Vapour-phase crystallisation of silica from SiF₄-bearing volcanic gases

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Abstract
Thermodynamic modelling of magmatic gases shows that SiF_4 may be an important F-bearing species at the high pressures typical of magma reservoirs. Upon decompression during degassing, SiF_4 will react with water vapour to form HF and silica. Common magmatic gases of high-T fumaroles seem to contain too little SiF_4 to be a significant source of silica, except if extremely large amounts of gas percolate through a small volume of rock, as is the case in lava domes. Only if fluorine contents of the gases exceed 1 mol% detectable amounts of silica may be formed, but such high fluorine contents have not yet been observed in natural gases. Alternatively, silica may be formed by heating of cool SiF_4-rich gases circulating in cooling lava bodies. We suggest that these mechanisms may be responsible for the deposition of crystalline silica, most probably cristobalite, observed in vesicles in lavas from Lewotolo volcano (Eastern Sunda Arc, Indonesia). Silica occurs as vapour-crystallised patches in vesicles, and is sometimes associated with F-phlogopite, which further supports F-rich conditions during deposition. Because of the connection between F-rich conditions and high-K volcanism, we propose that late-stage gaseous transport and deposition of silica may be more widespread in K-rich volcanoes than elsewhere, and long-term exposure to ash from eruptions of such volcanoes could therefore carry an increased risk for respiratory diseases. The dependence of SiF_4/HF on temperature reported here differs from the current calibration used for temperature measurements of fumarolic gases by remote sensing techniques, and we suggest an updated calibration.

Key words *SiF₄ – vapour crystallisation – silica – degassing*

1. Introduction

Silica minerals are frequently found as vesicle fillings in recently erupted volcanic products, and are commonly interpreted as late or post-magmatic secondary phases. In a study of Montserrat it was reported that groundmass silica phases occur in slowly cooled (dome) lavas only and not in pumice from explosive eruptions, indicating that crystalline silica was produced by vapour-phase crystallisation and devitrification within the lava dome (Baxter *et al*., 1999). As crystalline silica may pose a serious health threat to humans if it enters the respiratory system, it was suggested that volcanoes with lava domes may pose a greater risk for silicosis than other types of volcanoes (Baxter *et al*., 1999). Silica enrichment in hydrothermal aureoles around magma chambers is commonly interpreted as the result of crystallisation from silica-saturated solutions, and leaching of other elements by acidic hydrothermal fluids (*e.g*., Giggenbach, 1984). However, these processes are typical of post-intrusive alteration and it is unlikely that such processes act in erupting lava flows and domes. The importance of F species such as HF and SiF_4 in mass transport during degassing was demonstrated by White and Hochella (1992), who describe the depletion of weathering surfaces of basaltic lava flows in SiO_2 and enrichment in Ca,

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Al, and Mg during post-eruptive degassing of cooling magma bodies.

Here we present thermodynamic calculations that indicate that silica phases may form as a result of decompression of HF-rich gas during ascent of vapour-saturated magma, but also during heating of SiF_4-bearing gases. SiF_4 is a highly volatile compound at ambient pressures and temperatures (sublimation point $= -86°C$ at atmospheric pressure), which at elevated temperatures readily reacts with water vapour to form HF and silica. The reaction is very sensitive to temperature and is shifted in favour of SiF_4 at low temperatures ($< 400°C$; Rosenberg, 1973), whereas in high-temperature fumaroles HF is the dominant fluorine-bearing species. The results will be used to explain the presence of small patches of a crystalline silica phase, associated with fluorine-phlogopite, in vesicles in lavas from Lewotolo volcano (Eastern Sunda Arc, Indonesia).
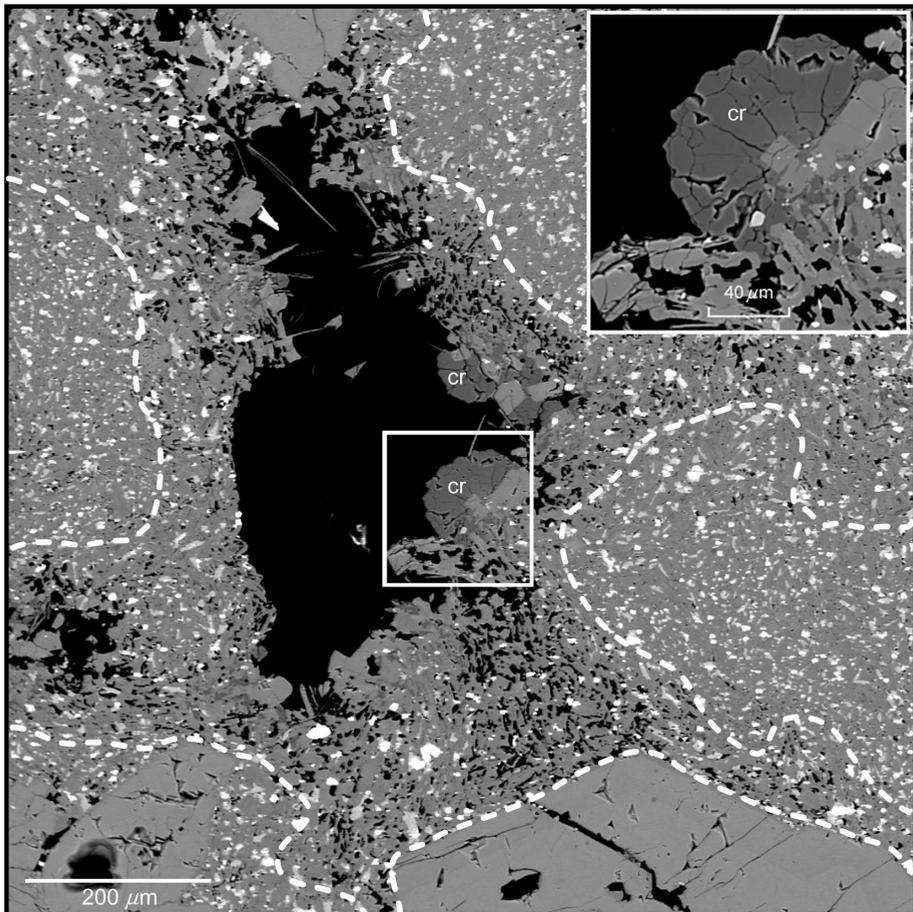

