2	(31)
11	Volcan/Pacayal 2	opx > cpx; <i>tr</i> . opq	Average	65.7	0.8	15.5	5.3	0.2	1.3	4.1	2.1	5.0	100.0
			St. Dev.	0.7	0.1	0.8	0.6	0.1	0.2	0.4	0.2	0.3	(33)
12	Volcan/Pacayal 2	opx >> cpx	Average	66.8	0.8	15.0	5.1	0.1	1.2	4.0	2.1	4.9	100.0
			St. Dev.	0.8	0.2	1.2	0.8	0.1	0.4	0.4	0.3	0.2	(33)
13	Pacayal 3 pumice	opx >> cpx; opq	Average	67.5	0.7	14.9	4.8	0.2	1.2	3.6	2.2	5.0	100.0
	(lower)		St. Dev.	0.4	0.1	0.2	0.2	0.1	0.1	0.2	0.1	0.2	(33)
	Pacayal 3 pumice (upper)	opx > cpx; opq	Average	68.0	0.7	14.6	4.8	0.2	1.2	3.5	2.2	4.9	100.0
14			St. Dev.	0.7	0.1	0.6	0.3	0.1	0.2	0.4	0.2	0.3	(34)
45	Pacayal 4	opx; <i>tr</i> . opq	Average	67.2	0.7	15.5	4.6	0.2	1.2	3.7	1.9	5.0	100.0
15			St. Dev.	0.8	0.1	0.7	0.6	0.1	0.5	0.4	0.2	0.3	(31)

Table 1 Analyses of volcanic glass from tephas in the Berlín-Chinameca volcanic area.

Minerals; opx: orthopyroxene, cpx: clinopyroxene, al: allanite, bi: biotite, opq: opaque minerals.

Sample number corresponds to the number with circle that indicates sampling level in fig. 3.

Chemical quantitative analysis was realized with a wave-length-dispersive electron microprobe analyzer (JEOL JXA-8800RL) in the Department of Earth and Environmental Science, Hirosaki University under the following conditions; beam current,  $3 \times 10^{-9}$  A; beam diameter,  $10 \ \mu$ m; accelerating voltage, 15 kV.

Oxide percentage was renormalized to 100%. The number with parentheses indicates quantity of analysis.

## IV. Methods of analysis

Volcanic glass and minerals were isolated from crushed pumice by supersonic washing and sieving. Mineral assemblage was investigated by polarized microscope. Chemical composition of volcanic glass was analyzed quantitatively with a wave-length-dispersive electron microprobe analyzer (JEOL JXA-8800RL) in the Department of Earth and Environmental Science, Hirosaki University. Beam currents of  $3 \times 10^{-9}$  A and beam diameters of  $10 \,\mu$ m were used at an accelerating voltage of 15 kV. Oxide percentage was renormalized to 100% and averaged with calculating standard deviation from the analysis in each sample, after removal of obvious anomalous results. For analyses, 30 or more glass shards of each sample were randomly selected, although unfortunately analysis could not reach target quantity in several sample.

#### V. Result

Mineral assemblage and chemical composition of the volcanic glass are shown in table 1. The result of chemical analysis of every glass shard is shown as a plot in Harker diagram (Fig. 4). To classify the tephras into several group and to compare with other tephras derived from other volcanic area, chemical analyses are replotted in the FeO-CaO and the FeO-K2O diagrams (Fig. 5), because the ratios of the three elements are more variable.

All tephras are mineralogically similar, because orthopyroxene and small amount of clinopyroxene and opaque minerals are commonly contained, despite the Blanca Rosa and the Jucuapa 4 pumices also bear allanite and the Pacayal 4 pumice lacks clinopyroxene.

