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# Reply to comment by T.M. Gerlach on "Mid-ocean ridge popping rocks: implications for degassing at ridge crests"

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## 1. Introduction

T.M. Gerlach [1] has raised an important point regarding the appropriate value for the bulk $CO_2$ concentration of Mid-Atlantic Ridge popping rocks, and we appreciate this opportunity to clarify several points.

In our original paper [2] we inferred that these popping rocks, in contrast to typical mid-ocean ridge basalts (MORB), had undergone essentially no gas loss prior to eruption. Evidence for this includes (1) the extreme vesicularity ($\sim 17\%$ by volume) and relatively primitive nature of popping rocks compared to most MORB (typically $\sim 1\%$ vesicularity); (2) the linear correlation of the logarithm of vesicle population density with decreasing vesicle size in the popping rocks; (3) a $^4\mathrm{He}/^{40}\mathrm{Ar}$ ratio in popping rocks which is the lowest value measured in MORB [3] (and similar to the production ratio appropriate for the upper mantle), consistent with rare gas solubilities and varying degrees of pre-eruptive vesicle loss for MORB; (4) a $\delta^{13}\mathrm{C} = -3.8\%o$, the highest value found in MORB [4]; and (5) the *highest* rare gas and $CO_2$ concentrations yet found in MORB. Our main point was that most MORB appear to be residual liquids which erupt after some gas loss has occurred, whereas popping rocks may represent a rare case where significant perturbations to bubble nucleation and growth have not occurred during magma ascent. The major implication is that pre-eruptive gas loss may be a significant form of degassing for MORB, as suggested previously [5].

Prior to the discovery of popping rocks, it was speculated that degassing occurred at depths up to $\sim 50$ km, because no MORBs contained enough He to account for the He flux at ridges estimated from the deep ocean excess of $^3\mathrm{He}$. We measured He contents in excess of $50\mu\mathrm{cm}^3$ STP/g in popping rocks from $14°$N on the Mid-Atlantic Ridge [2,3], and emphasized that such a high [He] could provide the He flux solely by degassing of newly created ocean crust. While it was not the major point of our paper, we also used the *measured* $[CO_2]$ reported by a different laboratory for these same samples [4,6] to show that the calculated carbon flux was within the range of previous estimates. We felt that using a measured $[CO_2]$ rather than a calculated value was a better approach for this flux estimate, which we presented as an order of magnitude estimate only. (There has been a considerable debate over the precise value of the mid-ocean ridge C flux, estimates of which are based on somewhat different measurements and lines of reasoning [5,7–10].)

Our calculations for nucleation and growth rate parameters used an *estimated* value for bulk $CO_2$ content of 1 wt.%. A value of $\sim 1$ wt.% for the initial $CO_2$ content is consistent with the vesicularity and depth of eruption [4,6]. We cited a value of 0.21 wt.% as the highest measured value for the bulk $CO_2$ content [6] (more recent measurements range up to 0.30 wt.% [4]). We did not suggest that 0.21 wt.% should be taken as representative of undegassed MORB magma. Obviously the determination of a true bulk gas content in popping rocks is extremely difficult owing to their vesicular nature and the potential for gas loss during sample preparation. Our model calculations were presented to illustrate the generality of the approach in arriving at order of magnitude estimates for

vesicle nucleation and growth rate parameters. As we pointed out, these estimates were probably uncertain by about a factor 5.

In the following we present some new results and calculations which address the discrepancy noted by Dr. Gerlach in the calculated and measured bulk $CO_2$ contents. First, we show that some degree of gas loss by natural decrepitation of vesicles after quenching, or during sample preparation, seems unavoidable. Second, we demonstrate that the partitioning of He between gas and melt is close to equilibrium in these popping rocks. Therefore, at least part of the discrepancy between measured and calculated $CO_2$ contents may be related to sample preparation techniques. Third, we present a mass balance for a mixture of gas components ($CO_2$-$H_2O$) and melt, which is constrained by new measurements of *dissolved* $CO_2$ and $H_2O$ in these same popping rocks, and by the experimentally-determined real properties of these gases. From these considerations, bulk $CO_2$ and $H_2O$ contents of 0.8 and 0.6 wt.%, respectively, are the most appropriate values for these magmas. The measurement of dissolved [He], [$H_2O$] and [$CO_2$] for the same samples allows a refined estimate to be made for the mid-ocean ridge C flux which closely agrees with that in [1], but we emphasize that the large uncertainties preclude the accuracy of this estimate to better than a factor of 3.

