

CO₂ fluxes from mid-ocean ridges, arcs and plumes

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Abstract

Estimates of CO₂ emissions at spreading centres, convergent margins, and plumes have been reviewed and upgraded using observed CO₂/³He ratios in magmatic volatiles, ³He content estimates in the magmatic sources, and magma emplacement rates in the different tectonic settings. The effect of volatile fractionation during magma degassing, investigated using new rare gas and CO₂ abundances determined simultaneously for a suite of Mid-Ocean Ridge (MOR) basalt glasses, is not the major factor controlling the spread of data, which mainly result from volatile heterogeneity in the mantle source. The computed C flux at ridges $(2.2 \pm 0.9) \times 10^{12}$ mol/a, is essentially similar to previous estimates based on a more restricted data base. Variation of the C flux in the past can be simply scaled to that of spreading rate since the computed C depends mainly on the volatile content of the mantle source, which can be considered constant during the last 10⁸ a. The flux of CO₂ from arcs may be approximated using the CO₂/³He ratios of volcanic gases at arcs and the magma emplacement rate, assuming that the ³He content of the mantle end-member is that of the MORB source. The resulting flux is $\sim 2.5 \times 10^{12}$ mol/a, with approx. 80% of carbon being derived from the subducting plate. The flux of CO₂ from plumes, based on time-averaged magma production rates and on estimated contributions of geochemical sources to plume magmatism, is $\leq 3 \times 10^{12}$ mol/a. Significant enhancements of the CO₂ flux from plumes might have occurred in the past during giant magma emplacements, depending on the duration of these events, although the time-integrated effect does not appear important. The global magmatic flux of CO₂ into the atmosphere and the hydrosphere is found to be 6×10^{12} mol/a, with a range of $(4-10) \times 10^{12}$ mol/a. Improvement on the precision of this estimate is linked to a better understanding of the volatile inventory at arcs on one hand, and on the dynamics of plumes and their mantle source contribution on the other hand. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The rate of CO₂ degassing from the Earth is considered to be a major factor controlling the partial

pressure of atmospheric CO₂ over geological time, and therefore the long-term variation of climate (Berner et al., 1983). The amount of gas transferred from a given reservoir into the atmosphere depends on: (1) the rate of melt production in this reservoir; (2) the abundance of volatile species in reservoir rocks and related melts; and (3) the degree of melt degassing. Consequently, the flux of CO₂ from the solid Earth might have fluctuated in the past follow-

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ing: (1) changes in the spreading rate of lithospheric plates, resulting in variations of the flux of mantle-derived CO₂ at mid-ocean ridges (MOR) and of the flux of subduction-derived CO₂ at convergent margins; and (2) variation of the frequency and volume of plume-derived lava emissions (PLUME) originating deep in the mantle.

It is of fundamental importance to evaluate quantitatively the relationship between CO₂ degassing and magmatism. MOR volcanism represents more than 60% of the total volume of lavas erupted at the Earth's surface and is potentially a major source of CO₂. The MOR lava eruption rate is known from the age–distance relationship of divergent plates and the MOR CO₂ flux can be computed if the initial C content of oceanic basalts is evaluated. The difficulty of this approach is that CO₂ solubility in magmas is low and this species is quantitatively degassed during eruptions, even in the case of oceanic basalts erupting under hydrostatic pressure. Hence the C content of the original magmas cannot be directly measured as in the case of non-volatile trace elements, and so must be reconstructed from observed residual, isotopically fractionated, carbon in oceanic basalts, necessitating a number of assumptions to be made. The CO₂/³He ratios in MOR hydrothermal fluids and rocks allow to constrain the CO₂ emission rate from MOR volcanism because the flux of ³He from ridges has been estimated (Craig et al., 1975; Welhan and Craig, 1983; Jean-Baptiste, 1992; Farley et al., 1995). CO₂/³He in hydrothermal fluids at MOR are available for only three locations (Welhan and Craig, 1983; Des Marais and Moore, 1984), and Des Marais (1985) and Marty and Jambon (1987) proposed to use CO₂/³He values of MOR basalt glasses (MORB) as proxies for CO₂/³He ratios at ridge crest emissions, increasing considerably the number of CO₂/³He data sets. This approach was questioned by Gerlach (1991) and Trull et al. (1993) who argued that a slight difference in CO₂ and He solubilities could cause a significant source of error in the calculated emission rate at ridges as a consequence of CO₂–He fractionation during pre-eruptive degassing.

The CO₂ flux of subaerial volcanoes (both arc and plume-type) is generally estimated by extrapolating the measured volatile fluxes of (few) individual volcanoes to the total number of presently active

volcanoes. Contrary to the case of MOR volcanism which has not significantly varied in volume rate on the time scale of 1–10 Ma, present-day emissions of subaerial volcanism can hardly be extrapolated over geological periods as episodic emissions of particularly volatile-rich or active (or both) volcanoes could have significantly increased the flux of volcanic CO₂ in the past. Active geothermal systems may also supply a considerable amount of CO₂ (Irwin and Barnes, 1980; Seward and Kerrick, 1996), but their contribution remains to be quantified. Further measurements on active volcanoes allow improvement of these estimates, but are limited by the requirement of a safe access to eruptive vents and plumes. Satellite remote sensing significantly improves the number of observations and their reliability, especially in the case of cataclysmic eruptions such as the recent ones from Pinatubo and Rabaul, but the major limitation advocated above, the connection between past and present activities, remains inescapable.

The role of plumes is even less constrained. The present-day CO₂ flux from plume volcanism appears low and comparable to that of arc volcanism (Gerlach, 1991; Allard, 1992; Marty and Le Cloarec, 1992). However, it is probable that major pulses of plume-related volcanic episodes which have produced continental flood basalts (CFB) and large igneous provinces (LIP) in the Cretaceous and in the Tertiary produced large-scale emissions of CO₂, the impacts of which on the climate are controversial (Caldeira and Rampino, 1990, 1991; Larson, 1991a,b; Heller et al., 1996). Quantification of these emissions requires a good geochronological control of the time interval during which these events took place, and knowledge of the initial volatile content of plume-derived magmas.

The first aim of this contribution is to review CO₂ fluxes and their uncertainties in the different tectonic environments. Secondly, the effect of magma degassing on He–CO₂ fractionation is quantitatively evaluated using new CO₂ and rare gas data, allowing a more detailed evaluation of the CO₂ flux at ridges to be made. Thirdly, the C content in the upper mantle feeding MOR magmatism is estimated, allowing to link the flux of CO₂ at ridges to the rate of spreading at mid-ocean ridges. Fourthly, the flux of CO₂ at convergent margins is derived from the volume of mantle-derived magmas and the contribu-

tion of the slab at arcs and scaled to the MOR spreading rate. Finally, the latest developments in rare gas systematics are used to constrain the fraction of volatiles, including C, uprising from deep regions in the mantle.

