Reconnaissance of Modal Proportions and Chemical Compositions of Heavy Minerals in Tuffs from the Boso Peninsula, Central Japan

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Abstract Modal proportions of heavy minerals in a tuff are different in fractions divided by grain size. Heavy minerals such as zircon and magnetite are strongly enriched in the fine-grained fractions. The proportion changes within a tuff layer even if it consists of the same mineral assemblage. Both chemical compositions and modal proportions of minerals in most of the tuffs depend more or less on grain size, due to the complex mixing of different volcanic fragments at eruption or at depositional stage. Only in a few tuffs, mineral composition and proportion are homogeneous within a layer and are not significantly affected by grain size.

There are many characteristic tuffs such as cummingtonite tuff and Fe-rich orthopyroxene-bearing tuff in the Tertiary-Quaternary sequence from the Boso Peninsula. Although simple correlation by mineral proportion may not be available, chemical compositions of minerals can be used as a correlation factor if they are specific. Otherwise it is better to correlate tuffs referring to modal proportion, mineral composition and lithology.

Key words: tuff, modal proportion, mineral composition, Boso Peninsula.

Introduction

Volcanic eruptions have occurred almost continuously in Quaternary in the Japanese Islands. Hence, volcanic ash layer has been commonly used as a key bed in a sedimentary sequence. Tephrochronology studies in Japan have mostly concentrated on the many widespread tephras. Most of the Quaternary key layers covering wide area in the Japanese Islands were summarized in detail by Machida and Arai (1992). Correlations of the tuffs were made mainly by the refractive index and shape of glass in addition to lithological work. Chemical composition of glass in a tuff was also used as a correlation factor. The analysis of glass was made by many methods: wavelength spectrometer (Furuta *et al.*, 1986), energy dispersive spectrometer (Tokui, 1989) and ICP (Kikkawa *et al.*, 1989). On the other hand, chemical composition of mineral has been rarely used as the factor in the study of tuff and ash layer. This is probably due to that volcanic glass is brought to a distance far from its eruption center and is observed in a wide area. Distribution of mineral depends on its size and

density and is restricted in contrast to that of glass. The other reason may be that glass is chemically homogeneous, whereas minerals are more or less heterogeneous.

In the Boso Peninsula, more than several hundreds tuff layers are observed in the Tertiary to Quaternary sequence. Geological map of the peninsula was proceeded referring many key tuff layers (Mitsunashi *et al.*, 1959, 1979). In this paper, we analyzed modal proportions and chemical compositions of heavy minerals to elucidate grain size effect of their parameters and to examine chemical variation of mineral in a volcanic fragment and in a tuff layer. This is reconnaissance to find out factors which are available for correlation of tuff in the sequence.

Analytical Method

Most of the tuffs from the lower part of the Kazusa Group in the Boso Peninsula are poorly consolidated and weakly cemented. They were disaggregated by boiling in water with 5% of hydrogen peroxide. Clay minerals and fine-grained particles were removed by several times of washing. The samples were subsequently dried and sieved into four fractions: A (0.5–0.25 mm), B (0.25–0.125 mm), C (0.125–0.063 mm), D (<0.063 mm). Fragments coarser than fraction A are small in mount in comparison with the other fractions. They are composed mainly of accidental volcanic fragment or undisaggregated mass of volcanic glass. Some well solidified tuffs were softly crushed in a stainless steel vessel with the same subsequent procedures as that mentioned above. Tuff is composed mainly of essential material with subordinate or trace mounts of accessary and accidental blocks. As most of the tuffs collected are too fine-grained to separate these materials, each fraction includes various minerals or glasses in origin.

Heavy minerals were separated from the fractions by mixing with methylene iodide. The specific gravity of the liquid was reduced to 2.82 to recover composite grain and aggregate of heavy mineral and glass. Micaceous and carbonate minerals are present in both heavy and light fractions. Hence, these minerals except for biotite were not include in the following mineral count. Pyrite and goethite are common in some tuffs. Most of them are considered to be secondary formed as an authigenic mineral or replacing magnetite. They are not included in the mineral proportion.