## 2. Post-eruptive gas loss

Figure 1 shows the cumulative volume fraction vs. vesicle size for the popping rocks based on our original data [table A1, ref. 2]. The volume fractions were computed assuming that all vesicles within each size class are spheres with radii equal to the midpoint of the size class, and the plotted values therefore only represent approximations. Most of the volume fraction of gas is clearly in the larger vesicles despite their much smaller abundance, as we pointed out previously [2]. Thus, for sample sizes of < 1 g (as typically analyzed for bulk gas content) potential gas loss either naturally or during sample preparation may be significant. For example, for a sample size of 0.5 g, there are only ~ 10 vesicles in the largest 2 size classes (calculated from data in our original table 2). Decrepitation of vesicles in these size groups would

lead to a loss of ~ 25% of the original bulk gas content. The problem is even worse if smaller samples are analyzed.

This effect can be quantified following several assumptions about sample and vesicle geometry. Consider a cube of edge-length $L$, and assume that the bubbles are spheres randomly distributed throughout the cube. For a bubble of diameter $D$, the center of the bubble must be placed at least a distance $(D/2 + \delta)$, where $\delta$ is very small, from the edge of the sample to ensure that the original vapor within the bubble is retained. Any bubbles closer to an edge than this will be opened to the atmosphere during sample preparation. The fraction of bubbles of size $D$ which are not opened during preparation is given by

$$f \cong \frac{(L - 2(D/2 + \delta))^3}{L^3} = \frac{(L - D)^3}{L^3}$$

Letting $D = \alpha L$, $f = (1 - \alpha)^3$ or $\alpha = 1 - f^{1/3}$. Thus, to ensure that $f > 0.95$ for any given grain size requires $\alpha < 0.017$. This means for example, that for retention of more than 95% of the bubbles in the 1 mm size class, the sample must be a cube with $L = 59$ mm (weight > 470 g).

In this way we estimate that the amount of gas loss for each sample we have analyzed for [He] is ~ 25–35%, based on the vesicle size distribution data [table A1, ref. 2] and the respective sample weights (~ 0.27–0.54 g; Table 1). Actual gas loss may be somewhat different from this rough estimate, because the calculation assumes a homogeneous distribution of vesicles, a simple geometry
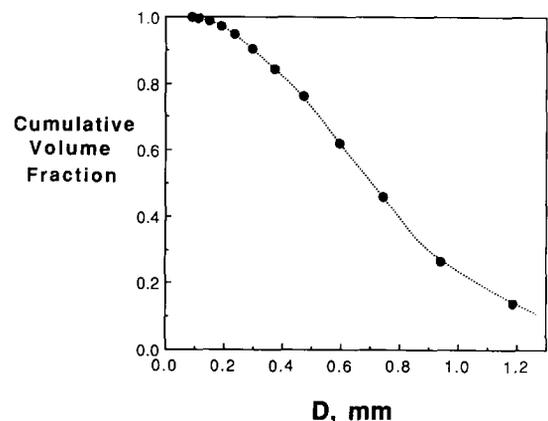


Fig. 1. Cumulative volume fraction of vesicles vs. vesicle diameter in mm.

for the samples analyzed, and the absence of microcracks.