2. Carbon flux at mid-ocean ridges

2.1. C and ^3He fluxes at MOR: a review

Estimates of CO_2 emission rates at MOR based on C content and isotopic ratios in MORB glasses are very variable from $(0.5\text{--}0.9) \times 10^{12}$ mol/a (Gerlach, 1991) up to 13×10^{12} mol/a (Javoy et al., 1982). The approach based on carbon calibration to ^3He requires determination of C/ ^3He ratios at MOR. Fig. 1 includes C/ ^3He data for MORB glasses (bulk fraction), in which case CO_2 and He have been determined separately in different laboratories and/or using separate extractions (Des Marais, 1985; Marty and Jambon, 1987; Kingsley and Schilling, 1995), and hydrothermal fluid data (Welhan and Craig, 1983; Des Marais and Moore, 1984; Gerlach, 1991). Gerlach (1991) noted that preferential degassing of He with respect to CO_2 could explain lower C/ ^3He ratios in hydrothermal fluids. Considering all data as a single population, the median CO_2 / ^3He ratio is 2.2×10^9 ($n = 26$), with a standard deviation ($2\sigma/\sqrt{n}$) of 0.7×10^9 , similar to the early estimate of Marty and Jambon (1987) based on a more restricted data base.

The present-day flux of ^3He has been estimated at 1000 ± 250 mol/a, using a single box oceanic model (Craig et al., 1975; Welhan and Craig, 1983). Jean-Baptiste (1992) proposed a significantly lower ^3He flux of 400–660 mol/a based on a three-ocean basin model. However, Farley et al. (1995) recently integrated ^3He data in a global oceanic circulation model and proposed a ^3He flux similar to the one originally suggested by Craig and co-workers. Thus the value of the ^3He flux depends critically on the oceanic model adopted and is subject to change in the future when models become more sophisticated. For a mean ^3He flux of 1000 ± 250 mol/a, and using the median C/ ^3He given above, the carbon flux at ridges becomes $(2.2 \pm 0.9) \times 10^{12}$ mol/a.

2.2. C/He fractionation in MORB?

MORB glasses have variable volatile contents, due to, e.g., variable vesicle density and previous degassing, and it is uncertain if CO_2 and He concentrations measured separately, as is the case of part of the data compiled in Fig. 1, are representative of the mantle volatile composition. Simultaneous analysis of CO_2 and He, together with Ar and N_2 , allows to circumvent the problem of volatile heterogeneity and to gain information on fractional degassing (Marty, 1995; Marty et al., 1995). In the latter case the radiogenic $^4\text{He}/^{40}\text{Ar}^*$ ratio (where ^4He is produced by the decay of U and Th, and $^{40}\text{Ar}^*$ is produced by the decay of ^{40}K) in the upper mantle can be anticipated from K/U (Jochum et al., 1983) and Th/U (O'Nions and McKenzie, 1993) ratios in the MORB source. $^4\text{He}/^{40}\text{Ar}^*$ ratios observed in MORB are generally higher than the computed upper mantle ratio of $3(\pm 1)$, possibly reflecting previous loss of Ar which is less soluble than He in silicate melts (Jambon et al., 1986). Assuming that such loss follows a Rayleigh distillation (Marty, 1995), then any fractionation effect between two volatiles can be scaled to the $^4\text{He}/^{40}\text{Ar}^*$ ratio and the initial ratio between two volatile species, e.g., CO_2 and ^3He , can be computed according to:

$$\left(\frac{\text{CO}_2}{^3\text{He}} \right)_{\text{init}} = \left(\frac{\text{CO}_2}{^3\text{He}} \right)_{\text{obs}} \times \left[\frac{(^4\text{He}/^{40}\text{Ar}^*)_{\text{obs}}}{(^4\text{He}/^{40}\text{Ar}^*)_{\text{init}}} \right]^{\frac{1-(K_{\text{He}}/K_{\text{CO}_2})}{1-(K_{\text{He}}/K_{\text{Ar}})}} \quad (1)$$

where K_{He} , K_{CO_2} and K_{Ar} are, respectively, the solubility coefficients equal to 2.5×10^{-11} mol g^{-1} hPa $^{-1}$, 9.0×10^{-12} mol g^{-1} hPa $^{-1}$ and 2.6×10^{-12} mol g^{-1} hPa $^{-1}$, for He, CO_2 and Ar in tholeiitic melt (e.g., Jambon et al., 1986; Holloway and Blank, 1994).

In our analysis (Table 1), we have taken into account chemical variation among MORB. It is now well established that some of MORB (N-MORB) are depleted (e.g., low K content, depletion in light Rare Earth Elements, $^{87}\text{Sr}/^{86}\text{Sr} < 0.7026$) and best represent the depleted upper mantle, whereas other MORB

