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► **To cite this version:**

M. Le Cloarec, M. Pennisi. Radionuclide behavior in high-temperature gases from Satsuma Iwojima volcano, Japan. *Earth Planets and Space*, 2002, 54 (3), pp.287-294. 10.1186/BF03353028. hal-03127141

**HAL Id: hal-03127141**

**<https://hal.science/hal-03127141>**

Submitted on 2 Jul 2021

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## Radionuclide behavior in high-temperature gases from Satsuma Iwojima volcano, Japan

M. F. Le Cloarec<sup>1</sup> and M. Pennisi<sup>2</sup>

<sup>1</sup>*LSCE, Laboratoire mixte CNRS-CEA, 91190 Gif sur Yvette, France*

<sup>2</sup>*Istituto di Geocronologia e Geochimica Isotopica, CNR, 56127 Pisa, Italy*

(Received November 13, 2000; Revised January 25, 2002; Accepted January 27, 2002)

Radionuclide and sulfur measurements were performed on samples from plume and hot fumarolic gas discharged from Satsuma Iwojima volcano, Japan. Such measurements in volcanic plumes contribute to a better understanding of degassing mechanisms (emanation coefficient of metals, degassing magma volume, residence time of the magma). At Satsuma Iwojima, inferred emanation coefficients of <sup>210</sup>Pb and <sup>210</sup>Po were estimated to be 0.07 and 2.5%, respectively, the lowest values obtained to date in volcanic gases. These values may be “apparent” emanation coefficients, due to the high viscosity of the degassing magma, which prevents efficient degassing of such low concentration components. The volume of the degassing reservoir (rhyolite layer) is estimated to be 0.24 km<sup>3</sup>, assuming no radionuclide recharge from the underlying basaltic reservoir to the degassing rhyolite.

### 1. Introduction

Radionuclide measurements in volcanic plumes provide useful indications of degassing processes such as volume of degassing magma or the escape time of gases (Lambert *et al.*, 1986; Gauthier *et al.*, 2000). The last decay products of the <sup>238</sup>U series, <sup>210</sup>Pb ( $T_{1/2} = 22$  years), <sup>210</sup>Po ( $T_{1/2} = 4.6$  months) and <sup>210</sup>Bi ( $T_{1/2} = 5$  days), which are assumed to be in radioactive equilibrium in the deep magma, are chemical species which are volatile at magmatic temperatures. They are enriched in gases, according to their specific volatility, leading to radioactive disequilibria in the gaseous phase. These radionuclides are thus potential tracers of events having different time scales, from as much as 100 years to a few years, and even a few weeks, according to their different half-lives.

Studies over long periods at Mount Etna and Stromboli allowed degassing models to be proposed (Lambert *et al.*, 1986; Gauthier *et al.*, 2000), based on the idea that the degassing takes place from a shallow reservoir located in the upper part of the magma chamber. This leads to the estimation of parameters such as emanation coefficients of Po, Bi and Pb between the gaseous phase and the magma, the time elapsed between the separation of gas from the magma and its emission to the atmosphere, or renewal of non-degassed magma in the degassing reservoir by convective movement. Radionuclide measurements performed during short periods at White Island volcano, New Zealand, and Mount St Helens, USA, allowed the volume of degassing magma at the time of sampling to be estimated, from the knowledge of <sup>210</sup>Po fluxes and <sup>210</sup>Po magmatic content before degassing. At White Island continuous renewal of the degassing reser-

voir was assumed (Le Cloarec *et al.*, 1992), whereas the reservoir at Mount St Helens was assumed to be nearly motionless (Le Cloarec *et al.*, 1986).

We have investigated radionuclide behavior in hot fumarolic gases emitted from Satsuma Iwojima volcano, Japan. The current activity of this volcano is described in detail by Saito *et al.* (2001). High-temperature fumarolic gases (up to 880°C) are emitted at Iwodake from a magma that is thought to be rhyolitic at 950–1000°C (Saito *et al.*, 1997). The last eruption occurred 1300 years ago. The high temperature of the gases, as well as the permanent flux of SO<sub>2</sub>, averaging 550 T/day (Kazahaya *et al.*, 2002), require that non-degassed magma convects in the shallow part of the reservoir where the degassing takes place. Kazahaya *et al.* (2002) propose that the degassing occurs from a two-layered reservoir: the degassed magma returns at depth, owing to its higher density, and is recharged in volatiles emitted by an underlying basaltic layer. The present rhyolite is thought to be fully degassed, and acts as the transporter of dissolved gases from the underlying basalt to the surface.

### 2. Sampling and Analysis

Sampling was performed in November 1997, either directly in the plume, at the rim of the crater (series 1 and 2), or at the end of silica tubes inserted into hot fumaroles to collect sublimates (series 3). Radionuclide sampling was performed at the same place and time together with SO<sub>2</sub>, Cl<sup>-</sup> and F<sup>-</sup> sampling. The techniques of sampling and radioactivity measurements were described by Polian and Lambert (1979). Several cubic meters of the diluted plume are filtered through a cellulose filter, at a flow rate of about 8 m<sup>3</sup> per hour. Subsequently, the gross  $\alpha$  and  $\beta$  radioactivities are measured during a period of several months and the <sup>210</sup>Pb, <sup>210</sup>Bi and <sup>210</sup>Po activities at the sampling time are calculated from the known rate of radioactivity decay. The sampling

Table 1(a). Radionuclides and SO<sub>2</sub> content in aerosols sampled at Satsuma Iwojima in November 1997.

