

Behavior of fluorine and chlorine in volcanic ash of Sakurajima volcano, Japan in the sequence of its eruptive activity

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At Sakurajima volcano, strombolian eruptions forerun vulcanian explosions, and vulcanian explosions are often followed by continuous ash eruptions. Change in the mode of its eruptive activity is drastic and release of volatiles from magma corresponding to its eruptive activity is examined by determination of fluorine and chlorine in volcanic ash. The F contents of all the ash samples are markedly higher than the arithmetic mean value of Japanese volcanic rocks (ca. 300 $\mu\text{g/g}$). Further, the water-soluble Cl contents of almost all the ash samples are also extremely higher than those of Japanese volcanic rocks (less than 50 $\mu\text{g/g}$). This is attributed to fixation of F and Cl in hot gas onto the volcanic ash particles in the crater and/or eruption plumes. The differences in those contents among the “strombolian eruption”-, “vulcanian explosion”- and “continuous ash eruption” groups are significant, which implies that hot gas rich in F and Cl are issued during strombolian eruptions, while those halogens are less concentrated in hot gas after strombolian eruptions. The water-insoluble Cl content of the “strombolian eruption” group is significantly higher than those of the other groups. This result implies that Cl and the other volatiles are intensely released from magma during the doming period before vulcanian eruptions. Yet, it is inferred that continuous ash eruption is the final phase of vulcanian one.

Key words: fluorine, chlorine, strombolian eruption, vulcanian explosion, Sakurajima.

1. Introduction

Sakurajima is an andesitic stratovolcano and one of the most active volcanoes in the world. It lies about 5 km east of the city of Kagoshima at the southern end of Kyushu, Japan (Fig. 1). Recent eruptive phase has been sustained at the summit crater of the central cone, “Minamidake” since October 1955. Typical vulcanian explosions have occurred repeatedly, yet strombolian and continuous ash eruptions have been frequently observed. Strombolian eruptions forerun vulcanian explosions, and vulcanian explosions are often followed by continuous ash eruptions, which is the ordinary sequence of the eruptive activity of Sakurajima volcano.

Volcanic earthquakes observed at this volcano are classified as A-type, B-type, and explosion earthquakes. A-type earthquakes have clear P- and S-phases similar to ordinary tectonic earthquakes. While B-type earthquakes are micro-scale and characterized by the absence of clear S-phases. Explosion earthquakes are observed at the onset of vulcanian explosions. A-type earthquakes often precede swarms of B-type earthquakes, and the swarms are usually followed by explosive activity (Kamo, 1978). Spectrum analysis discloses that A-type earthquakes occur in brittle regions, whereas B-type earthquakes swarm in ductile or molten regions (Ishihara and Iguchi, 1989).

Geophysical observation revealed distribution of

hypocenters of volcanic earthquakes at this volcano (Kamo, 1978; Ishihara, 1990; Iguchi, 1994). Hypocenters of explosion earthquakes are concentrated inside a cylindrical chamber with a radius of 200 m, at depths from 1 to 3 km beneath the summit crater. Those of B-type earthquakes are also concentrated inside the same chamber. Contrastively, tectonic-like A-type earthquakes occur around the chamber at depths from 1 to 4 km beneath the summit crater. Ishihara (1990) and Iguchi (1994) understood that the cylindrical chamber was a magma conduit, which connected the summit crater and a shallow magma reservoir, and that B-type and explosion earthquakes occurred at ductile regions inside the conduit, whereas A-type earthquakes occurred at brittle regions around the conduit.

Further, Ishihara and Iguchi (1989) subclassified B-type earthquakes into high (BH), and low frequency (BL) types, and examined the relationship between seismic activity and ground deformation. Hypocenters of BH-type earthquakes are usually distributed in the region deeper than those of BL-type earthquakes. Yet, BH-type earthquake swarm is associated with slow inflation of the summit without significant eruptive activity, whereas BL-type earthquake swarms during rapid deflation of the summit with strombolian eruptions. They inferred that BH-type earthquake swarms were caused by magma intrusion into the conduit, whereas BL-type earthquakes were related to degassing from ascending magma. Dominant frequencies of BH-type, BL-type, and explosion earthquakes are different from each other although hypocenters of these earthquakes distribute inside

