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The behaviour of fluorine, chlorine, and sulphur in the magma of Merapi Vulcano Central Java – Indonesia

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ABSTRACT

Merapi volcano, located at Central Java - Indonesia, is one of the world's most active volcano. In order to gain better understanding on volcanism and magmatism of this calc-alkaline volcano, various researches have been carried out. Some valuable information concerning volcanism of Merapi volcano can be indirectly obtained through the investigation of fluorine, chlorine and sulphur behavior in the magma. To accomplish this study, sixteen rock samples have been taken from the summit. Petrographic and chemical analysis of the rocks had been carried out. Major elements composition, analyzed by X-ray fluoresence method, shown that during the last 100 years chemical composition of magma have not been significantly changed, about 55 wt% of SiO_2. Chemical composition of individual minerals, determined by EPMA, suggested a constant composition the magma. Bulk compositions of fluorine and chlorine were determined by wet analytical methods, Ion-selective Electrode "by Trymethylsilylating distillation" method and spectrophotometer determination by Mercury Thiocyanate method respectively. On the other hand, sulphur was determined by a fluorescence instrumental method. The concentration of fluorine, chlorine and sulphur are 210 - 390 ppm, 60 - 540 ppm (water insoluble) and 17 - 82 ppm respectively. The relationship between Cl with Si02 and CaO could be observed. F in agreement with CaO, and in general correlate with the volume of hydrous minerals. Most of F/Cl atomic ratio of Merapi rocks >1, and decrease with increasing Si02, or F is more reactive than Cl to the magma, especially in the earlier stage of crystallization. The equal size of fluorine and hydroxyl ions permits fluorine to substitute easily for OH- in hydrous minerals or melt, Cl may be expelled during crystallization when in the fluorine present. In more residual magma the larger ionic radius of chlorine and its renown ability to form complex molecules should lead to greater concentration of chlorine than fluorine; these facts as well as the water solubility of chlorine compounds, that have been advanced as an explanation for the high Cl/F ratio obtained in volcanic gases. Sulphur has parallel correlation with FeO. It is shown that sulphur was more partioned into Fe rich magma, whereas Fe-S mineral is more likely. Therefore, the low sulphur content of Merapi lava might be as the characteristics of island arc volcanism.

Keywords: Composition magma of Merapi, chlorine, fluorine, sulphur

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SARI

Merapi yang berlokasi di Jawa Tengah merupakan salah satu dari gunung api paling aktif di dunia. Untuk memperoleh pengertian tentang kegunungapian dan magmatisme gunung api kalk alkalin, berbagai riset telah dilakukan. Informasi berharga berkenaan dengan vulkanisme Merapi dapat diperoleh secara tidak langsung melalui penyelidikan sifat fluorin, chlorin dan sulfur dalam magma. Untuk menyelesaikan studi ini, enam belas contoh batuan telah diambil dari puncak untuk dilakukan analisis petrografi dan kimia. Analisis dengan menggunakan metoda x-ray fluoresence elemen major menunjukkan bahwa dalam 100 tahun terakhir komposisi kimia magma merapi tidak mengalami perubahan siO_2 *yang signifikan yaitu sekitar 55%. Komposisi kimia dari setiap individu mineral ditentukan dengan EPMA menunjukkan komposisi magma yang konstan. Komposisi keseluruhan dari fluorin dan chlorin dilakukan dengan metoda analitik basah, elektroda ion selektif dengan metoda "destilasi trymethylsilylating" dan penentuan spektrofotometer berturut-turut dengan metoda Mercury thiocyanate. Di lain pihak, belerang ditentukan dengan metoda instrumental fluoresense. Konsentrasi fluorin, klorin dan sulfur berturut-turut adalah 210 – 390 ppm, 60-540 ppm (tidak larut air) dan 17-82 ppm. Hubungan antara Cl dengan* SiO_2 *dan CaO dapat diamati. F cocok dengan CaO, dan secara umum berkorelasi dengan mineral-mineral hidrous. Kebanyakan rasio antara F/Cl batuan Merapi >1, dan menurun dengan meningkatnya* SiO_2*, atau F lebih reaktif daripada Cl terhadap magma, khususnya pada tahap awal kristalisasi. Ukuran ion fluorin dan ion hidroksil yang sama memungkinkan fluorin bersubstitusi dengan mudah dalam lelehan dengan OH dalam mineral-mineral hidrous atau lelehan, Cl dikeluarkan sewaktu kristalisasi bila fluorin masih ada. Dalam magma sisa, makin besar radius ion chlorin dan kemampuannya membentuk molekul kompleks seharusnya mengarah ke konsentrasi chlorin lebih besar daripada fluorin; fakta-fakta ini begitu pula kelarutan air senyawa chlorin telah dimajukan sebagai penjelasan untuk rasio tinggi Cl/F yang diperoleh dalam gas-gas vulkanik. Belereng mempunyai korelasi paralel dengan FeO. Telah diperlihatkan bahwa belerang telah terpatrisi ke dalam fase magma yang kaya akan Fe, sedangkan mineral Fe-S lebih mirip. Kandungan sulfur yang rendah dari Lava Merapi mungkin mencirikan vulkanisme busur kepulauan.*

Kata Kunci: *komposisi magma merapi, chlorine, fluorine, sulfur*

INTRODUCTION

Merapi, an andesitic strato volcano, is one of the world's most active volcano. It is located 25 km to the north of Yogyakarta, Central Java Province, Indonesia. Geographic position are: 07˚.32'.44" south latitude and 110.26'.79" east longitude, rising to an elevation of 2968 M (asl). In order to gain better understanding on volcanism and magmatism of this island arc calc-alkaline volcano, various researches have been done.

In magma, volatile geochemistry is an important part in volcanology, because volcanic eruption is magma degassing process. Water and carbon dioxide comprise are the most abundant substance in magmas, anyhow volatile is also very significant. Other important substances found in volcanic gas is sulphur, which is closely related to volcanic activity. Yoshida et al., (1994) stated

Figure 1. Index map of Merapi Volcano, Yogyakarta, Indonesia.

