Hydrogen concentration in plagioclase as a hygrometer of arc basaltic melts: Approaches from melt inclusion analyses and hydrous melting experiments

Morihisa Hamada [a,*], Masashi Ushioda [a], Toshitsugu Fujii [b,c], Eiichi Takahashi [a]

[a] Magma Factory, Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan
[b] Earthquake Research Institute, University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-0033, Japan
[c] Crisis & Environmental Management Policy Institute, #505, 1-22 Wakaba, Shinjuku-ku, Tokyo 160-0011, Japan

A R T I C L E   I N F O

A B S T R A C T

The partition coefficients of hydrogen between plagioclase and basaltic melt were determined by two approaches. For the first part of this study, plagioclase-hosted melt inclusions in mid-ocean ridge basalt (MORB) from the Rodriguez Triple Junction in the Indian Ocean were analyzed. The hydrogen concentration in plagioclase is less than 60 wt ppm water, and the average H_2O concentration in melt inclusions is 0.3 wt%. Therefore, the apparent partition coefficient of hydrogen between plagioclase and melt is ≈ 0.01 on a molar basis. For the second part of this study, hydrous melting experiments of arc basaltic magma were performed at 0.35 GPa using an internally-heated pressure vessel at $f_{O_2} \approx NNO+3$. The starting material was hydrous basaltic glass with H_2O ranging from 0.8 to 5.5 wt%. A grain of Ca-rich plagioclase (≈ 1 mg) and 10 mg of powdered basaltic glass were sealed in a $Au_{80}Pd_{20}$ alloy capsule, and then kept at near the crystallization temperature of plagioclase as a liquidus phase to attain an equilibrium of hydrogen between plagioclase and melt. Combining the results of these two parts of this study, we formulated two linear equations to correlate the hydrogen concentration in plagioclase and the H_2O concentration in melt. When H_2O in melt is ≤ 1 wt%,

hydrogen in plagioclase (wt ppm water) $\approx 80 \times H_2O$ in melt (wt%).

When H_2O in melt is ≥ 4 wt%,

hydrogen in plagioclase (wt ppm water) $\approx 40 \times H_2O$ in melt (wt%).

Hydrogen concentration in plagioclase lies between two equations when H_2O in melt ranges from 1 to 4 wt%. In accordance with these formulations, the partition coefficients of hydrogen between plagioclase and basaltic melt switches from 0.01 ± 0.005 under H_2O-poor conditions (≤ 100 wt ppm water in plagioclase, ≤ 1 wt% H_2O in melt) to 0.005 ± 0.001 under H_2O-rich conditions (≥ 150 wt ppm water in plagioclase, ≥ 4 wt% H_2O in melt). Such switches of hydrogen partitioning with an increase in H_2O can be related to change of the atomic site for hydrogen in the crystal structure of plagioclase.

1. Introduction

Trace amounts of hydrogen are commonly accommodated in the crystal structure of nominally anhydrous minerals (NAMs). Since the 1960s, such hydrogen in NAMs has been used as an indicator of water–rock interaction and a proxy of H_2O dissolved in silicate melts (e.g., Dodd and Fraser, 1967; Wilkins and Sabine, 1973; Aines and Rossman, 1984; Bell and Rossman, 1992). In the last decade, partition coefficients of hydrogen between peridotite minerals (olivine, orthopyroxene, clinopyroxene, etc.) and melt have been determined by analyzing experimental products using secondary ion mass spectrometry (SIMS) to estimate the abundance of H_2O in the mantle and the behavior of H_2O during partial

melting of the mantle (e.g., Koga et al., 2003; Aubaud et al., 2004, 2008; Keppler and Bolfan-Casanova, 2006; Kohn and Grant, 2006; Tenner et al., 2009). For example, Aubaud et al. (2004) reported the partition coefficients of hydrogen between NAMs (olivine, orthopyroxene and clinopyroxene) and melt as $D_H^{(ol-melt)} = 0.0017$, $D_H^{(ol-melt)} = 0.019$, and $D_H^{(ol-melt)} = 0.023$, respectively, under upper-mantle P–T conditions (1–2 GPa and 1230–1380 °C).

