

H₂O loss from hydrous melts during fluid-absent piston cylinder experiments

ALBERTO E. PATIÑO DOUCE

Department of Geology, University of Georgia, Athens, Georgia 30602, U.S.A.

JAMES S. BEARD

Department of Earth Sciences, Virginia Museum of Natural History, Martinsville, Virginia 24112, U.S.A.

ABSTRACT

We have documented H₂O loss from vapor-absent melting (dehydration-melting) experiments with durations of 5–31 d in a piston cylinder apparatus at 7, 10, and 15 kbar and 925–1000 °C. In experiments on an amphibole gneiss (PB-92-2), the most obvious manifestation of H₂O loss is a decrease in melt fraction and an increase in plagioclase abundance with increasing temperature. In the most extreme case (at 10 kbar), the melt fraction decreases from 33 to 15% between 975 and 1000 °C, whereas modal plagioclase increases from 18 to 29 wt%. The total H₂O content of this sample, estimated from microprobe O analyses, decreased from a starting value of 1.4 wt% to 0.6 wt% at 1000 °C, although no such decrease was evident at 975 °C. Similar, but smaller, effects were observed in high-temperature experiments on the amphibole gneiss at 7 and 15 kbar. The bulk H₂O content of a sample containing a biotite gneiss composition (PB-92-1) decreased from 1.7 to 1.0% between 975 and 1000 °C at 10 kbar with no obvious effects on phase relations. Nominal H₂O losses observed in long-duration experiments (31 d, 10 kbar, 950 °C) on both starting compositions were not resolvable within analytical uncertainty.

Although dehydration is accompanied by an increase in f_{O_2} , that is attributable to H loss, the low abundance of Fe³⁺ and the low f_{O_2} (QFM – 1) of even the most dehydrated samples require a mechanism other than H loss for most of the observed dehydration. We suggest that molecular H₂O is diffusing out of the samples. Unlike H, molecular H₂O is a common species in hydrous silicate melts. The little information that exists on the diffusivities of large volatile species (e.g., O₂, N₂) in metals suggests that the diffusivities can approach that of H at high temperatures. If H₂O diffusivity is within even 2–3 orders of magnitude of H diffusivity at 1000 °C, diffusive loss of H₂O could account for our observations.

INTRODUCTION

The loss of H₂O from hydrous, but H₂O-undersaturated, silicate melts during the course of experimentation results in crystallization or resorption of phases, including melt, whose stabilities are functions of H₂O activity. This clearly undesirable result has been noted in the course of vapor-absent melting experiments on biotite- and amphibole-bearing gneisses. We present time and temperature studies that demonstrate H₂O loss during vapor-absent melting experiments of H₂O-bearing compositions sealed in Au capsules. H₂O loss is manifested by changes in phase relations and f_{O_2} , and is documented by electron probe analyses of O (Nash, 1992). Because the total H₂O content of the samples studied here is low (<50 µg), documentation of H₂O loss by gravimetric or manometric means is not feasible (D. Wenner, personal communication).

EXPERIMENTAL AND ANALYTICAL PROCEDURES

The results discussed here are part of an experimental study of the vapor-absent melting relationships of biotite-

and amphibole-bearing metamorphic rocks. Two starting materials have been studied and are both composed of mixtures of hand-picked minerals. One is a model biotite gneiss (PB-92-1: 37% biotite, 34% quartz, 27% plagioclase, 2% ilmenite) and the other a model amphibole gneiss (PB-92-2: 54% hornblende, 24% quartz, 20% plagioclase, 2% ilmenite). Samples of approximately 2–3 mg were contained in Au capsules 1.4 mm in outer diameter with a wall 0.2 mm thick. We conducted several isobaric temperature series and an isothermal, isobaric time series. Experimental conditions are shown in Table 1.

All experiments were done in a piston cylinder apparatus with 0.5-in. cell assemblies. The pressure medium was NaCl in all experiments except at 1000 °C and 10 kbar, where BaCl₂ was used. The small size of the capsules allowed us to pair them side by side within the cells, so that each experiment contained two samples, one of each composition. The hot piston-out technique was used in every case. Reported pressures are gauge pressures; friction loss is less than 0.5 kbar. The temperature was measured and controlled by means of W₇₄Re₂₆-W₉₅Re₂₅ thermocouples. Minerals and glasses were analyzed for