Fig. 1. Back-scatter electron images of a vesicle filling containing several patches of crystalline silica (cr), inferred to be cristobalite. The dashed lines indicate the approximate outline of the vesicle and interconnecting veins before the vesicle-filling assemblage was formed. Note the radial growth texture of the silica patches. The small needles sticking into the open space are F-phlogopite. Inset shows detail of one of the silica patches.

1.1. *Geological background*

Lewotolo volcano is located at Lomblen Island (8°27′S, 123°59′E) in the Nusa Tenggara (Lesser Sunda) Islands region of Indonesia. Strong fumarolic action at the summit produces a continuous outflow of hot (≤490°C) gases rich in H_2O, CO_2, H_2S, SO_2, HCl and HF (Poorter *et al.*, 1991), pointing to the presence of a degassing magma chamber at shallow depth. Lewotolo has erupted porphyritic, high-K calc-alkaline rocks over a wide range of silica contents from basalts to trachyandesites (47-62 wt% SiO_2; Stolz *et al.*, 1990; Hoogewerff, 1999). High fluorine contents of bulk rock (up to 800 ppm; Vroon, 1989), groundmass glass (up to 6000 ppm), apatite and phlogopite (De Hoog, 1995) indicate that the Lewotolo magmas are relatively rich in fluorine.

1.2. *Petrography of vesicle fillings*

A detailed description of the vesicle fillings was presented in De Hoog and Van Bergen (2000), in which the authors describe the presence of the rare mineral zirconolite in these fillings. We will summarize the relevant parts here.

Vesicles in about half of the lavas from Lewotolo volcano are partially to completely filled with an assemblage of mainly alkali feldspar, plagioclase and a silica phase. In addition the vesicles contain small amounts of clino- and orthopyroxene and magnetite, and trace amounts of zirconolite, ilmenite and apatite. These partially filled former vesicles will be referred to as *vesicle fillings* (fig. 1). The fillings have sieve-like textures and can be distinguished from the groundmass by a coarser grain-size, higher porosity, and the absence of glass. In samples with large amounts of vesicle fillings the whole network of former vesicles is interconnected. If the assemblage fills veinlets, the texture is denser, with a lower porosity close to that of the groundmass.

A crystalline silica phase grew as isotropic to low-birefringent patches with a radial structure into voids, or occupies interstitial spaces, *e.g.*, between crystals or near cracks (fig. 1). Individual patches can reach sizes up to 200 μm;

the total volume in the rock is small, however, and does not exceed 0.02 vol%. Optical microscopy did not conclusively distinguish between cristobalite and tridymite, but the common anisotropy and textures typical of shrinkage features point to cristobalite. Thin whiskers of phlogopite occasionally intrude into the left-open space within the former vesicles.

The vesicle fillings were probably deposited from a migrating fluid phase, possibly derived from deeper parts of the magma chamber, during a very late stage of magmatic evolution (De Hoog and Van Bergen, 2000). The morphology of later-stage minerals (crystalline silica, phlogopite) suggests that these may have crystallised from a less dense vapour phase.