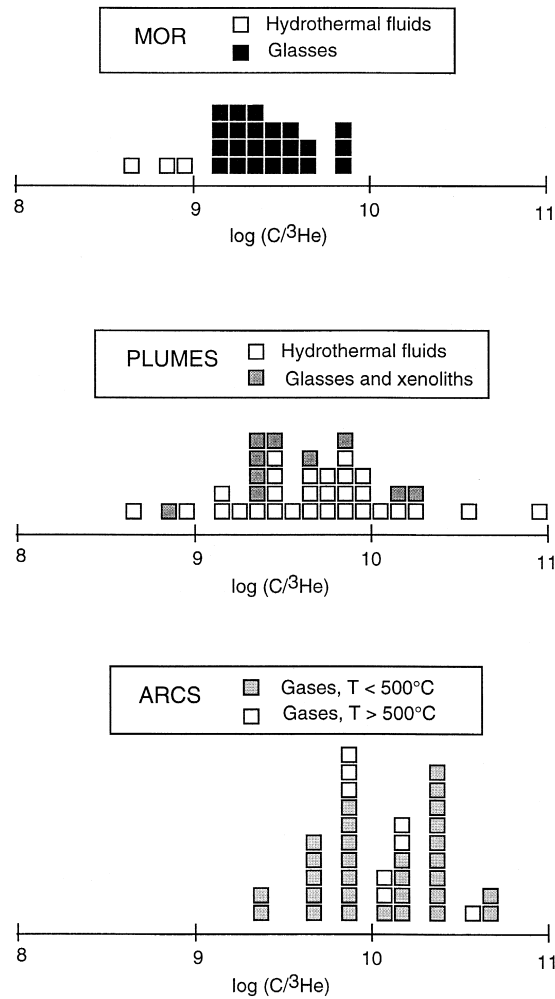


Fig. 1. $\text{CO}_2/{}^3\text{He}$ ratios ($\times 10^{-9}$) in rocks and fluids from various tectonic contexts. *MORB*. Data (whole-rock data) are from Des Marais (1985), Marty and Jambon (1987), Javoy and Pineau (1991) and Kingsley and Schilling (1995). All samples show ${}^3\text{He}/{}^4\text{He}$ within 8 ± 1 Ra (where Ra is the atmospheric ${}^3\text{He}/{}^4\text{He}$ value of 1.38×10^{-6}). *PLUMES*. Only samples showing ${}^3\text{He}/{}^4\text{He}$ ratios higher than those of MORB (> 9 Ra) are represented. Fluids comprise fumaroles from the Hengill area, Iceland (axis of the graben; Marty et al., 1991), the Piton de la Fournaise volcano, Réunion Island (Dolomieu crater; Marty et al., 1993a) and Kilauea (Sulphur Bank; Craig and Lupton, 1976). Hydrothermal fluids are represented by hot springs in the Cirque de Cilaos, Réunion (Marty et al., 1993a) and in Yellowstone (Mud Volcano, where the highest ${}^3\text{He}/{}^4\text{He}$ ratios were recorded; Craig et al., 1978). Loihi fluid data are from Craig et al. (1987). Rock data are from Marty and Jambon (1987) and references therein (Loihi seamount), Trull et al. (1993; Réunion and Hawaiian xenoliths), Marty et al. (1996; Red Sea basalts at 18°N) and B. Marty (Galapagos submarine glasses, unpublished data). *ARCS*. Subduction-type gases are represented by fumaroles and volcanic gases in the temperature range $95\text{--}880^\circ\text{C}$. Data are from Marty et al. (1989), Varekamp et al. (1992), Allard (1992), Sano and Marty (1995) and Sano and Williams (1996). High temperature ($> 500^\circ\text{C}$) may be more representative of magmatic volatiles as interactions with underground aquifers are less likely than for low-temperature gases. However, both sets of $\text{CO}_2/{}^3\text{He}$ ratios are indistinguishable, suggesting that low-temperature interactions are not responsible for the spread of data. The median value is ~ 8 times that of N-MORB, and ~ 3 times that of plumes, a clear evidence that subducted plates contribute C to arc volcanism.

(E-MORB) are termed enriched (e.g., enrichment in light Rare Earth Elements, ${}^{87}\text{Sr}/{}^{86}\text{Sr} > 0.7026$) (e.g., Le Roex, 1987). The origin of such enrichment is

generally attributed to long-term recycling of crustal material to the upper mantle. Volatiles such as C may be potentially subject to such enrichment, given

Table 1
New rare gas and CO₂ data of MORB glasses

Sample	Type	CO ₂ 10 ⁻⁶ mol/g	³ He 10 ⁻¹⁶ mol/g	⁴ He/ ⁴⁰ Ar*
<i>EPR 13°N</i>				
CY82 31 02	N	0.23	5.0	44
CL DRO 15V	N	2.39	35.4	15
CLDR01 5V-b	N	4.34	40.8	17.3
CY84 05 08	N	0.63	5.8	27.2
CY82 30	E	0.75	17.6	59.9
CY82 09 03	E	0.29	14.5	110
CY82 21 06	T	1.66	30.9	12.8
<i>MAR 14°N</i>				
2PD43	E	19.2	82.9	1.17
<i>MAR 30°N</i>				
CH98 DR11	N	1.42	10.7	6.2
CH98 DR12	N	1.43	12.9	6.6
CH98 DR15	N	4.55	49.9	4.5
CH98 DR17	N	4.37	55.7	7.7
<i>MAR 36°N</i>				
CH31DR01	E	30.8	60.7	25.6
CH31DR04	E	32.6	69.1	30
CH31DR10	E	0.41	27.4	472
CH31DR09	T	2.61	8.2	7.8
CH31DR11	E	15.7	43.0	13
CH31DR11 No. 4	E	41.8	146	18.7
<i>Red Sea 20.5°N</i>				
KS 11 A	E	7.35	30.2	96
KS 11 B	E	4.06	13.9	33.3
KS 12 A	E	0.21	0.80	24.5
KS 04 A	E	7.15	26.3	54.2

EPR = East Pacific Rise; MAR = Mid-Atlantic Ridge. Gases were extracted by vacuum crushing according to the procedure described in Marty (1995), and Marty et al. (1995). The CO₂ was condensed in a cold finger at liquid nitrogen temperature adjacent to the crusher. The powdered sample was heated for 5 min at 100°C after crushing. The CO₂ was then transferred to glass ampoules for volumetry and isotope determination (to be presented elsewhere). Rare gases were analysed on-line (Marty, 1995). The ³He content was computed from the measured He amount and ³He/⁴He ratio (all of them being in the MORB range of 8 ± 1 Ra). The amount of radiogenic ⁴⁰Ar* was computed from measurements of Ar content and ⁴⁰Ar/³⁶Ar ratio, assuming that all ³⁶Ar was atmosphere-derived. T-MORB stands for transitional MORB (Le Roex, 1987) and has been assimilated to E-MORB in Fig. 2b.

the possibility of volatile recycling in subduction zones.

Fig. 2 illustrates the correlation between CO₂ and ³He in N-MORB and E-MORB for gases extracted by crushing (Table 1). The excellent correlation in the case of N-MORB defines a CO₂/³He ratio of $(0.86 \pm 0.24) \times 10^9$ (Fig. 2a; computed using the York (1967) regression analysis with uncorrelated errors), 3 similar to values measured in hydrothermal fluids sampled at ridges. The CO₂/³He ratio cor-

rected for fractional degassing using Eq. (1) is $(1.06 \pm 0.3) \times 10^9$ (Fig. 3), quite similar to the uncorrected mean ratio. Thus the present data set suggests that fractional degassing has no discernible effect on the CO₂/³He ratio of N-MORB, a conclusion which will need to be re-examined when more data are available. In the case of E-MORB, the correction for fractional degassing increases the CO₂/³He ratio for E-MORB from $(3.3 \pm 1.1) \times 10^9$ (Fig. 2b) to $(4.5 \pm 1.3) \times 10^9$ (Fig. 3).