Figure 2. Lava dome on the top of Merapi Volcano.

that fluorine and chlorine are other most abundant volatile substance to water and the most important substances inhigh temperature volcanic gas.

In order to understand the degassing behavior of ascending magma, it is necessary to study the interaction between different volatile substance and the potential influence of all volatile matter in magmatic process.

Accordingly, some valuable information's concerning the volcanism can be indirectly obtained through the investigations of Fuorine, chlorine and sulfur behaviour in magma. To accomplish this objective: The rock samples had been taken from the summit, for Petrographic and chemical analysises had been carried out.

SAMPLES AND ANALYTICAL METHOD

Sixteen rock samples have been collected from the summit of Merapi, as representative of vulcanism products since 1883 until 1995. Then the samples named as Merapi Lava (ML) 1883, ML 1906, ML 1911, ML 1940, ML 1948, ML 1953, ML 1954, ML 1955, ML 1956, ML 1957, ML 1992, ML 1994-A, ML 1994-B, ML 1994-C, ML 1994-N (November) and ML 1995. The ML 1911 is a pyroclastic flow deposit, while the other are the dome lava.

Major elements composition, analyzed by X-ray fluoresence following the method of Fujii et al., 1988; Yoshida et al., 1994. Chemical composition of individual minerals, determined by EPMA, with the equipment of JEOL Model JXA 8800 R. Bulk compositions of fluorine, chlorine and water soluble chlorine were determined by wet analytical methods: Ion-selective Electrode "by Trymethylsilylating distillation" method (Tsuchiya et al., 1985), spectrophotometer determination by Mercurie Thiocyanate method (Yoshida et al., 1994) and Tomonari's method (Yoshida et al., 1994) respectively. On the ether hand, sulfur was determined by a Fluorescence instrumental method. The analytical procedures are described as follows:

Major elements

The glass bead were made by mixing one part of pulverized rock samples (about 400 mg) with ten parts of lithium tetra-borate ($LiB0_4$), mixed well and then transfered into the Pt-Au mold. Heat in a temperature of 1000°C until completely melted, and then cooled down. Eight standard rocks from, Geological Survey of Japan have been used to produce a calibration curve. Equipment: Philips Model PW 14047.

Fluorine

Weigh 250 mg of pulverized sample in a nickel crucible. Mix well with 2 g of Na_20_2. Heat until completely melt. After cooling add about 25 water, put in a beaker glass, heat in a hot plate for about 1 hour. When it is dissolved, transfer the solution into a 50 m1 polyethylene centrifugal tube and then centrifuge together with the suspended matter. Transfer the supernatant to a 100 m1 volumetric flask.Wash the residue with a small amount of water and re - centrifuge. Add the washing to the flask and dilute the solution to the mark.

The distillation apparatus made of boron silicate. Place 10 ml of water in the absorption tube. Transfer a 50 ml aliquot of the solution to the reaction tube of apparatus, add 2-3 drops of methyl orange. Adjust the pH to approximately 1 by the addition of perchloric acid until the color change from orange to rose. Connect the reaction tube to the adapter. Introduce helium at the rate of about 60 ml minute^{-1} for 10 minutes. After 10 minutes, close the Nitrogen gas. The purpose of this procedure is to expel CO_2 from samples solution.

Change the water in the absorption tube with 10 ml of 0.1 N NaOH. Re-connect the apparatus. Add 6 m1 of the pyrophosphoric acid solution to the sample solution; the concentration of the acid will become about 1 mol 1-^{1} in terms of orthophosphoric acid and the pH 0.5 - 1. Immediately after the addition of 55 micron liter of HMDS by microsyringe, connect the reaction tube to the adapter. Introduce helium at the rate about 60 ml minute^{-1} for 30 minute, and then remove the absorption tube. Transfer this solution quantitatively with a 25 ml volumetric flask containing 2.0 ml of modified TISAB and combine the washings of the absorption tube. Dilute to the mark. Add 2.0 ml of the 0.5 mol 1^{-1} nitric acid to the distillate prepared as above in the 25 m1 volumetric flask. Transfer this solution to a 50 m1 beaker.

Determine the concentration of fluoride with the calibrated ion meter by the single point method. The solutions used for calibration are prepared by adding 2.0 ml of modified TISAB A to 25 ml of standard fluoride solutions (i.e. : 0.1 ; 1; 10 ppm).

Chlorine

Weigh 150 - 200 mg of fine pulverized sample in a platinum crucible. Add 1.00 g of Na_2CO_3 and mix well. Heat until completely melting. After cooling, add 7 - 8 ml of water and 1 drop of ethanol (to reduce MnO_4^{2-}). Heat on a hot plate for about 30 minutes to 1 hour to extract soluble part of the cake. Crush the residue by small glass rod to facilitate the extraction. After being dissolved, transfer the solution (together with fine suspended matters) to a centrifugal tube (15 ml capacity). Shake well the centrifugal tube and then centrifuge.

Wash the crucible with small amounts of water for several times and combines the washing to the centrifugal tube with the remainder residue. Shake the tube to suspend the residue, put in a 200 ml beaker glass contain about 50 ml of distillate water, put on a hot-water bath for 20 to 30 minutes. Centrifuge and combine the supernatant to the volumetric flask.

Add 2 ml of 60% $HCIO_4$ and 4 ml of $Fe(N0_3)_3$. $9H_20$ solution in succession (to avoid precipitation of silica). Shake the flask to expel excess CO_2. Add 3 ml of $Hg(SCN)_2$ reagent solutions Dilute to the mark and mix well. Measure the absorbency at 460 nm.

Calibration curve: Take 5 ml of $NaClO_4$ solution (for matrix matching and for blank compensation) in 25 m1 volumetric flasks. Prepare Cl^- standard solutions (less than 10 ml) to contain 0, 20, 40, 80, 120, 160 and 200 ppm of Cl respectively. Add 4 ml of $Fe(N0_3)_3$. $9H_20$ and 3 ml of $Hg(SCN)_2$ reagent solutions. The calibration curve for this procedure must be almost linier.