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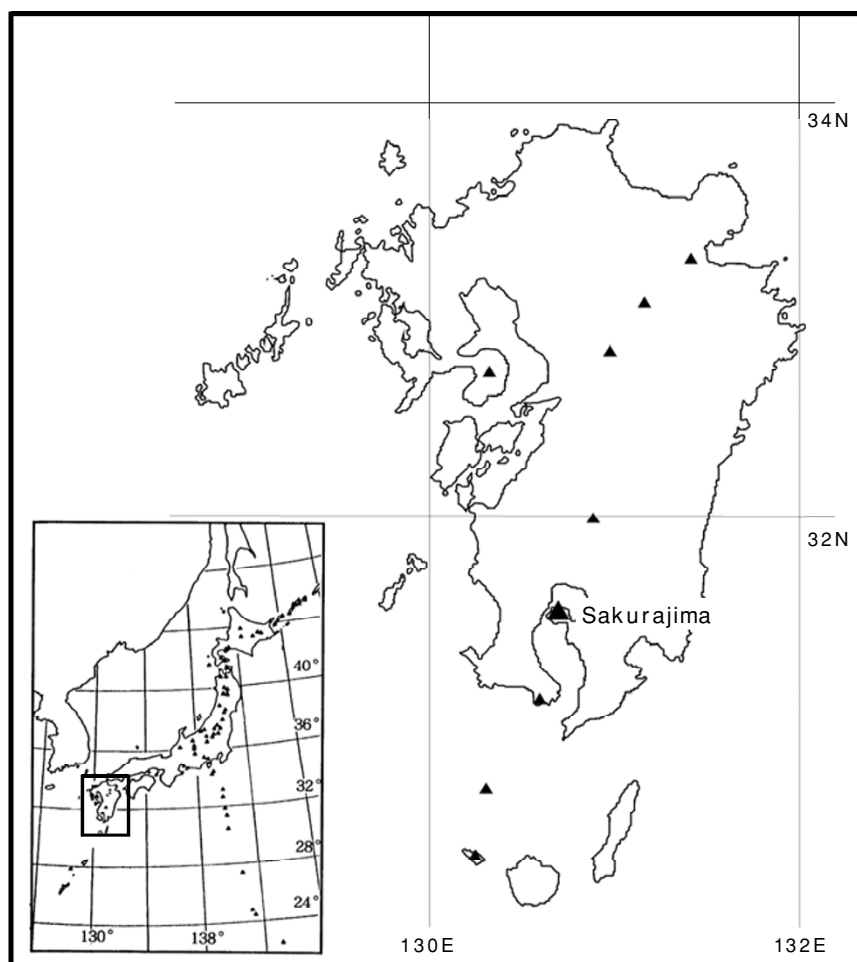


Fig. 1. Map showing location of Sakurajima volcano, southwest Kyushu, Japan.

the cylindrical chamber beneath the crater, which is attributed to difference in source processes affected by the state of the magma conduit including gas phase (Iguchi, 1994).

Magmatic volatiles are chemical substances dissolved in magma under pressure. Decompression of magma by moving toward Earth's surface causes exsolution of volatiles that become the driving force of explosive eruptions. Moreover, release of volatiles from magma changes its viscosity and density drastically, and these can influence violence of a volcanic eruption. Thus, examination of the behavior of volatiles will help us better understand eruptive activity of volcanoes.

Hydrogen fluoride (HF) and hydrogen chloride (HCl) are major constituents of high temperature volcanic gases. Moreover, F and Cl are the second-most abundant volatile components after water in volcanic rocks. Yoshida (1963) heated powdered rocks in nitrogen gas flow at temperatures from 400°C to 1200°C to examine volatility of fluorine and chlorine compounds from silicates. This experiment showed that F was less volatile than Cl. Yoshida (1975, 1990) performed further experiments for interaction between volcanic gases and rocks. These experiments revealed that F in gas phase was fixed onto rocks more easily than Cl, and that F and Cl were fractionated through volcanic emanation. Hence, F and Cl contents of volcanic

products could be good indicators of their behavior in volcanic processes. In this study, we determine F and Cl contents of volcanic ash issued by several types of eruptions of Sakurajima, and discuss release of volatiles from magma in the sequence of its eruptive activity.

2. Samples

The analyzed ash samples are the pristine products emitted by strombolian eruptions, vulcanian explosions and continuous ash eruptions from 1975 to 2002. These samples were collected at the foot of the volcano immediately after emission without contamination of soil and exposure to rain. All the ash samples are kept in plastic bags and cases. The ash samples of the strombolian eruptions are finer than 250 μm . While those of the other eruption types consist of particles finer than 250 μm (70%) and those from 250 μm to 500 μm (30%).