n°		<sup>210</sup> Pb Bq/m <sup>3</sup>	<sup>210</sup> Bi Bq/m <sup>3</sup>	<sup>210</sup> Po Bq/m <sup>3</sup>	SO <sub>2</sub> mg/m <sup>3</sup>	<sup>210</sup> Po/SO <sub>2</sub> Bq/mg	<sup>210</sup> Pb/SO <sub>2</sub> Bq/mg	<sup>210</sup> Po/ <sup>210</sup> Pb	<sup>210</sup> Bi/ <sup>210</sup> Pb
plume									
1.1	02/11	0.0031	0.065	0.040	9.51	0.0042	0.00033	13	21
1.2	02/11	0.0012	0.069	0.049	3.68	0.0134	0.00034	42	58
2.1	03/11	0.0037	0.047	0.170	21.63	0.0079	0.00017	44	13
2.2	03/11	0.0044	0.049	0.184	24.03	0.0076	0.00018	41	11
2.3	03/11	0.0058	0.073	0.209	24.41	0.0086	0.00024	37	13
2.4	03/11	0.0031	0.064	0.144	26.50	0.0054	0.00012	43	21
end of silica tube									
3.2	06/11	0.0375	2.921	1.650	216.93	0.0076	0.00017	47	78
3.3	06/11	0.0250	1.829	0.896	268.71	0.0033	0.00009	38	73
3.4	06/11	0.0583	3.071	2.750	58.29	0.0472	0.00100	47	53
mean value						0.0073*	0.00021*	39	
one standard deviation						0.0031	0.00009	10	

\*discarding point 3.4.

Table 1(b). Cl, F and S content in the plume sampled at Satsuma Iwojima, November 1997.

n°	1997	S mg/m <sup>3</sup>	Cl mg/m <sup>3</sup>	F mg/m <sup>3</sup>	Cl/F mg/mg	Cl/S mg/mg	F/S mg/mg
plume							
1.1	02/11	4.76	9.0	0.60	15.0	1.9	0.13
1.2	02/11	1.84	1.4	0.21	6.6	0.7	0.11
2.1	03/11	10.82	7.0	0.44	16.0	0.6	0.04
2.2	03/11	12.02	8.3	0.43	19.3	0.7	0.04
2.3	03/11	12.21	5.5	0.40	13.8	0.5	0.03
2.4	03/11	13.25	nd	nd	—	—	—
end of silica tube							
3.2	06/11	108.46	110.9	6.55	16.9	1.0	0.06
3.3	06/11	134.36	114.1	10.95	10.4	0.8	0.08
3.4	06/11	29.14	21.8	2.08	10.5	0.7	0.07

device for SO<sub>2</sub>, Cl<sup>-</sup> and F<sup>-</sup> consists of a filter holder connected to a small pump. The flow rates are 4.5 and 4.2 l/min for SO<sub>2</sub> and halogens, respectively. Sampling times vary from 3 to 20 minutes depending on the density of the plume. Each filter holder contains two Millipore filters in series impregnated following the techniques described by Faivre-Pierret (1983). After sampling, filters are washed and subsequently analyzed for Cl<sup>-</sup> by chromatography, for F<sup>-</sup> by specific electrode, and for SO<sub>2</sub> by colorimetry.

### 3. Analytical Results

All results are shown in Table 1. According to the sampling method, variations of the elemental content on filters are due to atmospheric dilution. Thus, if elemental addition or depletion do not occur during period between the gas emission at surface and the sampling time, elemental corre-

lations should follow linear trends, thus allowing the typical elemental ratios to be defined in the fluid. The radionuclide and S, Cl and F contents of the gases are far lower when the sampling is performed at the rim of the crater (series 1 and 2) compared with the samples collected near the output of the fumaroles (series 3), which experience less atmospheric dilution.

The (<sup>210</sup>Po/<sup>210</sup>Pb) ratios do not show a large range of variation, except for sample 1.1, and have a mean value of  $41.4 \pm 2.7$  in the diluted plume, and slightly higher mean value ( $44 \pm 5$ ) at the end of the silica tubes. The slopes of the lines <sup>210</sup>Po versus <sup>210</sup>Pb are 39 ( $r = 0.83$ ) and 45 ( $r = 0.98$ ) at the two locations respectively (Fig. 1), consistent with the hypothesis of atmospheric dilution of a single magmatic source of radionuclides.

The (<sup>210</sup>Po/SO<sub>2</sub>) and (<sup>210</sup>Pb/SO<sub>2</sub>) ratios have mean val-

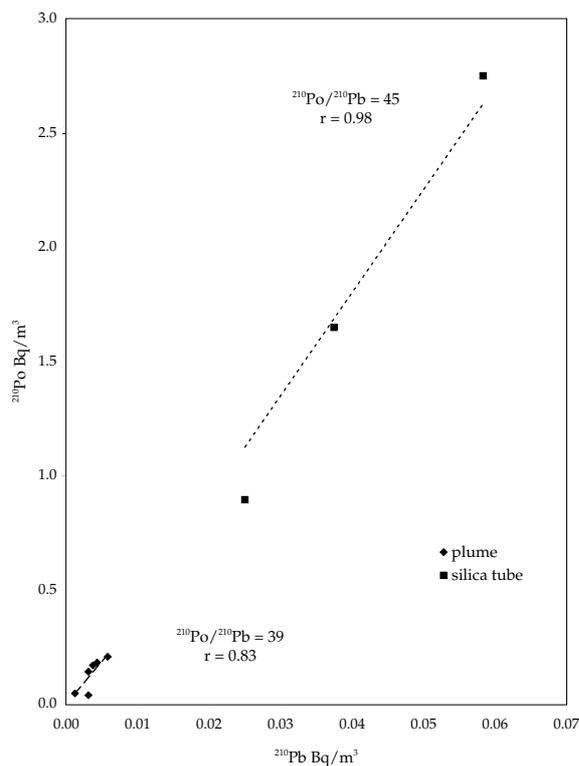


Fig. 1. Correlation between  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  in Satsuma Iwojima gases.