2. Thermodynamic modeling

We studied the formation of silica phases as a result of decompression of SiF$_4$-rich phases using the equilibrium reaction

$$SiO_2(s) + 4HF(g) \leftrightharpoons SiF_4(g) + 2H_2O(g). \quad (2.1)$$

Although equilibrium between a vapour phase and silica is a valid assumption for the formation of silica from a SiF$_4$-bearing gas, reaction (2.1) is only an approximation of equilibrium between vapour and siliceous melt. In the underlying paper we follow the deductions of White and Hochella (1992) that the net free-energy differences between silica and siliceous melt are negligible compared to temperature and pressure effects.

In the calculations it is assumed that the rest gases SO_2, H_2S, CO_2 and HCl do not participate in the equilibrium reaction given by reaction (2.1). However H_2S will react with H_2O to form SO_2 and H_2 following the reaction

$$H_2S(g) + 2H_2O(g) \leftrightharpoons SO_2(g) + 3H_2(g). \quad (2.2)$$

The equilibrium of the reaction shifts to the right with decreasing pressure, thus consuming H_2O. However, because the amount of S in volcanic gases is much smaller than the amount of H_2O, the effect of reaction (2.2) on reaction (2.1) will be negligible.

Applying the equilibrium condition to reaction (2.1) by setting the Gibbs energy of the reactants equal to that of the products results in

$$\Delta G(P,T) = RT \ln\left(\frac{P_{SiF_4}P^2_{H_2O}}{P^4_{HF}}P^\circ\right) = RT \ln(K) \quad (2.3)$$

$$\Delta G(P,T) = G_{SiO_2}(P,T) + 4G^\circ_{HF}(T) - G^\circ_{SiF_4}(T) + \\ - 2G^\circ_{H_2O}(T) \quad (2.4)$$

where P represents pressure, T thermodynamic temperature, R the gas constant, K the equilibrium constant and the superscript «°» refers to the reference pressure $P^\circ = 1$ bar and P_j represent the partial pressures of the substances $j = SiF_4$, H_2O and HF.

The Gibbs energies of the pure substances, $G^\circ_j(T)$, at 1 bar pressure are expressed in terms of the enthalpy of formation, $\Delta H^\circ_{f,j}$, absolute entropies, S°_j, and heat capacities $C^\circ_{P,j}$, as

$$G^\circ_j(T) = \Delta H^\circ_{f,j} + \int_{T_0}^T C^\circ_{P,j} dT - T \cdot \left\{ S^\circ_j + \int_{T_0}^T \frac{C^\circ_{P,j}}{T} dT \right\}. \quad (2.5)$$

The enthalpies of formation and absolute entropies refer to a common reference temperature $T_0 = 298.15$ K and are found in thermodynamic tables (JANAF, 1985; Barin, 1989). The heat capacity data in these tables were fitted with polynomial functions with an accuracy better than 0.1%.

The Gibbs energy of solid SiO_2 at arbitrary pressure and temperature conditions is calculated using

$$G_j(P,T) = \Delta H^\circ_{f,j} + \int_{T_0}^T C^\circ_{P,j} dT - T \cdot \left\{ S^\circ_j + \right. \\ \left. + \int_{T_0}^T \frac{C^\circ_{P,j}}{T} dT \right\} + \int_{P^\circ}^P V_j dP \quad (2.6)$$

where $j = SiO_2$ and V_j, the molar volume of SiO_2. The molar volume of a solid substance is calculated using a Murnaghan equation of state

$$V = V^\circ \left[1 + \frac{(K^\circ)'}{K^\circ}(P - P^\circ) \right]^{\frac{1}{(K^\circ)'}} \quad (2.7)$$

where K° represents the isothermal bulk modulus and $(K^\circ)'$ its pressure derivative at 1 bar pressure. The molar volume at 1 bar pressure, V°, is calculated using the expression

$$V^\circ(T) = V^\circ(T_o) \exp\left(\int_{T_0}^T \alpha^\circ(T) dT \right) \quad (2.8)$$

where α° represents the thermal expansivity at 1 bar pressure. Polynomial expressions for K°, $(K^\circ)'$ and α° as function of temperature and the molar volume of SiO_2 were taken from the work of Swamy *et al.* (1994).

Depending on pressure and temperature, SiO_2 may exist in the forms α-quartz, β-quartz, tridymite, cristobalite, coesite and stishovite. From these six forms of SiO_2 we considered only α-quartz, β-quartz and tridymite because our study was limited to a pressure range between 0-2.5 GPa and temperature range between 1100-1400 K. Note that cristobalite is not a stable phase at the pressure and temperature conditions of our investigation, although it is often observed to be the most common crystalline silica phase in volcanic rocks (*e.g.*, Baxter *et al.*, 1999). The crystallisation of cristobalite, instead of a stable silica form, has a negligible effect on the results of the thermodynamic calculations compared to effects associated with errors in thermodynamic data.

