

The degassing of Hawaiian tholeiite

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Abstract. Accepting the Gerlach and Graeber (1985) estimates of the initial CO₂ and H₂O concentrations, we have calculated the variation of the concentrations of these gases, dissolved and/or exsolved, in Hawaiian tholeiite from the moment it is generated until it solidifies at the Earth's surface. These computations are extensions of our previous work (Bottinga and Javoy 1989, 1990a, 1990b) on the nucleation, growth and ascent of bubbles in mid-oceanic ridge basalt. The present study is different in that we consider low-pressure ($P > 1$ bar) bubble nucleation and the presence of H₂O. Our results indicate that: (1) Hawaiian liquid tholeiite is supersaturated with respect to CO₂ when it erupts; (2) degassing of the basaltic liquid takes place during different stages, each of which gives rise to a compositionally distinct bubble population, which to a large extent is lost before the formation of a new population; (3) fumarolic gas compositions are affected by the pressure and temperature at which gas bubbles are released from the lava and the velocity with which lava is ejected from the magma chamber.

I Introduction

Water and carbon dioxide are present in Hawaiian tholeiite in minute quantities. Hence, it is probably justifiable to consider these volatiles being dissolved in the silicate liquid as in an ideal solution and to ignore speciation problems. The solubilities of CO₂ and H₂O in liquid basalt at pressures less than 1 kbar have not been measured yet, but the systematics shown by observations at higher pressures and for other silicate melt compositions permit simple extrapolations to pressures lower than 1 kbar (see Appendix). The properties of gaseous solutions of CO₂ and H₂O at $P < 1000$ bars and $T > 1000^\circ\text{C}$ can be reproduced quite well by means of a modified Redlich-Kwong equation of state (De Santis et al. 1974) with the interaction constants of Holloway (1977, 1981). These circumstances make it possible to treat with reasonable precision the system liquid basalt-

CO₂-H₂O, within the limits set by its natural occurrence at magmatic temperatures. The physical constants we have used for the computations are discussed briefly in the Appendix.

Most of the release of carbon dioxide and water from a magma body takes place via the stages - nucleation, growth, floating upward, and escape from the melt - of bubbles. The question of bubble nucleation in basalts is controversial and will be discussed here with special emphasis on nucleation at $P < 200$ bar. Previously, we have discussed the nucleation of CO₂ bubbles at higher pressures (Bottinga and Javoy 1990a). It is well known that bubble growth and dissolution in silicate liquids are rate-controlled by diffusion in the melt (e.g. Ramos 1986). Hence the problem of the growth of a stationary multicomponent gas bubble in a lava requires nothing more than a solution of the diffusion equation. For multicomponent gas bubbles, only numerical solutions are possible because the equations to be solved for the diffusional fluxes of the different volatile components are coupled (e.g. Krämer 1979). When a bubble has grown sufficiently for drag forces to be overcome by buoyancy, mass flow becomes important as a transport mechanism and then the diffusion equation should be replaced by a more general transport equation. This equation gives the flux of the dissolved volatile into the bubble as the product of a transport coefficient and the difference between the volatile concentrations directly at the melt side of the bubble-melt interface and far away from it. The usual procedure is to express the transport coefficient in terms of more fundamental constants using fluid dynamical relationships. This approach was taken by Ramos (1986); we have adopted his results to obtain an equation giving the transport coefficient as a function of the diffusion coefficient of the dissolved gas in the melt and of the bubble velocity with respect to a frame moving with the melt (Bottinga and Javoy 1990b). The velocity of a bubble in a silicate melt due to buoyancy is given by a Stokes-type equation, known as the Hadamard-Rybcynski law, which has been verified experimentally by Hornyak and Weinberg (1984) and Jucha et al. (1982).

Hence calculating the rate of growth of bubbles filled with CO_2 and H_2O does not pose particular problems.

The third major igneous gas present in bubbles in magma is a sulfur-containing compound. Lack of information on the physico-chemical constants for sulfur-bearing gases is the main reason that these gases have been neglected here. We do not think that this oversight will invalidate the results we present in this paper because:

1. the initial sulfur content of Hawaiian tholeiite is reported to be the smallest of the major gases: it amounts to only a half of the initial water content (Greenland et al. 1985; Gerlach and Graeber 1985).
2. igneous sulfur is present mainly in the form of exsolved liquid sulphides (Harris and Anderson 1983; Roedder 1981; Roedder and Weiblen 1971) with vapour pressures much smaller than those of CO_2 or H_2O under magmatic conditions.

In this paper we publish the results of our calculations on the nucleation, growth and ascent of bubbles containing CO_2 and H_2O in liquid tholeiite under magmatic conditions. Unless stated explicitly otherwise, all our computations were done for pressures and temperatures corresponding to those of the anhydrous liquidus of tholeiitic basalt (Ito and Kennedy 1968; Bottinga and Allègre 1978). For these calculations we have followed the formalism developed previously in Bottinga and Javoy (1990a, 1990b). We have already dealt with the degassing of mid-oceanic ridge tholeiite (MORB), which is dominated by the formation and escape of CO_2 -rich bubbles at $P > 150$ bars (Bottinga and Javoy 1989). At such pressures the roles of H_2O and SO_2 are unimportant. Now, we will discuss the degassing of Hawaiian tholeiite; for $P > 100$ bars the degassing scenario is similar to that for MORB, but at smaller pressures the exsolution of water from the basaltic liquid becomes predominant and gives rise to novel features. We have limited ourselves to discussing MORB and Hawaiian tholeiite, because we have for these two lava types reasonably good information on the initial concentrations of igneous CO_2 and H_2O . For reasons of simplicity, we have assumed that all of the CO_2 and H_2O present in Hawaiian tholeiite is purely igneous.

II Bubble birth pains in basalt

II-1 Supersaturation, large or small?

Gerlach (1986) asserts that: "Experimental data and theoretical studies indicate that bubble nucleation is an inevitable consequence of magma becoming slightly supersaturated in volatiles (Sparks 1978; Wilson and Head 1981)". Like Wright and Helz (1987), we disagree with this statement; we have searched in vain in the cited references for any real evidence to justify the qualification "slightly". Experimental data on bubble formation in natural silicate liquids have been reported by Murase and McBirney (1973) and Westrich (1982), and there have been discussions by Sparks (1978) and Bottinga and Javoy (1990a) on the theory of bubble nu-

cleation in natural silicate liquids. We are unaware of other recent work in which new results with a bearing on this question are reported.

Murase and McBirney (1973) observed the generation of numerous bubbles at different temperatures and deduced an apparent activation energy for bubble nucleation, which turns out to be compatible with a process rate-controlled by the diffusion of carbon in the melt (Bottinga and Javoy 1990a). However, their description does not exclude the possibility of heterogeneous bubble nucleation, and neither the composition of the volatiles involved nor the concentration of these compounds in their samples have been determined. Hence during bubble nucleation the degree of supersaturation is unknown for these observations.

Westrich (1982) reports in an abstract that he heated initially bubble-free obsidian samples from 600° to 1100°C in a muffle furnace and observed the generation of 10 to 1000 bubbles/ cm^3/s in a sample containing 0.1 wt.% water initially. Unfortunately he does not reveal the chemical composition of the content of the bubbles, and if the sample contained also other volatiles. The partial water pressure in the muffle furnace is not mentioned. Probably, it was equal to that of the laboratory atmosphere, that is to say, it was less than the water vapour pressure at 25°C . If this was the case, one may deduce that Westrich's sample was supersaturated by at least a factor of five, from a simple extrapolation of the water solubility observations by Burnham and Jahns (1962) on obsidian.

Fine and Stolper (1985) and Dixon et al. (1988) have observed that submarine tholeiite may be supersaturated in CO_2 by a factor of five. The only measurement of dissolved gas in subaerial tholeiite we know of is by Harris and Anderson (1983) for a sample of the Kilauea summit eruption of November 1959. Their sample was highly supersaturated with respect to CO_2 and probably also with respect to H_2O (see section IV-2).