## 3. Helium and carbon in popping rocks

This leads to the question of sample variability. While we have not performed the $CO_2$ measurements, we suggest that the *highest* gas concentrations in these rocks should be accepted as being closest to the representative value, based on the above discussion. $CO_2$ analyses of a large number of these samples are currently in progress in the stable isotope laboratory of Prof. M. Javoy at the University of Paris, and these data will provide a more reliable basis on which to address the issue raised by Gerlach [1]. In addition, *glass phase* $CO_2$ and $H_2O$ contents of the same samples analyzed for He have been measured at CalTech by FTIR spectroscopy. These samples have *dissolved* $CO_2$ contents of 180 ppm and $H_2O$ contents of 0.51 wt.% (Jacqueline Dixon, pers. commun.). The value of 180 ppm is very close to the equilibrium $CO_2$ solubility in basalt at $1200\,^{\circ}C$ and 360 bar [11].

We have attempted to address the questions of sample variability and vesicle decrepitation using He measurements. We performed repeated analyses of single glass chunks by crushing *in vacuo*, and also attempted to determine the state of He partitioning between glass and vesicle phases. If a large fraction of the vesicle gas has been lost by natural decrepitation or during sample preparation, He should appear to be concentrated in the glass phase in excess of the equilibrium partitioning value.

Our He results are presented in Table 1. All samples were analyzed by crushing at least once. The total range in crushed helium content is about a factor of 2, similar to that observed earlier [2]. The mean of 6 analyses is $60 \pm 14$ ($1\sigma$) $\mu cm^3STP/g$; agreement for replicate analyses of subsamples from the same chunk is even better, e.g., DG1 and DG2 (Table 1). Each of these samples were also crushed in vacuum sequentially, with > 99.9% of the He released in the first crushing step. Immediately following this analysis, the powders produced by crushing were transferred to Al foil boats and introduced to the all-metal sample loading system of a high-temperature rock furnace. (All the sample powder passed through a

**TABLE 1**

Helium in MAR popping rocks

| Sample | Wt. | Crushed [He] | Melted [He] | Dissolved [He] |
|---|---|---|---|---|
| DG1 | 0.352 | 64.3 | – | |
| | 0.405 | 68.8 | 0.88 | 1.05 |
| DG2 | 0.464 | 51.3 | – | |
| | 0.478 | 66.4 | 1.00 | 1.08 |
| PR-ya | 0.266 | 73.2 | – | – |
| PR-xc | 0.538 | 34.6 | – | – |

All analyses were performed at UCSB, on glass pieces recovered by dredge $2\pi D43$ of the Akademik Boris Petrov, from $14\,^{\circ}N$ on the Mid-Atlantic Ridge. Sample weight in g. [He] in $\mu cm^3STP/g$, determined by peak height comparison to laboratory running standards. Analytical precision is < 1%, and accuracy is ~ 1% based on repeated calibrations of the running standards against California marine air [19]. Vesicle He was extracted by crushing *in vacuo* of a single glass chunk. Melted He was extracted by fusion of the remaining powders, all of which passed through a 100 $\mu$m sieve. Dissolved content is the melted [He] plus the amount lost by diffusion between crushing and melting analyses, calculated from the measured rate of He loss from the powders in vacuum and the time interval between analyses (see text).

100 $\mu$m sieve, and the bulk of the powder had a grain size considerably smaller than this value.) The rock furnace was pumped overnight and baked to $1800\,^{\circ}C$ the next morning. Cold blanks for the furnace system clearly revealed the diffusion of He from the crushed rock powders (with the $^3He/^4He$ ratio characteristic of these popping rocks). Sample DG2 was analyzed after establishing this sample's diffusive loss rate, approximately 24 hours after its crushing. In a similar manner DG1 was analyzed the following day. Results of the melted analyses are presented in Table 1. The dissolved He content has been computed as the sum of the melted [He] plus the amount lost by diffusion during the time interval between crushing and melting analyses.