The calculations of the partial pressures of HF, SiF_4 and H_2O and the partial pressure of the rest gas at arbitrary pressure and temperature conditions proceeds as follows. When a pressure is applied to the system or when the temperature of the system is changed, the partial pressures of HF, H_2O and SiF_4 change and an amount of SiO_2 is consumed. At the condition (P°, T), the number of moles n°_{HF}, $n^\circ_{SiF_4}$ and $n^\circ_{H_2O}$ of each gas phase species is calculated from the measured partial pressures. According to eq. (2.1) at arbitrary conditions (P, T') an amount, m, of SiO_2 reacts with $4m$ moles of HF to form m moles of SiF_4 and $2m$ moles of H_2O. The amount of moles in the gas phase changes from $n^\circ_{HF} + n^\circ_{SiF_4} + n^\circ_{H_2O} + n^\circ_{restgas}$ to $n^\circ_{HF} + n^\circ_{SiF_4} + n^\circ_{H_2O} + n^\circ_{restgas} - m$. The partial pressures of the substances in the gas phase are

$$P_{HF} = \frac{(n^\circ_{HF} - 4m)P}{N} \quad P_{H_2O} = \frac{(n^\circ_{H_2O} + 2m)P}{N}$$

$$P_{\text{SiF}_4} = \frac{(n^{\circ}_{\text{SiF}_4} + m)P}{N} \quad P_{\text{restgas}} = \frac{n^{\circ}_{\text{restgas}} P}{N}$$

$$N = (n^{\circ}_{\text{HF}} + n^{\circ}_{\text{SiF}_4} + n^{\circ}_{\text{H}_2\text{O}} + n^{\circ}_{\text{restgas}} - m). \qquad (2.9)$$

Inserting these relations into eqs. (2.3) and (2.4) leads to

$$(n^{\circ}_{\text{SiF}_4} + m)(n^{\circ}_{\text{H}_2\text{O}} + 2m)^2 \, (n^{\circ}_{\text{HF}} + n^{\circ}_{\text{SiF}_4} + n^{\circ}_{\text{H}_2\text{O}} +$$

$$\frac{+ n^{\circ}_{\text{restgas}} - m)}{(n^{\circ}_{\text{HF}} - 4m)^4} = \frac{P}{P^{\circ}} \exp\left(\frac{\Delta G(P,T)}{RT}\right). \qquad (2.10)$$

The Gibbs energy difference $\Delta G(P,T)$ is calculated by eq. (2.4). It is constrained by thermodynamic data of the gas phase species and the solid forms of SiO_2. With n°_{HF}, $n^{\circ}_{\text{SiF}_4}$, $n^{\circ}_{\text{H}_2\text{O}}$ and $n^{\circ}_{\text{restgas}}$ measured at the experimental condition (P°,T), the amount m is calculated with eq. (2.10), leading to calculated partial pressures of the gas phase species at arbitrary pressure and temperature conditions. The algorithm of the computational procedure is included in the program XiPT, which is a successor of the program TXY-Calc (Jacobs *et al.*, 1996; Jacobs and Spencer, 1996).

Table I. Recalculated compositions of Lewotolo gas samples in mol% (after Poorter *et al.*, 1991).

	Average (n=4)	1σ
H_2O	73.5	4.4
CO_2	15.9	4.4
SO_2	7.76	2.5
H_2S	0.86	0.51
HCl	0.169	0.106
HF	0.0465	0.0175
N_2	1.39	1
H_2	0.34	0.355

Equilibrium temperatures are $950 \pm 50°C$; sampling temperatures were ~490°C at 50 cm depth. Ar, He and CH_4 are present at ppm-level. Calculated oxygen fugacities are $\pm 10^{-11}$ bar, slightly higher than the QFM-buffer.

The calculations were performed using the compositions of hot (up to 490°C) summit fumaroles from Lewotolo volcano (Poorter *et al.*, 1991). Equilibrium compositions and temperatures were recalculated by an iterative gas-restoration procedure (Poorter *et al.*, 1991) and are given in table I. HCl, HF and H_2 values are in the normal range of volcanoes related to subduction zones, but CO_2 and SO_2 values and HF/HCl ratios are high compared to world-wide high-temperature fumarole data given by Symonds *et al.* (1994). We note that, because of differences in solubility of the various volatiles, the composition of gases at higher pressures is potentially different from those at atmospheric pressure, but these effects are difficult to quantify and therefore not considered in the paper.