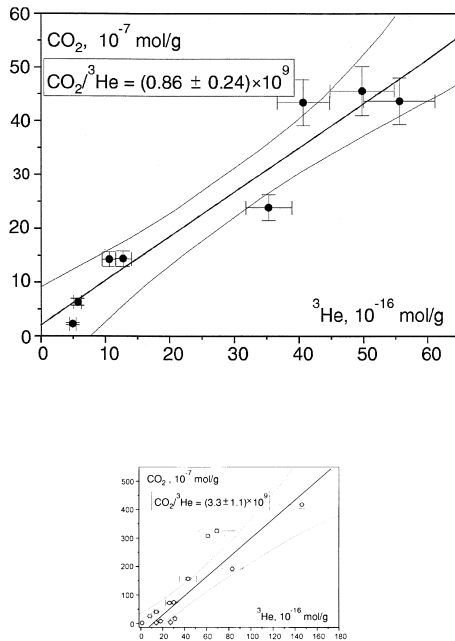


Fig. 2. ^3He versus CO_2 in vesicle gas extracted from MORB glasses (Table 1). (a) N-MORB. The correlation was computed using the York (1967) regression with uncorrelated errors corresponding to 95% confidence interval. (b) E-MORB. The correlation indicates a significantly higher $\text{CO}_2 / ^3\text{He}$ ratio.

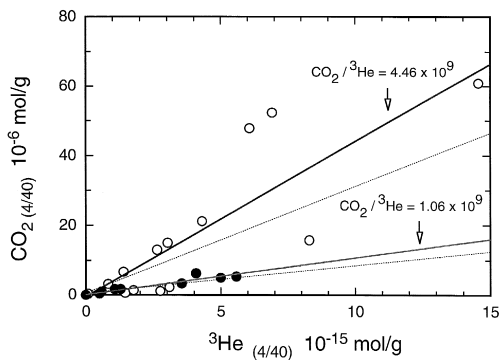


Fig. 3. ^3He versus CO_2 : effect of correction for fractional degassing. The ^3He concentrations are the same as in Fig. 2, and the CO_2 concentrations have been corrected using the radiogenic $^4\text{He}/^{40}\text{Ar}^*$ ratios. The correction assumes that the $^4\text{He}/^{40}\text{Ar}$ ratio in MORB glasses varies upon degassing because solubilities of He and Ar differ by one order of magnitude. The initial radiogenic $^4\text{He}/^{40}\text{Ar}$ value of the mantle is 3 (see text). For comparison, the uncorrected correlations are shown as dotted lines. The N-MORB correction is not significant, but correction of E-MORB data leads to a significantly higher mean $\text{CO}_2 / ^3\text{He}$ ratio of 4.5×10^9 .

2.3. Model flux of carbon at MOR

The mean MORB $\text{CO}_2 / ^3\text{He}$ ratio depends on the proportion of E-MORB relative to N-MORB. The proportion of E- to all MORB is around $30 \pm 10\%$ (e.g., compilation from Ito et al., 1987). The mean MORB $\text{CO}_2 / ^3\text{He}$ ratio is then $(2.2 \pm 1.0) \times 10^{12}$ mol/a, in fact similar to previous estimates.

The mean carbon content of the upper mantle can be then computed assuming that C is incompatible (e.g., Bottinga and Javoy, 1990) and that C is quantitatively degassed from MORB magmas (a reasonable assumption given the low solubility of C in basaltic melt). With a mass flux of $21 \text{ km}^3/\text{a}$ (e.g., Crisp, 1984) and a partial melting rate of $10 \pm 3\%$ at ridges, the corresponding mean C content of the upper mantle is computed to be $(3.1 \pm 1.9) \times 10^{-6}$ mol/g. The concentration of C in the upper mantle is unlikely to have changed on a time scale of 10^8 , given typical residence time of recycled material in the upper mantle on one hand, and that of trace elements in this reservoir on the other hand, both of which being of the order of 10^9 a.

The C content of the upper mantle can also be obtained from estimates of ^3He content of this reservoir as derived from rare gas systematics. Recent models propose that the residence time of He in the upper mantle is ~ 1 Ga (steady-state model; Kellogg and Wasserburg, 1990; O'Nions and Tolstikhin, 1994; Porcelli and Wasserburg, 1995a,b). Model results depend on assumptions of the U content of the upper mantle, steady or evolutionary regimes of mantle reservoirs, and give mean ^3He content within $(2.5 \pm 1.5) \times 10^{-15}$ mol/g (Allègre et al., 1983, 1986; Trull et al., 1993; Porcelli and Wasserburg, 1995b; Tolstikhin and Marty, 1998). The ^3He concentration in the upper mantle is unlikely to have significantly varied on the time-scale of 100 Ma, which is about 1/10 the rare gas residence time in the upper mantle. For the E-MORB type source, the ^3He content is assumed to be similar since $^3\text{He}/^4\text{He}$ ratios do not change by more than 10% and are due to contribution of crustal component containing radiogenic ^4He . In this case the C content of the upper mantle computed following this method is $(4.5 \pm 3.2) \times 10^{-6}$ mol/g, very similar to the concentration estimated above, but with a larger uncertainty related to assumptions inherent to rare gas models.

Although imprecise, this estimate has the advantage to be valid on a time scale of 10^7 – 10^8 a, and therefore applicable to the C cycle from the Mesozoic to the present.

3. Carbon flux at convergent margins

3.1. Previous estimates

Estimates of the C flux from arc and non-arc volcanoes (Table 2) vary over one order of magnitude (0.4×10^{12} mol/a to 3.3×10^{12} mol/a), depending on the method adopted. Part of the spread is due to the limited number of volcanoes on which direct measurements (by remote sensing measurement of CO_2 adsorption in volcanic plumes) are available. Besides this technical problem, there exists a fundamental question of the representativeness of present-day emissions over geological periods. For example, a single volcano like Mount Etna alone emits at present up to 0.5×10^{12} mol/a (Allard et

al., 1991), and the number of Etna-like degassing events in the past is completely unknown.