Both the heavy and light fractions were cemented in epoxy resin and prepared for modal and chemical analyses. Most of the minerals were identified by means of profiles obtained by energy dispersive spectrometer (EDS, LINK Systems). Orthopyroxene and cummingtonite were analyzed by wave-length spectrometer (JXA 8800 of JEOL) and their modal proportions were recalculated on the basis of the analytical results.

Among 100 tuffs studied, several thick tuff layers are described and discussed in detail here. They are 'Kd8', 'Kd38', 'Kd38CM', 'Kd38YK' and 'Kd39' from the lower part of the Kazusa Group in the Boso Peninsula, and 'Tokyo Pumice' bed.

Kd38 were originally denoted by Mitsunashi *et al.* (1959). Its locality is not certain now because of abundant tuff layers in the area. NHMIC (1990) and Yoshikawa (1996) described the different outcrops for Kd38. Characters CM and YK after the Kd38 denote the tuffs from the Kurotaki area described by NHMIC (1990) and by Yoshikawa (1996), respectively. Kd38 without any character shows a sample collected along the Yoro river and its locality was described by NHMIC (1990). Kd38 tuff occurs near the boundary between Tertiary and Quaternary (Takayama *et al.*, 1995). The tuffs from the Boso Peninsula are submarine deposits. On the other hand, the volcanic ash collected from the Tokyo Pumice bed was deposited on land.

Heavy and Light Minerals

In the heavy fractions, more than 12 minerals were observed from the tuffs. Orthopyroxene and clinopyroxene in addition to magnetite and ilmenite are ubiquitous (Table 1). Hornblende and cummingtonite are one of major phases in some tuffs. Allanite is common phase in one sample. Although both cummingtonite and allanite are common in some tuffs from the Niigata Prefecture, central Japan (Kurokawa *et al.*, 1983), they have not been reported from the Boso Peninsula (*e.g.* Satoguchi, 1995). They were euhedral and were surrounded by clear glass as well as pyroxenes and hornblende (Fig. 1 A), showing that they were formed as a phenocryst. Zircon and apatite were probably magmatic phase formed at the same time as the clear glass. As Watanabe and Danhara (1996) described zircon with older age than the sedimentary age, some are probable to be accessary or accidental materials. Kurokawa *et al.* (1983) described garnet-rich tuff from the Niigata Prefecture. As garnet is scarce in mount in the tuff from the Boso Peninsula, it is difficult to conclude whether it is magmatic or exotic in origin. Epidote and titanite are also too small in mount to discuss their mineral proportions and compositions here.

Light fraction of tuff is composed mostly of glass with small amounts of minerals. Plagioclase is common only in coarse-grained tuff. It is always the most abundant among the minerals in the light fractions (Table 1). Quartz, albite and K-feldspar are trace in amount, occurring mostly as an aggregate without any association of glass (Fig. 1B). They are clearly accidental block.

Modal Proportion of Heavy Minerals

Cross lamina, graded bedding and fine-banded structure, common in marine deposit, are observed in a thick tuff layer from the Boso Peninsula. Several samples were collected in such a thick layer to study variation of modal proportion and mineral composition within a layer. Mineral species and number of each mineral counted under EDS profile are shown in Table 1.

All the samples contain orthopyroxene. Four fractions divided by grain size in a

Table 1. Mineral species and number of mineral grain observed in the heavy and light fractions in tuffs from the Bosso Peninsula.