TABLE 1. H₂O contents of the high-temperature experiments

T (°C)	P (kbar)	t (d)	H ₂ O _c * (wt%)	Total** (wt%)	%Melt (wt%)	Bulk H ₂ O† (wt%)	Corr. factor‡
PB-92-1 (biotite gneiss, glass rhyolitic)							
950	10	15	3.2	100.3	50	1.2–2.0	1.040
950	10	31	3.2	99.9	46	1.1–1.9	1.017
975	10	11	3.6	100.1	48	1.3–2.2	0.980
1000	10	5	1.8	99.8	57	0.78–1.3	1.010
PB-92-2 (amphibole gneiss, glass rhyodacitic to dacitic)							
925	7	15	4.5	100.4	23	0.79–1.3	1.018
950	7	15	4.5	99.9	16	0.55–0.92	1.042
950	10	7	5.8	99.7	26	1.1–1.9	1.014
950	10	15	5.1	100.2	29	1.1–1.9	1.055
950	10	31	4.3	98.9	28	0.85–1.4	0.990
975	10	11	5.1	99.5	33	1.3–2.2	1.043
1000	10	5	4.4	101.0	15	0.48–0.82	1.078
950	15	15	5.5	100.0	22	0.92–1.5	1.018
975	15	15	5.1	100.0	21	0.82–1.4	1.020
1000	15	15	5.0	100.1	16	0.64–1.1	1.034

Note: additional information, including spot analyses, is available from the authors or from the *American Mineralogist* data repository.

* H₂O_c = H₂O content of the glass calculated from excess O in the glass analysis, with the assumption that all excess O₂ is held in H₂O and all Fe is Fe²⁺.

** Total of probe analysis including H₂O_c.

† Bulk sample H₂O calculated from H₂O_c and the melt fraction. Range of values reflects 20% relative error in H₂O_c and 6% relative error in melt fraction. Oxidation of all Fe in the glass to Fe³⁺ would lower these values an average of 7%.

‡ This factor corrects the O analysis for drift and for differences in the C coat between the sample and the standard. It is determined by periodically analyzing quartz in the sample during the analytical session and assumes perfect quartz stoichiometry.

major elements, including O, using the JEOL superprobe in the geology department at the University of Georgia. Modal abundances of melt, plagioclase, orthopyroxene, clinopyroxene, and ilmenite were calculated by simultaneous mass balance of K₂O, CaO, Al₂O₃, FeO, and MgO. The melt fraction was also calculated assuming that the K₂O not in plagioclase was in the melt. Melt fractions calculated by these two methods are almost identical, but the latter calculation allows the 6% relative error in the K₂O analysis to be assigned directly to the mode (Fig. 1).

We measured the O contents of the glasses with the electron microprobe using a JEOL LDE1 crystal (layered dispersion element) and a 3000- μ m slit (see Nash, 1992) to estimate the H₂O contents of the experimental products. Peak position and count rates for O were calibrated on a synthetic corundum standard for which we assumed a stoichiometric O content. The merit of this assumption was assessed by using this calibration to analyze synthetic spinel and enstatite standards. In both cases, we obtained values within 0.5 wt% of the respective stoichiometric O concentrations. Nash (1992) indicated that a critical factor in obtaining accurate O analyses is that the conductive C layers of standard and unknown be as similar as possible. Because it is not practical to coat standards and samples together before each probe session, we circumvented this difficulty by analyzing quartz crystals in the experimental samples and determining a correction factor from the ratio between the stoichiometric and analyzed O contents in quartz. This correction factor, ranging from 0.98 to 1.078, was then applied to O in the glass

