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► **To cite this version:**

Cyril Aubaud, Françoise Pineau, Roger Hékinian, Marc Javoy. Carbon and hydrogen isotope constraints on degassing of CO₂ and H₂O in submarine lavas from the Pitcairn hotspot (South Pacific). *Geophysical Research Letters*, American Geophysical Union, 2006, 33, 10.1029/2005GL024907 . insu-03603151

HAL Id: insu-03603151

<https://hal-insu.archives-ouvertes.fr/insu-03603151>

Submitted on 9 Mar 2022

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Carbon and hydrogen isotope constraints on degassing of CO₂ and H₂O in submarine lavas from the Pitcairn hotspot (South Pacific)

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Received 13 October 2005; revised 28 November 2005; accepted 13 December 2005; published 21 January 2006.

[1] The analysis of CO₂-δ¹³C-H₂O-δD in vesicles of 35 submarine volcanic glasses reveals that open-system degassing, following closed-system degassing, is responsible for the observed variations in volatile concentration and isotopic ratios. The least degassed samples allow the assessment of minimum estimates for the flux of CO₂ and H₂O from the Pitcairn hotspot: 2.24 ± 0.17 10⁴ tons C yr⁻¹ and 1.32 ± 0.82 10⁵ tons H₂O yr⁻¹. The results also suggest that the carbon in the source of the Pitcairn hotspot may have a δ¹³C value around -6‰, 2‰ lower than the source of mid-ocean ridge basalts. This indicates either a possible contribution from the lower mantle or the possible involvement of decarbonated recycled materials with an unusual carbon isotopic signature. **Citation:** Aubaud, C., F. Pineau, R. Hékinian, and M. Javoy (2006), Carbon and hydrogen isotope constraints on degassing of CO₂ and H₂O in submarine lavas from the Pitcairn hotspot (South Pacific), *Geophys. Res. Lett.*, 33, L02308, doi:10.1029/2005GL024907.

1. Introduction

[2] Volcanism is the principal process of transfer of CO₂ from the mantle to the surface [Javoy *et al.*, 1982]. Since CO₂ has climatic implications, it is important to estimate its flux for different types of volcanism.

[3] Among different approaches, estimates of the flux of CO₂ can be obtained by studying submarine volcanic glasses. However, these flux estimates are complicated by degassing processes. Due to its low solubility in magmas [Dixon *et al.*, 1995], carbon is responsible for the nucleation and growth of CO₂-rich vesicles upon decompression of magmas on their way to the surface [Bottinga and Javoy, 1990]. Since carbon isotopes are fractionated during this process [Javoy *et al.*, 1978; Matthey, 1991], δ¹³C values decrease during degassing. Therefore, carbon isotopes are a good tracer of degassing processes.

[4] Previous studies on the behavior of CO₂ in intraplate lavas have shown that a two-stage degassing model is probably the most appropriate to describe CO₂ degassing [Aubaud *et al.*, 2005; Bureau *et al.*, 1998; Gerlach and Taylor, 1990]. In this model, the first stage is a closed system, with degassing occurring from the depths of melting to a shallow magma chamber; this is followed by a

second stage of open-system degassing during the eruption of the magma [Aubaud *et al.*, 2005].

[5] Carbon isotopic studies for intraplate lavas are scarce. A study of submarine glasses from the Society hotspot [Aubaud *et al.*, 2005] has shown that the δ¹³C value of the source of these lavas is similar to that of the source of mid-ocean ridge basalts (MORB, -4.0 ± 0.5‰ [Javoy and Pineau, 1991]). However, the noble gases of these lavas showed a MORB signature suggesting that the MORB source dominates their volatile budget. Therefore, a study of intraplate lavas showing a clear hotspot signature is needed in order to identify a possible different carbon isotopic source than for MORB.

[6] Water is more soluble than CO₂ in natural magmas [Dixon *et al.*, 1995]. However, intraplate lavas have relatively high water contents, and even at great eruption depth (4000 m), significant degassing may occur [Aubaud *et al.*, 2005; Dixon *et al.*, 1997].