Water soluble chlorine

Weigh precisely 250 mg of pulverized sample, immersed over night in 10 ml water in a 15 m1 centrifugal tube. Prepare other 15 m1 centrifugal tube (second centrifugal tube). Transfer supernatant into the second centrifugal tube, add small amount of $NaN0_3$ to coagulate the suspended matters and then re-centrifuge. Transfer the "re-supernatant" into a 25 m1 volumetric flask.

Add some water to the residue in first centrifugal tube until the volume of about 10 ml Centrifuge. Transfer the supernatant into the second centrifugal tube, add small amount of $NaN0_3$ and then re-centrifuge. Combine the second "re-supernatant" to the volumetric flask. Dilute with water until the mark.

Take 10 ml of aliquot into a 25 m1 tube, add a 2 ml of $Fe(N0_3)_3$. $9H_2O$ and 1.5 ml of $Hg(SCN)_2$ solutions. The determination is using $Hg(SCN)_2$ photometric method. Measure the absorbance at 460 nm. Prepare CI standard solutions of 0; 1; 2; and 4 ppm respectively. Add a 2 ml of $Fe(N0_3)_3$. 9 H_20 and $Hg(SCN)_2$ solutions into standard solutions. Measure the absorbance at 460 nm. The calibration curve must be almost linier.

Sulphur

Sulfur content in the rocks of Merapi volcano were determined using a fluorescence instrumental method. The sample were vaporized and combined with oxygen at a temperature of 1100°C. Oxidation products include CO_2. H_20, and various other oxides (MOx) as hown by equation:

$$R\text{-}S + 0_2 \longrightarrow H_20 + SO_2 + MOx + C0_2$$

The conversion of chemically bound of sulfur to SO_2 is quantitative. The SO_2 is exposed to ultraviolet radiation of a specific wave length as shown by equation:

$$SO_2 + hv' \longrightarrow SO_2 + hv''$$

This fluorescent emission is completely specific for sulfur and is proportional to the amount of sulfur in the original sample. Sulfur calibration standard were analyzed to produce internal calibration curves.

RESULT

From petrographic evidence such as mineral inclusion patterns, crystallization sequence of the rock sample is inferred as follows; plagioclase ==> orthopyroxene ==> Fe-Ti oxides => clinopyroxene => hornblende ==> biotite. Hydrous minerals such as apatite, amphibole and biotite are always present, reflecting the volatile-rich nature of magmas.

The analytical results for major elements listed in table 1. All the analytical results of bulk rocks major element composition are for total iron to be FeO and normalized on H_20 free base. The analytical error have determined of ± 0.5%. On the K_20 versus $Si0_2$ Harker diagram, the rocks fall into high K calc-alkaline series with basaltic andesite typically. The high Ca contents have been attributed to the high water contents of island arc magma. EPMA determination for major elements composition of individual minerals is shown in Figure 3.

The fluorine, total chlorine, water soluble chlorine, sulfur contents and F/Cl atomic ratios of Merapi rocks are shown in Table 2. The analytical error determinations for both F and Cl are of 10 ppm at the contents levels, while the error for S is determined of ± 3%. Concentration of F are ranges continuously from 210 - 390 ppm, while ML 1957 has the highest content of 710 ppm. The contents of total chlorine shown a wider range from 80 ppm to 860 ppm (ML 1911 sample). The ML 1991 is a pyroclastic flow deposit, and shown most basaltic composition (53 wt. % SiO_2). Concentration of water soluble Cl in most sample is low, the highest is 80 ppm. Further discussion will be made on the water insoluble CL The sulfur contents ranged from 17 - 82 ppm. ML 1883 and ML 1955 have high contents of 8910 and 399 ppm respectively, these of high value might be caused by contamination or decomposition during and or after rocks solidification. In fact,a few percent of pyrite mineral in ML 1883 was detectable by X-ray diffraction analysis. Therefore, further discussion will be made by neglected the ML 1883 and ML 1955.

DISCUSSION

A model for subsurface structure of Merapi volcano have been summarised that the internal volcanic system at Merapi consist of two reservoirs, so called shallow reservoir and deep reservoir, where the shallow reservoir was much smaller than the deep one (Kirbani et al., 1990). From the hypocentral distribution of volcanic earthquakes

Table 1. Major Element Compositions and Calculated CIPW of Merapi Rocks.