Sample	1	Кд38 1	88 upper		d38 ;	Kd38 middle		Kd38 lower	lower		Kd38	Kd38CM upper	ıpper		Kd38CM middle	CM n	niddle	4.	Kd3	8CM	Kd38CM lower	_	Kd8	Kd8 upper	i.
size*	\ \	A* B*	*	<		В	C	A B	C	Y	В		C D	V	A B		С	, d	A	В	C	D	V	В	C
Heavy mineral																									
**xdo	∞	81 80	82		75 5	99	31 2	20 3		2 57		101	91 5	56 107	7 111		74	55	95	11	63	29	83	93	68
cnm	7	0 30	12		32 4		53 9	94 99		09														5	5
cpx	7	3 27			6	6	14 3	36 5	10	1 34		68 3	34 11		57 3	37 2	27	21	46	25	10	3	53	25	16
hb	3	0 26	10		30 2	28	22 1	12 9	(7	4	7	∞	9	3	3 1	10	5	9	2	7	3	39	62	75
biotite																									
mt	25	5 42	108		42 7	79 1	191	2 89	9 178		4	11 4	42 133		11 4	43 8	80 18	182	6	31	75 2	205	\mathcal{C}	∞	30
ilm		6 14	34		16 2	25	51 1	10 47	7 44	4		_	9 3	30		5 2	22	Ξ		4	40	32	_	9	18
zircon							_			_			11	_			2	2			9	7			
apatite			. 4	2	_	_	2									_	_	_		-		4			
epidote		_			2	_		4	61											-	7		7	_	2
garnet													_				_								
titanite						_							_												
Light mineral																									
quartz		5 2				_	_	6 2	C 1	3	1	7	7 1	14		_		7		9	∞	14	4	7	3
Ca-pl	6	94 97	66	9 100		66	6 66	94 97	7 97	7 36		46 4	44 5	50 7	77 (66 4	40		100	80	46		63	93	26
albite				_								7		7			_				_	3	_	-	
K-feld		1										7	6	9			4	2		9	∞	18			

* Fraction size: A (0.5–0.25 mm), B (0.25–0.125), C (0.125–0.063), D (<0.063)

^{**} Mineral abbreviations: opx=orthopyroxene, cum=cummingtonite, cpx=clinopyroxene, hb=Ca-rich amphibole, mt=magnetite, ilm=ilmenite, Capl=calcic plagioclase (An>10), K-feld=K-feldspar.

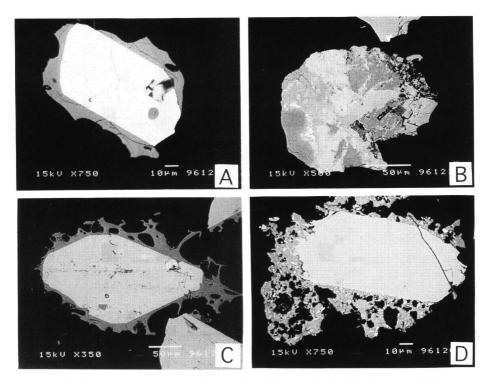


Fig. 1. Back-scattered photographs of minerals and fragments. A: allanite surrounded by clear glass. B: aggregate consisting mainly of quartz, K-feldspar and albite. C: Orthopyroxene surrounded by clear glass. D: orthopyroxene surrounded by devitrified glass.

sample have different modal proportion. Relative proportions of minerals against orthopyroxene are presented in Figs. 2 and 3. Striking feature is that magnetite, ilmenite and zircon which are heavier than the other heavy minerals, are usually enriched in fractions of small grain size. Kurokawa *et al.* (1983) reported the enrichments of magnetite and zircon in the fine-grained fraction and concluded that their original sizes crystallized from a magma were as fine-grained as that of the fraction. As the other reason, it may be explained by that coarse-grained magnetite and zircon can not brought far from the eruption center compared with less heavy minerals such as pyroxenes and amphiboles.

Orthopyroxene is similar in density with clinopyroxene and amphiboles. Their relative abundances, however, are also different from fraction to fraction and they have not always regular relationships with the grain size (Fig. 2). These features are not explained simply as grain size effect as do magnetite and zircon. On the basis of thin section observation of volcanic rocks, it seems that grain sizes of phenocrysts of pyroxenes are not strongly variable. Unsteady relation of mineral proportion will be explained by different distribution of original grain size of mineral as suggested by

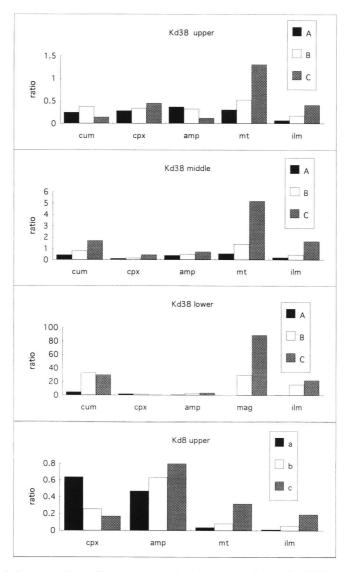


Fig. 2. Relative proportions of heavy minerals in the coarse-grained tuffs, Kd38 and Kd8, from the Boso Peninsula. Vertical axis is a ratio of modal proportion of each mineral divided by orthopyroxene. Grain size A: 0.5–0.25 mm, B: 0.25–0.125. C: 0.125–0.063, D: <0.063. Mineral abbreviations: cum=cummingtonite,.cpx=clinopyroxene, amp=Ca-rich amphibole, mt=magnetite, ilm=ilmenite.