3. Results and discussion

3.1. *Temperature dependence of HF/SiF₄*

The variation of HF/SiF₄ with T for various partial pressures of HF in the system SiO_2-HF-H_2O-SiF₄ is plotted in fig. 2. Note that the *x*-axis in fig. 2 is in a log scale, so that the increase in HF/SiF₄ between two markers (2 units) corresponds to a 100-fold increase of HF/SiF₄. The temperature dependence of reaction (2.1) at 1 bar has been documented earlier by Rosenberg (1973) and White and Hochella (1992), and SiF₄ and HF are also included in the GAS-WORKS program used to calculate equilibrium compositions of volcanic gases (Symonds *et al.*, 1992). As shown in fig. 2, our results closely match those of Rosenberg (1973), except for a slight deviation at lower temperatures. A few data points published by Symonds *et al.* (1992) are consistent with these trends. However, the calculations of White and Hochella (1992) deviate, showing a straight line with a slope which is considerably less steep than the curves predicted by Rosenberg (1973) and our data. As largely the same thermodynamic databases were used in all cases, we hypothesize that the trends of White and Hochella (1992) were based on models or assumptions that are not documented in their paper, which makes it difficult to verify their calculations. The agreement
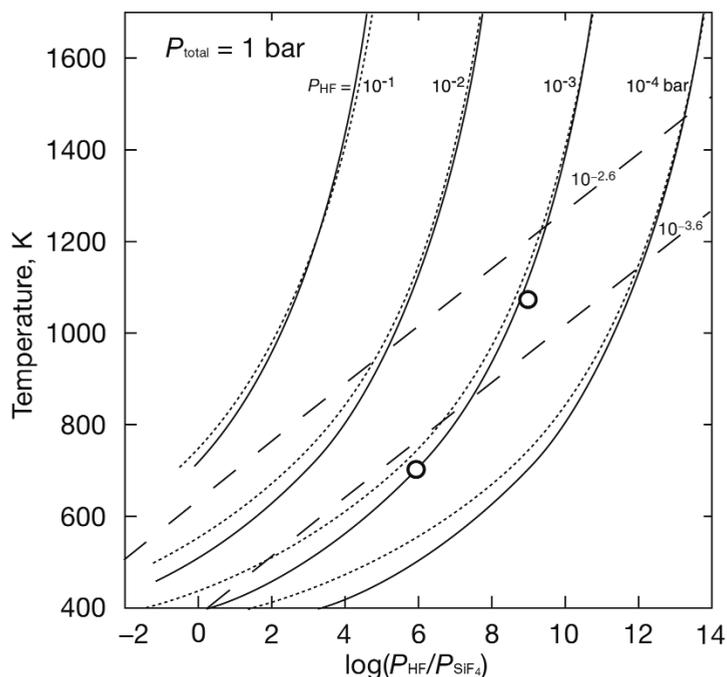
Fig. 2. Variation of SiF$_4$/HF (expressed as log[P_{HF}/P_{SiF_4}]) with T (in K) at different partial pressures of HF, and 1 bar total vapour pressure ($P_{HF}+P_{SiF_4}+P_{H_2O} = 1$). Continuous lines are from our own calculations, whereas dotted lines are data from Rosenberg (1973), dashed lines are after White and Hochella (1993), and the two circles are data points from Symonds *et al*. (1992) with $P_{HF} = 10^{-3.07}$ bar. Uncertainties in our data due to uncertainties in heat of formation and enthalpy of SiO$_2$, HF, H$_2$O and SiF$_4$ are about 25° and 0.2 log units. Note that the relative importance of SiF$_4$ increases both with total amount of F in the system (*i.e*., P_{HF}), and with decreasing temperature. White and Hochella (1992) trends are clearly offset and predict HF/SiF$_4$ variations with temperature that are much larger than other models.

with the data of Rosenberg (1973) and Symonds *et al*. (1992) supports that our model is valid for 1 bar, and can be used to predict equilibria at higher pressures (see below).

The curves in fig. 2 show the variation of HF/SiF$_4$ with T for a fixed value of P_{HF} and at a total vapour pressure of 1 bar. As production of SiF$_4$ consumes HF, P_{HF} is not constant, and the curves do therefore not represent cooling paths. However, HF consumption by production of SiF$_4$ is important only if P_{SiF_4} is close to P_{HF}, so that in fig. 2 only the bottom part of the curves would be noticeably influenced.