	1883	1906	1911	1940	1948	1953	1954	1955	1956	1957	1992	1994F	1994L	1994G	1994N	1995
SiO_2	55	54.9	53.7	55.5	55.5	56.1	55.2	55.6	55.4	55.4	55.7	55.6	55.6	55.6	55.9	55.8
TiO_2	0.84	0.84	0.84	0.77	0.77	0.79	0.77	0.75	0.77	0.77	0.74	0.76	0.76	0.78	0.75	0.84
Al_2O_3	19.7	19.2	19.2	19.3	19.3	19.2	19.6	19.7	19.4	19.6	19.5	19.5	19.4	19.5	19.4	19.2
FeO	7.78	7.49	8.12	7.12	7.19	7.13	7.24	6.97	7.16	7.11	6.89	6.97	7.07	7.2	6.91	8.12
MnO	0.19	0.19	0.19	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.19	0.18	0.19	0.19
MgO	2.81	2.65	3.09	2.48	2.53	2.34	2.47	2.4	2.47	2.45	2.41	2.45	2.44	2.37	2.38	3.09
CaO	7.6	8.57	9.18	8.23	8.39	7.81	8.38	8.25	8.37	8.4	8.42	8.41	8.43	8.27	8.25	8.18
Na_2O	3.66	3.73	3.29	3.96	3.76	3.78	3.87	3.69	3.77	3.69	3.76	3.74	3.66	3.74	3.78	3.71
K_2O	2.1	2.08	2.02	2.15	2.1	2.28	2.11	2.14	2.12	2.09	2.12	2.08	2.08	2.1	2.14	2.14
P_2O_5	0.33	0.33	0.31	0.31	0.32	0.32	0.32	0.33	0.35	0.35	0.32	0.3	0.31	0.31	0.3	0.31
Total	100	100	99.99	100	99.99	99.99	100	100.01	99.99	100	100	100	99.99	99.99	100.01	100
il	1.67	1.52	1.67	1.5	1.52	1.52	1.52	1.3	1.52	1.3	1.52	1.52	1.52	1.52	1.52	1.5
mt	3.7	3.5	3.8	3	3.2	3.2	3.5	3.5	3	3.2	3	3	3	3	3	3
ap	0.62	0.6	0.62	0.6	0.62	0.62	0.62	0.62	0.8	0.8	0.62	0.62	0.62	0.62	0.62	0.62
or	12.2	12.2	11.68	13	12.2	13.35	12.2	13	13	12.2	13	12.2	12.2	12.2	13	13
ab	30.09	31.4	27.77	34	32	32	32	31.4	32	31.4	32	31.4	30.9	31.4	32	32
an	31.1	29.8	31.97	28	29.5	28.6	30.6	30.6	30	31	29.8	30.5	30.5	30.5	29.5	29.6
di(wo)	2.1	4.6	4.9	4.6	4.5	3.9	3.6	4.8	3.7	4.3	4.2	4.2	4.2	3.8	4.3	4.3
di(en)	0.8	1.9	2.14	1.8	1.8	2	1.6	1.4	2.1	1.6	1.8	1.7	1.6	1.7	1.7	1.7
di(fs)	1.2	2.7	2.8	2.6	2.4	1.1	2.1	2.1	2.4	1.8	2.4	2.3	2.5	2.2	2.5	2.4
hy(en)	5.1	3.4	5.19	3.4	3.4	2.7	3.7	3.7	3.1	3.2	3.3	3.4	3.6	3.4	3.4	3.35
hy(fs)	6.4	4.9	6.69	4.6	4.9	3.7	4.7	4.9	4.7	6.8	4.4	4.7	5.6	4.6	4.6	4.5
Q	4.1	3.4	1.2	3	4	6.1	3.7	4.3	2.94	4	4.1	4.5	4.3	4.8	4.3	4.2

il = ilmenite; mt = magnetite; ap = apatite; or = orthoclase; ab = albite; an = anorthite; di = diopside

wo = wolastonite; en = enstatite; fs = fostarite; Q = quartz.

Table 2. Major element compositions and calculated CIPW of Merapi rocks.

Sample	F (ppm)	Cl [H2O-sol] (ppm)	S (ppm)	F/Cl*	Phen (%)	Gms (%)	Hornblende (%)	biotite (%)
1883	220	80 [20]	8910	6.84	64.5	35.5	0.5<	0.5<
1906	370	110 [30]	61	8.63	73.5	26.5	1	0.5<
1911	310	860 [30]	19	0.7	45	55	0.5<	3
1940	210	180 [30]	40	2.61	65.5	34.5	0.5<	0.5<
1948	320	200 [30]	28	3.51	68.5	31.5	0.5-1	0.5
1953	280	90 [20]	26	7.46	60	40	0.5<	0.5<
1954	380	150 [20]	33	5.45	73.5	26.5	0.5-1	1
1955	270	170 [20]	399	3.36	80	20	0.5<	0.5<
1956	280	200 [20]	51	2.9	78	22	0.5<	0.5
1957	710	390 [40]	82	3.78	74.5	25.5	1-2.0	0.5<
1992	300	400 [50]	22	1.6	74	26	0.5-1	0.5<
1994-F	390	620 [80]	72	1.32	77.5	22.5	0.5-1	1
1994-L	360	520 [10]	20	1.35	81	19	0.5<	1
1994-G	360	530 [20]	56	1.32	73	27	0.5-1	1
1994-N	350	490 [10]	17	1.36	80	20	0.5<	1-1.5
1995	220	160 [20]	26	2.93	-	-	-	-

* Atomic ratio, Cl Insoluble water

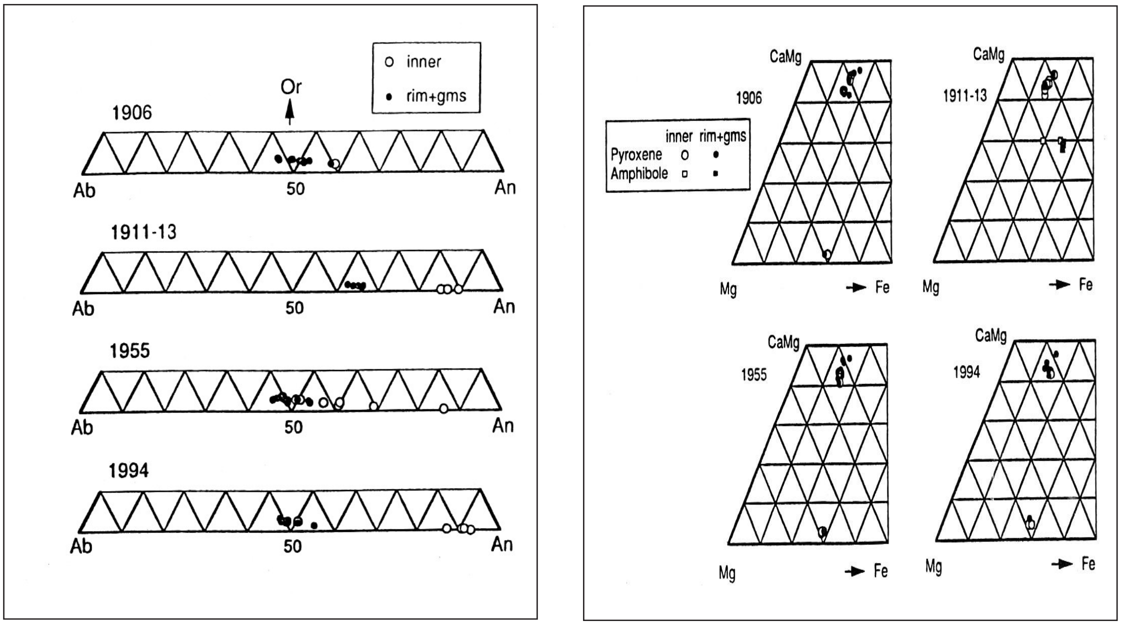

Figure 3. Chemical composition of plagioclase and pyroxene of some Merapi lavas, and composition of amphibole of ML 1911.