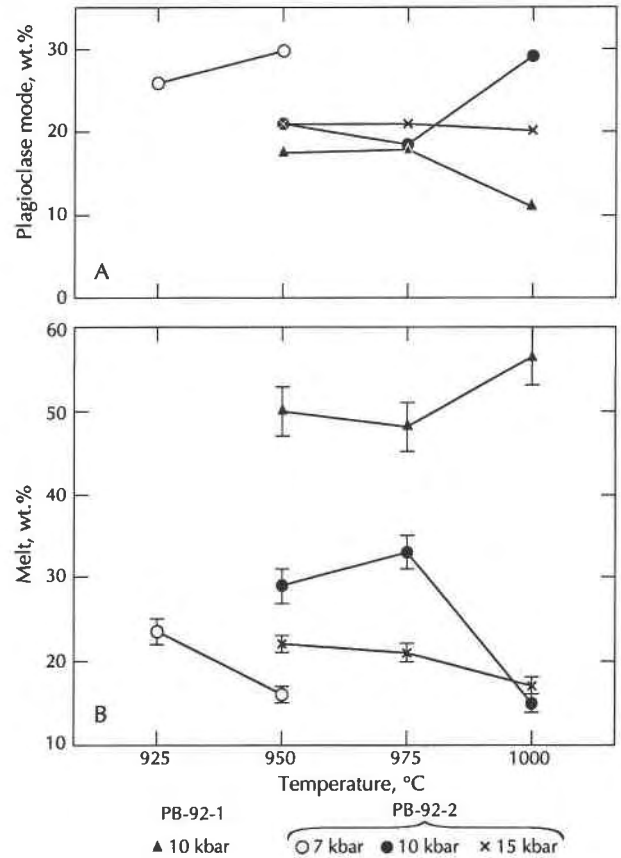


Fig. 1. Plagioclase mode (A) and melt fraction (B) vs. temperature. PB-92-1 is biotite gneiss; PB-92-2 is amphibole gneiss.

analyses. The corrected O contents of the glasses were combined stoichiometrically with the analyzed cation contents, and the excess O was recalculated as H₂O (cf. Nash, 1992). These recalculated values are shown as H₂O_c in Table 1. The average relative error (2 sd) for the O analyses is 2% (Table 2¹). If all this error is propagated into the excess O, then the resulting relative error in H₂O_c is ~20%. The weight-percent totals obtained when H₂O_c values are included in the analyses (see Table 1) range from 98.9 to 101.0 wt%, with a mean of 100.0 wt%. The bulk H₂O contents of the experimental products (Table 1) were calculated from H₂O_c values and the melt fraction. Initial H₂O contents were calculated from O analyses of high-pressure superliquidus glasses and are 1.6 ± 0.3 and 1.4 ± 0.3 wt% for the biotite gneiss and amphibole gneiss, respectively. The H₂O_c and bulk H₂O contents given in Table 1 were calculated assuming that all Fe is Fe²⁺. For our experiments (*f*_{O₂} < QFM), very little Fe (<5%; e.g., Kress and Carmichael, 1988) is likely to be trivalent. However, because *f*_{O₂} increases as dehydration proceeds (see below), Fe³⁺ in the melt should be highest in the most dehydrated samples. Thus, H₂O losses

¹ A copy of Tables 2 and 3 may be ordered as Document AM-94-560 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

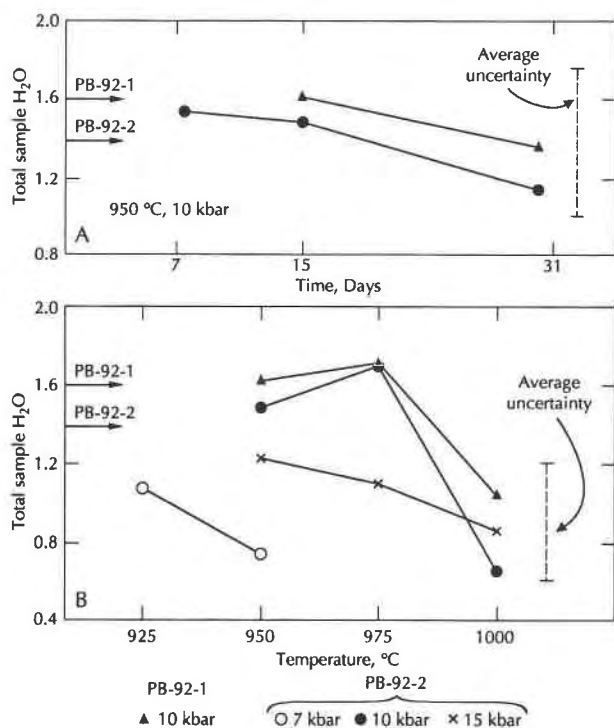


Fig. 2. Total H₂O content as a function of (A) time and (B) temperature. Average error encompasses a 20% relative error in microprobe O determination and a 6% relative error in the calculation of the melt fraction. See text and Table 1.

determined assuming no change in oxidation state are probably minima.

EVIDENCE FOR H₂O LOSS

The first indications that dehydration was occurring in these experiments were decreases in melt fraction (a drop of > 50% in one case) with increasing temperature in several experiments on the amphibole gneiss (PB-92-2: Fig. 1, Table 1). At 7 and 10 kbar, the decrease in melt fraction is accompanied by an increase in the plagioclase mode (Fig. 1). The increase in modal plagioclase is manifested by the appearance of interstitial plagioclase and of thick, calcic overgrowths on plagioclase grains. There are no unambiguous indications from phase relations for decreased H₂O activity in either the time series or in the temperature series on the biotite gneiss (PB-92-1: Fig. 1, Table 1). However, calcic rims on some plagioclase grains were noted in some of these experiments as well.

