Earth and Planetary Science Letters 361 (2013) 183–194

Contents lists available at SciVerse ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Mechanisms of magma degassing at mid-oceanic ridges and the local volatile composition (^{4}He–^{40}Ar*–CO_2) of the mantle by laser ablation analysis of individual MORB vesicles

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ARTICLE INFO

Article history:
Received 6 July 2012
Received in revised form
21 October 2012
Accepted 24 October 2012
Editor: T.M. Harrison
Available online 22 November 2012

Keywords:
MORB volatiles
individual vesicle analysis
degassing processes
mantle heterogeneity
magma

ABSTRACT

Individual vesicles in <1 cm^3 samples of MORB glasses commonly preserve significantly different volatile (He, Ar, CO_2) compositions. Five separate MORB glass samples from different ridges were investigated, selectively opening targeted vesicles using a 193 nm excimer laser. One sample shows evidence of syn-emplacement selective helium loss from the vesicles in the glass rim close to the crystallised zone of the pillow lava, proving that He contents and low He/Ar ratios do not always reflect mantle and/or magmatic processes. However the composition of the different vesicles of three of these samples covers large ranges in He/Ar and Ar/CO_2 with linear variations in plots of ln(He/Ar) vs. ln(Ar/CO_2) which are consistent with a Rayleigh distillation at equilibrium and allow the relative abundances of the volatiles in the MORB mantle source to be estimated by correcting for degassing processes on a sample-by-sample basis. This technique presents a new tool for characterising and correcting for volatile fractionation processes that have modified the initial mantle source composition. The results confirm a heterogeneous $CO_2/^3$He ratio in the MORB source regions with the Azores mantle source enriched in C/^{3}He compared to that of N-MORBs. The considerable heterogeneity in vesicle compositions within such a small volume (<1 cm^3) requires injection of less degassed magma at shallow level before eruption. The maximum time interval between magma mixing and quenching on the seafloor is of the order of a few hours.

1. Introduction

Mid-oceanic ridge volcanism represents about 75% of the total magma emplaced on Earth (Crisp, 1984). Volatiles in the source of this magma, i.e. the Earth's mantle, influence the physical properties (viscosity, melting point etc.) of the mantle and are key for understanding how the Earth's mantle formed and evolved through time, the origin of the atmosphere and oceans, and for constraining the present day volcanic CO_2 flux to the atmosphere.

Analyses of volatiles trapped in oceanic basalts provide fundamental constraints on the composition and structure of the Earth's mantle (e.g. Allègre et al. 1987, 1983; Bottinga and Javoy, 1990; Cartigny et al., 2008; Craig and Lupton, 1976; Fisher, 1997; Honda et al., 1993; Javoy and Pineau, 1991; Javoy et al., 1982; Kurz et al., 1982; Marty and Humbert, 1997; Marty and Ozima, 1986; Moreira et al., 1998; Ozima and Zashu, 1983; Poreda and Arnorsson, 1992; Sakai et al., 1984; Sarda et al., 1988; Starkey et al., 2009; Staudacher et al., 1990 etc.). The mantle volatile composition is heterogeneous; for instance, the MORB source has a well-defined and homogeneous ^{3}He/^{4}He ratio in contrast to the OIB source (e.g. review by Graham 2002). The MORB reservoir itself presents heterogeneities, not only for incompatible elements but also for volatiles (e.g. Cartigny et al., 2001; Dosso et al., 1999; Marty, 2012; Marty and Zimmermann, 1999; Nishio et al., 1999). On the other hand there is geophysical evidence for whole mantle convection (Grand et al., 1997; Van der Hilst et al., 1997).

Constraining the basalt source region volatile variations is notoriously problematic because virtually all mantle-derived melts have been strongly modified by magmatic degassing (Clarke et al., 1969). During submarine eruptions, the chilled margins of pillow basalts trap a fraction of mantle derived gases in CO_2-rich vesicles (Kurz et al., 1982; Marty and Ozima, 1986). However ^{4}He/^{40}Ar ratios in vesicles are fractionated relative to the mantle ratio. Because ^{4}He and ^{40}Ar are radiogenic isotopes, produced by U, Th and K decay, respectively, and because the mantle U/K ratio is relatively constant (Arevalo et al., 2009; Jochum et al., 1983) the ^{4}He/^{40}Ar ratio of the mantle is relatively well constrained with values of 2–4 (Jambon et al., 1985; Marty 2012; Staudacher et al., 1989). Despite this, ^{4}He/^{40}Ar* ratios (^{40*}Ar is the ^{40}Ar corrected for

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http://dx.doi.org/10.1016/j.epsl.2012.10.022

Table 1
Location of basaltic glasses sampled along the Mid-Atlantic Ridge (MAR) and the East Pacific Rise (EPR). The samples are classified as N, T and E-MORB according to their La/Sm ratios, normalised to the "primitive mantle" (normalisation to the composition of CI carbonaceous chondrites, 237 ppb and 148 ppb for La and Sm respectively from McDonough and Sun (1995)). $^4He/^{40}Ar^*$, $^3He/^4He$ and $^{87}Sr/^{86}Sr$ ratios from the literature are also given for information. ~ indicates that the data was not available for the sample studied here, but was measured in the same ridge area, and – indicates that the data is not available. The vesicularity was calculated using the microtomographic images and the software ImageJ.