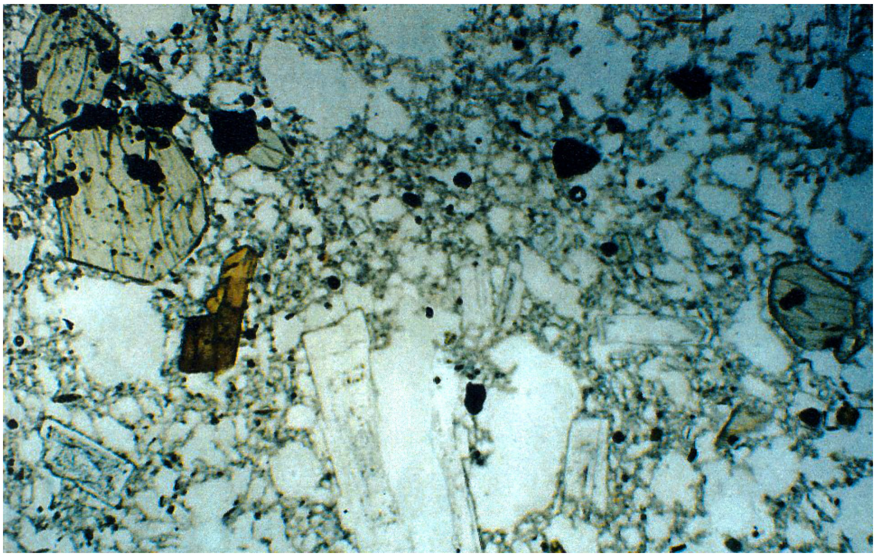

Figure 4. ML1911 Phenocrysts of plagioclase (colorless), taken in plane-polarized light.

(Kamo et al., 1994) has also inferred the existance of vertical magma conduit of 5 km long from magma reservoirs to the summit of Merapi and a magma pocket around 2-3 km deep. It could be taken as a hypothesis.

Major elements composition shown that during the last 100 years chemical compositions of the lava have not been significantly changed, about 55 wt. % of $Si0_2$ as shown in figure 5, chemical composition of individual minerals is also suggested a constant composition of magma. A continuous basaltic magma supply from the chamber; mixed up with and influenced of reminded magma in the pocket may have occurred.

Fluorine

In this work, fluorine contents varied in a narrow range, continued from 280 to 390 ppm. (table 2), and in general fluorine contents in almost of samples correlate with the CaO contents. It is well known that fluorine may occur in crystalline phase as a single crystal like apatite or to replace hydrous minerals like amphibole and mica. The equal size of fluorine and hydroxyl ions permits fluorine to substitute easily for OH^- in hydrous minerals or melt (Greenland and Lovering,1964; Johns and Huang 1967; Carmichael, 1974; Metrich, 1990). The hydrous minerals have been detect in thin section of Merapi lava, the hydrous minerals commonly associated with plagioclase and pyroxene. Hornblende associated with pyroxene and plagioclase as xenocrysts and

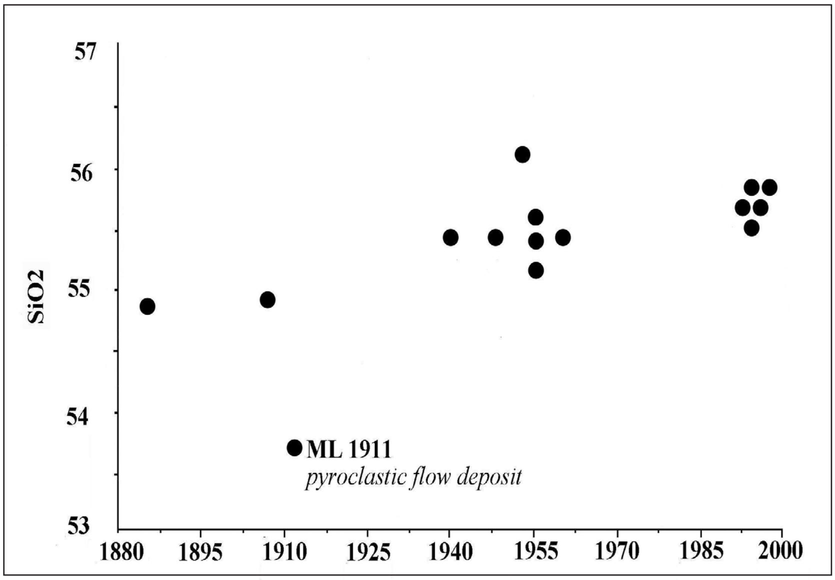

Figure 5. SiO_2 contents of Merapi rocks during 100 years.

also some crystal of hornblende rimmed by microcrysts of plagioclase. Apatite occurs as inclusion in plagioclase and pyroxene. Biotite appeared in the fractures and crystal edge of plagioclase, or as a single pseudomorph plagioclase crystal. Accordingly fluorine is fractionated with Ca rich phases in the magma and associated with hydrous minerals, and may exist in cystalline phases such as hornblende [Na ca_2 (Mg,Fe) Al $Si_6Al_2O_{22}$ $(OH,F)_2$] apatite [$Ca_5(F,C1,OH)(P0_4)_3$] and biotite [$K(Mg,Fe)_3$,$AISi_30_{10}(OH,F)_2$]. ML 1911 has the highest CaO content among the samples, and contains 310 ppm of F as shown in figure 6. This sample is a low crystalinity pyroclastic flow deposit. Possibly some amount of F were lost during the eruption. ML 1957 contain 710 ppm of F, this content is about two times higher than the average content. This rock is also have high Cl and S content. Petrographically contains about 2% of hornblende and about 1% of biotite, and a small portion of brown glass derived from basaltic melt have been detected.