By 1000 °C at 10 kbar, the total H₂O contents of the amphibole and biotite gneisses have decreased to 0.6 and 1.0 wt%, respectively (Fig. 2). These numbers reflect a 57% H₂O loss in the amphibole gneiss and a 38% H₂O loss in the biotite gneiss, relative to the initial H₂O content. These losses can be resolved within the uncertainty of the H₂O content calculation (Fig. 2, Table 1). No such losses were observed in either composition at 10 kbar and 975 °C or in experiments of 7 and 15 d at 950 °C (Fig. 2). Nominal H₂O losses are observed in the amphibole gneiss at 7 kbar and 950 °C and at 15 kbar and 1000 °C

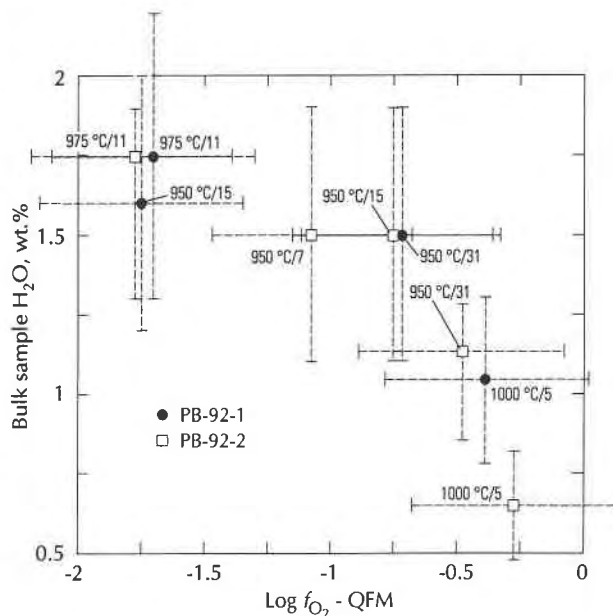


Fig. 3. The *f*_{O₂} relative to QFM as a function of sample H₂O content for the 10-kbar experiments.

and in long-duration experiments (31 d) at 950 °C on both the amphibole and biotite gneisses (Fig. 2). Although these losses are not resolvable within the uncertainty of the calculation, their consistency qualitatively supports the conclusion that some H₂O loss generally occurs in high-temperature and long-duration experiments.

The *f*_{O₂} was calculated using the equilibrium $2\text{FeSiO}_3 + \frac{1}{2}\text{O}_2 = \text{Fe}_2\text{O}_3 + 2\text{SiO}_2$. Standard-state properties were taken from Berman (1988), and activities were calculated with the models of Sack and Ghiorso (1989) for orthopyroxene and Ghiorso (1990) for ilmenite. Mineral compositions are given in Table 3.¹

There is a strong correlation between log *f*_{O₂}, calculated from mineral equilibria, and H₂O content, calculated from modal data and microprobe O analyses (Fig. 3). This correlation indicates that the samples became more oxidized as they became more dehydrated and is a strong indication of open-system behavior. In particular, the experiments at 1000 °C, despite having durations of only 5 d, are considerably more oxidized and dehydrated than all the lower-temperature experiments.

MECHANISMS FOR H₂O LOSS

Beard and Patiño Douce (1993) initially thought that H loss was responsible for the desiccation of the experiments. The correlation between *f*_{O₂} and H₂O content suggests that some net H loss did occur (Fig. 3), albeit at a rate several orders of magnitude below that observed by Chou (1986) in systems containing an aqueous fluid phase. Mass-balance calculations, however, require that 2 mol of FeO be oxidized to Fe₂O₃ for each mole of H₂ that diffuses out of the system. If the 0.8 wt% loss from PB-92-2 between 975 and 1000 °C reflected H₂ loss alone, then 6.3 wt% of Fe₂O₃ would have to have formed to

have consumed the excess O. The ilmenite in the high-temperature experiment is more abundant and more oxidized than in the low-temperature experiment (Π_{94} vs. Π_{99}), but there is no magnetite or hematite present. Generous estimates of Fe₂O₃ content suggest that it increased <0.5 wt% between 975 and 1000 °C, i.e., less than one-tenth of the amount required if H were the only component leaving the system. This modest increase in Fe³⁺ is consistent with the observation that f_{O_2} in the most oxidized experiments at 1000 °C is still below QFM (Fig. 3). One interpretation of these observations is that a net loss of H₂O occurred during the experiments.