ues of  $0.0073 (\pm 0.0031)$  Bq/mg and  $0.00021 (\pm 0.00009)$  Bq/mg, respectively, discarding sample 3.4, which is out of the variation range of the ratios. The slope of the lines  $^{210}\text{Po}$  versus  $\text{SO}_2$  and  $^{210}\text{Pb}$  versus  $\text{SO}_2$  are  $0.0072$  Bq/mg ( $r = 0.90$ ) and  $0.00018$  Bq/mg ( $r = 0.62$ ), respectively, suggesting a common magmatic origin for  $^{210}\text{Po}$ ,  $^{210}\text{Pb}$  and  $\text{SO}_2$  (Fig. 2).

The case of  $^{210}\text{Bi}$  appears to be different. The ( $^{210}\text{Bi}/^{210}\text{Pb}$ ) ratios are lower at the crater rim ( $23 \pm 18$ ) than in gases sampled at the end of silica tubes ( $68 \pm 13$ ). In the plume, the ( $^{210}\text{Bi}/^{210}\text{Pb}$ ) ratios can be compared to those observed in plumes from an open conduit volcano: about 20 at Stromboli in 1996 (Gauthier *et al.*, 2000) and about 25 at Mount Etna during the period 1976–1995 (Le Cloarec and Pennisi, 2001). Higher ( $^{210}\text{Bi}/^{210}\text{Pb}$ ) ratios are currently observed in fumarolic gases, and are ascribed to the decay of  $^{210}\text{Pb}$  sublimates deposited along the pathway of the gases toward the surface (Le Cloarec and Gauthier, 2001). New  $^{210}\text{Bi}$  atoms are created which enter the gaseous phase, due to the higher volatility of this element compared to that of  $^{210}\text{Pb}$ , leading to the observed ( $^{210}\text{Bi}/^{210}\text{Pb}$ ) ratios being higher than those measured directly in the plume.

Elemental ratios Cl/S and F/S are the slopes of the lines Cl versus S and F versus S, respectively. Correlations between Cl and S, Cl and F, and F and S are shown in Fig. 3. On Figs. 3(a) and 3(b), all correlations define linear trends, with  $0.96 < r < 0.99$ . This result confirms that a common magmatic source is feeding the fumarolic fluids emitted at Iwodake crater. The Cl/F ratio is 12, somewhat lower than the value of about 20 reported by Shinohara *et al.* (1993). The Cl/S ratio is 0.9 (Fig. 3(b)), in agreement with Cl/S =

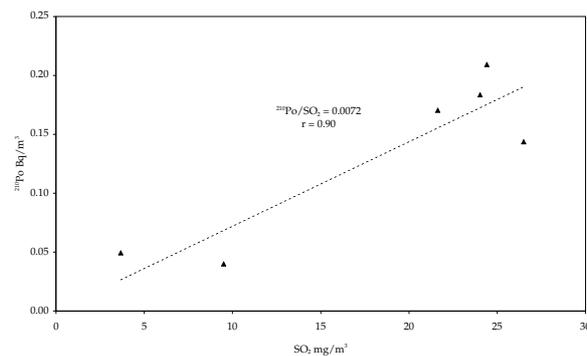


Fig. 2(a). Correlation between  $^{210}\text{Po}$  and  $\text{SO}_2$  in series 1 and 2 in Satsuma Iwojima gases.

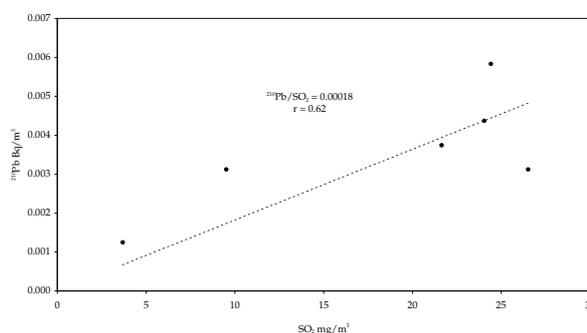


Fig. 2(b). Correlation between  $^{210}\text{Pb}$  and  $\text{SO}_2$  in series 1 and 2 in Satsuma Iwojima gases.

0.6 reported by Shinohara *et al.* (1993) and Cl/S = 0.7 reported by Hedenquist *et al.* (1994). The F/S ratio is 0.07, twice that reported by Shinohara *et al.* (1993).

#### 4. Emanation Coefficients ( $\varepsilon$ )

The radionuclide ratios measured in volcanic gases are controlled by characteristic emanation coefficients ( $\varepsilon$ ) of radionuclides defined as a partition between gas and lava (Gill *et al.*, 1985):

$$\varepsilon = (C_i - C_f)/C_i$$

where  $C_i$  is the initial radionuclide concentration in magma before degassing and  $C_f$  its final concentration in degassed magma. At a given volcano emanation coefficients can be inferred from the knowledge of one,  $\varepsilon_M$ , following the equation:

$$\begin{aligned} (X/M)_{\text{gas}}/(X/M)_{\text{lava}} \\ = (\varepsilon_X/\varepsilon_M)/[(1 - \varepsilon_X)/(1 - \varepsilon_M)]. \end{aligned} \quad (1)$$

The difficulty is to determine  $\varepsilon_M$  properly.