Reaction (2.1) is strongly dependent on temperature and on partial HF pressure. For example, a drop in temperature from 1400 to 800

K will decrease HF/SiF$_4$ by over 3 log units (~1250 times). The amount of SiF$_4$ will be higher than HF below 500 K if P_{HF}=0.01 bar. Therefore, at atmospheric pressure, SiF$_4$ does occur only in significant amounts at high partial pressures of HF and low temperatures. Dilution of HF-rich gas with HF-poor gas of the same temperature will have a strong effect on SiF$_4$, *e.g*., diluting a gas 10 times will decrease P_{SiF_4} by a factor 10000. Dilution of volcanic with atmospheric gases will lower T and P_{HF}, two parameters with opposing effects on SiF$_4$ production. Modelling shows that conservative mixing of high-T volcanic gases with air will increase the relative amount of SiF$_4$, because the temperature effect outweighs the dilution effect.

3.2. *Pressure dependence of HF/SiF₄*

Figure 3 illustrates the variation of P_{HF}/P_{SiF_4} with pressure at $P^*_{HF} = 10^{-2.5}$ and $10^{-1.0}$ and temperatures typical of magmatic gases (where P^*_{HF} is the partial pressure of $HF(P_{HF}/P_{total})$; $P^*_{HF}=$ $=P_{HF}$ at atmospheric pressure). The ratio P_{HF}/P_{SiF_4} increases strongly with decreasing pressure, especially in the low-pressure part of the system. The various curves that were calculated for different temperatures between 1100 and 1400 K are close to parallel. Applying a pressure of 860 bar to a system initially at atmospheric pressure will shift the equilibrium by 3 log units, equivalent to a 10-fold increase in P_{HF} in fig. 2. Therefore, at this pressure the figure is similar to the one at 1 bar, except that the

continuous lines are valid at P^*_{HF} values that are ten times lower than indicated at 1 bar.

Even though the relative amount of SiF₄ increases at high pressure, the absolute quantities are still very low in volcanic gases, as HF concentrations are generally low ($P_{HF}<10^{-2}$) and the total amount of SiF₄ is even smaller than HF (as $P_{HF}/P_{SiF_4}>10^5$ at magmatic temperatures, see fig. 2). However, if gases would be more HF-rich, SiF₄ would become a significant component even at moderate pressures (fig. 3). For example, if $P^*_{HF}=10^{-1}$ then SiF₄ contains more than 1% of the total amount of fluorine over the whole temperature and pressure interval studied here, except at pressures lower than ~100 bar, and at 1100 K it is the dominant fluorine species at pressures higher than 500 bar. We
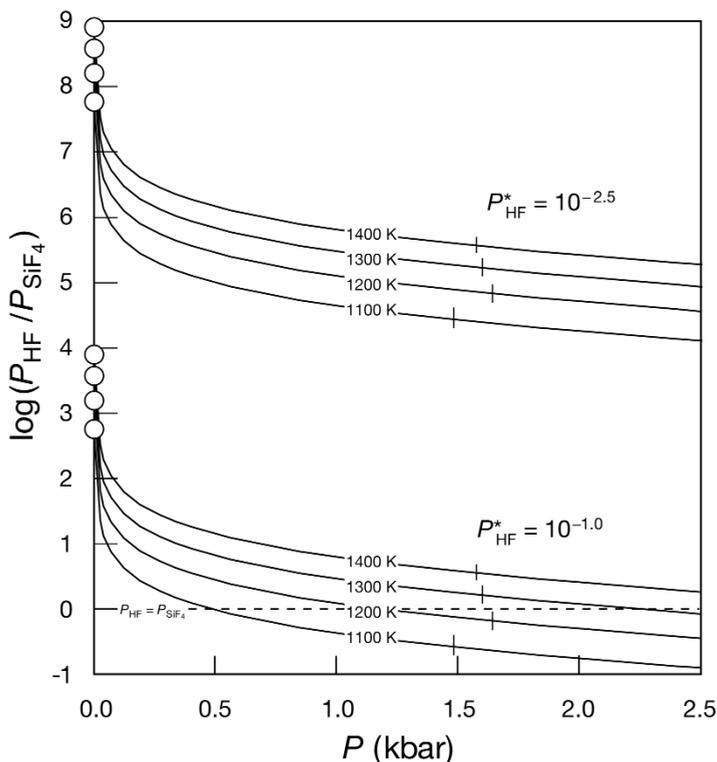

Fig. 3. Variation of log (P_{HF}/P_{SiF_4}) with total pressure for various temperatures at $P^*_{HF} = 10^{-2.5}$ and $P^*_{HF} = 10^{-1.0}$, respectively. The importance of SiF₄ increases with decreasing temperature, increasing P_{HF}, and increasing pressure. The circles represent data at 1 bar, and are equivalent to the values in fig. 2 at the same temperature and P^*_{HF}.

note, however, that such high partial HF pressures have never been observed in nature.