3. Analytical Procedure

Fluorine and chlorine that are not exsolved from volcanic ash are tightly sealed within ash particles in water-insoluble forms. While HF and HCl in volcanic gas react with volcanic ash in an eruption plume, certain proportions of F and Cl are fixed onto the surfaces of the ash particles in water-soluble forms. Water-soluble Cl compounds are stabilized on the surface of the ash, whereas F compounds consider-

Table 1(a). Contents (in $\mu\text{g/g}$) of F and Cl of the ash issued by strombolian eruptions.

Date	F	s-Cl	ins-Cl
1975/3/12 ^{a)}	1140	1840	350
1975/6/22	790	1640	450
1985/4/13	1050	1780	430
1985/7/29 ^{b)}	890	2080	370
a.m. ¹⁾	967.5	1835.0	400.0
s.d. ²⁾	157.14	183.58	47.61
g.m. ³⁾	957.8	1823.3	397.9

^{a)} water-soluble Na: 378 $\mu\text{g/g}$ and water-soluble K: 96.3 $\mu\text{g/g}$

^{b)} water-soluble Na: 384 $\mu\text{g/g}$ and water-soluble K: 85.8 $\mu\text{g/g}$

¹⁾ Arithmetic mean

²⁾ Standard deviation

³⁾ Geometric mean

ably become water-insoluble with the lapse of time due to its high reactivity with silicates (e.g. Kamada, 1980). In the present case, the oldest samples were collected in the middle of 1970's, and F compounds on the ash particles are probably water-insoluble. Hence, total F, water-soluble Cl, and water-insoluble Cl contents are determined.

Fluorine is determined by the method of Tsuchiya *et al.* (1985). A powdered sample is weighed correctly and fused with Na_2O_2 in a nickel crucible. The cake is dissolved in pure water and the resulting suspension is centrifuged. Fluorine in the solution is distilled as trimethylfluorosilane and the fluoride concentration in the distillate is determined with an ion selective electrode.

Water-soluble chlorine is extracted by immersing a powdered sample overnight in pure water and the powder is centrifuged. Chloride in the solution is determined by mercuric thiocyanate-spectrophotometry (Tomonari, 1962). Water-insoluble Cl content is usually calculated as the difference between total Cl and water-soluble Cl content. In this case, water-soluble Cl contents of the ash samples are very high, which will be shown later. For the determination of water-insoluble Cl, powdered samples are pretreated for removal of water-soluble Cl by washing with pure water. Total Cl is determined by the method of Iwasaki *et al.* (1955) as improved by Ozawa (Yoshida *et al.*, 1994; Oshima and Yoshida, 2005). A pretreated sample is weighed correctly and fused with Na_2CO_3 in a platinum crucible. The cake is dissolved in pure water and the resulting suspension is centrifuged. Chloride in the solution is determined by mercuric thiocyanate-spectrophotometry. Water-soluble Cl contents of the pretreated samples are also determined and water-insoluble Cl contents are calculated. The errors in the determination of both F and Cl are $\pm 10 \mu\text{g/g}$.

Sakurajima is a maritime volcano and sea salt contamination may increase water-soluble Cl contents of the ash samples. Thus, water-soluble Na and K of some ash samples having particularly high water-soluble Cl contents are also determined by atomic absorption spectrometry for examination of contamination of sea salt.

Table 1(b). Contents (in $\mu\text{g/g}$) of F and Cl of the ash issued by vulcanian explosions.

Date	F	s-Cl	ins-Cl
1975/3/19	600	340	250
1977/8/28	670	1010	310
1980/4/6	470	60	230
1980/5/5	970	1130	250
1980/7/18 ^{c)}	1520	2800	260
1981/11/22	700	590	230
1982/8/21	480	750	230
1983/5/22	960	2120	320
1983/6/22	680	2140	290
1983/8/22	560	500	180
1984/6/4	810	1150	280
1984/7/21 ^{d)}	1270	2830	220
1985/9/4	390	200	200
1999/12/10	520	140	280
2000/10/7	1440	1930	300
2002/11/13	570	490	270
a.m. ¹⁾	788.1	1136.3	256.3
s.d. ²⁾	351.27	937.72	39.81
g.m. ³⁾	725.3	723.5	253.2

^{c)} water-soluble Na: 543 $\mu\text{g/g}$ and water-soluble K: 153 $\mu\text{g/g}$

^{d)} water-soluble Na: 1010 $\mu\text{g/g}$ and water-soluble K: 269 $\mu\text{g/g}$

¹⁾–³⁾ Same as in Table 1(a)

Table 1(c). Contents (in $\mu\text{g/g}$) of F and Cl of the ash issued by continuous ash eruptions.