[7] In this contribution, we report analysis of CO₂ and H₂O and their corresponding carbon and hydrogen isotopic ratios in vesicles of 35 submarine volcanic glasses from the Pitcairn hotspot. These lavas show a clear hotspot type noble gas signature [Honda and Woodhead, 2005]. The focus of the present study is to characterize the mode of the degassing process. We also assess the flux of CO₂ and H₂O from the Pitcairn hotspot and discuss its possible original δ¹³C signature.

2. Geological Setting and Sample Description

[8] The volcanic chain of the Duke of Gloucester-Pitcairn volcanic alignment, located in the South Pacific, is about 1500 km long. The progressive decrease in age of the volcanics eastward is in accordance with a fixed hotspot origin for the chain [Binard *et al.*, 2004]. The present activity of the hotspot is now located 70–100 km to the southeast of the Pitcairn Island in an area that includes two major volcanoes—namely Bounty and Adams—and several small edifices.

[9] The 35 fresh submarine glasses selected for the present study consist of 16 alkalic basalts, 11 trachyandesites, and 8 trachytes. These samples were collected on Bounty and Adams volcanoes and 6 small volcanoes during the POLYNAUT cruise in 1999. Description, depth and location of the samples are given by Devey *et al.* [2003] and Hékinian *et al.* [2003].

3. Analytical Techniques

[10] The analytical techniques used to analyze the gases in the vesicles have been described in a previous publication [Aubaud *et al.*, 2005]. The international graphite standard USGS24 repeatedly measured (n = 10) gave a δ¹³C value of

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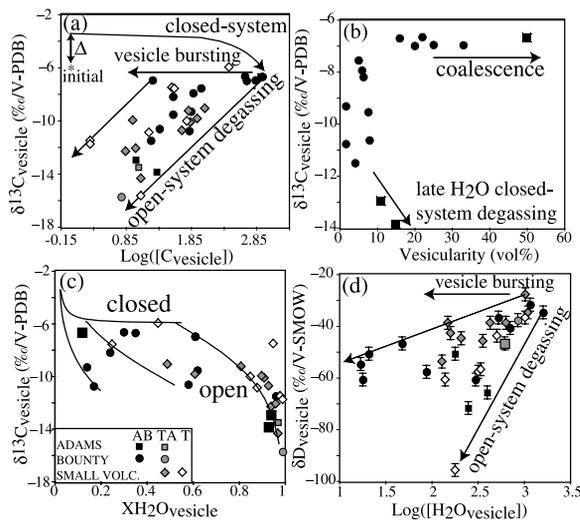


Figure 1. (a) The open-system degassing process was modeled with a $\Delta^{13}\text{C}$ of +2.5‰. (b) Increase of vesicularity at high $\delta^{13}\text{C}$ -values is due to vesicle coalescence. Increase of vesicularity at low $\delta^{13}\text{C}$ -values is due to late H_2O closed-system degassing. (c) The closed and open-system degassing curves were calculated with VolatileCalc. (d) The open-system degassing process was modeled with a ΔD of +28‰ starting from the sample PN03-08 (lower line) and a ΔD of +6‰ starting from the sample PN DR03-01 (upper line). The Δ values were selected because they best fit the data. Abbreviations are: AB = alkalic basalt, TA = trachyandesite, T = trachyte.

$-15.96 \pm 0.03\text{‰}$ (certified value is -15.994‰). For hydrogen, the international standard NBS30 (certified δD value is -65.7‰) gave a δD value of $-61.6 \pm 3.1\text{‰}$ ($n = 6$).

4. Results

[11] Observation of the samples in thin section reveals important information about the distribution and evolution of the vesicles in the erupting lavas. The vesicles in most of the alkalic basalt glasses are generally spherical and isotropically distributed throughout the samples whereas those in trachyandesitic and trachytic glasses are elongated, concentrated in regions following lava flow and therefore are not isotropically distributed in the samples. This can be ascribed to differences in viscosity of these melts. If most of the alkalic basalts show spherical vesicles all isolated from one another, two samples do not obey this rule and deserve special attention. (1) The sample PN03-11 has spherical vesicles that are not all isolated from one another. Most of the vesicles in this sample are interpenetrated, suggesting an early stage of coalescence. (2) The vesicles in the sample PNDR06-04 are rounded but not spherical most of them being reniform. This is suggestive of an advanced stage of coalescence.