Chlorine

Many investigators have shown that volatile solubilities depend on large number of controlling variables, as for chlorine and sulfur: pressure, temperature, major element composition, major volatile species composition, and the fugacities of oxygen, sulfur and chlorine. Actually there are many other variables involved: variation of the fractionation factors, entry of chlorine into minerals by means other than isomorphous

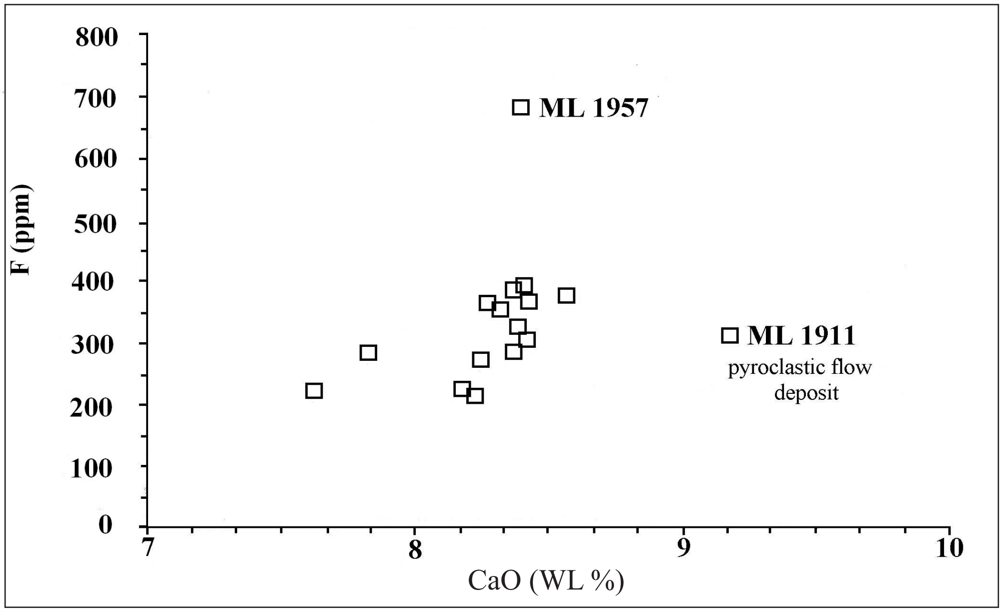

Figure 6. Relation between F and CaO contents in Merapi rocks.

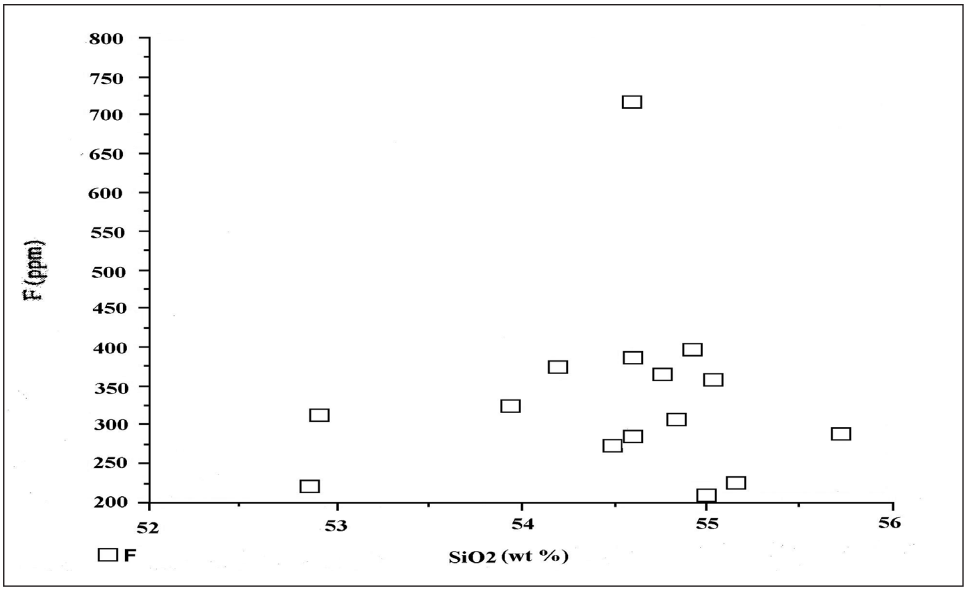

Figure 7. Plot of SiO_2 againts fluorine of Merapi rocks.

substitution, escape of water and chlorine from the magma (Kuroda and Sandell, 1953). Some investigators also found that behaviorally of Cl has greater influence on properties of hydrothermal fluids in a magmatic system.

It is well known that chlorine exists predominantly in micas, hornblende and apatite, replacing hydroxyl ion and dissolved in volcanic glass (Greenland and Lovering, 1964; Johns and Huang, 1967; Metrich, 1990; Stix et al., 1995). According to Kuroda and Sandell (1953), despite the large difference in the ionic radius of OH^- (1.33) and $C1^-$ (1.81A), chlorine appears to substitute for hydroxyl (or oxygen) in such common rock minerals as biotite and amphibole, and to some extent in apatite. Chlorine can occur in rocks in a various of ways:

1. In minerals in which it is an essential or predominant constituent, as in sodalite or scapolite
2. Isomorphously replacing OH^- and 0^-, as in micas and apatite
3. In aqueous inclusions, as in feldsfar and quatz
4. In "solid" solution, as in glasses

In Merapi rocks the C1 contents ranges continuously from 60 until 180 ppm, and immediately increase to 350 - 540 ppm. The correlation with $Si0_2$ and CaO are observable. That is, chlorine in Merapi rocks exist in Ca and silica rich phases of magmas.