On the other hand, the chemical composition of the eleven tephras are variable. The SiO<sub>2</sub> and the Al<sub>2</sub>O<sub>3</sub> content ranges from 65.6 to 74.1 percent and from 13.5 to 16.5, respectively, in average. The Pacayal 1 pumice is chemically unique and it is remarkably higher in SiO<sub>2</sub> content than other tephras, consequently its chemical plots are located separately from the plots of other tephras (Fig.4). The chemical plots of other tephras, however, are clustered in Harker diagram.

The Jucuapa 4 is so similar to the Blanca Rosa in chemistry that it is difficult to distinguish them chemically, although the stratigraphic positions and the eruptive ages are quite different (Table 1 & fig. 3). The Unit/Unidad-A and the Twin/Las Gemelas that are stratigraphically close are also similar in chemistry. The chemical plots of the Jucuapa 3 and the Pacayal 3 is almost separated in Harker diagram as the inconsistency of SiO<sub>2</sub> content in the range of standard deviation (Table 1). The Jucuapa 1, the Volcan/Pacayal 2 and the Pacayal 4 are assumed to be chemically intermediate between them. The Jucuapa 2 is chemically similar to the Pacayal 3 but shows larger chemical variation than any other tephras (Table 1).

Chemical plots are found to form into four clusters in the FeO-CaO and the FeO-K2O diagrams (Fig.5), so that the eleven tephras can be classified into four groups; Group I includes more than half of the tephras, which are the Jucuapa 1, the Jucuapa 2, the Jucuapa 3, the Volcan/Pacayal 2, the Pacayal 3 and the Pacayal 4 pumices. Overlapped by one another, the chemical plots of these tephras form a broad cluster in the diagrams. The chemistry of the group can be characterized by relatively higer FeO and CaO, and lower K2O than other groups; Group II is composed of the Twin/Las Gemelas and the Unit/Unidad-A pumices, whose stratigraphic positions are also close as chemistry. FeO and CaO contents are slightly lower and K2O content is slightly higher than those of group I; Group III comprises the Blanca Rosa and

the Jucuapa 4, whose chemistry is quite similar as mentioned above. FeO and CaO contents are slightly lower and K2O content is slightly higher than those of group II, although the difference of FeO content is quite small; Only the Pacayal 1 pumice that shows unique chemistry as mentioned above belongs to group IV. While FeO and CaO contents are lower than those of other groups, K2O content is not so different with that of group III.

Chemical plots of tephras derived from other volcanic areas such as Ilopango, Coatepeque and Atitlán calderas (Fig. 1) occupy a place different from those of the groups I to IV in the FeO-CaO and the FeO-K2O diagrams (Fig. 5). Four groups mentioned above are clearly separated from them in those diagrams, even the group IV closest to those among the four.

#### VI. Summary and discussion

The eleven pumice layers identified by field survey in the Berlín-Chinameca volcanic area was analyzed to clarify mineral assemblage and chemical composition of volcanic glass using polarized microscope and X-ray microprobe analyzer.

While the great difference was not recognized in mineral assemblage, the eleven pumices can be classified chemically into four groups and differentiated from tephras originating from Ilopango, Coatepeque and Atitlán calderas, in the FeO-CaO and the FeO-K2O diagrams.

Therefore, several tephras of the eleven are presumably traceable to the remote area. The Pacayal 1 pumice, only the member of group IV shows unique chemistry, so that it is easy to detect in other places outside Berlín-Chinameca volcanic area by the chemical analysis. The Blanca Rosa and the Jucuapa 4 pumices belonging to group III are chemically too similar to be distinguished. However, they are stratigraphically, or temporally, different, consequently each of them would be possible to be differentiated from each other. Although the Twin/Las Gemelas and Unit/Unidad-A pumices belonging to group II would not be distinguished chemically, nor stratigraphically, in remote area, they are still valuable because they are stratigraphically and temporally so close to be assumed to form almost an isochronous surface. Chemistry of other tephras of group I is so similar to utilize them as a time marker, then several additional data, other than chemical composition of volcanic glass, are necessary; the Jucuapa 1 and the Jucuapa 2 pumices are stratigraphically close to the Chinameca 2 ash and the Los Chocoyos ash, respectively, which are uniquely identifiable by their chemistry; the Pacayal 4 pumice is mineralogically different from other tephra of the group I; between the Jucuapa 3 and the Pacayal 3 pumices, there are chemical and temporal differences.