[12] The results of the crushing experiments are reported in Table S1¹. The gases extracted from the vesicles in all the samples are predominantly CO_2 and H_2O . [$\text{C}_{\text{vesicle}}$]

¹Auxiliary material is available at <ftp://ftp.agu.org/apend/g/l/2005GL024907>.

varies over three orders of magnitude (from 2 to 870 ppm C), a range similar to that determined for glasses from the Society hotspot [Aubaud *et al.*, 2005]. The $\delta^{13}\text{C}_{\text{vesicle}}$ values vary from -6.0 to -15.7‰ , the latter value being the lowest measured for volcanic submarine glasses by the crushing technique. The highest $\delta^{13}\text{C}_{\text{vesicle}}$ value is 2‰ lower than that generally attributed to the source of MORB and the Society hotspot (-4‰ [Aubaud *et al.*, 2005; Javoy and Pineau, 1991]). As illustrated by Figure 1a, the $\delta^{13}\text{C}_{\text{vesicle}}$ values show a broad decrease with decreasing $\text{Log}([\text{C}_{\text{vesicle}}])$, a result similar to that obtained for Society hotspot lavas [Aubaud *et al.*, 2005].

[13] As shown by Figure 1b, among the basalts, the samples with the highest $\delta^{13}\text{C}_{\text{vesicle}}$ have the largest vesicularity. It is worth noting that the two alkalic basalts showing evidence of vesicle coalescence show the largest vesicularity. The $\delta^{13}\text{C}_{\text{vesicle}}$ values lower than -7.5‰ are restricted to low vesicularity basalts. The vesicularity increases towards lower $\delta^{13}\text{C}_{\text{vesicle}}$ due to the increasing proportion of H_2O in the vesicles (Figure 1c).

[14] The $\text{H}_2\text{O}_{\text{vesicle}}$ varies from <10 to 1610 ppm H_2O , and δD from -28 to -96‰ in the range of previous measurements for glasses from the Society hotspot [Aubaud *et al.*, 2005]. In a plot $\delta\text{D}_{\text{vesicle}}$ vs. $\text{Log}([\text{H}_2\text{O}_{\text{vesicle}}])$ (Figure 1d), the $\delta\text{D}_{\text{vesicle}}$ values show a broad decrease with decreasing $\text{Log}([\text{H}_2\text{O}_{\text{vesicle}}])$, an observation similar to that previously made for Society hotspot lavas [Aubaud *et al.*, 2005].

5. Degassing of CO_2 and H_2O

[15] The measured vesicularities for the alkalic basalts (Figure 1) together with the observation that significant amounts of gas are released by crushing under vacuum show that degassing has affected all the samples analyzed in the present study. The observations that $\delta^{13}\text{C}_{\text{vesicle}}$ decreases with $\text{Log}([\text{C}_{\text{vesicle}}])$, vesicularity and increasing $\text{XH}_2\text{O}_{\text{vesicle}}$ and that the $\delta\text{D}_{\text{vesicle}}$ values decrease with $\text{Log}([\text{H}_2\text{O}_{\text{vesicle}}])$ (Figure 1) suggest that degassing is the chief process controlling the variations of volatile concentration and chemical and isotopic ratios in the vesicles of all the glasses.

[16] From a theoretical point of view, there are two main types of degassing styles: (1) closed-system degassing where vesicles form from the melt and remain in equilibrium with it, (2) open-system degassing (or Rayleigh distillation) where vesicles escape continuously from the magma during their formation.

[17] The high vesicularity and high $\delta^{13}\text{C}_{\text{vesicle}}$ values of the samples PNDR06-04, PN03-05, PN03-06, PN03-07, PN03-08, and PN03-11 suggest that these magmas have suffered the least amount of vesicle loss. They have probably degassed closer to a closed-system degassing process.