3.3. Formation of SiO_2

3.3.1. Pressure-release induced crystallisation of SiO_2

Because of the temperature and pressure dependence of the SiF_4/HF ratio, SiO_2 can be produced in two ways: 1) by an increase of the temperature of the system, or 2) by a decrease of pressure. As pressure decrease is common during magmatic degassing, whereby exsolved vapour rises through a magma column, we will discuss this process in more detail.

When magma becomes volatile saturated, $e.g.$, in response to decompression or fractional crystallisation, a separate fluid phase forms in which volatile components, including HF, will be concentrated. HF is a very reactive gas, and it will react with the melt to form SiF_4, following reaction (2.1), and other less volatile species, such as MgF_2, CaF_2 and AlF_3 (White and Hochella, 1992). This way, appreciable amounts of silica may be entrained in the volatile phase, the exact amount being determined by thermodynamic equilibrium and by the solubility and concentration of fluorine in the system. Here we assume that thermodynamic properties during reaction with siliceous melt are not significantly different from reaction with pure SiO_2 (White and Hochella, 1992; see Methods). If the magma starts or continues to rise, vapour pressure decreases and Reaction 1 will shift to the left resulting in precipitation (sublimation) of silica from the vapour.

If we assume a magma which contains a vapour phase with $P_{HF} = 10^{-2.6}$ bar, an isothermal pressure decrease from 1000 to 1 bar at 1400 K would cause a shift in $\log P_{SiF_4}$ from -8.5 to -11.6, and would result in the production of SiO_2. However, as the total amount of SiF_4 in the system is very small, the amount of SiO_2 formed during pressure release is limited. Under the assumed conditions 1 mol SiO_2 would be formed from ~794 kmol HF, or, expressed in weight, ~260 kg HF is needed to form 1 g silica. This amount of HF is equivalent to ~105 000

kg magmatic vapour. A dynamic model in which large amounts of gas percolate through a relatively small rock volume is therefore needed to deposit significant amounts of silica. In our example from Lewotolo, a gas/rock ratio of 1300 is needed to deposit 0.2‰ silica by volume (the estimated amount of silica in some of the samples). However, while such as scenario might work for dome lavas, it is difficult to reconcile with the presence of silica patches within vesicles in lavas on the flanks of Lewotolo volcano. If we apply the model to Mt. Etna (Sicily, Italy), which is one of the larger gas-producing volcanoes on Earth, with an average HF production of 100-300 ton per day (Francis et $al.$, 1998; Pennisi and Le Cloarec, 1998), the amount of silica formed during decompression of SiF_4-bearing gas could be about 1 kg per day, depending on assumptions regarding P^*_{HF} at depth. Clearly, these amounts are exceedingly small.

3.3.2. The effect of changing temperatures

In the above calculations we assumed that the temperature of the magmatic gas phase is constant. Because the HF/SiF_4 ratio is strongly temperature dependent, a temperature decrease during degassing will counteract the formation of SiO_2 induced by pressure release. Thermodynamic calculations on ascending magma-gas mixtures (Mastin and Ghiorso, 1998) for water-saturated magmas decompressing from 50 MPa to 1 atm suggest that temperature changes may vary between a 50°C decrease to an almost 10°C increase, depending on whether degassing takes place below the fragmentation depth and whether the magma is mafic or silicic. In the case of passive degassing (no fragmentation) the process is isenthalpic for silicic magmas (temperature may increase) and isentropic for basaltic magmas (temperature decreases). However, the temperature effect is small compared to the pressure effect (fig. 3). For example, in order to balance P_{HF}/P_{SiF_4} in a 1400 K vapour during decompression from 1 kbar to atmospheric pressure, a simultaneous temperature decrease of almost 600°C would be needed. We conclude therefore that any tempera-

tures variations during decompression and degassing have an effect on the formation of SiO$_2$ that is negligible compared to that of pressure release.