3.2. Model flux of carbon

In order to avoid this problem, C flux estimates may be based on magma production rates for arc volcanoes together with estimates of C content in the magma sources and of partial melting rates at arcs. In this case, the fraction of carbon deriving from the mantle wedge as well as that originating in the descending slab needs to be documented. This approach was attempted by Varekamp et al. (1992) and by Sano and Williams (1996) and is further investigated here. Volcanic gases from subduction-type volcanism show $\text{CO}_2/{}^3\text{He}$ ratios higher than those observed in MOR- and plume-type gases (Marty and Jambon, 1987; Marty et al., 1989; Varekamp et al., 1992; Sano and Marty, 1995; Sano and Williams, 1996; see also Table 1), an observation attributed to addition of slab-derived carbon. The median $\text{CO}_2/{}^3\text{He}$ ratio of gases from 37 subduction-type

Table 2
Available estimates of the flux of CO_2 from subaerial volcanoes

Authors	Arc volcanoes 10^{12} mol/a	Non arc volcanoes 10^{12} mol/a	Total 10^{12} mol/a	Method	Notes ^a
Le Guern (1982)			1.1	Flux measurement	
Marty et al. (1989)	0.3			C/S plus S flux	b
Williams et al. (1990, 1992)			0.4–2.5	C/S plus S flux	c
Gerlach (1991)			1.8	Flux measurement	d
Allard (1992)	0.7	0.82	1.5	Flux measurement	e
Marty and Le Cloarec (1992)			1.5–2.5	C/ ²¹⁰ Po plus Po flux	f
Varekamp et al. (1992)	1.5		3.3	C/ ³ He, mass flux	g
Brantley and Koepenick (1995)			2–3	Flux measurement	h
Sano and Williams (1996)	3.1	0.03	3.1	C/ ³ He, ³ He flux	i

^a Compilation of geochemical data for 30 volcanoes, including direct measurements of CO_2 fluxes (Barringer radiometer, artificial tracing, aircraft sampling).

^b Assuming a mean C/S ratio of 1.5 (best estimate for MORB) and using the Berresheim and Jaeschke (1983) SO_2 flux from active volcanoes.

^c Compilation of measurements of SO_2 fluxes and C/S ratios in volcanic gases and extrapolation to the total number of volcanoes.

^d Compilation of direct CO_2 flux measurements from 7 volcanoes and extrapolation using statistical (median) analysis.

^e Compilation of measured or estimated CO_2 fluxes from 17 volcanoes.

^f Measurement of the C/²¹⁰Po ratios for 5 volcanoes and using the global volcanic ²¹⁰Po budget of the atmosphere.

^g Computation involving the respective fractions of mantle-derived C and slab-derived C at arcs, and the mass flux of volcanic material at arcs relative to that at ridges.

^h Fractal analysis of volcanic CO_2 fluxes.

ⁱ Compilation of C/³He ratios in volcanic gases. The C flux was computed using the Torgersen (1989)'s ³He flux estimate based on the ratio between arc and ridge mass fluxes.

volcanoes (Fig. 1) is $(11.0 \pm 3.3) \times 10^9$ ($n = 37$, median value, uncertainty as $2\sigma/\sqrt{n}$), similar to a previous estimate made by Sano and Williams (1996), and about five times higher than the mean MOR ratio. This difference suggests the proportion of metamorphic carbon relative to total carbon to be approximately 80%, in agreement with the conclusions of Varekamp et al. (1992), Sano and Marty (1995) and Sano and Williams (1996).

The flux of carbon at subduction zones can be computed according to:

$$\phi_{C,arc} = \phi_{arc} \times [{}^3\text{He}]_{um} \times (C/{}^3\text{He})_{arc} \times r_{arc}^{-1} \quad (2)$$

where ϕ_{arc} is the flux of magmas and r_{arc} is the mean partial melting rate at arcs. The range of extent of partial melting is inferred to be 10–25% from consideration of major subduction systems in the world (Plank and Langmuir, 1988). The best available estimate of the rate of magma emplacement at accreting plate margins is $0.5 \pm 0.1 \text{ km}^3/\text{a}$ for volcanism, and 2.5–8.0 km^3/a for plutonism (Crisp, 1984). If we consider only the rate of lava production, we obtain a mean $\phi_{C,arc}$ of $1.5 \times 10^{11} \text{ mol/a}$. This figure is significantly lower than that derived from volcanic emissions (Table 2). If we now include plutonism, then the flux of C at arcs becomes $\sim 2.5 \times 10^{12} \text{ mol/a}$. As for previous estimates, the uncertainty pertinent to this approach is considerable. Having said that, there are a number of points which merit consideration.

First, the flux of carbon computed in the present work using the mass flux of lavas is an order of magnitude lower than the volcanic flux. Only when plutonism is included is the correct order of magnitude obtained, suggesting that considerably more magma outgasses CO_2 at depth than that seen erupting (Allard et al., 1991, 1994). It also agrees with the idea that magma underplating is a significant source of volatiles contributing to the atmosphere (O'Nions and Oxburgh, 1988; Hilton et al., 1993).

Second, the CO_2 flux at convergent margins appears to be comparable to that at divergent margins, but with different origin for carbon (mantle-derived for the former, mainly exogenic for the latter).

We would like to emphasise at this stage that all methods listed in this section, including ours, yield C flux estimates for arcs which are not better defined than at best a factor of 2. Progress in this domain

may arise from a better knowledge of magmatic processes at arcs as well as from direct volatile analysis in magmas at depth (e.g., in melt inclusions trapped in mafic minerals).

4. Carbon flux from plumes

4.1. Observations

Two different lines of observations suggest low volatile flux from plumes. Direct observations of hydrothermal activity at the top of the most active present-day plume-type volcano, Loihi Seamount, Hawaii (Craig et al., 1987; Koreda et al., 1988) documented a very low ${}^3\text{He}$ flux. The amount of warm (30°C) water which penetrates on the southwestern rim of the summit Loihi crater and further flows downward is so small that a reasonably reliable estimate of the helium flux is not possible (H. Craig, pers. commun, 1995). This is in sharp contrast with the powerful hydrothermal activity at the East Pacific Rise (Craig et al., 1975) and several other MOR hydrothermal manifestations. Moreover, worldwide observations of ${}^3\text{He}$ excesses in seawater, together with recent modelling on mantle ${}^3\text{He}$ flux shows mid-ocean ridges to be the dominant source of mantle He (Farley et al., 1995).

For non-arc subaerial volcanism, and therefore including plume-type volcanoes, Allard (1992) estimates the flux of ${}^3\text{He}$ at 160–240 mol/a, a factor of 5 lower than the ${}^3\text{He}$ flux at spreading centres and, for PLUME-type volcanoes alone, probably an order of magnitude lower than the ${}^3\text{He}$ flux at MOR (in the compilation of Allard, Mount Etna, which does not show PLUME-type He (Marty et al., 1991), supplies $\sim 58 \text{ mol } {}^3\text{He/a}$).