The presence of more than one generation of bubbles in lavas is an indication that bubble nucleation requires more than a "slight" supersaturation. Pineau et al. (1976) measured different carbon isotopic compositions of two coexisting bubble populations in a tholeiite from the Mid-Atlantic Ridge. Other occurrences of at least two bubble populations in basaltic rocks are mentioned in McMillan et al. (1987) for the Cohasset basalt flow in south-central Washington and in Walker (1989) for Hawaiian pahoehoe. The photographs in Friedman (1967) of pumice from the 1959–1960 eruption of Kilauea show also evidence for the presence of at least two different bubble populations. Three distinct pore-size populations were reported to be present in individual samples of plinian deposits from five volcanoes by Sparks and Brazier (1982) and interpreted to be due to different vesiculation events.

Sparks (1978) has remarked that the application of the classical theory for homogeneous nucleation to bubble formation in natural silicate liquids leads to serious contradictions. He suggested that at least some of these difficulties would disappear if bubble nucleation

in lavas occurred heterogeneously, i.e. if bubble nucleation took place on crystal faces in the wall rocks or of phenocrysts in the liquid. It seems unlikely that this could lead to the formation of the abundant bubbles in Hawaiian spongy pahoehoe lava, because heterogeneous nucleation gives rise to spatially characteristic bubble distributions. Besides, Delaney et al. (1978) noticed that only 30% of the bubbles in submarine basalts were attached to crystals. Also the decompression experiments at high pressures by Sakuyama and Kushiro (1979) on hydrous andesitic liquids gave rise to bubble distributions, which are incompatible with nucleation being predominantly heterogeneous.

Another suggestion by Sparks (1978) to alleviate the problems associated with the classical nucleation theory, is that the presence of "surface active agents" dissolved in basalt could cause bubble nucleation to occur readily once saturation has been reached. Water is a well known surface active agent, but it is present in Hawaiian tholeiites only at very low concentrations levels (Swanson and Fabbi 1973; Harris and Anderson 1983). Moreover the deduced initial water content of Hawaiian tholeiite is very small, i.e. 0.3 wt.% (Greenland et al. 1985; Gerlach and Graeber 1985). The measurements of Khitarov et al. (1979) indicate that such small concentrations of dissolved water have very little influence on the surface energy of liquid basalt.

II-2 Nucleation thermodynamics

The thermodynamically stable population of bubble nuclei containing i molecules of a volatile substance dissolved in the melt is given by Frenkel (1955):

$$n_b(i) = C \exp(-\Delta G(i)/k_B T) \quad (1)$$

$n_b(i)$ is the number density of bubble nuclei in the melt, C is the concentration of the volatile substance in solution, $\Delta G(i)$ is the free energy of formation of a nucleus containing i molecules, and k_B is the Boltzmann constant. $\Delta G(i)$ is a function of i , the energy associated with the melt-nucleus interface, and $\Delta\mu(P_n, P_m)$ is the chemical potential difference between the volatile in the nucleus and dissolved in the melt:

$$\Delta G(i) = i\Delta\mu(P_n, P_m) + A(i)\sigma \quad (2)$$

and

$$\Delta\mu(P_n, P_m) = \mu'_g(P_n) - \mu'_m(P_m) \quad (3)$$

$\mu'_g(P_n)$ is the chemical potential per molecule of the pure volatile substance in the nucleus at pressure P_n and $\mu'_m(P_m)$ the chemical potential per molecule of volatile dissolved in the melt at pressure P_m . The quantities marked by a prime are per molecule. $A(i)$ is the surface area of the nucleus containing i molecules and σ is the surface energy of the melt in contact with the volatile. P_n is the pressure on the vapour in the nucleus; it is not equal to P_m , which is the pressure on the melt. These two pressures are related:

$$P_n = P_m + 2\gamma/r \quad (4)$$

where γ is the surface tension and r is the radius of the spherical nucleus. The chemical potential difference $\Delta\mu'(P_n, P_m)$ depends on i . When i increases r grows and the difference between P_n and P_m vanishes. If at the same time solution equilibrium is attained we will have $\Delta\mu'(P_n, P_m) = 0$. But for small values of i with $P_n > P_m$, $\Delta\mu'(P_n, P_m)$ becomes zero or negative when the melt is sufficiently supersaturated.

$\Delta G(i)$ is equal to the difference in free energy between a volume of melt with one bubble nucleus with i molecules of a given gas and that of the same melt volume containing the i molecules of the gas in solution. $\partial\Delta G(i)/\partial i < 0$ is the requirement for thermodynamically stable nuclei. Later we will also consider embryos, which are thermodynamically unstable bubble nuclei. An embryo contains less gaseous molecules than a nucleus, but enough for $\Delta\mu'(P_n, P_m) < 0$, where now P_n is the pressure on the gas in the embryo. Therefore, the chemical potential of the gas in an embryo at the pressure P_n is smaller than the chemical potential of the same gas dissolved in the melt at pressure P_m . Thus embryos are chemically stable: their presence is only possible if the melt is supersaturated.

To calculate the nucleation number density, one needs to solve simultaneously: (a) Eqs. 1-4, (b) an equation of state for the free volatile (i.e. the Redlich-Kwong equation), and (c) an equation giving the solubility of the volatile in the melt. Usually in nucleation research, one is preoccupied with the determination of the mean nucleation rate (J) at a given moment.

$$J = \sum J(i) n_b(i) / \sum n_b(i) \quad (5)$$

where $J(i)$ is the nucleation rate for nuclei containing i molecules.

$$J(i) = n_b(i) / \tau(i)$$

$\tau(i)$ is the average time it takes to produce a nucleus containing i volatile molecules. The nucleation rate can be measured directly. From a practical point of view, rates smaller than one nucleus per cm^3 of melt per second are not observable (Sparks 1978).

II-3 Extension of the classical nucleation theory

The classical theory of bubble nucleation (Frenkel 1955; Toshev 1973) is based exclusively on Eqs. 1-4. It describes adequately bubble nucleation when the surface energy is small. But for liquids with high surface energies (silicate liquids, liquid metals, etc.) the observed rates of nucleation are much higher than one calculates with Eq. 1 (Richardson 1974).

A large surface energy means that $\Delta G(i)$ is large and that n_b is small (see Eqs. 1, 2). But if one lets i increase to offset the large surface energy term in Eq. 2 then $\tau(i)$ will increase, because it is determined by the time it takes to produce a concentration fluctuation giving rise to a cluster of i volatile molecules. The supersaturation ratio is an observed quantity; thus it can not be considered as an adjustable variable to obtain agreement between theory and observations.

To reduce $\tau(i)$ without reducing i or changing the supersaturation ratio, we proposed (Bottinga and Javoy 1990a) that nuclei are formed via an embryo stage. We recall that i is fixed by Eq. 1 and the condition of having $n_b > 1$. For embryos we have $\Delta\mu(P_n, P_m) < 0$, therefore the dissolved volatile molecules diffuse into them. Thus embryos will become thermodynamically stable nuclei, provided that their mean life time is sufficiently large. Probably, this will be the case, because no mechanisms causing their destruction have been identified. At constant supersaturation, the number of CO₂ molecules needed for the formation of an embryo is significantly smaller than that for a stable nucleus, i.e. 5×10^3 versus 10^5 . Hence the quantity $\tau(i)$ may be much smaller than is conventionally estimated.

The question is how these embryos can be formed, because the formation of their interface with the basaltic liquid requires also a certain quantity of surface energy. This is the reason that nuclei have to contain so many molecules before they can be stable. To circumvent this difficulty we noted that normally occurring temperature fluctuations in a cubic centimeter of melt represent energy changes which are greater than the quantities of energy required for the formation of the total interfacial area of several thousands of embryos in the same melt volume (Bottinga and Javoy 1990a). Hence a spatial and timely coincidence of these normal thermodynamic temperature fluctuations and of cooperative fluctuations of the concentration of the volatile substance in solution could lead to the formation of embryos.