Radionuclide measurements at the same time as  $\text{SO}_2$  measurements in a plume provide a way to estimate the emanation coefficient of  $^{210}\text{Pb}$ ,  $\varepsilon_{\text{Pb}}$ , owing to its very long half-life which prevents it from decaying appreciably after its emission from the magma. Any X component in the gases is related to its initial concentration in the magma by

$$(C_X)_{\text{gas}} = \varepsilon_X * (C_X)_{\text{magma}} * f \quad (2)$$

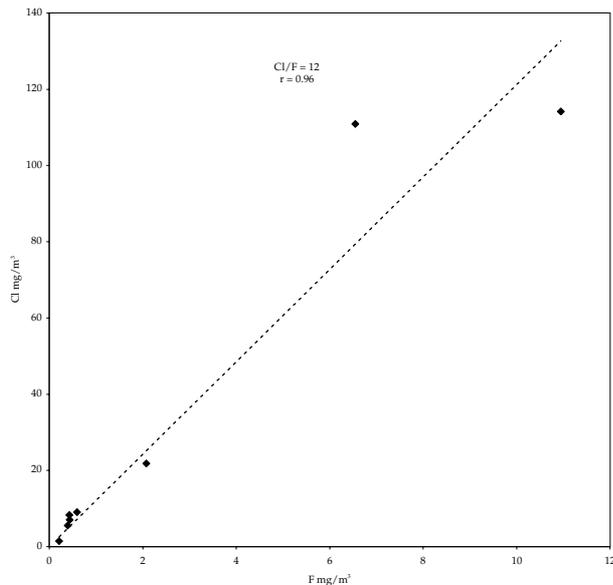


Fig. 3(a). Correlation between Cl and F in Satsuma Iwojima gases.

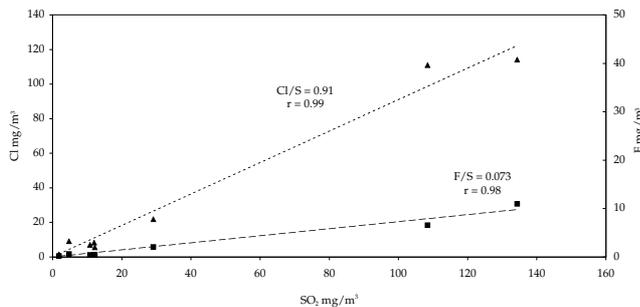


Fig. 3(b). Correlation between Cl and S (full triangles) and F and S (full squares) in Satsuma Iwojima gases (series 1, 2, 3).

where  $f$  is a factor relating the degassing volume to its gas content. Thus  $^{210}\text{Pb}/\text{SO}_2$  ratio in the main plume is

$$(^{210}\text{Pb}/\text{SO}_2) = \varepsilon_{\text{Pb}} * A_{\text{Pb}}/\varepsilon_{\text{SO}_2} * C_{\text{SO}_2} \quad (3)$$

where  $A_{\text{Pb}}$  is the activity of  $^{210}\text{Pb}$  and  $C_{\text{SO}_2}$  the  $\text{SO}_2$  concentration in the magma before degassing. The estimation of  $\varepsilon_{\text{Pb}}$  inferred from Eq. (3) leads to the estimation of any  $\varepsilon_M$ , using Eq. (1), provided that  $M$  has been measured in gases and associated lavas.

#### 4.1 Emanation coefficient of Pb

Saito *et al.* (2001), present a detailed analysis of melt inclusions in different lavas emitted by the volcano in the past. They emphasize that the volatile composition of Showa Iwojima rhyolitic melt agrees with that of the presently discharging high-temperature volcanic gases, suggesting a magma with similar composition as the source of the volcanic gases. Thus  $C_{\text{SO}_2}$  will be taken equal to the mean value in Showa Iwojima melt inclusions, 0.220 mg/g (Saito *et al.*, 2001);  $\varepsilon_{\text{SO}_2}$  will be taken equal to 0.82 ( $\pm 0.09$ ), as suggested by S concentration measurements in Showa Iwojima melt inclusions ( $0.110 \pm 0.020$  mg/g) and matrix glass (maximum  $0.020 \pm 0.010$  mg/g; Shinohara and Saito, pers.

Table 2. Abundance of trace Pb and Bi in Satsuma Iwojima lava and associated gases.

Element	rhyolite ppm	sample 2.1 $\mu\text{g}/\text{m}^3$	sample 2.2 $\mu\text{g}/\text{m}^3$
Bi	0.74 <sup>1</sup>	1.44 <sup>1</sup>	1.56 <sup>1</sup>
Pb	17.7 <sup>1</sup>	12.11 <sup>2</sup>	16.00 <sup>2</sup>
Bi/Pb	0.042	0.12	0.10

<sup>1</sup>measurements performed by ICP-MS (A. Gaudry, pers. comm., 2000).

<sup>2</sup>measurements performed by atomic absorption spectrometry, this work.

comm., 2001). We measured the  $^{210}\text{Pb}$  activity in the rhyolite, 0.058 ( $\pm 0.002$ ) Bq/g, and we assume that this value is very close to the  $^{210}\text{Pb}$  activity in non degassed magma; indeed, our studies on other volcanoes indicate that  $\varepsilon_{\text{Pb}}$  is not higher than 1% (Pennisi *et al.*, 1988; Le Cloarec *et al.*, 1992; Gauthier *et al.*, 2000), which is less than the uncertainty of activities analysis. From  $^{210}\text{Pb}/\text{SO}_2 = 0.00021$  ( $\pm 0.00009$ ), the value of  $\varepsilon_{\text{Pb}} = 0.07$  ( $\pm 0.04$ )%, about ten times lower than typical values.