4.2. Mass flux

There are several estimates of the rate of magmatism at MOR and PLUME developed on ocean plates (Parsons, 1982; Reymer and Schubert, 1984; Crisp, 1984) and all of them result in a MOR/PLUME mass ratio of ~ 10 . For example, Crisp (1984) inferred a PLUME magma emplacement rate of $(5\text{--}7) \times 10^{15} \text{ g/a}$ ($1.8\text{--}2.4 \text{ km}^3/\text{a}$; to be compared with a

Table 3

Large igneous provinces during the last 250 Ma (after Mohr and Zanettin, 1988; Coffin and Eldholm, 1993; White and McKenzie, 1995)

Locality	Age (Ma)	Duration (Ma)	Volume (10^6 km^3)	Rate during active phase (10^{15} g/a)
Columbia River (W&M)	17.2–15.5	1.7	0.174	0.28
Columbia River (C&E)	17.2–15.7	1.5	1.0	1.9
Ethiopia (M&Z)	32–29.5	2.5	1	1.2
North Atlantic Tertiary Province (W&M)	57.5–54.5	3	1.8	1.7
North Atlantic Tertiary Province (C&E)	57.5–54.5	3	7	6.5
Deccan (W&M)	66 ± 1	1	2.5	7.0
Deccan (C&E)	69–65	1	8	22
Ontong Java (C&E)	124–121	3	38	35
Ontong Java LIP (C&E)	–	–	53	50
Parana (W&M)	137–127	2	1.5	2.1
Siberian Traps (W&M)	248 ± 3	1	2	5.6
Kergulen (C&E)	–	–	15	8.4
Kerg LIP (C&E)	–	–	23	14
Total	250	250	95.5	1.1

rate of $21 \text{ km}^3/\text{a}$ for MOR) from mapping the oceanic crust and this range is used hereafter. The rate of magmatism required to form continental flood basalt (CFB) provinces and averaged over geological periods, $1 \times 10^{15} \text{ g/a}$ (the mean flux during 250 Ma; Table 3), does not change this proportion. Kellogg and Wasserburg (1990) inferred somewhat higher mass flux of $(1-10) \times 10^{17} \text{ g/a}$, based on geophysical estimates of the buoyancy flux (the flux of matter necessary to induce topographic deformation) associated with plumes (e.g., Sleep, 1990). Such flux would correspond to the flux of matter invading the upper mantle and not necessarily reaching the surface.

4.3. ^3He content of the plume source

The development of plumes and CFB requires thermal anomalies which are likely to originate from the lower mantle, possibly from the core–mantle boundary. Thus the lower mantle appears to be an important contributor of volatiles to PLUME, a view corroborated by the occurrence of ^3He enrichments in OIB (e.g., Lupton, 1983) and in CFB (Basu et al., 1993, 1995; Marty et al., 1996). We first assume that PLUME originate from the lower mantle, and then discuss this assumption using available data for PLUME-related lavas and fluids. The abundance of

^3He in the lower mantle can be estimated from steady-state (Kellogg and Wasserburg, 1990; O’Nions and Tolstikhin, 1994; Porcelli and Wasserburg, 1995b) and evolutionary (Allègre et al., 1983, 1986; Azbel and Tolstikhin, 1990; Tolstikhin and Marty, 1998) models, with the most acceptable value of $[^3\text{He}]_{\text{LM}} = (2.2 \pm 1.0) \times 10^{-13} \text{ mol/g}$, a factor of ~ 100 higher than the value inferred for the MORB source (Section 2.3).

In contrast to these expectations isotopic He–Sr–Nd–Pb correlations show that He abundances (relative to those of the lithophile trace elements shown) in PLUME melts are similar to or even lower than those in MORB (Kurz et al., 1983, 1987; Poreda et al., 1993; Farley et al., 1995; Graham et al., 1996; Marty et al., 1996). This apparent contradiction between expected and observed abundances of He isotopes in PLUME is depicted in Fig. 4, which shows a selection of He–Sr isotope relationships observed in plume and seamount basaltic lavas of several localities. As a first approximation, these correlations can be treated as resulting from mixing between two end-member materials. The first one, UM, is a proxy of the depleted upper mantle, for which He and Sr abundances can be considered as known and fixed parameters ($^4\text{He}/^3\text{He} = 90,000$, $[^3\text{He}]_{\text{UM}} = 2 \times 10^{-15} \text{ mol/g}$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7024$, $^{86}\text{Sr} = 15 \text{ ppm}$; Ito et al., 1987; O’Nions and Tolstikhin, 1994, 1996).

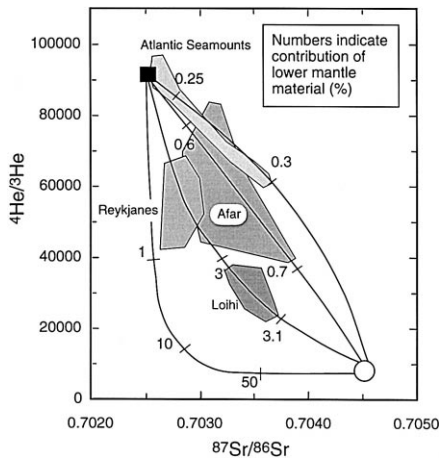


Fig. 4. Sr–He isotope relationships for selected hot spots and seamount lavas. Areas were selected to cover the largest range of variations. Observed He and Sr isotope abundances at hot spot and seamount basalts can be roughly approximated by binary mixing, one end-member being the depleted upper mantle (UM) (source of MORB), and another one, plume source (PS), could be a mixture of the bulk silicate earth Sr (see text) and He with: (1) constant ${}^4\text{He}/{}^3\text{He} = 5.5 \times 10^3$ as inferred from the evolutionary modelling of light rare gases (Tolstikhin and Marty, 1998); and (2) variable concentrations of helium. The choice of Sr abundance in PS is not crucial: Sr abundance in reasonable PS end-members are not expected to differ greatly from that in the MORB source. Numbers along the curves are fractions of mixing (portion of lower mantle material in the mixture). The calculated mixing lines fit the observed relationships only if $[{}^3\text{He}]_{\text{PS}} \ll [{}^3\text{He}]_{\text{LM}}$: the lower mantle material involved in mixing must be diluted or degassed before mixing occurred. This issue has been already discussed by Kurz et al. (1983, 1987), Poreda et al. (1993), and others (see text). Sources of data: Atlantic Seamounts, Graham et al. (1996) and Castillo and Batiza (1989); Loihi, Kurz et al. (1983); Afar, Marty et al. (1996); Reykjanes, Poreda et al. (1986); Loihi, Kurz et al. (1983).

The second end-member is the plume source (PS) which could be some hypothetical mixture of He from the lower mantle (${}^4\text{He}/{}^3\text{He} = 5500$, $[{}^3\text{He}]_{\text{LM}} = 2.2 \times 10^{-13}$; O’Nions and Tolstikhin, 1994, 1996; Tolstikhin and Marty, 1998), and the bulk mantle Sr (${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.7045$, $[{}^{86}\text{Sr}]_{\text{BM}} = 20$ ppm; Jacobsen and Wasserburg, 1979; McKenzie and O’Nions, 1995). These abundances give the mixing parameter $R_{\text{PS}/\text{UM}} = ({}^3\text{He}_{\text{LM}} \cdot {}^{86}\text{Sr}_{\text{UM}}) / ({}^3\text{He}_{\text{UM}} \cdot {}^{86}\text{Sr}_{\text{LM}}) = 62$. The choice of the Sr abundances in the plume source is not crucial and the conclusions which follow are valid even if Sr abundances typical of aged oceanic crust are used (${}^{87}\text{Sr}/{}^{86}\text{Sr} \sim 0.707$, $[{}^{86}\text{Sr}]_{\text{OC}} \sim 100$ ppm).