Although several magma chambers located several position are assumed to explain the origin of the four chemical groups of tephra, it is not clarified which crater ejected each tephra. A summit caldera of Berlín-Tecapa Volcano and a lager crater at the top of Chinameca-Pacayal Volcano called "Laguna Seca El Pacayal" are recognizable topographically, so that they are candidates for a vent which ejected pumice fall. However, there may be any invisible crater that was covered by volcanic activity succeeding the crater formation. Further field survey is necessary to locate the vents that ejected the eleven tephras and to clarify how the four chemical groups of the tephras correspond to the vents and the volcanic history.

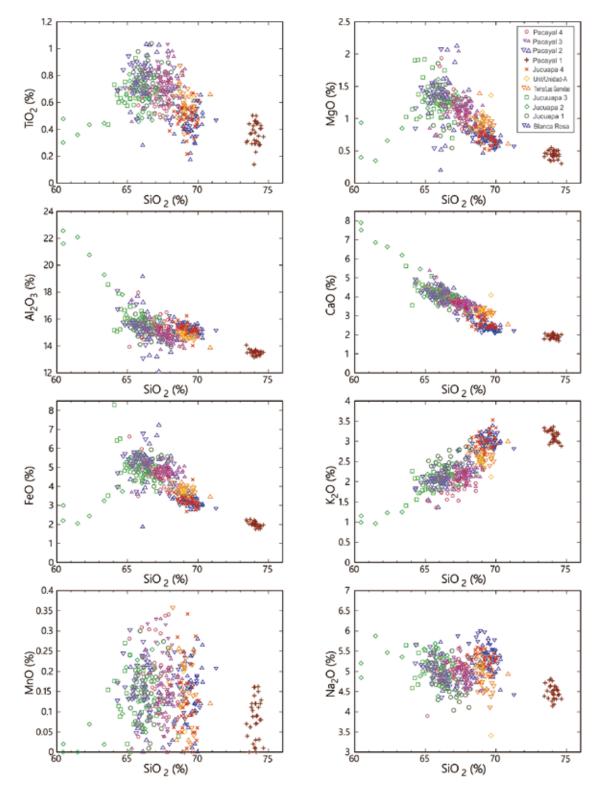


Fig. 4 Chemical composition of volcanic glass from the eleven tephras in study area See text and table 1 for analytical conditions. Sampling level is shown in fig. 3. The pair of triangle and reverse triangle show each chemical composition of volcanic glass from the upper unit and the lower unit, respectively, of the same tephra.

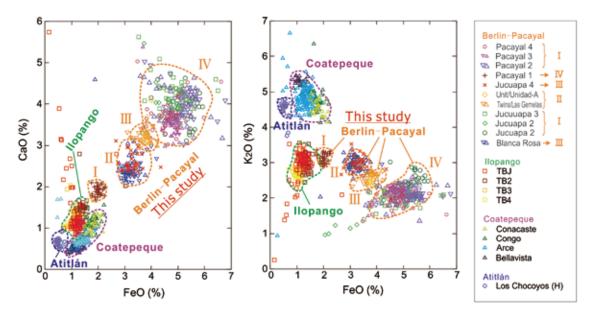


Fig. 5 Comparison of chemical composition of volcanic glass from tephras in the FeO-CaO and the FeO-K<sub>2</sub>O diagrams.

See text for classification of tephras into the four groups of I to IV. The chemistry of tephras from Atitlán Caldera, Coatepeque Caldera and Ilopango Caldera are also shown for comparison (Kitamura, 2006; Kitamura, 2016; Kitamura, 2017; Kitamura, 2018).

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