Plagioclase is one of the most common NAMs in crustal rocks, including volcanic rocks. While the composition of plagioclase and/or Ca/Na partitioning between plagioclase and melt have been applied as a hygrometer of melts (e.g., Housh and Luhr, 1991; Putirka, 2005; Lange et al., 2009), there have been few studies that used hydrogen concentration in plagioclase as a hygrometer, because the partition coefficient of hydrogen between coexisting plagioclase and melt was not constrained. Hydrogen is accommodated in plagioclase as either structural OH

or structural H_2O. While structural H_2O is found in pegmatite feldspars (Johnson and Rossman, 2004) and stable only at low temperature conditions (less than about 700 °C; Aines and Rossman, 1985), plagioclase in volcanic rocks accommodates hydrogen as structural OH. Johnson (2005) estimated the partition coefficient of hydrogen between plagioclase and melt to be 0.004 on a molar basis, using the hydrogen concentrations in host plagioclase and the H_2O concentration in coexisting dacitic melt inclusions (up to 8 wt% H_2O) obtained from the series of eruptions at the Mount St. Helens in 1980–1981. On the other hand, Seaman et al. (2006) estimated the partition coefficient of hydrogen to be 0.1 between anorthoclase crystals and low-H_2O phonolitic melt inclusions ($H_2O \leq 0.4$ wt%) from Mount Erebas, Antarctica. As introduced above, the estimated hydrogen partition coefficients between feldspars and melt seem to be inconsistent.

The purpose of this study is to determine the partition coefficient of hydrogen between coexisting plagioclase and basaltic melt, $D_H^{(plag\text{-}melt)}$, by equilibrating plagioclase with hydrous melt. In order to achieve this purpose, this study was performed in two parts. The first part of this study is analyses of plagioclase and low-H_2O basaltic melt inclusions ($H_2O \approx 0.3$ wt%) collected from the Indian mid-ocean ridge basalt (MORB). The second part of this study is hydrogen partitioning experiments between plagioclase and hydrous basaltic melt (0.8 wt% $\leq$ bulk $H_2O \leq 5.5$ wt%). Nominally dry experiments were not performed because of the difficulty in reaching completely dry conditions under pressure, except when using a graphite-lined capsule (e.g., Médard and Grove, 2008; Almeev et al., 2012). A possible reason for the difficulty in performing completely dry experiments would be the diffusive uptake of hydrogen into the sample capsule to reduce Fe^{3+} to Fe^{2+} in melt. Combining the results of these two parts of this study, we will propose to use hydrogen concentration in plagioclase as a hygrometer of melt.

The concentration of hydrous species accommodated in plagioclase is usually quantified as "wt ppm H_2O" (e.g., Johnson and Rossman 2003, 2004). However, this description is sometimes confusing because readers may interpret that hydrogen is accommodated in plagioclase as molecular H_2O. In this paper, we quantify hydrogen in volcanic plagioclase (as structural OH) following the procedures by Johnson and Rossman (2003, 2004) and describe it in "wt ppm water". We also describe hydrous species in plagioclase simply as "hydrogen". Many possible incorporation mechanisms of hydrogen in feldspars have been proposed so far (e.g., Kronenberg et al., 1996; Johnson, 2006; Yang, 2012) and thus, we cannot assume a certain reaction involving hydrogen between plagioclase and melt. In this paper, we simply define the partitioning of hydrogen on a molar basis, as follows:

$$D_H^{plag\text{-}melt} = \frac{C_H^{plag}}{C_H^{melt}} = \frac{C_{water}^{plag}}{C_{H_2O}^{melt}}. \tag{1}$$

2. Analyses of plagioclase and melt inclusions in MORB

2.1. Outline of the studied sample

Melt inclusions trapped in phenocrysts are often regarded as melt preserving pre-eruptive volatile concentration because the host mineral acts as a tiny pressure vessel. Advantage of using melt inclusions in MORB is that MORB is instantaneously quenched on the ocean floor under the confining pressure of several hundred bars, and therefore, post-entrapment loss of hydrogen from minerals and/or H_2O from melt inclusions is expected to be minimal. In this study, we analyzed plagioclase-hosted melt inclusions in MORB (sample #KH93-3-DR9, Table 1)

Table 1

Whole-rock composition of DR9-9 F-1, dredged MORB sample from Rodriguez Triple Junction (RTJ), and three plagioclase-hosted melt inclusions. Data are normalized to 100 wt% total.