The curve corresponding to mixing between the UM and PS = LM end-members defined above ($R_{\text{PS}/\text{UM}} = 62$ corresponds to the solid curve in Fig. 4) can only accommodate the least radiogenic samples of the Reykjanes Ridge. In this case, the observed trend needs an upper mantle/lower mantle mass ratio > 100 . The trends for the other regions (Fig. 4) can be reproduced if R varies from ~ 20 (Loihi) to ~ 200 (Atlantic Seamounts) times lower than $R_{\text{PS}/\text{UM}}$. Because the Sr abundances could hardly account for these dramatic variations, the low R values imply either much lower concentrations of ${}^3\text{He}_{\text{LM}}$ in mixed materials or high ${}^3\text{He}_{\text{UM}}$ in MOR-sourced melts (e.g., Kurz et al., 1983; Graham et al., 1996; Marty et al., 1996).

The second alternative can be ruled out: to increase the He/Sr ratio by a factor of about 100, an unrealistically small fraction of melt would have been necessary. Assuming a bulk solid/melt partition coefficient for Sr of 0.03 (Jacobsen and Wasserburg, 1979) and an infinitely small value for He, then a melt fraction of $\sim 0.01\%$ is derived, which would be almost immobile. Investigation of trace element abundances in melt inclusions in olivine shows that both depleted and enriched melts could be derived by continuous melting within a single mantle column having a melt fraction between 3 and 20% (Sobolev and Shimizu, 1993; Gurenko and Chaussidon, 1995).

We therefore favour the first possibility that the low R values imply He abundance in the PLUME end-member much lower than that of the lower mantle and, in some cases, even lower than that of the upper mantle. Such decrease could be due either to pre-degassing of the PLUME end-member, or to dilution of lower mantle material by upper mantle, sub-oceanic lithosphere, or recycled material.

If the original PLUME material would have been advected upwards, underwent melting, degassing, and subsequently mixed with upper mantle melts/rocks, then the total amount of He transferred into the atmosphere by PLUME would be a factor of ~ 10 larger than that outgassing through MOR (approximately ten times less magma emission rate, but ~ 100 -fold enrichment in ${}^3\text{He}$). However, there is no evidence for such elevated ${}^3\text{He}$ flux from PLUME (Section 4.1), neither for high ${}^3\text{He}$ concentrations in PLUME-related rocks and minerals. Indeed compari-

son of ^3He abundances in olivine from PLUME basalts and those from subcontinental xenoliths and mafic–ultramafic rocks does not show any evidence for ^3He -rich melts in PLUME-related crystallisation differentiation processes (Fig. 5).

Secondly, high abundances of ^3He have not been observed so far in basalt glasses sampled at hot spots. Fig. 6 summarises the concentrations of ^3He

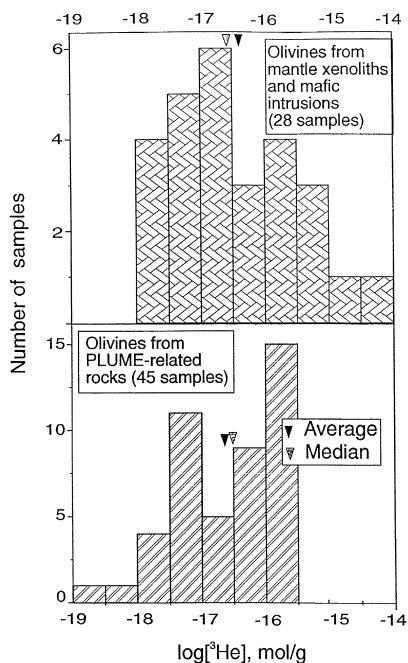


Fig. 5. ^3He abundance in olivines from xenoliths and ultramafic rocks. The abundance of $[^3\text{He}]_{\text{LM}}$ required to maintain low $^4\text{He}/^3\text{He}$ ratios in the lower mantle should be high $(2.5 \pm 1.5) \times 10^{-13}$ mol/g as computed from steady-state and evolutionary rare gas models (see text for references). In contrast, $^4\text{He}/^3\text{He}$ ratios in subcontinental xenoliths are higher than those in MORB, implying the ^3He concentration in subcontinental mantle to be similar to, or even lower than, that in the MORB source, $(2 \pm 1) \times 10^{-15}$ mol/g. However, this dramatic difference has not been recorded in olivine separates from PLUME-sourced xenoliths. The main conclusion is the same as that drawn from Fig. 4: lower mantle He should be diluted, or degassed, before the xenoliths were formed. If the PLUME-sourced olivines were formed at depths precluding intense degassing of upwelling plume material, then the scenario involving dilution appears to be preferable. Sources of data: (top plot) Porcelli et al. (1986), Tolstikhin et al. (1992), Dunai and Baur (1995); (bottom plot) Kurz et al. (1983), Rison and Craig (1983), Kaneoka et al. (1986), Poreda and Farley (1992), Marty et al. (1993a), Hiyagon et al. (1992), Moreira et al. (1995), Valbracht et al. (1996).

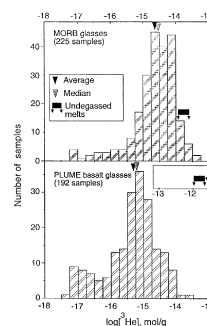


Fig. 6. ^3He abundance in MOR and PLUME basalt glasses. The concentrations of ^3He in MOR glasses (top) are almost always lower (by one order of magnitude for the mean and median values) than those expected in undegassed melts, assuming a melt fraction of 10%, a ^3He abundance of $(2.5 \pm 1.5) \times 10^{-15}$ mol/g for the MORB source, and an incompatible behaviour for helium. However in a few cases, the observed concentrations are similar to the undegassed values. If PLUME had entrained lower mantle material to a level where melting occurred, then the melts would have to contain a very high concentration of $^3\text{He} > 1 \times 10^{-12}$ mol/g, which is two orders of magnitude higher than the highest observed concentrations. In contrast to MORB, PLUME basalt glasses never preserved a record of lower mantle-derived concentrations. A possible explanation of this contrast is that He in PLUME material was diluted before melt generation and degassing. Sources of data: Kurz and Jenkins (1981), Kurz et al. (1982a,b, 1983), Ozima and Zashu (1983), Rison and Craig (1983), Poreda et al. (1986, 1993), Staudacher et al. (1986, 1989), Sarda et al. (1988), Staudacher and Allègre (1989), Trull et al. (1990), Honda et al. (1991, 1993), Graham et al. (1992), Hiyagon et al. (1992), Poreda and Farley (1992), Lupton et al. (1993), Marty et al. (1993b), Moreira et al. (1995), Valbracht et al. (1996).