Date	F	s-Cl	ins-Cl
1982/7/25	650	880	230
1982/7/29	670	910	240
1983/7/13	720	810	260
1983/7/29	590	1060	220
a.m. ¹⁾	657.5	915.0	237.5
s.d. ²⁾	53.77	105.36	17.08
g.m. ³⁾	655.8	910.6	237.0

¹⁾–³⁾ Same as in Table 1(a)

4. Results

Analytical results and statistical parameters are listed in Table 1(a)–1(c) according to the mode of eruption. Water-soluble Na and K contents of the selected samples are footnoted in Table 1(a) and 1(b). Their weight ratios of Na to K range from 3.54 to 4.48, and they are much lower than that of seawater (ca. 27.5). This shows that all the ash samples are probably free from sea salt contamination.

Halogen contents of volcanic rocks in Japan have approximately lognormal distributions (Iwasaki *et al.*, 1957; Yoshida *et al.*, 1971). It is appropriate to take logarithmic values for applying statistical analysis to the data for the halogen contents. However, some samples of the “vul-

canian explosion" group have low water-soluble Cl contents and the deviations from the other values are exaggerated when we take logarithms of those values. The differences between the arithmetic mean values and corresponding geometric mean values are very small except for water-soluble Cl in the "vulcanian explosion" group as shown in Table 1(a)–1(c). Hence, we can use the normal distribution approximation for the following discussion.

5. Discussion

5.1 Differences in F and water-soluble Cl contents among the three types of eruption

The arithmetic mean values of F and water-soluble Cl contents of Japanese volcanic rocks are ca. 300 $\mu\text{g/g}$ (Yoshida and Tsuchiya, 2004), and less than 50 $\mu\text{g/g}$ (Iwasaki *et al.*, 1957; Yoshida *et al.*, 1971), respectively. The F and water-soluble Cl contents of all the ash samples shown in Table 1(a)–1(c) are extremely higher than these values. Kamada (1957, 1980) found that the volcanic ash issued by the 1955 eruption of Sakurajima had considerably high F and Cl contents, and that F and Cl compounds were considerably fixed on the ash in water-soluble forms. He inferred that fixation of F and Cl in hot gas onto the ash particles, within the crater and/or eruption columns, increased those contents of the ash markedly. Moreover, Yoshida *et al.* (1968) exposed powdered rocks to fumarolic gases containing HF and HCl in a certain period. They evidenced that F and Cl contents of the employed rocks highly increased, and that F was mainly stabilized in water-insoluble form. Whereas Cl was mostly fixed in water-soluble form. Thus, the present ash samples are highly enriched in F and water-soluble Cl, which is probably attributed to fixation of volcanic gases onto the ash particles.

The F and water-soluble Cl contents of the "strombolian eruption", "vulcanian explosion", and "continuous ash eruption" groups are different from one another (Fig. 2). This may suggest change in F and Cl concentrations in hot gas in the sequence of the eruptive activity. Those contents of the "vulcanian explosion" group range widely, however, Dixon's Q-test for outliers (Dixon, 1953) shows that all the samples of this group belong to the same normal distribution at the 1% significance level. The significance of dissimilarity in the arithmetic mean values among the three groups is examined by t-test (Table 2). Yet, differences in the variances among them are also examined by F-test (Table 3).

The arithmetic mean values of the F and water-soluble Cl contents of the "strombolian eruption" group are significantly higher than those values of the other groups. While those values of the "continuous ash eruption" group do not differ from those of the "vulcanian explosion" group at the 5% significance level. These results support the deduction from Fig. 2 that F and water-soluble Cl contents of the volcanic ash depend on the mode of the eruption. They imply transition of F and Cl concentrations in hot gas issued from magma in the sequence of the eruptive activity. Hot gas enriched in F and Cl was issued from magma during strombolian eruptions, while it was depleted in the halogens after this stage. Fluorine and chlorine concentrations in hot gas did not change significantly between vulcanian