II-4 Nucleation of CO₂ bubbles

Our previous calculations showed that for dissolved CO₂ in silicate melts, the bubble-number density depends very strongly on i . Small increases in i cause enormous increases in n_b , from infinitely small to exceedingly large, when $\partial\Delta G(i)/\partial i < 0$ (Bottinga and Javoy 1990a). Under natural circumstances n_b should be greater than one nucleus per cm³ of melt, if an observable number of bubbles is to be produced as a result of a nucleation event. When we are dealing with small bubbles (diameters of less than 0.1 mm) the difference between bubble and nucleation number densities cannot be important. Bubble-number densities in MORB vary considerably from about 10 bubbles/cm³ to more than 10^6 bubbles/cm³ of melt according to the data of Kurz and Jenkins (1981), Marty and Ozima (1986) and Dixon et al. (1988). The latter authors report that MORB dredged from depth between 2 and 3 km can be supersaturated in CO₂ by a factor of five. This observation indicates that the CO₂ supersaturation ratio should be five or larger before CO₂ bubbles nucleate under magmatic conditions at pressures of 200 to 300 bars. This conclusion and calculations similar to those plotted on Fig. 1, make it possible to estimate the number of CO₂ molecules in a stable nucleus to be about 10^5 , under natural conditions in tholeiitic melts (Bottinga and Javoy 1990a; Fig. 2).

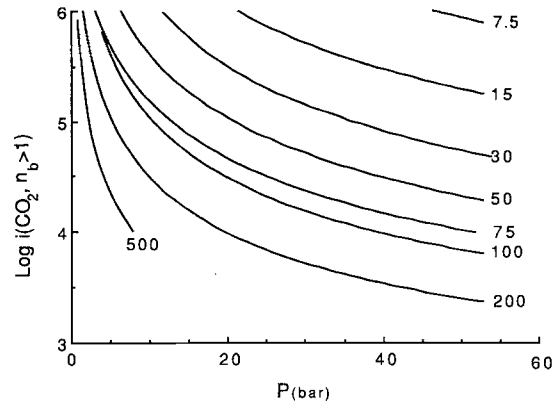


Fig. 1. The decimal logarithmic value of the number of CO₂ molecules in stable nuclei when the nucleation number density is larger than 1 nucleus/cm³, at CO₂ supersaturation degrees varying from 7.5 to 500, plotted against pressure (bar)

We anticipate that the number of molecules (i) in stable nuclei produced at an observable rate is kinetically controlled and does not depend very much on pressure under natural conditions. This implies according to the calculated results plotted on Fig. 1 that when pressure increases, bubble nucleation will take place at smaller supersaturation ratios, and that close to the surface of the Earth the nucleation of bubbles in basalt occurs only when supersaturation is considerable. This conclusion is nothing else than a consequence of the fact that the surface area of a nucleus, containing a constant number of volatile molecules, increases when the pressure decreases because the molecular volume of the volatile in the nucleus becomes larger during decompression. The variation with pressure of the surface area of a bubble nucleus causes concomitant variations in the surface energy and in the nucleation-number density (see Eq. 1).

In Bottinga and Javoy (1990a), we have given an expression for the supersaturation ratio needed for CO₂ bubble nucleation in liquid basalt as a function of pressure. This expression is only valid for $200 < P(\text{bar}) < 5000$; for $P > 5000$ bar the required supersaturation ratio becomes virtually independent of pressure, because the molecular volume of CO₂ changes very little with P . At that time we considered exclusively pressures greater than 200 bar, but for the purpose of this paper we have decreased the lower limit of these calculations to $P=2$ bar. The results are plotted in Fig. 1, and are expressed as

$$\text{Log}(C_n/C_e) = 3.281 - 1.4511 \text{Log}(P) + 0.1672[\text{Log}(P)]^2$$

where C_e is the CO₂ solubility in basalt at the basalt liquidus temperature and pressure $P(\text{bar})$. C_n is the CO₂ concentration needed for the formation of stable nuclei with 10^5 CO₂ molecules and a nucleation-number density larger than one nucleus/cm³ of melt.

II-5 Nucleation of water vapour bubbles

The surface energy of liquid basalt in contact with H₂O or CO₂ is known (see Appendix). The solubility of wa-

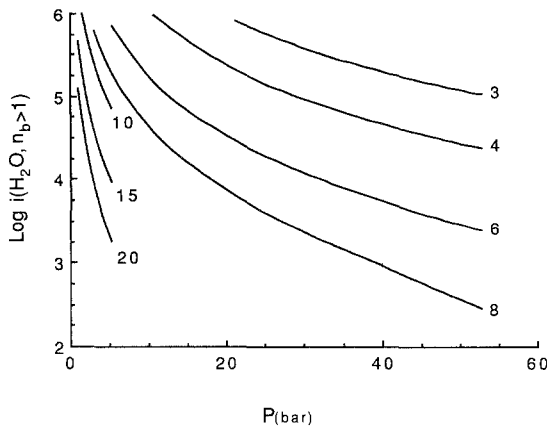


Fig. 2. Same as Fig. 1, but for H₂O and supersaturation degrees varying from 3 to 20

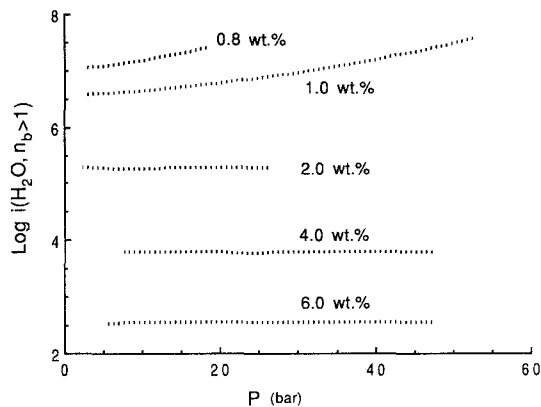


Fig. 3. The decimal logarithmic value of the number of H₂O molecules in a stable nucleus when the nucleation density is larger than 1 nucleus/cm³ for constant concentrations of dissolved H₂O varying from 0.8 to 6.0 wt.%, plotted against pressure

ter in molten basalt has been determined by Hamilton et al. (1964) and the CO₂ solubility by Mysen et al. (1975) and Stolper and Holloway (1988). With these data we have calculated the results for CO₂ (Fig. 1) and H₂O (Fig. 2). Values of $i(\text{CO}_2)$ and $i(\text{H}_2\text{O})$, for which $n_b > 1$, as a function of pressure for different supersaturation ratios are shown. Fig. 3 is a replot of Fig. 2, with $i(\text{H}_2\text{O})$ values for constant dissolved water concentrations instead of supersaturation ratios. Evidently, even at low pressures, the presence of a stable population of water nuclei with $i(\text{H}_2\text{O}) < 10^6$ is very unlikely, given that the initial water concentration in Hawaiian tholeiite is reported to be 0.3 wt.% (Greenland et al. 1985; Gerlach and Graeber 1985). Hence the nucleation of water bubbles in Hawaiian tholeiite seems to be excluded according to the classical theory.