Whole-rock composition of the sample #DR9-9 F-1[a]		Plagioclase-hosted melt inclusions[b]		
		#pl19-MI	#pl21-MI	#pl22-MI
SiO_2	50.5	51.6	51.6	51.5
TiO_2	1.52	1.70	1.41	1.50
Al_2O_3	15.1	14.3	13.4	14.5
FeO^{*c}	11.1	9.55	10.70	8.06
MnO	0.19	0.16	0.21	0.16
MgO	7.44	8.09	8.18	9.44
CaO	11.1	10.9	10.9	11.4
Na_2O	2.80	2.74	2.70	2.68
K_2O	0.10	0.08	0.07	0.05
P_2O_5	0.15	0.11	0.11	0.11
Cr_2O_3	0.04	0.05	0.07	0.04
NiO	0.02	0.04	0.05	0.02
SO_3	–	0.27	0.30	0.24
molecular H_2O[d]	0.04	0	0	0.04
OH[d]	0.30	0.32	0.24	0.26
CO_2[d]	0.02	0.06	0.07	0.05
Total	100 (wt%)	100 (wt%)	100 (wt%)	100 (wt%)
FeO*/MgO	1.5	1.2	1.3	0.9
		Host plagioclase[b]		
An content[e]		An86	An73	An82
OH concentration (wt ppm water)		29	20	31

[a] Major element composition was analyzed using XRF. H_2O and CO_2 were analyzed using FTIR.
[b] Plagioclase crystal and melt inclusions were analyzed using EPMA. H_2O and CO_2 were analyzed using FTIR.
[c] Fe content is given as FeO* (total iron).
[d] Molecular H_2O, OH and CO_2 concentrations were analyzed using FTIR.
[e] Anorthite content of plagioclase = $100 \times Ca/(Ca + Na)$.

dredged from the Rodriguez Triple Junction (RTJ) in the Indian Ocean ($\approx 25.5°$S, $\approx 70.0°$E, ≈ 4000 m deep) during the KH93-3 Research Cruise by the R/V Hakuho-maru of the Ocean Research Institute, University of Tokyo in 1993 (Tamaki and Fujimoto, 1995). At RTJ, the Central Indian Ridge, the Southeast Indian Ridge and the Southwest Indian Ridge meet. This MORB sample is glassy aphyric rock, containing 5 vol% of plagioclase (An_{74-89}, from ≤ 0.1 mm to 5 mm long) and 1 vol% of olivine (Fo_{90}, less than 1 mm in diameter).

2.2. Analytical procedures using XRF and EPMA

The whole-rock composition of the MORB sample was analyzed with a RIGAKU 3070 X-ray fluorescence (XRF) spectrometer at the Institute for Geothermal Sciences, Kyoto University, following the procedures outlined by Sugimoto et al. (2007). The operating conditions were 15 kV and 5.0×10^{-8} A, and the data were corrected using a ZAF correction.

Plagioclase crystals were hand-picked from a crushed MORB sample under a binocular microscope, then were mounted on epoxy, cut, and polished on one side. The major element compositions of plagioclase and plagioclase-hosted melt inclusions were analyzed using a JEOL JXA-8800 electron probe microanalyzer (EPMA) at the Department of Earth and Planetary Sciences, Tokyo Institute of Technology, operated at 15 kV and 1.2×10^{-8} A. Plagioclase was analyzed with a focused beam, and melt inclusion was analyzed with a defocused beam (10 μm in diameter, as usual). For all the elements except for Na, the counting times were 20 s on peak and 10 s for background on each side. In order to minimize Na loss from melt inclusions during analysis, Na was analyzed first, and for shorter counting times (10 s on peak and 5 s for background on each side). The peak position of Na was determined in advance and fixed to also minimize Na loss during