3.3.3. The effect of P_{HF}

As almost all SiF$_4$ is converted to SiO$_2$ during decompression, the amount of SiO$_2$ formed is essentially limited by the amount of silicon initially present in the gas phase. At partial pressures of HF common in high-T fumaroles the amount of SiO$_2$ formed is extremely small. Increasing the amount of SiF$_4$ in the gas phase in response to 1) a higher fluorine activity in the vapour, or 2) lower gas temperatures would increase the amount of SiO$_2$ formed. A temperature decrease of about 350 K would result in a ten times higher SiO$_2$ production, which is still rather insignificant. The effect of P^*_{HF}, however, is much stronger: an increase of P^*_{HF} from 0.001 to 0.01 results in a decrease of 3 log units of P_{HF}/P_{SiF_4}. In other words, while the amount of HF increases by a factor of 10, the amount of SiF$_4$ increases by a factor of 10000. If we assume an initial $P^*_{HF}=0.05$ and $T=1250$ K, the amount of SiO$_2$ formed during decompression is about 2.5 mol% (or 7.5 wt%) of the amount of HF present in the gas. The validity of such a scenario is difficult to evaluate, as little is known about the concentration of fluorine in late-stage magmatic vapours at high pressures. It is of interest to note that silica patches in the vesicles in Lewotolo lavas are often associated with thin whiskers of F-phlogopite that stick out of the silica mass. This suggests a common origin of both phases and a very high fluorine activity during crystallisation (De Hoog and Van Bergen, 2000). Although such F-rich compositions have yet to be observed in volcanic gases, the co-existence with F-phlogopite makes crystallisation of silica from F-rich vapour an attractive hypothesis.

As an alternative, silica may have been deposited from within the lava flow, *i.e.*, not in response to depressurisation but as a result of the large temperature gradients in the cooling lava. Although in cooling gases SiF$_4$/HF will increase and therefore the lava surface may become depleted in silica (White and Hochella, 1992), the heating of SiF$_4$-rich gases is an efficient way of producing silica because of the large SiF$_4$/HF ratios of these gases compared to hot, pressurized magmatic vapour. For example, SiF$_4$/HF ratios of up to 0.2 and SiF$_4$ fluxes of up to 1 kton have been measured in the plume of Popocatepetl (Love *et al*., 1998), and because of the steep slope of SiF$_4$/HF ratios with temperature at low T (fig. 2), heating of these gases by only 100°C would convert most SiF$_4$ to SiO$_2$. In a similar manner, silica may be deposited locally by gas circulating in cooling lava bodies.

It is of interest to emphasize that Lewotolo is a high-K volcano, as K-rich magmatic systems are considered to be often enriched in fluorine as well (*e.g*., Edgar *et al*., 1996; Strecher, 1998). Therefore, silica deposited during vapour decompression might be relatively common in volcanoes with high-K characteristics. We discovered silica patches (without F-phlogopite) similar in texture and appearance to those of Lewotolo, in lavas from Rinjani, a K-rich volcano on Lombok, which supports this supposition. Exposure to ash from eruptions of high-K volcanoes could therefore pose an increased risk for respiratory diseases, in a similar manner as eruptions from dome-forming lavas raised concerns about adverse health effects because of their high contents of crystalline silica (Baxter *et al*., 1999). We note that Lewotolo does not form lava domes, yet crystalline silica is present in many of its lavas.

3.4. *Implications for measurements of fumarole temperatures by remote sensing*

Figure 2 shows that the equilibrium temperature can be calculated if P_{HF} and P_{SiF_4} are known. This relation was used by Francis *et al*. (1996) to remotely determine fumarole temperatures at Vulcano (Italy). The authors calculated that fumarole temperatures were 200-450°C, which was in good agreement with directly measured temperatures of 210-690°C.

Francis *et al*. (1996) used the thermodynamic calculations of White and Hochella (1992), which, as discussed above, are inconsistent with

the results of Rosenberg (1973), Symonds *et al*. (1992) and the calculations presented here (fig. 2). Our thermodynamic model (*cf*. reaction (2.3)) predicts the temperature dependence of SiF_4/HF as follows:

$$T(°C) = \frac{-5574}{\log\left(\frac{P_{HF}}{P_{SiF_4}}\right) + 3\log P_{HF} - 4.755} - 273$$

(3.1)

in which it is assumed that $P_{H_2O} = 0.8$ bar and P_{HF}, $P_{SiF_4} << P_{H_2O}$, which are common conditions in volcanic plumes and fumaroles.

Repeating the calculations of Francis *et al*. (1996) with our thermodynamic data yields equilibrium temperatures around 100°C, with a maximum of ~180°C. These values are much lower than the findings of Francis *et al*. (1996) and directly measured temperatures of 250-600°C. In addition, the calculated range of temperatures for the different fumaroles is much smaller than observed. We hypothesize that the initial match between remotely measured and observed fumarole temperatures was fortuitous, and suggest that more work is needed to confirm that the remote-sensing approach can be reliably used to estimate fumarole temperatures. The discrepancy might be due to the absence of equilibrium between the gas components (which is more likely for heterogeneous equilibria, in which case one of the phases in the reaction is a solid, here silica). Alternatively, in view of our inferred temperature of ~100°C, the remote-sensing results may represent the temperature of condensing water vapour (steam), as water is the main component of the gases. Irrespective of these considerations, the strong influence of P_{HF} on calculated temperatures implies that errors in remote-sensing thermometry will be large unless HF can be measured simultaneously with SiF_4.

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