Kurokawa *et al.* (1983). As the tuffs include accessary and accidental blocks, the modal proportion in a sample should be more complex than that we expected. Grain size distribution is complex and modal proportions were affected by the distance

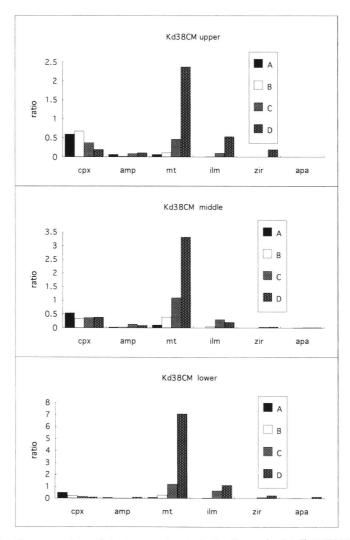


Fig. 3. Relative proportions of the heavy minerals in the fine-grained tuff, Kd38CM, from the Boso Peninsula. Explanations of axes and legend are shown in Fig. 2. zir=zircon, apa=apatite.

from the eruption center. Hence, it will be hard to use modal proportion as a correlation factor of each tuff. It may be useful only if the grain size is fixed and the tuffs in a narrow region are treated.

Variations of modal proportions within a thick tuff layer are shown in Fig. 4. In Kd38 tuff, cummingtonite is predominant in its lower part and small in its upper part. It is not responsible for gravity settling because of that the fractions with the same grain size are compared and all the minerals presented have similar density each



Fig. 4. Variations of modal proportions among pyroxenes and amphiboles in thick tuff layers. F. S.: grain size of fraction. U: upper part, L: lower part.

other. As cross lamina develops in the layer, the variation is probably due to the mixing of two tuffs during the sedimentation rather than successive eruption of magma with different modal proportions. Variations of modal proportions within a layer are recognized in both the Kd38CM and KD38YK (Fig. 4) where the chemical compositions of orthopyroxenes are also variable in each fraction as discussed later. The variation in a layer is explained by mixing of various volcanic fragments. Relatively steady mineral proportion is found in Kd39 tuff layer where a thin hornblende-bearing layer is intercalated in its upper part (Fig. 4).

These results show that a few samples in a thick layer are not enough for correlation of tuff by mineral proportions.

Compositional Variation of Orthopyroxene

Orthopyroxene is usually present in the tuffs from the Tertiary to Quaternary se-

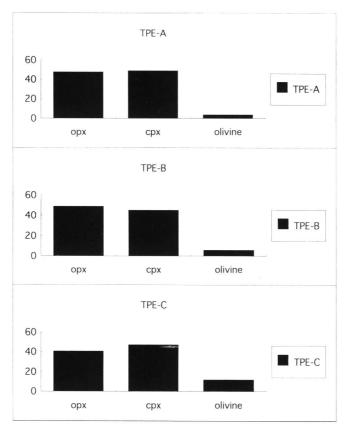


Fig. 5. Variations of modal proportions of pyroxenes and olivine in the Tokyo Pumice bed. Grain sizes, A, B and C, are in Fig. 2. Vertical axes are relative proportion (%) among the minerals.

quence from the Kanto Province. It is present mostly as an euhedral grain in a heavy fraction and is less weathered material than glass. Plagioclase and clinopyroxene are also major phases among the minerals in the tuffs. The former displays usually strong oscillatory zoning and the latter has more complex chemistry than orthopyroxene. Hence, they were not targeted in this study. To determine variation of orthopyroxene composition in a grain, detailed work was carried out in the Tokyo Pumice bed which contains pyroxenes, olivine, magnetite and ilmenite in the heavy fraction. Modal proportions of minerals in the pumice bed are shown in Fig. 5. Olivine, heavier than pyroxenes, is enriched in a fine-grained fraction as do the magnetite and zircon in the other tuffs mentioned above.