One may wonder whether or not the presence of aqueous embryos can resolve this contradiction between theory and the unequivocal observations of H₂O degassing by Swanson and Fabbi (1973) at a pressure of about 1 bar. For this reason, we have calculated minimum i values for H₂O bubble embryos. These $i(\text{H}_2\text{O})$ values are plotted against pressure in Fig. 4 for differ-

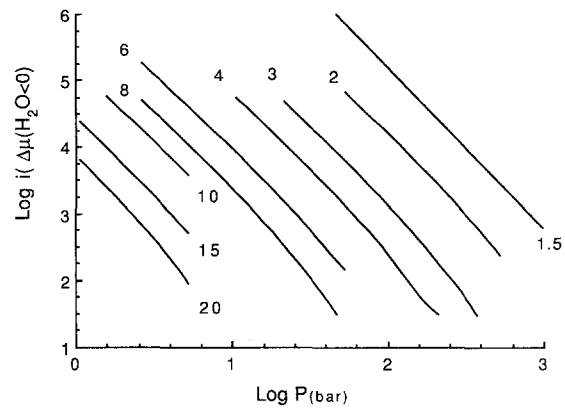


Fig. 4. The decimal logarithmic value of the minimum number of H₂O molecules in an embryo, when the chemical potential of melt dissolved H₂O is larger than that of gaseous H₂O in the embryo, plotted against pressure at constant supersaturation. Supersaturation ratios vary from 1.5 to 20

ent supersaturation ratios. It is obvious that even at $P < 10$ bar, $i(\text{H}_2\text{O})$ will be larger than 10^5 for a water supersaturation of four or smaller. But with an initial concentration of 0.3 wt.% H₂O and a fixed temperature of 1150° C, the water supersaturation ratio can not attain a value as large as four at $P > 1$ bar according to the available solubility data. For this reason $i(\text{H}_2\text{O})$ for embryos should be much larger than 10^5 (see Fig. 4). Consequently, this mechanism will not lead to the formation of numerous stable water nuclei in Hawaiian tholeiites. However, the common occurrence of spongy pahoehoe on Hawaii, is a clear proof that bubbles were formed in these tholeiitic liquids at atmospheric pressure (Walker 1989).

Figure 1 shows that CO₂ supersaturation should be very large for the formation of stable CO₂ bubble nuclei, at $P < 10$ bar and $i(\text{CO}_2) < 10^6$ molecules per nucleus. Actually it turns out that for small P , i.e. close to the Earth's surface, the surface energy contribution to $\Delta G(i)$ for CO₂, increases more rapidly with diminishing pressure than the energy contribution due to supersaturation for all reasonable values of $i(\text{CO}_2)$. Hence it becomes really impossible to have stable CO₂ bubble nuclei with $n_b < 1$ and $i(\text{CO}_2) > 10^6$. However, it is possible to form embryos for CO₂ bubbles with $i(\text{CO}_2) < 10^4$ (Fig. 5) because the CO₂ solubility is very small, and during eruption large degrees of CO₂ supersaturation may be attained. Harris and Anderson (1983) reported a dissolved CO₂ concentration in freshly erupted Kilauean tholeiite equivalent to a supersaturation ratio of more than 1000 (see section IV-2). Hence, the formation of CO₂ embryos eventually giving birth to stable CO₂ nuclei, is a possibility at $P < 10$ bars. Of course the growth and stabilization of these embryos will be enhanced by an additional diffusional flux of water into them. Thus at low pressures, the initiation of water-rich bubbles in Hawaiian tholeiite can occur because of the formation of CO₂ embryos.

In this discussion we have neglected to consider the likelihood of nuclei containing both CO₂ and H₂O. A

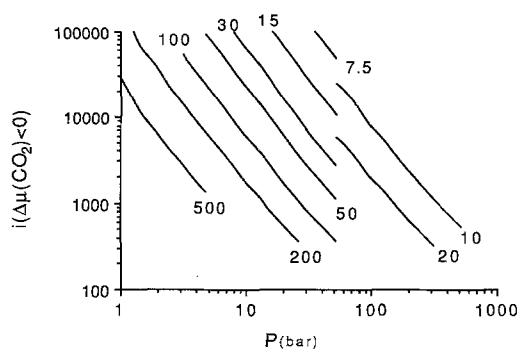


Fig. 5. The decimal logarithmic value of the minimum number of molecules in a CO_2 embryo with the chemical potential of melt-dissolved CO_2 larger than that of gaseous CO_2 in the embryo, versus pressure for constant supersaturation ratios varying from 7.5 to 500

general solution of this problem is outside the scope of this paper. For the purpose of our discussion certain simplifications are justified because of the low concentrations of dissolved CO_2 and H_2O of approximately 0.02 and 0.3 wt.%, respectively (see section III-2). Because of these low concentrations, the main effect due to the presence of a second volatile species will be a decrease in the term $\Delta\mu(P_n, P_m)$ (see Eq. 3). This is the consequence of the introduction of an entropy term, affecting the chemical potentials of the gases in the nucleus. The chemical potential of CO_2 dissolved in the melt will not be really affected by the presence of a small amount of H_2O ; likewise the chemical potential of H_2O dissolved in the melt will be virtually independent of the small quantity of CO_2 also present. Hence the term $\Delta\mu(P_n, P_m)$ for the different gases in the nucleus will be smaller than for the case that only a pure gas is present and the free energy of formation of the nucleus will diminish. This means a reduction of the total amount of gas needed to form a stable nucleus or an embryo with $\Delta\mu(P_n, P_m) < 0$, at constant supersaturations of the different gases. Hence at low P , bubble formation will take place at pressures somewhat higher than those calculated for pure CO_2 . The presence of a sulfur-containing gas will enhance this effect.

III CO_2 and H_2O in Hawaiian liquid tholeiite

III-1 Before degassing

In this section we will trace the development of bubbles in Hawaiian tholeiite and calculate the evolution of the concentrations of carbon and H_2O dissolved in the melt and in the bubbles while the melt moves from its source region to the surface. The quantity of carbon dissolved in the melt or exsolved as CO_2 in bubbles is expressed as gram of CO_2 per 100 grammes of basaltic liquid containing the bubbles.

The inferred depth of magma generation underneath Hawaii is about 70 km (Eaton 1962), in agreement with the estimate of 60–100 km of the Basaltic

Volcanism Study Project (1981). The initial CO_2 concentration of 0.65 wt.% in Hawaiian tholeiite (Gerlach and Graeber 1985) corresponds roughly to the CO_2 solubility in a tholeiitic liquid (Mysen et al. 1975; Stolper and Holloway 1988) at its liquidus temperature and at a pressure equal to the lithostatic pressure in the source region of Hawaiian basalt. Hence it is reasonable to suppose that Hawaiian tholeiite is CO_2 saturated when it is generated (Bottinga and Javoy 1989). For H_2O this is not the case, because its solubility in liquid tholeiite under the P and T conditions in the upper mantle source region is much larger (Hamilton et al. 1964) than its inferred initial concentration of 0.30 wt.% (Gerlach and Graeber 1985; Greenland et al. 1985). In effect, H_2O gives the impression of behaving like an incompatible substance when tholeiite is formed by partial melting. When Hawaiian tholeiite enters the magma chamber it will be saturated in CO_2 and undersaturated in H_2O .

The growth and rise of bubbles in magmas have been described in Bottinga and Javoy (1990b); the results we present here were calculated in the same way. We have assumed that the speed with which the magma rises from its source region to the magma chamber is constant and equal to 2 cm/s. This assumption is harmless because equilibrium between bubbles and melt is fairly rapidly attained. Thus from a geological point of view the melt will always be in equilibrium with the bubbles as long as melt velocities are smaller than 10 cm/s and bubble-number densities greater than or equal to 10^3 bubbles/cm³ (Bottinga and Javoy 1990b).

III-2 Preeruptive degassing

Before magma enters the chamber, bubble nucleation will have taken place when the CO_2 supersaturation ratio became larger than 1.5 (Bottinga and Javoy 1990a). We have assumed that the bubble-number density for the magma before entering the magma chamber amounted to 10^4 bubbles per cm³; this value may seem large but is typical for values observed for oceanic ridge basalts. In the magma chamber, the magma vesicularity would be on the average somewhat less than 4 vol.% if the bubbles were stationary, but due to their buoyancy the bubbles will rise at speeds ranging from 100 to 200 m/year with respect to the slowly convecting magma (Huppert et al. 1986; Jaupart and Brandeis 1986) depending on where they are in the magma chamber. According to Ryan (1987) the summital chambers of Kilauea and Mauna Loa are at similar depths (2–7 km) below their calderas. For reasons of simplicity, we have assumed an isobaric magma chamber at 600 bars pressure, i.e. at 2.25 km below the caldera. At this pressure the bubbles have a diameter of 0.26 mm, assuming that they all have the same size; this agrees with the estimate based on fluid dynamics by Vergnolle and Jaupart (1990). In reality the bubbles will show a gaussian size distribution (Walker 1989; Nordlie et al. 1989), as long as they are stationary, because the spatial distribution of nuclei giving rise to the

observed population is most likely random. But once they start to move with respect to the melt, the larger the bubble the faster it will grow due to the combined effects of diffusion and decompression. The growth rate of non-stationary bubbles is size dependent.