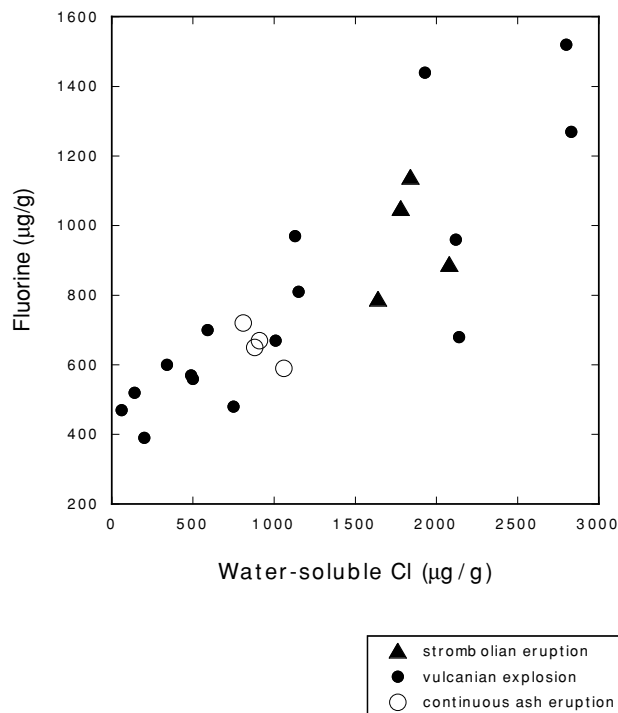


Fig. 2. Variation of F and water-soluble Cl contents of the ash samples issued by strombolian eruption, vulcanian explosion and continuous ash eruption.

eruption stage and continuous eruption stage.

5.2 Difference in water-insoluble Cl contents among the three types of eruptions

Figure 3 shows range of the water-insoluble Cl contents of the three groups. The water-insoluble Cl contents of the "strombolian eruption" group are higher than those of the other groups. While that of the "continuous ash eruption" group is within the range of that of the "vulcanian explosion" group. Significance of dissimilarity in the arithmetic mean value among the three groups is examined by t-test (Table 2). Difference in the variance among them is also examined by F-test (Table 3).

The arithmetic mean value of the water-insoluble Cl content of the "strombolian eruption" group is higher than those values of the others at 1% significance level. While the difference in the value between the "vulcanian explosion"- and "continuous ash eruption" groups is not recognizable at the 5% level. These statistic examinations support the deduction from Fig. 3 as shown above. The difference in the value among the three groups indicates that degassing of Cl is intensive before vulcanian explosion, while it is less intensive after this stage.

One might attempt to explain the difference in the water-insoluble Cl contents among the three groups as indicating state of the magma conduit in the sequence of the volcanic activity (Fig. 4). During strombolian eruption, the conduit is filled with fluid magma. Volatiles that are non-explosively exsolved from magma rise upward in the magma conduit. Therefore, the upper part of the magma column has high volatile contents (Fig. 4(a)). Formation of a lava dome at the crater bottom is frequently observed before vulcanian explosions. Chlorine and the other volatiles

Table 2. Differences in the arithmetic mean values among the groups examined by t-test.

Fluorine	strombolian eruption \gg , vulcanian explosion \sim continuous ash eruption
Water-soluble Chlorine	strombolian eruption $>$ vulcanian explosion \sim continuous ash eruption strombolian eruption \gg , continuous ash eruption
Water-insoluble Chlorine	strombolian eruption \gg , vulcanian explosion \sim continuous ash eruption

\gg , and $>$ mean that the difference is significant at the 1% level and the 5% level, respectively.
 \sim means the difference is not significant at the 5% level.

Table 3. Differences in the variances among the groups examined by F-test.

Fluorine	vulcanian explosion \sim strombolian eruption \sim continuous ash eruption vulcanian explosion \gg , continuous ash eruption
Water-soluble Chlorine	vulcanian explosion $>$ strombolian eruption \sim continuous ash eruption vulcanian explosion \gg , continuous ash eruption
Water-insoluble Chlorine	vulcanian explosion \sim strombolian eruption \sim continuous ash eruption

\gg , and $>$ mean that the difference is significant at the 1% level and the 5% level, respectively.
 \sim means the difference is not significant at the 5% level.