[18] The variations observed in Figures 1a and 1d suggest that the samples with lower vesicularity and lower $\delta^{13}\text{C}$ -values have experienced vesicle loss, i.e., degassing under open system. During open-system degassing, the isotopic composition ($\delta_{\text{open} - \text{system}}$) of a volatile element or species (C or H_2O) in the melt and in the vesicles can be described by the general equation: $\delta_{\text{open} - \text{system}} = \delta_{\text{initial}} + \Delta \text{Ln} (\text{C}/\text{C}_{\text{initial}})$ where δ_{initial} is the initial isotopic composition of the magma before degassing (or that of the first vesicle formed), Δ is the vapor-melt equilibrium

fractionation, C is the concentration in the residual reservoir, and C_{initial} is the initial concentration of the element or species in the magma before degassing. During this process isotopic ratios vary exponentially with C -contents, i.e., the data in diagrams expressing δ vs. $\text{Log}(C)$ (Figures 1a and 1d) define straight lines. Since during degassing, the heavy isotope is enriched in the vapor phase compared to the melt (see *Javoy et al.* [1978] and *Mathey* [1991] for carbon and *Pineau et al.* [1998] for hydrogen), the $\delta^{13}\text{C}$ and δD values should decrease with C and H_2O , respectively. This is what we observed in the case of water and carbon and their associated isotopic ratios ($\delta^{13}\text{C}_{\text{vesicle}}$ and $\delta\text{D}_{\text{vesicle}}$, respectively) for the Pitcairn glasses (Figures 1a and 1d). Although some scatter in the data exists, modelling of this open degassing process starting from the least degassed samples essentially reproduces the observed variations (Figures 1a and 1d). It should be noted that part of the scatter is probably due to vesicle bursting during sampling or sample preparation [*Javoy and Pineau*, 1991]. It therefore appears that the samples with progressive decrease in vesicularity and $\delta^{13}\text{C}$ -values recorded different extents of open-system degassing (i.e., vesicle loss) process starting from the magmas having the volatile characteristics of the least degassed samples.

[19] Due to their different solubilities in basaltic magmas, degassing of CO_2 and H_2O are not synchronous. CO_2 is degassed first due to its lower solubility in basaltic melts. This explains why the lowest $\delta^{13}\text{C}_{\text{vesicle}}$ values are observed only at high $\text{XH}_2\text{O}_{\text{vesicle}}$ (Figure 1c), i.e. that degassing of H_2O becomes predominant only when carbon is extensively degassed.

[20] In summary, the samples analyzed in the present study have all been affected by degassing. The degassing process recorded in the vesicles of these samples can essentially be described by a two-stage degassing process, similar to that already described for other natural magmas [*Aubaud et al.*, 2005; *Gerlach and Taylor*, 1990; *Shaw et al.*, 2004].

6. Flux of Carbon and Water From the Pitcairn Hotspot

[21] The least degassed samples (PNDR06-04, PN03-05, PN03-06, PN03-07, PN03-08, and PN03-11) are the most appropriate to give constraints on the flux of carbon and H_2O from the Pitcairn hotspot. Because part of the gas enclosed in vesicles is usually lost during sampling or during sample preparation [see *Aubaud et al.*, 2005], the samples need first to be corrected for vesicle bursting. We also estimate the concentration of carbon and water dissolved in the glass. Estimation of the flux of carbon and H_2O requires the total concentrations ($C_{\text{vesicle}} + C_{\text{glass}} = C_{\text{total}}$) also to be corrected for crystal fractionation (see caption of Table S2 for details on these calculations).

[22] The corrected carbon concentrations vary from 810 to 9450 ppm C (Table S2), a range similar to previous studies [*Aubaud et al.*, 2005; *Javoy and Pineau*, 1991]. It is important to note that in the case of the sample showing evidence of an advanced stage of vesicle coalescence (PNDR06-04), this calculation leads to a concentration much larger than for all the other samples. The calculated

concentration for the sample PN03-11 (showing evidence of an early stage of vesicle coalescence) is slightly above but more similar to that of the other samples (Table S2). These two samples probably overestimate the carbon (and H_2O) concentration due to the process of coalescence and will therefore be discarded for calculating the flux of CO_2 and H_2O . A role for gas accumulation cannot be totally excluded in other samples. However, for the sake of simplicity, we will take the observed coalescence as an indication of vesicle accumulation and will make the assumption that the absence of coalescence indicates that gas accumulation was a limited process.