The eruption dynamics of Kilauea have been treated by Vergnolle and Jaupart (1990) and Jaupart and Vergnolle (1988, 1989); these authors have shown that the accumulation of gas in the roof zone of the magma chamber can trigger eruptions. This gas accumulation is the result of the buoyancy-induced upward movement of bubbles present in the magma. Part of this gas will not be retained in the chamber but escapes to the atmosphere prior to eruption. Evidence for pre-eruption degassing of the Kilauean summit magma chamber has been given by Greenland et al. (1985) and Casdevall et al. (1987); the latter authors monitored the gas emission rate from fumaroles in the Kilauea caldera. The major constituents of this gas plume are CO₂, H₂O and SO₂ (Caddle 1980), with an atomic C/S ratio larger than ten (Casdevall et al. 1987). Such large C/S ratios are due in part to the small vapour pressure of liquid iron sulphides and to the precocious exsolution of gaseous CO₂; they suggest that this gas has escaped from the magma at relatively high pressure. During eruptions at the summit this ratio decreased to less than five, and in the rift zone it became less than one (Casdevall et al. 1987). This indicates the progressive loss of CO₂ from the magma. We have assumed that 90% of the gas bubbles entering the magma chamber from below manages to escape from the liquid tholeiite, before the eruption starts. This estimate is inspired by observations on MORB (Pineau et al. 1976; Pineau and Javoy 1983; Bottinga and Javoy 1989) and is in fair agreement with Gerlach and Graeber (1985). According to our calculations, uncontaminated chamber gas and bubbles in the magma in the chamber contain 97 vol.% CO₂ and 3 vol.% H₂O, ignoring the presence of SO₂. When the magma leaves the chamber, it is in equilibrium with the free gas phase and carries 0.021 wt.% CO₂ and 0.3 wt.% H₂O in solution and 10³ bubbles/cm³ in suspension.

III-3 Syneruptive degassing

During an eruption, lava rises at large vertical velocities towards the caldera (Vergnolle and Jaupart 1990); this is suggested by speeds of greater than 10 cm/s at which it exits from the vent and may even attain 200 cm/s (Thorarinsson 1968). Under such conditions equilibrium between bubbles and the basaltic liquid is not any longer possible. The main reasons for this are:

1. due to the high lava velocity the CO₂ and H₂O solubilities will decrease rapidly;
2. the bubble population of the magma is reduced because of the escape of bubbles in the magma chamber;
3. bubble nucleation becomes increasingly more difficult when the pressure diminishes;
4. the faster the magma moves the sooner it arrives at

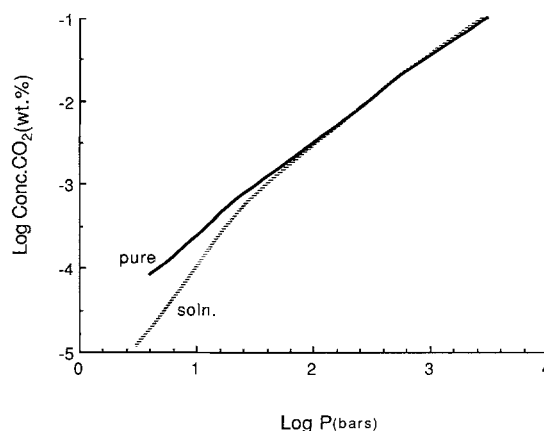


Fig. 6. The decimal logarithmic value of the dissolved CO₂ concentration (wt.%) as a function of pressure, when CO₂ is the only gas present (pure), and when the melt contains 0.3 wt.% H₂O (soln.) at $P = 1000$ bar

the surface of the Earth and the less time is available to reestablish equilibrium.

Another complicating feature is that at low pressures the exsolution of H₂O from the silicate melt becomes important and the small vapour pressure of the exsolved liquid sulphide phase becomes relatively more important, hence the partial pressures of H₂O and presumably SO₂ in the bubbles become non-negligible.

When magma is expelled from the chamber the assumption of a constant magma velocity becomes unrealistic and should be relaxed. Similarly, when the vesicularity becomes larger than 50 vol.% some of the approximations we have used (Bottinga and Javoy 1990b) are no longer completely valid. For these reasons our results for pressures of less than 30 bars are only qualitative.

Figure 6 shows the concentration of dissolved CO₂ in basaltic liquid ejected from the magma chamber at a speed of 2 cm/s and with initial concentrations of dissolved CO₂ and H₂O of 0.021 and 0.3 wt.%, respectively, in equilibrium with bubbles containing both gases or only carbon dioxide. The curve marked "pure" is for the simplified case that only CO₂ is present, while the other curve marked "soln." is for the presence of the two gases. At $P > 100$ bars the quantity of CO₂ in solution corresponds to the solubility of pure CO₂ in the basaltic liquid, but at lower pressures the decrease in the effective CO₂ solubility due to the presence of H₂O is evident. This effect is due to a decrease of $f(\text{CO}_2)$ in the bubbles when the relative H₂O concentration becomes larger at a given total pressure. Figure 7 indicates how the effective solubility of H₂O diminishes due to the presence of CO₂. The onset of H₂O exsolution in the presence of CO₂ is also quite evident from Fig. 8, depicting results of calculations for a melt-upward velocity of 10 cm/s. At this speed, CO₂ in the bubbles is not in equilibrium with that dissolved in the melt, but there is still equilibrium between exsolved and dissolved H₂O. This is due to the fact that the diffusion constant for H₂O is larger than for that for CO₂. Clear-

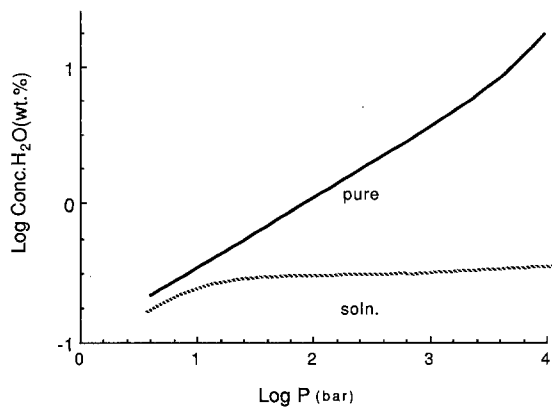


Fig. 7. Similar to Fig. 6, but for H₂O (pure) and H₂O in the presence of CO₂ (soln). For the latter case the melt is saturated with respect to CO₂

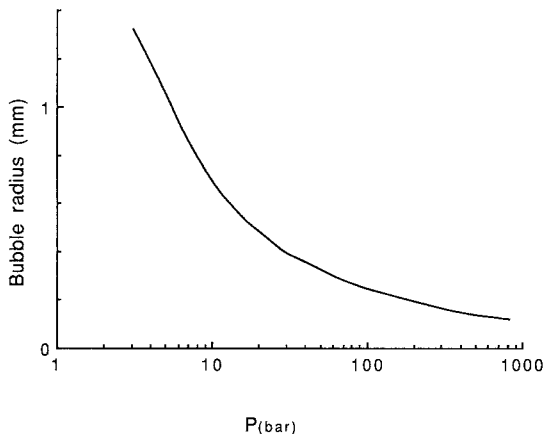


Fig. 8. Bubble radius (mm) versus pressure (bar), vertical upward melt velocity equals 10 cm/s. Bubble number density is equal to 1000

ly, H₂O exsolution in Hawaiian tholeiite becomes important at pressures less than 10 bars, although this value will increase somewhat when the inevitable presence of SO₂ has been taken into account. Hence the depth at which H₂O exsolution becomes important depends on the initial concentrations of the igneous gases, the speed at which the magma moves towards the Earth's surface and, in a minor way, on the bubble-number density.