#### 4.2 Emanation coefficient of $^{210}\text{Bi}$

$^{210}\text{Bi}$  has a very short half-life, about 5 days, which allows it to be continuously renewed from the parent  $^{210}\text{Pb}$  present in the degassing magma. Thus, the ( $^{210}\text{Bi}/^{210}\text{Pb}$ ) ratio cannot be used to infer the emanation coefficient of Bi from that of  $^{210}\text{Pb}$ . Assuming that  $\varepsilon_{^{210}\text{Pb}} = \varepsilon_{\text{Pb}}$  and that  $\varepsilon_{^{210}\text{Bi}} = \varepsilon_{\text{Bi}}$ , the emanation coefficient of  $^{210}\text{Bi}$  is estimated from stable Bi and Pb measurements in aerosols collected from the plume in 1997, and in old rhyolitic lavas (Table 2), following Eq. (1)

$$\frac{(\text{Bi}/\text{Pb})_{\text{gas}}/(\text{Bi}/\text{Pb})_{\text{lava}}}{= (\varepsilon_{\text{Bi}}/\varepsilon_{\text{Pb}})/[(1 - \varepsilon_{\text{Bi}})/(1 - \varepsilon_{\text{Pb}})]}. \quad (4)$$

From  $\varepsilon_{\text{Pb}} = 0.07\%$ , we calculate a mean value for  $\varepsilon_{\text{Bi}} = 0.18$  ( $\pm 0.13$ )%, which again is low compared to that observed at Etna and Stromboli, and much lower than at Merapi (about 4%).

#### 4.3 Emanation coefficient of $^{210}\text{Po}$

The case of  $^{210}\text{Po}$  is more complicated, as it has no stable isotope, and a short half-life, which allows it to decay in the gaseous phase, or to grow from  $^{210}\text{Pb}$  decay in the shallow degassing reservoir. The resulting  $^{210}\text{Po}$  content measured in the aerosols is thus the budget of these two events, depending not only on  $\varepsilon_{\text{Po}}$ , but also on the escape time,  $\theta$ , for the decreasing component, and on the residence time of the degassing magma reservoir,  $\tau$ , for the increasing component (Gauthier *et al.*, 2000). When both  $\theta$  and  $\tau$  are low compared to the  $^{210}\text{Po}$  half-life (138 days), the  $^{210}\text{Po}/^{210}\text{Pb}$  ratio in the gas phase allows  $\varepsilon_{\text{Po}}$  to be estimated after Eq. (2) following:

$$^{210}\text{Po}/^{210}\text{Pb} = \varepsilon_{\text{Po}} * A_{\text{Po}}/\varepsilon_{\text{Pb}} * A_{\text{Pb}} \quad (5)$$

which gives  $\varepsilon_{\text{Po}} = 2.5\%$ , assuming radioactive equilibrium in the deep magma before degassing (equal activities).

Taking into account the escape time  $\theta$ ,  $\varepsilon_{\text{Po}}$  has an apparent value equal to  $\varepsilon_{\text{Po}} * \exp(-\lambda_{^{210}\text{Po}} * \theta)$ . Moreover, due to the

Table 3. Melting and boiling temperatures of the main volatile species of Pb, Bi and Po in the range of magma temperatures.

Species	Pb		Bi		Po	
	$T_m$ °C	$T_e$ °C	$T_m$ °C	$T_e$ °C	$T_m$ °C	$T_e$ °C
Metal	327	1749	271	1564	254	962
Chloride	501	951	230	447	300	390
Fluoride	830	1293	725	900	—	—
Sulfide	1118	—	850	—	—	—

viscous nature of the rhyolitic magma, it seems reasonable to conclude that the rate of convection is low. Therefore, there will be a long residence time of the shallow degassing reservoir ( $\tau$ ). In these conditions, the production of  $^{210}\text{Po}$  atoms from  $^{210}\text{Pb}$  decay cannot be neglected, which makes the above estimated value for  $\varepsilon_{\text{Po}}$  likely to be higher than in reality.

#### 4.4 Discussion

Emanation coefficients ( $\varepsilon$ ) are closely related to the temperature of the magma and to its composition, for instance the presence or lack of  $\text{F}^-$  (Gauthier *et al.*, 2000). The emanation coefficient of Pb was shown to be 1% at Mount Etna (Pennisi *et al.*, 1988), 1.5% at Stromboli (Gauthier *et al.*, 2000) and only 0.8% at White Island (Le Cloarec *et al.*, 1992).  $\varepsilon_{\text{Bi}}$  varies from 22% in the Mount Etna plume, to 14% at Stromboli and 12% at White Island (same references, respectively). The emanation coefficient of  $^{210}\text{Po}$  is very high at Etna and Stromboli, about 100%, and 80–100% at White Island. From Table 3, it appears that Pb chloride, Bi fluoride and Po metal emission can be affected by the temperature of the magma, lower at Satsuma Iwojima than at Mount Etna, one of the possible causes of the very low emanation coefficients calculated for Satsuma Iwojima.