Results of the He partitioning experiment are displayed in Fig. 2, along with previously published MORB glass data [12]. Samples which display equilibrium vesicle–glass (v–g) partitioning will fall along a line in this diagram according to

$$[He]_v/[He]_g = (1/\rho K_d)(V_v/V_g),$$

where $K_d$ is the partition coefficient (in the sense described in the appendix to [13]), and $V_v/V_g$ is related to the vesicularity. Our results are con-
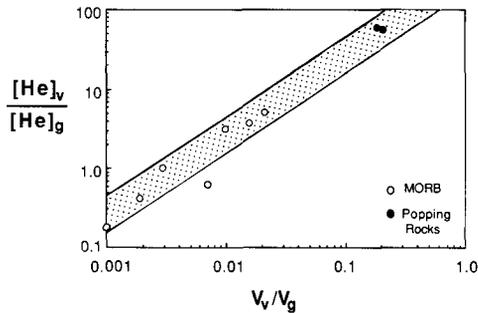
Fig. 2. Ratio of helium concentration in vesicles to helium concentration in glass vs. the volume ratio of vesicles to glass. Open symbols are MORB glass data from [12]. Samples in equilibrium will define a line with slope of $1/(\rho K_d)$, where $\rho$ is melt density and $K_d$ is the partition coefficient [12,13]. Shaded area is the best estimate for the MORB data including its uncertainty. $V_v/V_g$ is equivalent to the vesicle volume fraction at low vesicularities, but for the popping rocks with vesicularities of ~17%, $V_v/V_g = 0.17/(1-0.17) \cong 0.20$ (see text for discussion).

sistent with equilibrium partitioning of He in these popping rocks. Note that our analyses have not been adjusted for possible gas loss effects related to sample size as discussed in section 2. This would serve to move the data points upward on Fig. 2, in a direction opposite to that expected if natural vesicle decrepitation was significant. In contrast, the uncertainties in the Henry's Law constant estimated from the MORB data ($K_{He} = 3.7 \pm 1.8 \times 10^{-4}$ cm$^3$ STP/g-atm; [12]) are large, and do not preclude the possibility of some natural gas loss prior to our He analyses. Overall the He results suggest, but do not prove, that much of the discrepancy in measured and calculated bulk $CO_2$ contents may be due to analyses of small grain sizes where vesicle loss can be significant.

The measurements of dissolved He and $CO_2$ contents of the same glass samples do not suffer from this problem. This allows us to calculate more precisely the $C/^3He$ ratio of the popping rock magma. This ratio in the glass phase of the popping rocks is $7.5 \times 10^9$, higher than the average MORB value of ~$2 \times 10^9$ [9].

## 4. Volatile mass balance

Following methods outlined in Spera [14], a bulk-system mass balance, for $CO_2$ and $H_2O$ under real (non-ideal) conditions can be written as

$$Z_i^0 = \phi w_i^v + (1 - \phi) w_i^m \tag{1}$$

$$\theta = \phi \frac{\rho_0}{\rho_v} \tag{2}$$

$$\frac{1}{\rho_0} = \frac{\phi}{\rho_v} + \frac{1 - \phi}{\rho_m} \tag{3}$$

where $Z_i^0$ is the mass fraction of species $i$ in the bulk system, $\phi$ is the mass fraction of vapor phase, $\theta$ is the volume of the vapor phase (or vesicularity), $\rho$ is density, $w$'s are mass fractions, and subscripts v, m and 0 refer to vapor, melt and bulk system, respectively.

We have calculated $\rho_m$ (the density of the volatile-saturated melt) using coefficients given in [15], popping rock compositions from [2], and the measured $H_2O$ and $CO_2$ contents of 0.51 wt.% and 180 ppm, respectively. At 1200°C (magmatic conditions) $\rho_m$ is 2697 kg/m$^3$, and at 360 bar (seafloor) pressure $\rho_{CO_2}$ is 119.2 kg/m$^3$ [16] and $\rho_{H_2O}$ is 52.86 kg/m$^3$ [17].