In Figs. 9 and 10 the development of supersaturation of the melt with respect to CO₂ and H₂O is shown for different melt velocities as a function of pressure. The H₂O supersaturation ratio, like that of CO₂, increases with diminishing pressure, but for a melt velocity of 10 cm/s the supersaturation ratio for water remains very close to unity. The CO₂ supersaturation ratio is already somewhat larger than unity at $P=600$ bars and starts to increase rapidly at pressures less than 20 bars. For these calculations, we have supposed that only residual primary, i.e. pre-eruption, bubbles were present. In reality one should anticipate the nucleation of new, secondary, bubbles occurring at these small

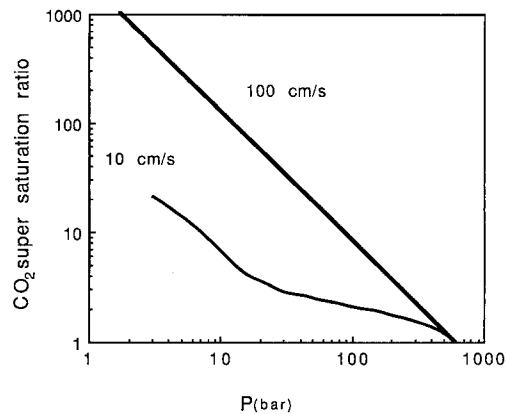


Fig. 9. CO₂ supersaturation ratio as a function of pressure and vertical-upward velocities of the melt of 10 cm/s and 100 cm/s. The melt is in equilibrium with respect to CO₂ at $P=600$ bar. Bubble-number density equals 1000 bubbles/cm³ of melt

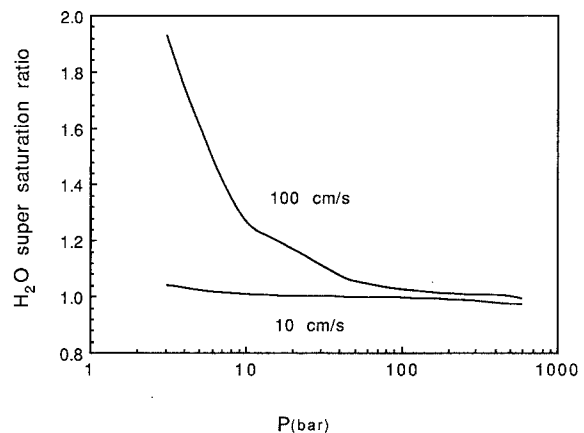


Fig. 10. Similar to Fig. 9, but for H₂O. Note that for $V_{\text{melt}}=10$ cm/s, the melt remains in equilibrium with respect to H₂O

pressures. The discussion in section II-5, the data plotted in Fig. 9 and the calculated i values for CO₂ embryos (Fig. 5) indicate that generation of secondary bubbles can take place only very close to the Earth's surface and when the bubble-number density of the residual primary bubbles is smaller than 10⁴ bubbles/cm³ of melt (see Eq. 14 in Bottinga and Javoy 1990b). Volumetrically these secondary bubbles will be non-negligible because of the low pressure. The accumulation of gas in the bubbles is rate controlled by diffusion, hence the total molecular content of these secondary bubbles can not be very important when the magma moves with vertical velocities greater than 10 cm/s (see Vergnolle and Jaupart 1990). The principal message of Figs. 9 and 10 is that the presence of water is of no importance during the triggering of Hawaiian tholeiitic eruptions but that it contributes to propelling the magma when the Earth's surface is approached. Gerlach and Graeber (1985) and Greenland (1987a,b) have drawn attention to this aspect already.

Figure 8 shows that at about 5 bars pressure the radius of the residual primary bubbles will be about 1.0

mm, and thus the total bubble volume per cm^3 of melt would be about 4 cm^3 . According to the Sparks (1978), criterion magma disruption should have taken place at $P > 6$ bars when the bubble to melt volume ratio became greater than three. Our calculated total bubble volume per cm^3 of melt depends on: (1) the supposition that the bubble-number density remains constant at 1000 since the magma left its reservoir; (2) that the melt velocity is not greater than 10 cm/s. Nucleation of secondary bubbles should not really affect this conclusion because the amount of gas molecules in the new bubbles will be much smaller than in the primary residual ones. It seems reasonable that the bubble-number density of the primary residual bubbles in the melt remains constant after ejection from the magma chamber because bubble velocities with respect to the moving melt are relatively small; however this may change if bubble coalescence takes place. Higher melt velocities result in smaller bubbles; if the melt velocity is 200 cm/s the total bubble volume/melt ratio will be equal to three only at 3 bars. The inevitable, but ignored, presence of SO_2 is a reason for melt disruption to take place at somewhat higher pressures than we calculate using the Sparks (1978) criterion. Interestingly enough, Decker (1987) wrote that Gerlach "determined that magmatic gases of the volume and composition normally occurring in flank eruptions of Kilauea Volcano begin to boil rapidly out of the magma at pressures equivalent to depths of only 40–100 m", that is to say at pressures varying from 10 to 26 bars.

The exsolution of melt-dissolved water is rate-controlled by the diffusion of H_2O in the melt. The most effective way to speed up such a process is by enlarging the surface across which H_2O diffuses to escape from the melt. Therefore the exsolution of water into bubbles is a process with positive feedback, accelerated by diminishing pressure. The propulsive action of the exsolving water vapour is due to the difference between the molecular volume of water vapour at low pressure and magmatic temperature and the partial molar volume of H_2O dissolved in the melt, i.e. approx. $20 \text{ cm}^3/\text{mol}$ (Silver and Stolper 1985). The effect is optimal at $P = 1$ bar when the molecular volume of water vapour at magmatic temperature is $1.13 \times 10^5 \text{ cm}^3/\text{mol}$. When the melt arrives at the Earth's surface and fountaining takes place, most of the secondary and residual primary bubbles will be lost to the atmosphere.

IV Volcanic gas

IV-1 Molecular composition

Gerlach and Graeber (1985) give four restored analyses for gas samples collected by Jaggar from "sustained lava lake activity" at Halemaumau. They consider these to be "the most reliable volcanic gas data". These gases were collected at about the same pressure and have similar chemical equilibrium temperatures, ranging from 1140° to 1185°C . However, their compositions are significantly different; their volume ratios $\text{CO}_2/$

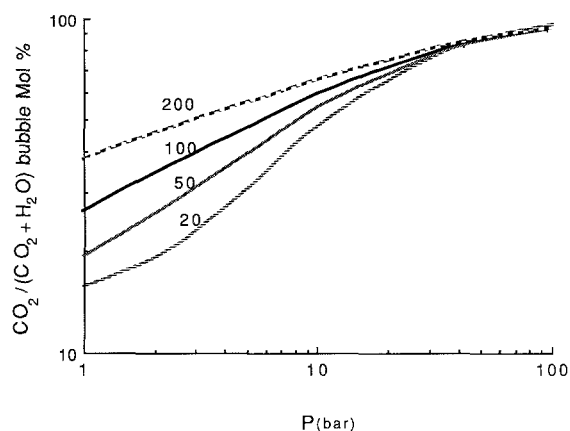


Fig. 11. Mol% CO_2 in primary bubbles as a function of pressure and for vertical upward melt velocities varying from 20 to 200 cm/s. Bubble number density is equal to 1000