However, the lowest value for  $\varepsilon_{\text{Po}}$  prior to this study was found in Merapi emissions, at about 50% (Le Cloarec and Gauthier, 2001), from which it was concluded that  $^{210}\text{Po}$  is volatilized mostly as metal (Table 3). In the case of Satsuma Iwojima, the low  $\varepsilon_{\text{Po}}$  is unexpected considering the magma temperature ( $967^\circ \pm 17$ , Saito *et al.*, 2001), higher than that of Merapi ( $900^\circ\text{C}$ , Le Guern *et al.*, 1982). The radiogenic origin of  $^{210}\text{Po}$  atoms, issued from  $^{210}\text{Pb}$  and  $^{210}\text{Bi}$  decay, together with the high viscosity of the magma can be invoked to suggest that these isolated atoms remain trapped in the degassing magma at the place they are formed. They then decay to stable Pb before having time to reach the surface. Thus the emanation coefficient of  $^{210}\text{Po}$ , and probably also those of  $^{210}\text{Pb}$  and  $^{210}\text{Bi}$ , for the same reasons, are “apparent” emanation coefficients, and relate only to those atoms which are able to join the degassing flux.

## 5. Fluxes

An average  $\text{SO}_2$  flux of 650 Mg/day was measured by F. Le Guern (pers. comm., 1997) at Satsuma Iwojima in November 1997. This measurement allows estimations of other elemental fluxes from the knowledge of the concentration ratio  $C_X/C_{\text{SO}_2}$  in the plume according to:

$$\Phi_X = \Phi_{\text{SO}_2} * (C_X/C_{\text{SO}_2}). \quad (6)$$

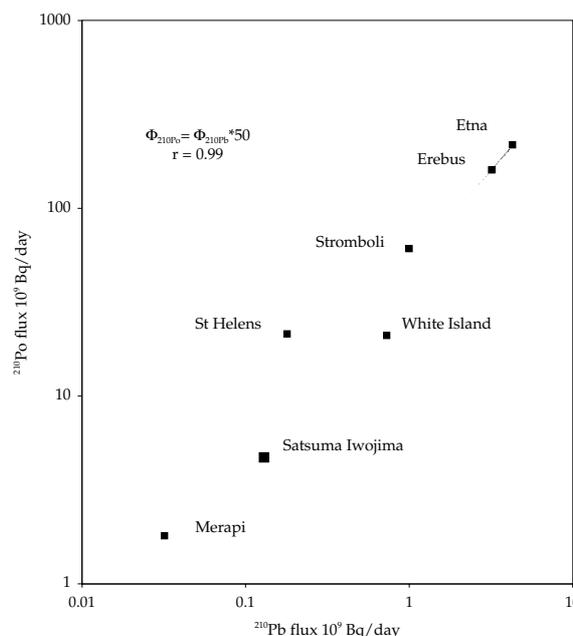


Fig. 4. Correlation between  $^{210}\text{Po}$  flux and  $^{210}\text{Pb}$  flux emitted from different volcanoes.

The results for halogens, 280 Mg/day HCl and 23 Mg/day HF, are calculated from an average  $\text{Cl/S} = 0.86$  and  $\text{F/S} = 0.07$ . The HCl flux is in agreement with data reported for activity in 1990,  $0.06 * 10^6$  Mg/year (Hedenquist and Lowenstern, 1994).

For radionuclides, we obtain 4.7 and  $0.13 * 10^9$  Bq/day of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ , respectively. These results indicate that very low activities are produced through the degassing of the Satsuma Iwojima magma. A comparison of present data with published results on volcanoes in different geological settings (Table 4) show a large variation in flux, in the range from 1.8 to 550 and from  $0.032$  to  $9.6 * 10^9$  Bq/day, for  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ , respectively. The plot  $\Phi_{^{210}\text{Po}}$  versus  $\Phi_{^{210}\text{Pb}}$  shows a positive correlation (Fig. 4) between the fluxes of the two elements ( $r = 0.99$ ) in worldwide volcanic gases, and suggests that the “law” that controls the degassing of the radionuclides does not differ significantly from one volcano to another, despite the large compositional differences between the selected volcanoes (Table 4).

According to preliminary data on radionuclide activities in lavas (Table 4), the calculated  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  fluxes are apparently not controlled by their activities in the magma. Rather fluxes may more reasonably be related to changes of

Table 4. Fluxes of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  associated to various lava compositions from different volcanoes.

	$\text{SiO}_2$ %	$^{210}\text{Pb}$ Bq/g lava	Pb in lava ppm	$\frac{^{210}\text{Po}}{^{210}\text{Pb}}$	$\Phi\text{SO}_2$ Mg/day	$^{210}\text{Po}/\text{SO}_2$ Bq/mg	$^{210}\text{Pb}/\text{SO}_2$ Bq/mg	$\Phi^{210}\text{Po}$ * $10^9$ Bq/d	$\Phi^{210}\text{Pb}$ * $10^9$ Bq/d
Hawaii 1987 (1)	46.9 (2)	0.004	4.2	232					
Etna 1992 (3)	47.4 (2)	0.075	9.4	65	10,000	0.055	0.00096	550	9.6
Etna 1993 (3)	47.4 (2)	0.075	9.4	91	2,000	0.037	0.00045	74	0.9
Etna 1994 (3)	47.4 (2)	0.075	9.4	36	3,000	0.045	0.00124	135	3.7
Etna 1995 (3)	47.4 (2)	0.075	9.4	37	4,000	0.027	0.00074	108	3
Stromboli 1996 (4)	47 (2)	0.14		70	125	0.215	0.0031	27	0.77
Stromboli 1997 (4)	47 (2)	0.14		73	250	0.38	0.0052	95	1.3
Merapi 1995 (5)	56 (2)	0.055	23	54	100	0.018	0.00032	1.8	0.032
Erebus 1994 (4)	57 (6)	0.004		35	50	3.2	0.064	160	3.2
White Island 1988 (7)	62 (2)	0.010	6.2	28	350	0.06	0.0021	21	0.73
St Helens 1981 (8)	65.6 (2)	0.016		121	230	0.093	0.00077	21.4	0.18
Satsuma I. 1997 (9)	75–77 (10)	0.058	17.7	37	650 (11)	0.0073	0.00021	4.6	0.13