In thin section of Merapi lavas, apatite found as inclusions in plagioclase and or pyroxene. The hydrous minerals hornblende appeared as xenocrysts, rimmed by iron oxides or pyroxenes, and associated with Ca-plagioclase. Biotite are altered to other anhydrous phase (plagioclase pseudomrph) due to low-pressure instability at surface conditions. Imagine that basaltic magmas from the depth bring hydrous minerals like hornblende and biotite, then mix up with more silicic magma in the reservoir. A stable crystallizing phase from volatile-rich basic magmas at depth becomes unstable and is subsequently resorted as the magmas ascend towards the surface. This condition had caused broken down of hydrous minerals and degassing of volatiles components. Thus, all of hydrous minerals in Merapi rocs always associated with Ca bearing minerals. Accordingly, most chlorine in Merapi magma have been associated with hydrous minerals and ground mass glass.

The ML 1911, has the most basaltic composition among the samples ($Si0_2$ of 53 wt. %), in fact this rock shown the highest contents of CI (830 ppm). Petrographically contains about 3 % of biotite (the highest among the sample) and has the lowest crystalinity. It is suggested that most of the chlorine in this rock exists in glass groundmass and hydrous minerals, especially biotite. In contrast, the chlorine content of ML 1953 is only 70 ppm, inspire of highest $Si0_2$ content. Under the microscope this rock figure out an alteration state, some amount of chlorine had lost after the rock solidified by secondary process.

F/Cl atomic values for most sample, except ML 1911, are larger than 1, and decreasing by the increase of $Si0_2$. Therefore, in most samples fluorine are generally more abundant than chlorine in molten silicate magma phase or more partitioned into the melt, while CI becomes aqueous fluids. Cl could be expelled during crystallization when fluorine presenct. In more residual magma the larger ionic radius of chlorine and its well known ability to form complex molecules should lead to greater concentration of chlorine than fluorine; these facts as well as the water solubility of chlorine compounds, have been advanced as an explanation for the high Cl/F ratio obtained in volcanic gases. In present state, the Cl/F ratio in volcanic gas of Merapi volcano is very large, in contrast with chlorine, the fluorine is almost undetectable.

The sulphur contents in Merapi rocks ranges from 17 to 82 ppm, these values are much lower compared with chlorine and fluorine. This sulphur content of Merapi rocks are equal with sulfur contents in Japanese andesitic rocks of 10 to 130 ppm (Arikawa, 1987). The low sulfur contents in Japanis volcanic rocks seems to be a characteristic of island arc volcanism. Accordingly, this feature is probably attributed (1) to the extent of the degassing of sulfur during the course of magmatic emanation or solidification, (2) to the difference of the magma source of the island arc from those of other, (3) to the isolation of the sulphur containing during fractional crystallization of magma and (4) to the heterogeneous distribution of sulfur in the upper mantle. However, this must be discussed more carefully in correlation with the contents of other volatile compounds (Ueda & Sakai 1984).

Allard et al., (1995) reported that sulphur content in the magma of Merapi is more than 950 ppm. If we use the 1991 - 1992 data of SO_2 discharge rate, magma extrusion rate and sulfur contents in bulk rocks (20 ppm) to estimate the sulfur concentration in the magma, we obtain the sulfur content of about 1400 ppm.

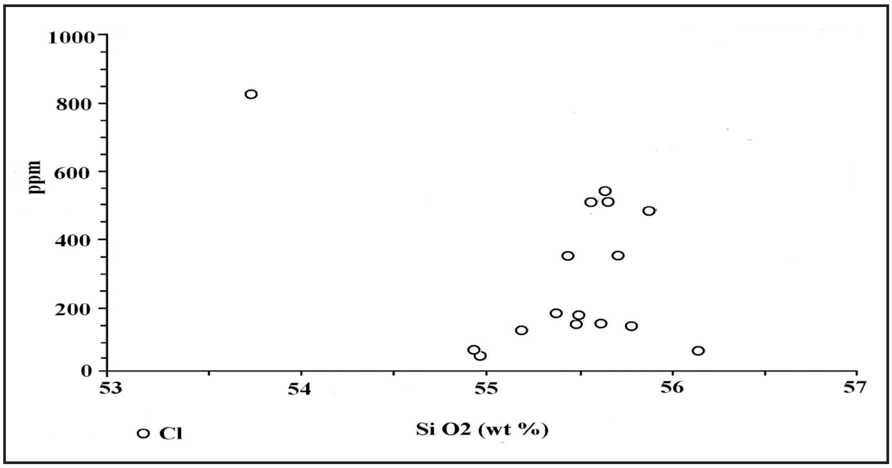

Figure 8. Plot of Chlorine content againts SiO_2 contents in bulk rocks.

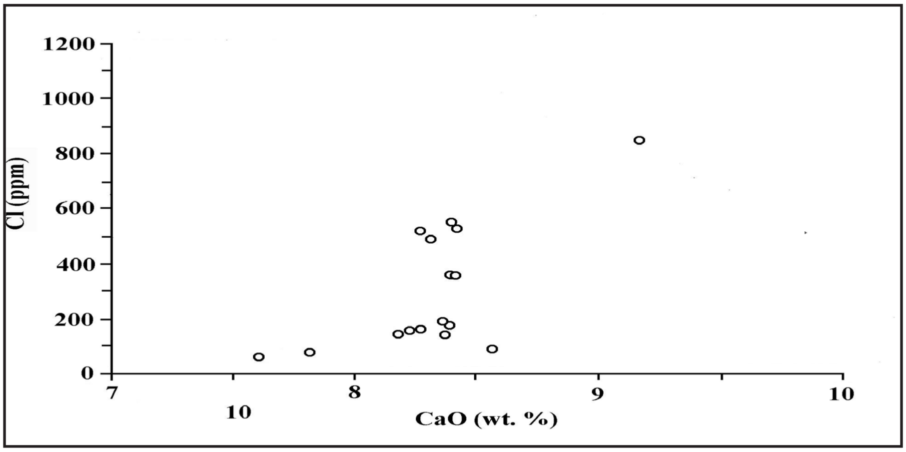

Figure 9. The correlat againts Siion between bulk CaO againts Cl in Merapi rocks.