($\text{CO}_2 + \text{H}_2\text{O}$) range from 0.20 to 0.57. If these compositions represent uncontaminated igneous gases, why are they so different? Probably, they came from bubbles which have escaped from a tholeiitic liquid. We have calculated how the composition of an igneous bubble in erupting Hawaiian tholeiite changes due to differences in magma-rise velocity and due to differences in the pressure at which it escapes from the melt. The results of the computations for magma-rise velocities varying from 2 to 200 cm/s are plotted on Fig. 11. Because the results for speeds less than or equal to 20 cm/s are indistinguishable, only those for 20 cm/s and larger have been reproduced. At $P = 1$ bar the $\text{CO}_2/(\text{CO}_2 + \text{H}_2\text{O})$ molecular ratio may vary by more than a factor of two, depending on the velocity. A similar compositional variation is caused by a change in the pressure at which bubbles are released, from 1 to 10 bars. The first effect is kinetic: it is due to the difference in the diffusion constants for CO_2 and H_2O in liquid basalt. The second effect is due to differences in the solubilities and their pressure dependences for CO_2

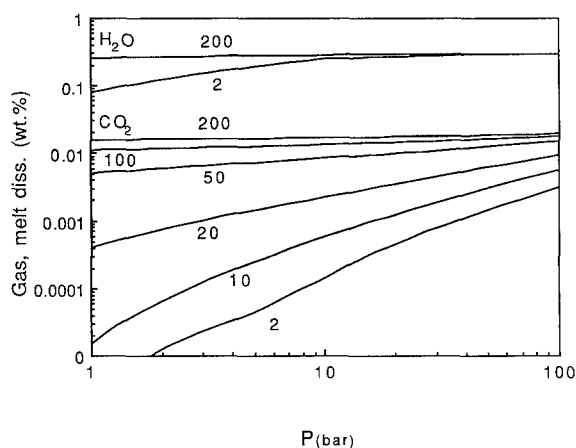


Fig. 12. Dissolved H_2O and CO_2 in the melt as a function of pressure, for melt velocities varying from 2 to 200 cm/s. See text for the conditions adopted for the calculation

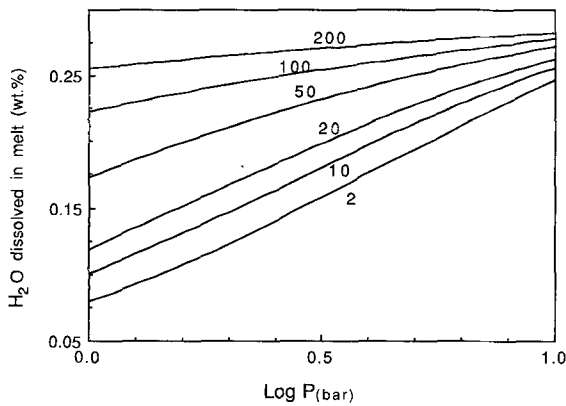


Fig. 13. Same as Fig. 13, but for H₂O and $P < 10$ bar

and H₂O in tholeiitic melts. These two causes may explain the observed differences in the "J samples" of Gerlach and Graeber (1985). Similar effects have been observed by Greenland (1987a) in gases collected at Mauna Loa, and were attributed by him also to these two causes. These bubble-gas compositional variations are accompanied by concentration changes of the residual dissolved volatiles in the basaltic liquid; these have been plotted in Figs. 12 and 13.

IV-2 Lava flow degassing

The escape of gases from Hawaiian lava flows has been described by Swanson (1973) and Swanson and Fabbi (1973), but their observations are difficult to interpret in terms of physical mechanisms because they do not contain information on the quantity of gas dissolved in the lava and on how much gas is in the bubbles. The only measurement we are aware of the amount of dissolved gas in a subaerially erupted lava, is by Harris and Anderson 1983, on the sample Iki-22, which is a "glassy scoria ... typical of the hot, olivine rich basalt" from the Kilauea summit eruption on 18 November 1959. The matrix glass of this sample contains in solution 0.063 wt.% H₂O and 0.004 wt.% CO₂ (Harris and Anderson 1983). Upon comparison of these results with the equilibrium solubility of these gases at 1150° C and $P = 1$ bar, one arrives at the conclusion that this sample was supersaturated with respect to CO₂ by a factor of more than 1000, and with respect to H₂O by a factor 3, approximately. These conclusions are qualitatively in good agreement with the observations by Swanson and Fabbi (1973) and Swanson (1973).

The very interesting results of Harris and Anderson (1983) should be confirmed and more measurements of the dissolved CO₂ and H₂O contents of subaerial lavas are really needed. The accuracy or precision of the Harris and Anderson results are not known, but it is well established (Eaton et al. 1987) that their sample Iki-22 has been exposed to conditions not considered in our calculations. Therefore, one should not be surprised that the results plotted in Fig. 12, for the concentrations of dissolved CO₂ and H₂O in subaerial Hawaiian tho-

leite, are incompatible with the Harris and Anderson observations for this sample. Besides, the reported concentrations for these two major igneous gases in Iki-22 are in disagreement with the initial concentrations for CO₂ and H₂O, deduced by Gerlach and Graeber (1985), if the evolution of this sample has been as simple as we have assumed here.

Apparently, Walker's (1989) paper on spongy pahoehoe at Hawaii is the first contribution devoted to the study of vesicles in lavas from Hawaii, where this type of rock seems to be quite common everywhere, except close to the vent from which the lava was issued. In near-vent lavas, Walker (1989) reports the presence of early formed centimeter-size bubbles. These seem to escape from the lava before bubble nucleation and growth occur, causing the formation of the spongy pahoehoe. Walker (1989) observed that the size distribution of the vesicles in these spongy lavas in a given horizontal plane is "normal". The relatively low viscosity of Hawaiian tholeiite close to the vent allows centimeter-size bubbles to reach the upper surface of the flow fairly rapidly ($V_{\text{bubble}} = 1$ cm/s) and in this way these early bubbles disappear. While the lava flows away from the vent, its temperature decreases and the supersaturation of the dissolved gases, in particular CO₂, augments. This increase results in the generation and growth of a new generation of bubbles, which is responsible for the formation of spongy pahoehoe. It is to be expected that this phase of bubble nucleation takes place in the same way as we have described in section II-5.

The newly formed bubbles show a number density of about 1000 bubbles/cm³ of melt. Variations of this number can be explained as being due to variations in the rate at which the temperature diminishes with distance from the upper and lower limits of the flow and due to shearing as has been pointed out and illustrated by Walker (1989). When this third generation of bubbles is being formed the viscosity of the lava, which is now non-Newtonian, increases rapidly by about a factor 20 according to the Einstein-Roscoe equation (Roscoe 1952). The vesicularity of the magma may now attain 50% and we are dealing with a phenomenon of two-phase flow. But the increase in viscosity will prevent the newly formed bubbles from floating over distances of more than 20 cm. Therefore the bubble-number density profile vertically across spongy pahoehoe is close to symmetrical. Several of these profiles have been described in detail in this remarkable paper by Walker (1989).

V Conclusions

Classical nucleation theory prohibits the formation of bubble nuclei in Hawaiian tholeiitic lava at low pressure because of the large surface energy of liquid tholeiite and the low initial dissolved water content. This difficulty may be circumvented with the formation of CO₂ embryos, which grow mainly due to a diffusion influx of H₂O. In the calculation of the degree of super-

saturation of a lava with respect to CO_2 , H_2O or SO_2 , one should take into account the presence of all the major igneous gases. In addition, one should indicate if the supersaturation is with respect to the content of bubbles at a given total pressure or with respect to the atmosphere. The observations on gases dissolved in liquid tholeiites on Hawaii (Harris and Anderson 1983) suggest strongly that these liquids contain too much dissolved CO_2 with respect to bubbles at $P=1$ atm. or with respect to the atmosphere, to be compatible with extrapolations of laboratory-determined solubility relationships (see section IV-2). This situation is probably due to bubble-nucleation difficulties at low pressure. The available scanty evidence indicates that more than one distinct population of bubbles are usually present in glassy volcanic rocks.