(1) Hinkley *et al.* (1994); (2) Allard (1983); (3) Le Cloarec and Pennisi (2001); (4) Le Cloarec, unpublished results; (5) Le Cloarec and Gauthier (2001); (6) Le Masurier and Thomson (1987); (7) Le Cloarec *et al.* (1992); (8) Le Cloarec *et al.* (1986); (9) this work; (10) Saito *et al.* (2001); (11) F. Le Guern, pers. comm. (1997).

emanation coefficients controlled by the physical properties of the magma. Radionuclide fluxes determined for Satsuma Iwojima correspond to one of the lowest radionuclide fluxes yet measured, the lowest being observed at Merapi, although the corresponding SO<sub>2</sub> flux is 2–3 times that of Stromboli, Merapi, White Island and Mount St. Helens. As observed above, the calculated emanation coefficients at Satsuma Iwojima are more than one order of magnitude lower than other silica-rich volcanoes. Comparing to basaltic volcanoes, a 40-fold difference is observed in  $\varepsilon_{\text{Po}}$  ( $\varepsilon_{\text{Po}} = 2.5\%$  at Satsuma Iwojima and 100% at Mount Etna), whereas the difference in the emanation coefficients of SO<sub>2</sub> is only about 15% ( $\varepsilon_{\text{SO}_2} = 90\%$  at Mount Etna and 82% at Satsuma Iwojima).

As a working hypothesis, we suggest that the silica content of the magma may represent a key factor in the observed range of variation of radionuclide fluxes due to the role played by increasing viscosity on elemental partition coefficients. Satsuma Iwojima represents the most silica-rich system investigated to date for the short-period and volatile radionuclides of the <sup>238</sup>U family.

Alternatively, the presence of hypersaline liquid condensed from high-pressure vapor beneath Satsuma Iwojima could be a sink for chloride-complexed metals. Hedenquist *et al.* (1994) suggested that this could be the reason that the flux of NaCl and metals measured during passive degassing of Satsuma Iwojima is about three orders of magnitude less than at White Island volcano, although the fluxes of SO<sub>2</sub>, H<sub>2</sub>O and other volatile species are similar.

## 6. Volume of Degassing Reservoir

According to the degassing model of Kazahaya *et al.* (2002), the shallow rhyolitic magma has a long residence time, as it was not renewed over the past 800 years. We assume that gases emitted at 3–5 km depth from the basaltic layer do not contain significant <sup>210</sup>Pb, <sup>210</sup>Bi or <sup>210</sup>Po, due to their very low vapor pressure at 90 MPa (Pennisi and Le Cloarec, 1998). Therefore, these radionuclides are here considered to be emitted mainly from the rhyolitic magma. Thus, it is possible to estimate the volume of the rhyolitic reservoir, using the argument developed by Le Cloarec *et al.* (1986) to estimate the degassing volume at Mount St. Helens. Radionuclides are continuously emitted in the plume. The measured flux of <sup>210</sup>Po must then be balanced by an equal production of its radioactive precursors, <sup>210</sup>Pb and <sup>210</sup>Bi. As <sup>210</sup>Pb has a very low emanation coefficient, most of this radionuclide remains in the rhyolite and decays to <sup>210</sup>Bi, which in turn decays to <sup>210</sup>Po. Bi compounds are more volatile, but the short half-life of <sup>210</sup>Bi prevents most of these atoms from reaching the atmosphere. Let  $x$  be the proportion of degassed <sup>210</sup>Bi atoms and  $y$  the proportion remaining in the degassing magma. The  $x$  factor accounts for the emanation coefficient of <sup>210</sup>Bi, and also for its decay before reaching the atmosphere, which cannot be neglected due to its short half-life. We measured <sup>210</sup>Pb activity in Satsuma Iwojima rhyolitic lava, 0.058 Bq/g. This means that each gram of magma produces  $N^{210\text{Bi}} = 0.058$  atom of <sup>210</sup>Bi per second (1 Bq = 1 disintegration/sec). Thus, the <sup>210</sup>Bi flux produced in the magma is  $y * 0.058$  atom/sec\*g. In a steady state, all <sup>210</sup>Bi atoms are transformed to <sup>210</sup>Po

atoms, and the flux of <sup>210</sup>Po produced in the magma is also  $y * 0.058$  atom/sec\*g. We know that only 2.5% of these atoms are emitted in the gases, that is  $0.025 * y * 0.058$  atom/sec\*g. Therefore the (<sup>210</sup>Bi/<sup>210</sup>Po) activity ratio in the plume is:

$$\begin{aligned} (^{210}\text{Bi}/^{210}\text{Po}) &= \lambda_{210\text{Bi}} * (x * 0.058) / \\ &\lambda_{210\text{Po}} * (y * 0.025 * 0.058) \\ x + y &= 1 \end{aligned}$$

where  $\lambda$  are the radioactive constants.