in PLUME and MOR basalt glasses and compares these to the concentrations expected for PLUME and MOR melts. The highest ^3He concentrations in MORB samples are in reasonable agreement with those predicted from the model-derived ^3He abundance in the depleted upper mantle and related magmas (Sarda et al., 1988; Staudacher et al., 1989; Sarda and Graham, 1990), whereas lower He contents in MORB glasses can be reasonably attributed to pre- and syn-eruptive degassing of volatiles. The ^3He concentrations in PLUME basalt glasses are generally lower than those in MORB, and, notably, are at least two orders of magnitude lower than the value predicted for partial melting of an uplifted lower mantle-type material. One possible reason is

that the He content in submarine lavas is in fact controlled by the saturation of the major volatile exsolving at the depth of eruption, namely CO₂ for below ~ 500 m. Several studies on carbon in oceanic basalts have shown that the CO₂ content of such samples is within a factor of 2–3 times that expected for CO₂ saturation at the relevant water depth (e.g., Pineau and Javoy, 1983; Blank et al., 1993). If CO₂ saturation is controlling the amount of He in oceanic basalts, then the observed He concentration should in fact reflect the depth of eruption rather than the initial He content in the primary magma. Therefore, the factor of ~ 5 difference for the mean ³He content between MORB and PLUME glasses (Fig. 6) may be due to the generally shallower depth of eruption of PLUME lavas which occur within topographic heights characteristic of hot spot centres (e.g., Hawaii, Galapagos, Reykjanes Ridge) rather than to a lower He content of the source. In addition, the CO₂/³He ratios of PLUME are a factor of 2–3 higher than those of N-MORB (Fig. 1), allowing less ³He to be retained at a given CO₂ saturation depth. However, there remains to be explained why there are no PLUME basalts analysed so far which show high ³He contents whereas some MORB glasses have retained He concentrations comparable with those expected for melting of their respective sources. In addition, if volatile degassing is extremely efficient in the case of PLUME, then such degassing should be apparent either in underwater volcanic emissions, or in the integrated flux of subaerial volcanism.

Given this evidence and observations of low ³He flux from plumes, we consider the low He abundance in PLUME to be a consequence of very low fraction of lower mantle material involved in PLUME generation, of the order of a few percent. The corresponding ³He flux to the upper mantle is maintaining the amount of ³He in this reservoir at steady-state, leaving little contribution of ³He to PLUME degassing flux. Assuming that the ³He PLUME/MOR flux ratio is ~ 0.1, approximately only $\leq 2 \times 10^{15}$ g/a of lower mantle material is involved in magma generation at PLUME, which can account for only $\leq 4\%$ of the PLUME magma generation rate. Consequently, the concentrations of ³He in PLUME and MOR melts are probably comparable within a factor of 2, as indicated by He–Sr isotope relationships in

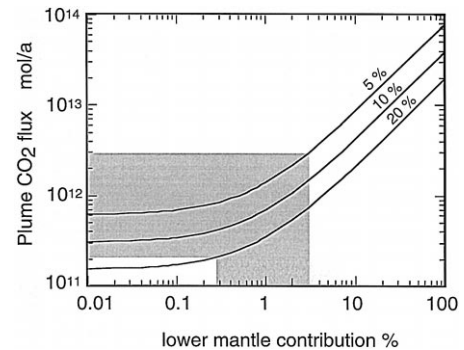


Fig. 7. Flux of CO₂ from PLUME volcanism as a function of the mass contribution of lower mantle material to PLUME magmas. The CO₂ flux is computed using estimated ³He contents of the upper and lower mantle regions, the mean CO₂/³He ratio in plumes, the PLUME magma generation rate (see text) and the partial melting rate (numbers along the curves) for PLUME generation.

magmatic provinces (Kurz et al., 1983; Poreda et al., 1993; Graham et al., 1996; Marty et al., 1996).

4.4. CO₂ flux

We compute the flux from PLUME in the same way as for arc:

$$\phi_{C,PL} = \phi_{PL} \times [^3\text{He}]_{PL} \times (C/^3\text{He})_{PL} \times r_{PL}^{-1} \quad (3)$$

An upper limit for the flux of carbon at PLUME is obtained by taking a maximum lower mantle contribution of 3% (Fig. 7), a lower limit of 5% for the melt fraction (e.g., White and McKenzie, 1995), and a PLUME CO₂/³He ratio of 3.0×10^9 . Then a CO₂ flux of 3×10^{12} mol/a is obtained (Fig. 7), comparable to the carbon flux at ridges. Although imprecise, these estimates suggest that the magnitude of PLUME degassing of CO₂ is at best similar to that of spreading centres.

5. Concluding remarks

We have attempted to evaluate CO₂ fluxes from spreading centres, plume-related volcanism, and subduction zones using rates of magma emplacement, CO₂–³He relationships in volatile emissions from these environments, and rare gas abundances in mantle reservoirs. Some of the parameters used in this

approach do not specifically depend on time for a range up to 10^8 a, although some of them (i.e., $\text{CO}_2/{}^3\text{He}$ ratios in volcanic gases) are instantaneous values. However, given the relative constancy of the processes in action (e.g., types of materials involved in subduction processes), we do not feel that those parameters could have experienced drastic variations in the past.

The maximum CO_2 flux resulting from magmatic processes is found to be 10×10^{12} mol/a, and our preferred estimate is 6×10^{12} mol/a. Arcs, spreading centres and plume may provide comparable flux of CO_2 . The activity of plumes in the past is unlikely to have dramatically increased these fluxes because time-integrated contributions of large-scale magmatic events such as CFB, appear minor with respect to steady-state degassing. However, enhanced plume activity such as CFB episodes might have injected CO_2 directly into the atmosphere, on a time scale that remains to be determined in more detail.

Such estimates are in agreement with early atmospheric balancing calculations which implied present-day (pre-industrial) CO_2 degassing rates of $(6-7) \times 10^{12}$ mol/a (Holland, 1978; Berner et al., 1983) and, more recently, of 11×10^{12} mol/a (Berner, 1990).

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