Hawaiian tholeiite becomes saturated with respect to CO_2 when it is formed by partial melting in the upper mantle. While it migrates to a magma chamber, initial nucleation of bubbles occurs because CO_2 supersaturation exceeds a pressure-sensitive critical value. In the Hawaiian magma chamber these primary bubbles move up under the influence of buoyancy. Some of these bubbles will get lost during volcanically quiet periods when they escape to the atmosphere via active fumaroles. Others escape from the magma chamber during the occurrence of lava expulsion, caused by the stabilisation of a foam layer. This foam is formed by the accumulation of primary bubbles under the roof of the magma chamber as has been described by Jaupart and Vergnolle (1988, 1989) and Vergnolle and Jaupart (1990). But a small fraction of these primary bubbles does not manage to escape and is transported in suspension to the vent.

While an eruption takes place, the upward-rushing tholeiite becomes greatly supersaturated in CO_2 because of the pressure dependence of the CO_2 solubility and the large velocity of the lava, and because the small CO_2 diffusion constant precludes fast reestablishment of equilibrium with the reduced quantity of remaining primary bubbles. The low pressure and the small dissolved CO_2 concentration make the formation of abundant stable nuclei difficult, but H_2O will contribute greatly to stabilize newly formed CO_2 embryos. Most of the secondary bubbles formed at low pressure and the residual primary bubbles formed at high pressure, will escape from the magma when it leaves the vent, in particular when fountaining takes place. However, degassing during this event can be incomplete because this process is rate-controlled by diffusion of the dissolved volatiles in the liquid basalt. In Hawaiian subaerial liquid tholeiite a third generation of bubbles may be formed because of increasing CO_2 supersaturation when the lava cools. These different bubble populations or their remnants show up because of their distinct size distribution and chemical and isotopic composition.

In geochemical research on fumarolic or volcanic gases, one should be aware that the temperature and pressure at which the gases are released, and the velocity with which the tholeiite has risen to the Earth's sur-

face, play an important role in determining the chemical composition of these gases. Much of the compositional variability shown by Hawaiian volcanic gas samples of superior quality may be due to these causes.

Acknowledgements. We would like to thank Françoise Pineau, Claude Jaupart and Ed Mathez for the very useful discussions we have had with them on the subjects treated in this paper. Our work was financially supported by the INSU-CNRS D.B.T. programme.

Appendix

We have ignored the problem of speciation of the dissolved CO_2 (Fine and Stolper 1985) and H_2O (Silver and Stolper 1985) in silicate melts. Because of the very small concentrations of these gases, this neglect can be justified in the light of the observations by the before-mentioned authors. For the same reason, we may consider as being ideal the mixing of the CO_2 and H_2O dissolved in the basaltic liquid. For the solubility of CO_2 in liquid basalt, we have followed Stolper and Holloway (1988), combining their low-pressure observations at 1200°C with the high T and P observations by Mysen et al. (1975). The constants in the solubility expression:

$$RT \ln[X(\text{CO}_2)/f(\text{CO}_2)] = A_1 + A_2 T + A_3 T \ln(T) + A_4 P \quad (\text{A-1})$$

were obtained by least squares fitting, $A_1 = -0.8897$ J/mol, $A_2 = -410.9$ J/(K·mol), $A_3 = 52.54$ J/(K·mol) and $A_4 = -3271$ J/(kbar·mol). $X(\text{CO}_2)$, wt.%, is the CO_2 solubility; $f(\text{CO}_2)$, kbar, is the CO_2 fugacity and $R = 8.3143$ J/(K·mol). This solubility expression reproduces the observations to within the reported error margins. Eq. A-1 indicates for $P < 1$ kbar and magmatic temperatures, that the solubility of CO_2 in the melt is proportional to $f(\text{CO}_2)$, as would be anticipated intuitively. The CO_2 solubility in liquid basalt varies sympathetically with temperature (Mysen et al. 1975).

The observations by Hamilton et al. (1964) were used to determine by fitting the constants in the solubility expression (A-2) for water in liquid basalt.

$$X(\text{H}_2\text{O}) = [B_1 f^{1/2}(\text{H}_2\text{O}) - B_2] \text{ wt.} \% \quad (\text{A-2})$$

$X(\text{H}_2\text{O})$ is the water solubility; $B_1 = 3.437$ kbar $^{-1/2}$; $B_2 = 0.115$. The Hamilton et al. (1964) data are for $P = P(\text{H}_2\text{O}) > 1$ kbar; extrapolation to zero water fugacity gives a residual solubility of 0.115 wt.% H_2O . This is not completely in agreement with the general observation that the water solubility of silicate melts at small water fugacities varies linearly with the square root of $f(\text{H}_2\text{O})$ and approaches zero when $f(\text{H}_2\text{O})$ tends to zero. For molten diopside at solidus temperatures this relation is well obeyed (Eggler and Rosenhauer 1978, Fig. 14). Data for simple silicate melts show this relationship also (Turkdogan 1983). Therefore in the absence of data for liquid basalt, we have assumed that for $f(\text{H}_2\text{O}) < 1.22$ kbar $B_1 = 3.333$ kbar $^{-1/2}$ and $B_2 = 0$ in Eq. (A-2); these adjustments are really minor. Because of lack of observational evidence we have ig-

nored the temperature dependence of the water solubility of liquid basalt. This may be justified because metalurgists have shown that the temperature dependence of the water solubility in simple silicate melts is negligible (Turkdogan 1983).

The surface energy of liquid tholeiite has been measured by:

– Murase and McBirney (1973) at $P=1$ atm. for $1250 < T < 1450^\circ\text{C}$ in the presence of air, they reported values varying from 3.5×10^{-5} to 4.0×10^{-5} J/cm²;

– Walker and Mullins (1981) at $P=1$ atm. for $1250 < T < 1500^\circ\text{C}$, in the presence of air or CO₂; the surface energy varied from 3.5×10^{-5} to 4×10^{-5} J/cm²;

– Khitarov et al. (1979) at 1200°C in the presence of H₂O they reported values varying non linearly from 4.0×10^{-5} at $P=1$ atm. to 10^{-5} J/cm² at $P=5000$ atm.

The surface energy changes somewhat with temperature, but is pressure sensitive, as suggested by Khitarov et al. (1979). Their observations indicate that water vapour lowers the surface energy. The surface energy values for basalt in contact with water (Khitarov et al. 1979) are for $P=P(\text{H}_2\text{O})$; evidently that is not the case for Hawaiian tholeiite at $P > 50$ bars. Because of the presence of some water and because of the pressure, we have assumed that the surface energy amounted to 3×10^{-5} J/cm² instead of the larger value of 3.5×10^{-5} J/cm² suggested by the observations of Murase and McBirney (1973) and Walker and Mullins (1981).

The diffusion constant for dissolved CO₂ in liquid basalt was calculated with the expression:

$$D(\text{CO}_2) = 3.723 \exp[(-1.95 \times 10^5 - 1102P)/RT] \text{ cm}^2/\text{s}$$

where P is expressed in kbar. This expression can be derived from the relationships given in Watson et al. (1982), based on their experimental observations.

There are no published measurements on the diffusion of water in basaltic melts. Besides, the diffusion constant for H₂O depends on the water concentration (Jambon 1983). For our calculations we have fitted a simple Arrhenius equation to the observations by Lapham et al. (1984) on an obsidian melt composition and by Scholze and Mulfingher (1959) on a soda lime silicate melt.

$$D(\text{H}_2\text{O}) = 0.00552 \exp(-98300/RT) \text{ cm}^2/\text{s}$$

These few data suggest that the water diffusion constant in basaltic liquids is larger than the CO₂ diffusion constant, therefore the precise value of $D(\text{H}_2\text{O})$ may not be really important for us.

The melt viscosity value was evaluated with the expression:

$$\eta = 3.228 \times 10^{-7} \exp(2.482 \times 10^5/RT) \text{ poise}$$

which reproduces adequately the observed viscosity of liquid basalt at low pressure; the pressure dependence of the basalt viscosity was ignored. As a matter of fact the viscosity of liquid basalt is only of minor importance in the context of this paper.

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