Compositional variations of core and rim of orthopyroxene are presented in Fig. 6. The core in this analysis is a center of randomly cut grain, i.e. apparent core. The rim is not always associated with glass. Peak of the core's data is 69 in X_{Me} , $100 \times$

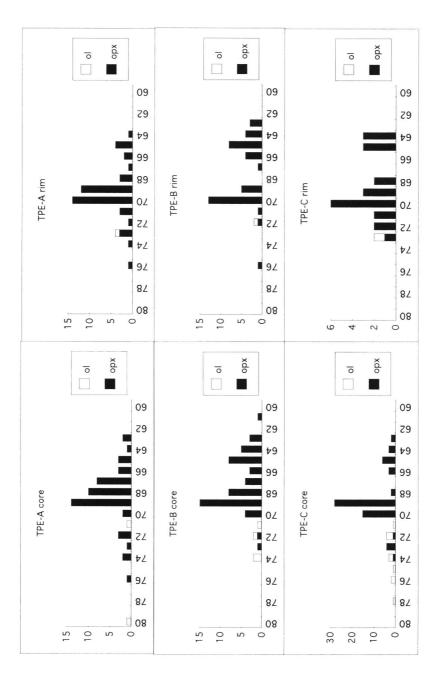


Fig. 6. Chemical compositions of orthopyroxene and olivine in each fractions of the Tokyo Pumice bed. Vertical axis is a number of grain analyzed. Horizontal axis is X_{Mg} , $100 \times Mg/(Mg + Fe)$, in mineral.

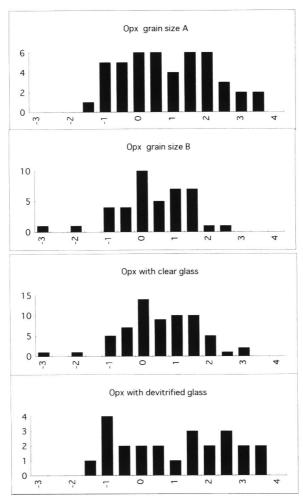


Fig. 7. Difference of X_{Mg} between core and rim in orthopyroxene grain. Upper part shows effect of grain size, whereas lower part is divided by a type of surrounding glass. Vertical axis is number of grain analyzed. Horizontal axis is difference of X_{Mg} between core and rim. Positive side indicates reverse zoning.

Mg/(Mg+Fe), in all fractions, whereas it is 70 in rim. The difference of X_{Mg} in orthopyroxene between core and rim is studied in detail in fractions A and B. It depends on the grain size as shown in Fig. 7. Coarse-grained orthopyroxene has a wider variation. The range is from -1.5 to 3.5 in X_{Mg} , whereas in the fine-grained size the difference is from -1.5 to 2.0. Composition at the rim is mostly more magnesian than the core's one; i.e. reverse zoning.

Orthopyroxene has been surrounded by two types of glasses, clear and devitri-

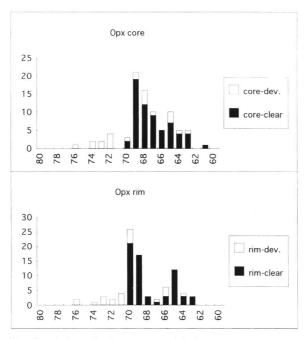


Fig. 8. Compositional variation of orthopyroxene with clear or devitrified glass. Explanations of axes are in Fig. 6.

fied (Fig. 1 C, D). Wider variation of difference of X_{Mg} is found in orthopyroxene with devitrified glass. In spite of these differences, it is noteworthy that both orthopyroxenes have reverse zoning and difference between core and rim is less than 2.0 in the fine-grained fraction B and in the group with clear grass.