Assuming that mixing in a binary ($CO_2-H_2O$) vapor phase is ideal,

$$\frac{1}{\rho_v} = \frac{w_{CO_2}^v}{\rho_{CO_2}} + \frac{w_{H_2O}^v}{\rho_{H_2O}} \tag{4}$$

By definition, the mole fractions ($X^v$) of $CO_2$ and $H_2O$ in the vapor are

$$X_{CO_2}^v = \frac{18 w_{CO_2}^v}{44(1 - w_{CO_2}^v) + 18 w_{CO_2}^v} \tag{5}$$

$$X_{H_2O}^v = \frac{44 w_{H_2O}^v}{18(1 - w_{H_2O}^v) + 44 w_{H_2O}^v} \tag{6}$$

where 18 and 44 are the molecular weights of $H_2O$ and $CO_2$, respectively, and $w_{H_2O}^v = 1 - w_{CO_2}^v$.

For the conditions of interest ($P = 360$ bar, $T = 1200°C$, $\rho_m = 2697$ kg/m$^3$) with measured parameters $\theta = 0.17$, $w_{CO_2}^m = 180$ ppm, $w_{H_2O}^m = 0.51$ wt.%, and $X_{CO_2}^v = 0.80$ (from [2,4]), we calculate that $w_{CO_2}^v = 0.907$, $w_{H_2O}^v = 0.093$ and $\rho_v = 106.8$ kg/m$^3$. Solving equations (2) and (3) simultaneously gives $\phi = 0.00804$ and $\rho_0 = 2257$ kg/m$^3$. Then, from eq. 1, $Z_{CO_2}^0 = 0.0075$ and $Z_{H_2O}^0 = 0.0058$. Therefore, for an undegassed popping rock magma under these conditions our best estimates for bulk $CO_2$ and $H_2O$ contents are 0.75 and 0.58 wt.%, respectively. At a "rigid temperature" of 1000°C the above method gives bulk $CO_2$ and $H_2O$ contents of 0.85 and 0.59 wt.%, respectively.

## 5. Implications for the carbon flux at mid-ocean ridges

Adopting the glass phase $C/^3He$ ratio of $7.5 \times 10^9$ measured in the popping rocks, and a global $^3He$ flux at mid-ocean ridges of $4 \pm 1$ atom per $cm^2$ of seafloor per second [18] ($\sim 760$ mol/yr) gives a calculated C flux of $\sim 5.7 \times 10^{12}$ mol/yr. This value is 3–10 times larger than estimated by Des Marais and Moore [8], Gerlach [5], and Marty and Jambon [9], but within the range of the values given by Javoy et al. [7] and Des Marais [10]. This calculation assumes that the $C/^3He$ ratio dissolved in the glass phase of the popping rocks is representative of a global value, which we consider unlikely. Adopting the average MORB value of $2 \times 10^9$ [8] for this ratio instead gives a C flux of $1.5 \times 10^{12}$ mol/yr.

A second method of calculation follows our original procedure [2]. Using the above estimate of $\sim 0.8$ wt.% $CO_2$ for the popping rock magma, a MORB He deficit of $\sim 50$ $\mu cm^3STP/g$ relative to popping rocks (i.e., a [He] of $\sim 60$ $\mu cm^3STP/g$ and bulk $C/^3He$ of $6.0 \times 10^9$ in the popping rocks), and the oceanic crustal production rate ($1.6–4.0 \times 10^{16}$ g/yr, assuming a crustal thickness of $2 \times 5$ km) yields a $^3He$ flux of 400–1000 mol/yr, and a C flux of $2.4–6.0 \times 10^{12}$ mol/yr. This value is larger than our original estimate of $0.4–1 \times 10^{12}$ [2], and a correctly pointed out by Gerlach [1] falls into the group of estimates which are $> 2 \times 10^{12}$ mol/yr.

These calculations demonstrate that somewhat different lines of reasoning using data from the same samples lead to calculated fluxes which differ by at least a factor of 3. At the present time we feel that vesicle distributions in MORB need more study, and the variability in $C/^3He$ ratios for MORB, popping rocks and hydrothermal vent fluids from a variety of locations needs to be thoroughly assessed before we can constrain the mid-ocean ridge carbon flux more precisely.

## Acknowledgments

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