From these equations, and from the (<sup>210</sup>Po/<sup>210</sup>Bi) activity ratio (0.6 calculated from Table 1), we calculate  $x = 0.0005$  and  $y = 0.9995$ , which confirms that very few <sup>210</sup>Bi atoms reach the atmosphere. The corresponding flux of <sup>210</sup>Po emitted per gram of magma is:

$$\phi_{210\text{Po}} = \lambda_{210\text{Po}} * y * 0.025 * 0.058 = 7.3 * 10^{-6} \text{ Bq/g * day.}$$

The total <sup>210</sup>Po flux, inferred from the SO<sub>2</sub> flux of 650 Mg/day (measured during the sampling; F. Le Guern, pers. comm., 1997) and the <sup>210</sup>Po/SO<sub>2</sub> concentration ratio, 0.0070 Bq/mg, is  $\Phi_{210\text{Po}} = 4.6 * 10^9$  Bq/day. The  $(\Phi/\phi)^{210\text{Po}}$  ratio is the volume of the shallow degassing reservoir, about 0.24 km<sup>3</sup>, taking 2.7 as the magma density. This estimation is a minimum value, keeping in mind that  $\varepsilon_{210\text{Po}}$  is probably lower than 2.5%.

Assuming that Satsuma Iwojima rhyolitic magma is undersaturated in gases (Kazahaya *et al.*, 2002), then SO<sub>2</sub> exsolved from the underlying basaltic layer dissolves in the upper 0.24 km<sup>3</sup> rhyolite. Assuming a continuous SO<sub>2</sub> degassing of 550 T/day over 800 years, the ratio between the amount of SO<sub>2</sub> in the estimated rhyolite volume and the mean SO<sub>2</sub> flux allows to roughly estimate the “residence time” of SO<sub>2</sub> in the rhyolitic reservoir. Considering a SO<sub>2</sub> content of 0.220 mg/g SO<sub>2</sub> in melt inclusions (Saito *et al.*, 2001), and taking into account the 82% rate of SO<sub>2</sub> degassing from magma to the plume (Shinohara and Saito, pers. comm., 2001), the “residence time” is calculated as 200 days. This time represents a complete turn-over of the rhyolitic magma by convection.

It is worth noting that the rhyolitic magma reservoir at Satsuma Iwojima appears to be larger than the volumes of degassing magmas from andesitic volcanoes: 0.005 km<sup>3</sup> at White island in 1988 (Le Cloarec *et al.*, 1992), 0.0002 km<sup>3</sup> at Vulcano in 1988–90 (Le Cloarec *et al.*, 1994) and 0.02 km<sup>3</sup> at Merapi in 1995 (Le Cloarec and Gauthier, 2001).

## 7. Conclusions

Measurements of radionuclides were performed on fumarolic gases at Satsuma Iwojima, Japan, for the first time. The observed high concentrations of radionuclides in the plume, and correlations between <sup>210</sup>Po and <sup>210</sup>Pb and between radionuclides and SO<sub>2</sub>, suggest that radionuclides and SO<sub>2</sub> have a magmatic origin. The observed enrichment in <sup>210</sup>Bi in fumarolic samples is attributed to the decay of <sup>210</sup>Pb sublimates deposited along the path of the gases before reaching the atmosphere.

A single set of measurements does not allow a degassing model to be developed, such as that proposed by Gauthier *et*

al. (2000), even if the current activity did not change over a long period of time.

Emanation coefficients during the sampling period were estimated for Pb and Bi, 0.07 and 0.18%, respectively, lower than any value measured to date at other volcanoes. The maximum value of the  $^{210}\text{Po}$  emanation coefficient is 2.5%, and is likely lower, as our estimation does not take into account the long residence time of the degassing reservoir, nor the escape time of the gases. Such very low emanation coefficients are probably “apparent” emanation coefficients. Indeed, since the magma temperature at Satsuma Iwojima (960–970°C) is higher than that determined at Merapi volcano, the emanation coefficients should be of the same order of magnitude at both volcanoes, based on the boiling temperatures of Pb and Bi halides and of Po metal. It is worthy to note that  $^{210}\text{Pb}$  is produced as atoms, at a concentration in the magma about  $\sim 10^{-9}$  times lower than the stable Pb concentration; likewise, the  $^{210}\text{Po}$  concentration in the magma is about  $10^{-15}$  g/g. Therefore, the high viscosity of the Satsuma Iwojima rhyolite may prevent these isolated atoms from being incorporated by the bubble flux, causing them to remain in the magma. The “apparent” emanation coefficient of radiogenic atoms corresponds to those atoms of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  that reach the surface. The low value of the Bi emanation coefficient is related to that of  $^{210}\text{Pb}$ , owing to the way it is calculated. Moreover, the trapping of metal chlorides by subsurface brines cannot be ruled out, which would also result in the lowering of emanation coefficients.

The implied long residence time of the rhyolitic layer allows an estimate of its volume, about  $0.24 \text{ km}^3$ , which is the volume of magma that will produce the observed continuous flux of  $^{210}\text{Po}$ . The turn-over time of the rhyolitic magma inferred from its volume is estimated to be about 200 days.

Our conclusions are consistent with the degassing model proposed by Kazahaya *et al.* (2002), provided the viscosity of the rhyolitic layer is high enough to trap isolated radionuclide atoms, but is not so high that convection of the rhyolitic magma is impeded.

**Acknowledgments.** The authors are grateful to all those who contributed to the sampling, particularly Dr. F. Le Guern and Dr. H. Shinohara. We appreciate the useful comments of Dr. H. Shinohara, Dr. Y. Taran, Dr. U. Fehn and Dr. J. Hedenquist who helped to greatly improve the manuscript. We thank Dr. H. Shinohara and Dr. G. Saito for communicating unpublished S contents in melt inclusions and matrix glass. Contribution LSCE 0730.

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M. F. Le Cloarec (e-mail: Marie-Francoise.Le-Cloarec@lsce.cnrs-gif.fr) and M. Pennisi