Composition of orthopyroxene with glass is summarized in Fig. 8. Orthopyroxene with X_{Mg} more than 70 is always associated with devitrified glass. Referring that olivine compositions are more than 70 (Fig. 6), the fragment containing olivine and Mg-rich orthopyroxene is considered to be accidental. Bimodal distribution is observed in orthopyroxene with clear glass (Fig. 8). One is orthopyroxene with X_{Mg} around 70 and the other one around 65. Such a bimodal feature is ambiguous in the core's data. Even in the random analyses of core and rim (Fig. 6), bimodal nature is recognized in the fractions B and C. It is obscured in the coarse-grained fraction A. At least three groups of orthopyroxene grains are recognized in the sample. This is due to mixture of essential, accessary and accidental fragments. It is reasonable to conclude that the most common orthopyroxene, with X_{Mg} around 70, was derived from the essential fragment. The other orthopyroxene around 65 may be accessary. As an alternative idea, it is probable that such Fe-rich pyroxene was derived also as an essential fragment from a mixed magma which is not uncommon in volcanic rocks.

If we apply the orthopyroxene composition as a correlation factor for tuff, the most selected position of analysis will be rim of the mineral with clear glass. However, the mineral is not always surrounded by the clear glass in the tuffs from the Boso Peninsula. And also it is hard for all the grains to be identified quickly whether which type of glass is associated with. Difference between core and rim is less than 2 in X_{Mg} in a fine-grained fraction (Fig. 7). Furthermore, bimodal distribution observed in the group with clear glass is also recognized in the data of the core's composition in the fine-grained fractions B and C (Fig. 6). Hence, we tentatively analyze a central part of the randomly cut grain in a fine-grained fraction and investigate whether the data are useful as a correlation factor for the tuffs from the Boso Peninsula.

Tuffs from the Boso Peninsula

Among 100 tuffs studied, two types of thick tuff layers are described. One is Kd39 tuff. It is homogeneous tuff in modal proportion and chemical composition of orthopyroxene. The other tuffs are Kd38CM and Kd38YK, variable in the parameters. Kd39 was collected from a tributary of the Hirasawa river, running at eastern side of the Yoro river. Its locality and lithology were described by NHMIC (1990). Kd38CM and Kd38YK were collected along a road and at a river bed from the Kurotaki area, respectively, and are different from Kd38, cummingtonite-bearing tuff, in the Yoro river. Kd38CM is about 100 m apart from Kd38YK, but the former is 100 cm in thickness whereas the latter 40 cm.

Kd39 tuff is roughly similar in modal proportion within a layer (Fig. 4). Even though it includes a hornblende-bearing thin layer at the upper part and different sizes of fractions were used for analyses, orthopyroxene is homogeneous throughout the layer (Fig. 9). Range of $X_{\rm Mg}$ ratio is from 54 to 56, narrower than the differences between core and rim in orthopyroxene in the fraction B from the Tokyo Pumice bed. It indicates that the mineral composition is a useful correlation factor for such a homogeneous tuff.

On the other hand, X_{Mg} of Kd38CM is different from fraction to fraction and is variable in each fraction in addition to variation of the modal proportion within a layer (Fig. 4). Composition of orthopyroxene from the lower part of the Kd38CM tuff layer is shown in Fig. 10. Orthopyroxenes in the coarse-grained fractions A and B are plotted in Mg-rich side, whereas the fine-grained fractions consist of Fe-rich orthopyroxenes with X_{Mg} around 58 and 26 with a small amount of Mg-rich one. In spite of such differences among the fractions, it can be concluded that the tuff has trimodal proportion in the pyroxene and includes three different fragments in origin. Peaks of X_{Mg} from the three groups are 68, 55 and 25. Fe-rich pyroxene is not observed in the most coarse-grained fraction. If we select only a specific fraction, different conclusions will be deduced as a origin for orthopyroxene.

Orthopyroxene in the Kd38YK tuff is presented at the bottom of Fig. 10 com-

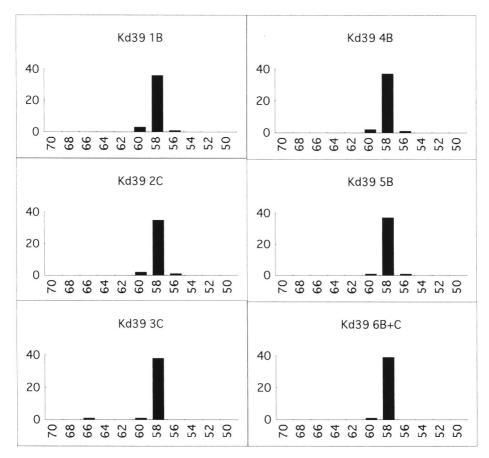


Fig. 9. Chemical compositions of orthopyroxenes in a thick tuff layer, Kd39, from the Boso Peninsula. Six samples were collected successively in the layer. Kd39-1 is from the uppermost part of the layer and Kd39-6 is from its bottom. Modal proportions of pyroxenes and amphibole in the layer are presented in Fig. 4. Explanations of axes are in Fig. 6.