Sample	Latitude	Longitude	Depth (m)	Vesicularity	$^4He/^{40}Ar^*$	La/Sm_N	$^3He/^4He$ (R/Ra)	$^{87}Sr/^{86}Sr$	Type	Comment
MAR 16–31°N										Geochemical anomaly between
RD87DR10	16°09N	46°40O	3650	1.9 ± 0.19	–	1–1.2[a]	~8.7[d]	0.7026[h]	T	10–17°N (Dosso et al., 1991)
CH98DR11	30°40N	41°49O	3500–3640	0.5 ± 0.05	6.2[k]	0.53[b]	8.24[e]	0.70254[i]	N	
MAR 36°N										Geochemical anomaly due to Azores'
CH31DR01	36°52N	33°14O	2540	2.7 ± 0.27	25.6[f]	1.4–2[c]	8 ± 1[f]	–	E	plume (Kurz and Jenkins, 1981;
CH31DR10	36°50N	33°16O	2700–2800	–	472[k]	1.4–2[c]	8 ± 1[f]	0.7032[j]	E	Dosso et al., 1999)
EPR 18°S										Geochemical anomaly centred at
ND21-4	18°45S	113°25O	2723	0.5 ± 0.05	19[g]	0.58[b]	9.1 ± 0.4[g]	0.70264[h]	N	17°S (Mahoney et al., 1994; Kurz et al., 2005)

[a] Dosso et al., 1993.
[b] David et al., 2000.
[c] Schilling, 1975.
[d] Staudacher et al., 1989.
[e] Nishio et al., 1998.
[f] Marty and Tolstikhin, 1998.
[g] Marty and Zimmermann, 1999.
[h] Schiano et al., 1997.
[i] Nishio et al., 2007.
[j] Dupré et al., 1981
[k] Marty, 1995.

atmospheric contamination, assuming that all ^{36}Ar comes from atmosphere) measured in MORB glasses vary over three orders of magnitude, between 1 and a few hundred (e.g. Aubaud et al., 2004; Burnard et al., 2003, 2002; Colin et al., 2011; Jambon et al., 1985; Marty and Zimmermann, 1999; Matsuda and Marty, 1995; Moreira and Sarda, 2000; Sarda and Moreira, 2002). This is because Ar is considerably less soluble than He in silicate magmas (Jambon et al., 1986; Lux, 1987; Nuccio and Paonita, 2000), therefore Ar is expected to be lost more rapidly than He from a degassing magma: thus high $^4He/^{40}Ar^*$ ratios observed in the residual phase (the basaltic glasses) are consistent with major gas loss via solubility determined distillation from the magma. However, the exact mechanisms of gas loss are uncertain, with some studies suggesting that disequilibrium processes could play a significant role during degassing (Aubaud et al., 2004; Gonnermann and Mukhopadhyay, 2007; Matsuda and Marty, 1995; Paonita and Martelli, 2007). In addition, post-eruptive processes could further fractionate the composition measured in the glasses (Kumagai and Kaneoka, 1998).

Laser microanalysis of individual vesicles allows the mechanisms of degassing to be studied on the magma chamber scale (Burnard, 1999) in contrast to classical extraction methods (crushing or fusion under vacuum) where each analysis is the average of many different generations of vesicles. Here we show how analysis of the abundances of ^4He–$^{40}Ar^*$–CO_2 in individual vesicles allows us to: (1) investigate the modes of degassing as well as the impact of post-eruptive processes on MOR volatile compositions and (2) use the trends of degassing obtained by individual vesicle analyses to correct measured compositions for degassing fractionation and thus calculate the local mantle source composition and heterogeneity.

2. Samples and analytical technique

Five MORB glass samples were investigated; the sample locations and their descriptions (vesicularity, degassing index—$^4He/^{40}Ar^*$, geochemical characteristics—La/Sm_N, $^{87}Sr/^{86}Sr$ and $^3He/^4He$ ratios) are given in Table 1. The fresh MORB glass samples were cut into cubes ~5 mm each side and imaged by X-ray microtomography either at the Swiss Light Source synchrotron facility (TOMCAT beamline, voxel resolution of 3.7 μm), or on a benchtop microtomograph (Mateis laboratory, France, voxel resolution of 5 μm). The resulting images allowed the size and position of individual vesicles to be identified (Fig. 1).

Then the samples were loaded in a laser cell with a CaF_2 window transparent to the laser beam and were pumped overnight while baking at 100 °C. The sample could be positioned using a X–Y stage to place the vesicle selected under the laser beam. We used a 193 nm (ArF) UV excimer laser (Lambda Physics Optex Pro) with an energy of about 1.3 mJ per pulse which reduces local heating of the surrounding glass. The resulting laser spot was $\sim 200 \times 100$ μm with about 6.5 J/cm^2 at the sample surface. The sample was ablated at a frequency of 20 Hz for 5 s; each pulse drilled ~140 nm into the glass. If the bubble was not opened during the 5 s ablation, the laser chamber was simply pumped at the end of each step (except when representative "ablation blanks" were measured; Table 2) and ablation continued after pumping.

When a vesicle was pierced, there was an immediate increase of pressure within the laser chamber due to release of gases from the vesicle, recorded by a capacitance manometer (MKS, type 6288XU1TCE18, 1 Torr). When this occurred, ablation was stopped and the gases analysed. Because CO_2 is the major gas in MORB vesicles (e.g., they have a low water content $<5\%$, e.g. Cartigny et al. 2008; Javoy and Pineau 1991; Pineau and Javoy 1994), we estimated the quantity of CO_2 from the pressure jump (the laser cell volume was well calibrated at 130 ± 0.7 cm^3 by expanding a known volume of gas into the laser cell and measuring the pressure change with a capacitance manometer). The minimum measurable CO_2 content (for an error of $\leq 10\%$) was $\sim 10^{-9}$ mol corresponding to a vesicle of ~100 μm diameter at seafloor pressure at 2.5 km depth.

The gases released were purified using a cold Ti-sponge and two hot and cold SAES^{TM} Ti–Al getters. Argon was separated from helium by absorption on a stainless steel frit at 77 K. ^4He and then the isotopes and abundances of argon were analysed using