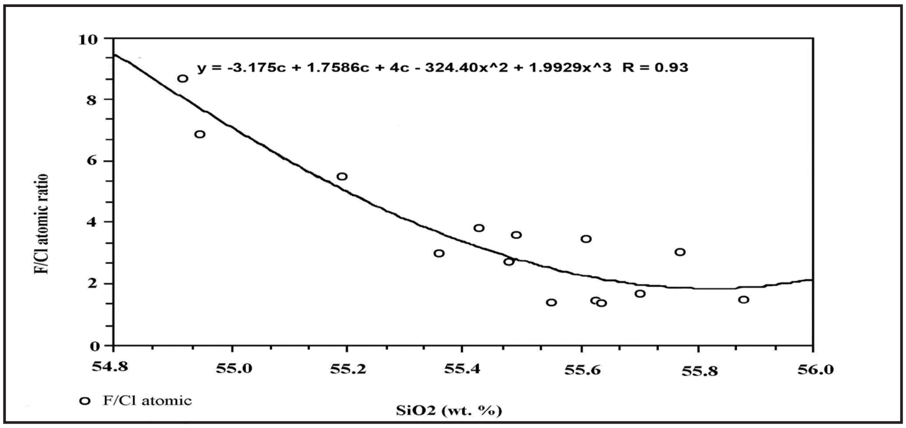

Figure 10. Plot of F/Cl atomic ratio (ML 1911 and ML 1953 are neglected) againts SiO_2.

This value does not include the sulphur discharged as H_2S. Accordingly, most of sulphur were lost from the magma during the 1991 - 1992 activity, and some amount may have been degassed by uneruptive magmas. Thus, the low sulphur contents of Merapi rocks may due to high degassing rate of magma.

Carrol & Webster (1995) have described that naturally-occurring basaltic magmas the dissolution of sulfur as sulfide is strongly depending on FeO melt content, as described by an equilibrium form:

FeO melt + $1/2\ S_2$ = FeS *melt* + $1/2\ 0_2$

In hydrous natural melts the solution mechanism for H_2S may involve reaction such as:

H_2S gas + FeO *melt* = FeS + H_2O gas

Sulfur contents of Merapi lava increasing by the increase of FeO as shown in figure 11, and decreases as SiO_2 increases. Thus, FeO have been strongly controlled by sulfur solubility in the magma of Merapi, wheres sulfur was more partitioned into Fe rich phases magmas, coordinated to the iron to form FeS minerals is likely.

In general the solubility of sulfur in silicate liquids is controlled essentially by the activity of the FeO component; the addition of silica or any other oxide, or an increase in the oxidation state (increased oxygen content), will depress the solubility of sulfur in a silicate liquid (Carmichae1, 1974).

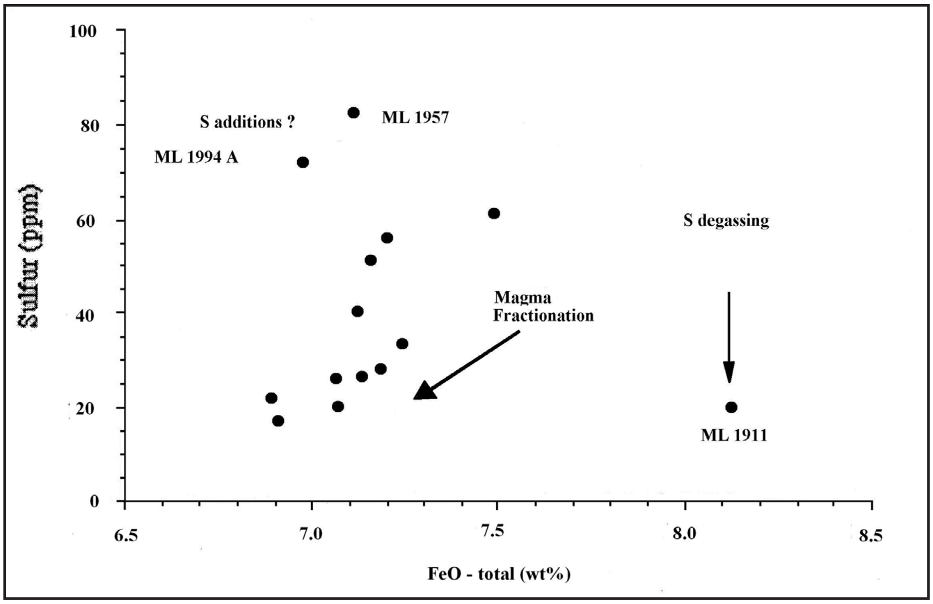

Figure 11. Plot of Sulphur concentrations againts FeO total

CONCLUSION

Through this work some conclusions can be drawn concerning the behaviour of some volatiles in relation with magmatism and volcanism of Merapi volcano.

During the last 100 years major elements composition of Merapi magma have not been significantly changed. The constant of major elements composition of individual minerals plagioclase and pyroxene phenocrysts are also suggested as a constant composition of magma. A continuous basaltic magma supply from the chamber; mixing with and influenced of remainded magma in the pocket may have been occured.

The correlation of volatile components with major elements composition have been observed. Most of F/Cl atomic ratio of Merapi rocks >1, decreasing with the increase $Si0_2$. This suggests that F is more reactive than C1 to the magma, especially in the earlier stage of crystallization. Fluorine were partitioned in CaO rich phases of magmas and exist in hydrous minerals. While C1 exist in hydrous minerals and ground mass glass. S content shows a parallel correlation with FeO and inverse with $Si0_{2.}$ That is, sulfur was more fractionated into Fe rich phases of magmas, as Fe-S minerals is likely. The low sulfur content of Merapi lava might be as a characteristics of island arc volcanism, in consequence of high degassing rate of magma. However, the addition of volatiles rich magma caused enrichment of some volatiles component.

In order to gain better understanding on volatile contents and its behavior in the magma of Merapi volcano, the future study is suggested. Rock samples augmentation, further chemical and mineralogical analysis, fluid inclusion study and determination of volatile concentration in hydrous minerals are required.

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