paring with those from the Kd38CM. Fraction B from the Kd38YK has trimodal distribution similar to those in the fractions C and D in the Kd38CM. Even though thickness of the tuffs and analyzed fractions are different between them. It is clear that Kd38CM is a extension of the Kd38YK because of paucity of Fe-rich pyroxenes and trimodal distribution in the tuffs from the Boso Peninsula.

Summary

Tuff has been used as a key bed in a sequence of the Boso Peninsula where numerous tuff layers are intercalated. Modal proportion is one of the indicators for the

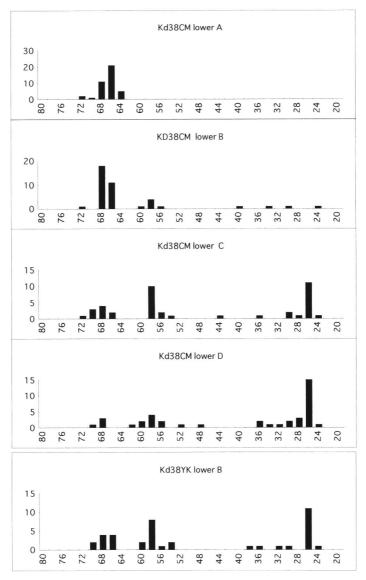


Fig. 10. Compositional variations of orthopyroxenes in lower parts of thick tuffs, Kd38CM and Kd38YK, from the Boso Peninsula, showing strong differences by grain size. Explanations of axes are in Fig. 6.

correlations of the tuff layers, but it depends largely on the fraction size (Figs. 2, 3). Especially, proportions of heavy minerals such as magnetite and zircon depend strongly on the grain size of the fraction. It seems apparently that relative proportions among the minerals with similar density can be used as a practical factor. However,

the proportions are also dependent on grain size even if the minerals were selected (Figs. 2, 5). It may be explained by that grain size of a mineral formed as a phenocryst is different from that of the other phenocryst. As far as the mineral proportions is concerned, the relative proportions of selected minerals may be only useful in the narrow area.

In the Boso Peninsula, cummingtonite, biotite and allanite are specific minerals in some tuffs. They are available as a correlation of a tuff if lithology and chemical composition are referred together. Variation of the modal proportion within a tuff layer is often recognized (Fig. 4). It will be due to sedimentary processes such as graded bedding, cross lamina and reworking of tuff. Many sampling is required in such a thick layer when modal proportion is used only as a correlation.

The tuffs contain accidental and accessary fragments in addition to the essential product. It is difficult to separate these blocks in a tuff layer. Many tuffs are complex modal proportions and chemical compositions of minerals because of the mixtures of the three component. In addition, mixed magma is not ignored in the volcanic rocks. These components also induce complex mineral assemblage, modal proportion and mineral composition.

Composition of orthopyroxene is complex as well as the modal proportion. Rim's composition of orthopyroxene with clear glass is characteristics and probably represents a essential fragment of the tuff (Fig. 8). Orthopyroxene grain is not always associated with the clear glass and it is hard to distinguish the grains quickly whether they are associated with clear glass derived mainly from essential fragment or devitrified glass probably from accidental or accessary ones. It is, however, fortunate that composition of apparent core of orthopyroxene is not so variable from that in its rim. The difference is mostly less than 2 in X_{Mg} in the fine-grained fraction (Fig. 7). Data of the apparent cores show that orthopyroxenes in some tuffs are homogeneous, but they are variable in X_{Mg} in most of the tuffs. Even if the variation is recognized, composition at the apparent core is a useful factor to distinguish or classify tuffs if it is characteristic as found in the Kd38CM and Kd38YK (Fig. 10).

Acknowledgement

The authors are very grateful to Mrs. M. Shigeoka for her help in modal and chemical analyses and heavy mineral separations throughout this study.

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