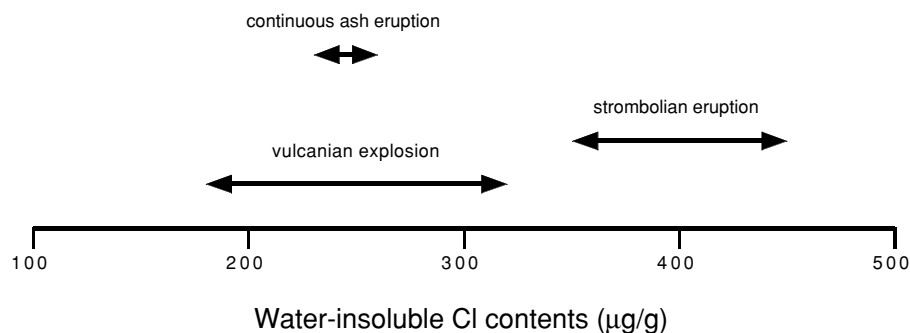


Fig. 3. Range of water-insoluble Cl contents of the ash samples issued by strombolian eruption, vulcanian explosion and continuous ash eruption.

are intensely exsolved from magma during the doming period and they are chambered beneath a lava dome. Release of volatiles from magma increases its viscosity, which furthers dome formation there (Fig. 4(b)). Then, vulcanian explosions eject pyroclastics of degassed magma (Fig. 4(c)). The difference in volatile contents of pyroclastics between vulcanian explosions and continuous ash eruptions is not recognizable, which suggests that continuous ash eruption is the final phase of vulcanian explosion. Ishihara (1985) deduced from geophysical observation that a lava dome plugged the magma conduit and hot gas was trapped in gas pockets beneath the dome, and that this stage might correspond to decrease of smoke before vulcanian explosions. Further, Iguchi (1994) implied that the conduit was filled with fluid magma during BL-type earthquakes, whereas the conduit was filled with a mixture of viscous magma and gases after BL-type earthquakes.

6. Conclusions

Determination of F and Cl contents of the ash issued from Sakurajima volcano by strombolian eruption, vulcanian explosion, and continuous ash eruption leads to the following conclusions.

The F and water-soluble Cl contents of the ash samples are extremely higher than those of Japanese volcanic rocks, which can be attributed to fixation of F and Cl in hot gas onto the ash particles. The sequence of the eruptive activity from strombolian eruption to vulcanian explosions, and then to continuous ash eruptions are closely related to release of volatiles from magma. During strombolian eruptions, volatile-rich fluid magma fills the conduit. Volatiles that are non-explosively exsolved from magma rise upward in the magma conduit. Then, F, Cl and probably other volatile components are concentrated in hot gas issued from magma in this stage. Volatiles are intensely released from

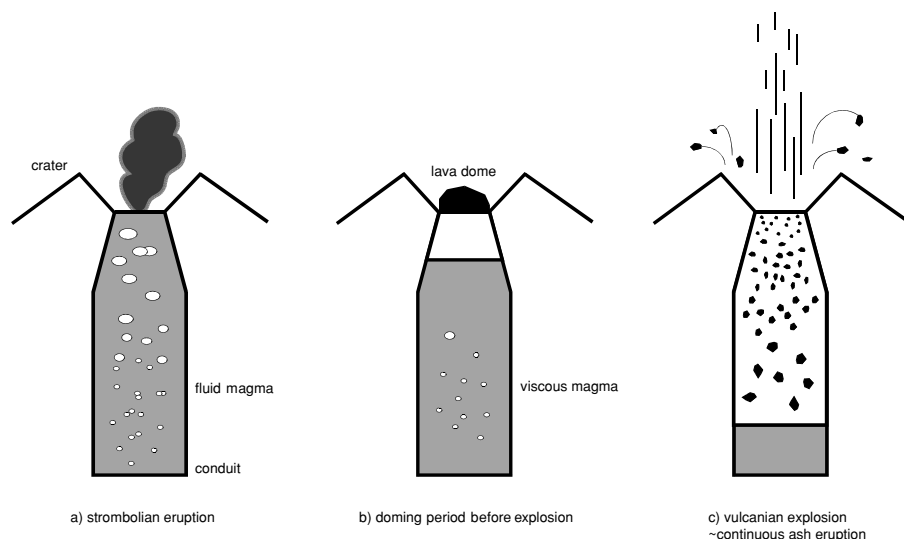


Fig. 4. Inferred state of the magma conduit including gas phase during strombolian eruption (a), doming period before vulcanian explosion (b) and vulcanian explosion to continuous ash eruption (c).

magma during doming periods before vulcanian explosions, and they are chambered beneath lava domes to become the driving force of vulcanian explosion. At the onset of vulcanian explosions, pyroclastics of degassed magma are ejected, and hot gas is depleted in F and Cl after this stage. After vulcanian eruption, the change in F and Cl concentrations in hot gas is not significant. And pyroclastics of continuous ash eruptions are less different from those of vulcanian explosions in volatile contents, which suggests that continuous ash eruption is the final phase of vulcanian explosions.

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