[23] Similar calculations and assumptions can be made in the case of H_2O (Table S2). Discarding sample PNDR06-04 and PN03-11, reconstructed H_2O concentrations vary from 6330 to 10360 ppm similar to other alkalic basalts [*Dixon et al.*, 1997].

[24] Taking the volcanic accumulation rate of $0.0054 \text{ km}^3/\text{yr}$ for the Pitcairn hotspot [*Hékinian et al.*, 2003] and excluding samples PNDR06-04 and PN03-11 from the calculation give average C and H_2O fluxes of $2.24 \pm 0.17 \cdot 10^4 \text{ tons C yr}^{-1}$ and $1.32 \pm 0.82 \cdot 10^5 \text{ tons H}_2\text{O yr}^{-1}$, values similar to previous estimates for the Réunion and the Society hotspots [*Aubaud et al.*, 2005; *Bureau et al.*, 1998]. It should be noted that if these magmas had an initial $\delta^{13}\text{C}$ value higher than the ones measured, the initial reconstructed concentrations would be higher. We therefore take these estimates as minimum. Assuming a range of partial melting between 5 and 10%, these estimates imply minimum C and H_2O concentrations of the source of 70–140 ppm C and 410–820 ppm H_2O respectively, similar to previous studies on other hotspots [*Aubaud et al.*, 2005; *Bureau et al.*, 1998; *Dixon et al.*, 1997].

7. Is the Initial $\delta^{13}\text{C}$ Value for the EM-I Pitcairn Hotspot Source Lower Than the MORB Source?

[25] The highest $\delta^{13}\text{C}$ value measured in the present study (-6.0‰) suggest that the source of carbon of the Pitcairn hotspot is 2‰ lower than both the MORB source and the source contributing to the volcanic gases at Kilauea volcano ($-4.0 \pm 0.5\text{‰}$ [*Gerlach and Taylor*, 1990; *Javoy and Pineau*, 1991]). The hypothesis of an hotspot source having an isotopic ratio of -6‰ has already been proposed previously [*Exley et al.*, 1986; *MacPherson et al.*, 2005]. It is therefore worth considering this possibility for the Pitcairn hotspot. Several hypotheses (not mutually exclusive) could be proposed to explain this particular $\delta^{13}\text{C}$ signature.

[26] First, it could represent primordial carbon acquired since the accretion of the Earth. The range of $\delta^{13}\text{C}$ values of chondrites (0 to -25.2‰ [*Kerridge*, 1985]), however, cannot precisely constrain the $\delta^{13}\text{C}$ value of the primordial mantle but this fact does not contradict the primordial carbon hypothesis. This hypothesis remains a possibility since a lower mantle noble gas signature have been measured for the Pitcairn lavas [*Honda and Woodhead*, 2005].

[27] A second possible origin is recycled carbon different in proportion from that at the origin of the MORB source. Recycled carbon is essentially a mixture of organic carbon ($\delta^{13}\text{C}$ value of -25‰) and carbonate ($\delta^{13}\text{C}$ value of 0‰) [*Deines*, 2002]. A more important fraction of recycled

organic carbon in the Pitcairn source could account for its relatively low $\delta^{13}\text{C}$ value.

[28] Finally, extensive decarbonation in subduction zones could lead to recycled material with low $\delta^{13}\text{C}$ values. On the basis of relatively low $\text{H}_2\text{O}/\text{Ce}$ ratios in EM-I like hotspots, some researchers have suggested that the EM-I component resulted from severe dehydration of material upon its passage through subduction zone [Dixon and Clague, 2001; Wallace, 2002]. This could occur in subduction zones with geothermal gradients where decarbonation is also likely to occur [Kerrick and Connolly, 2001]. Such a process would imply modification of the $\delta^{13}\text{C}$ value of the subducted material during decarbonation—a process which remains to be tested experimentally.

[29] At present, it is impossible to establish with certainty the origin of this relatively low $\delta^{13}\text{C}$ value in the Pitcairn source. Nevertheless, the present study suggests that the analysis of carbon in hotspots can lead to new constraints on the distribution of its isotopic ratio in the mantle.

[30] **Acknowledgments.** This manuscript is dedicated to the memory of Jean-Louis Cheminée. IGP contribution 2106.

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