Molecular H₂O is an abundant species in silicic melts containing >1–2% total dissolved H₂O (Stolper, 1982; Newman et al., 1986; Silver and Stolper, 1989; Mysen and Virgo, 1987). The mole fraction of molecular H₂O in the amphibolite melt at 1000 °C (calculated after Silver and Stolper, 1989, with the assumption that a speciation model for albite melt is applicable to our melt compositions) should be about 0.041. This corresponds to a f_{H_2O} of 6000 bars for equilibrium between dissolved H₂O and H₂O vapor (Silver and Stolper, 1989). At the f_{O_2} of our experiments, the corresponding f_{H_2} is 55 bars. The f_{H_2} and f_{O_2} outside the capsule are unknown, but neither should be high in a graphite-halide cell. We argue that the chemical potential difference driving H₂O diffusion in our experiments is at least 100 times that for H. Thus, comparable rates of H₂O and H loss would be observed even if the diffusivity of H₂O is 100 times less than that of H.

Experimental data on diffusion of gaseous species through metals are relatively scarce (e.g., Smithells, 1967), and, to the best of our knowledge, no measurements exist of H₂O diffusivities in precious metals. Some inferences about the behavior of large gaseous species can be drawn from studies of O₂ and N₂. Activation energies for H are typically about one-fifth of those for larger, diatomic gases (Volkl and Alefeld, 1978), and the diffusivities of larger species converge with those of H with increasing temperature. Although we have been unable to locate diffusion data for O₂ and N₂ in Au, the diffusivities of H in Ag and Nb at 1000 °C are, respectively, three and 2000 times higher than those of O₂ at the same temperature (Smithells, 1967; Hauffe, 1965). These values bracket the ratio of about 100 suggested by our experimental observations.

If desiccation occurred by H₂O diffusion, then the difference between the rates of H₂O loss from the two bulk compositions can be explained in terms of the speciation mechanism of H₂O in the melt. The relatively dry melts of the biotite gneiss (1.8% H₂O at 1000 °C) have OH⁻ as the dominant dissolved species and should contain less than one-fifth the dissolved molecular H₂O of the more hydrous melts of the amphibole gneiss (4.4% H₂O at 1000 °C) (Stolper, 1982; Silver and Stolper, 1989). Because OH⁻ is relatively immobile (Zhang et al., 1991), the rate of H₂O loss should be primarily controlled by the concentration of molecular H₂O, explaining the greater desiccation

in experiments on the amphibole gneiss. The overall higher diffusivity of dacitic vs. rhyolitic melts (e.g., Holloway et al., 1984) may also accelerate volatile loss from experiments with the amphibole gneiss starting material, which produced melts that were relatively poor in K₂O. We cannot adequately explain why the diffusive loss of H₂O accelerated markedly over a narrow temperature interval. We speculate that it may be related to annealing or some other temperature-sensitive change in the Au capsule material.

ACKNOWLEDGMENTS

Thanks to Ellen Compton-Gooding for drafting the figures and to L. Anovitz and T. Labotka for careful reviews of the manuscript. This work was supported by National Science Foundation grants EAR-9118418 to A.E.P.D. and EAR-9120035 to J.S.B.

REFERENCES CITED

- Beard, J.S., and Patiño Douce, A.E. (1993) Hydrogen loss from hydrous melts during fluid-absent piston cylinder experiments at 10 kb and 925–1000 °C. *Eos*, 74, 656.
- Berman, R.G. (1988) Internally-consistent thermodynamic data for stoichiometric minerals in the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂. *Journal of Petrology*, 29, 445–522.
- Chou, I-Ming (1986) Permeability of precious metals to hydrogen at 2 kb total pressure and elevated temperatures. *American Journal of Science*, 286, 638–658.
- Ghiorso, M.S. (1990) Thermodynamic properties of hematite-ilmenite-geikielite solid solutions. *Contributions to Mineralogy and Petrology*, 104, 645–667.
- Hauffe, K. (1965) *Oxidation of metals*, 452 p. Plenum, New York.
- Holloway, J.R., Delaney, J.D., Karsten, J.L., Lapham, K.E., and Stanton, T. (1984) Diffusion of H₂O in rhyolite melt: A model for silicic crustal magmas. *Geological Society of America Abstracts with Programs*, 16, 543.
- Kress, V.C., and Carmichael, I.S.E. (1988) Stoichiometry of the iron oxidation reaction in silicate melts. *American Mineralogist*, 73, 1267–1274.
- Mysen, B.O., and Virgo, D. (1987) Volatiles in silicate melts at high pressure and temperature. I. Interaction between OH groups and Si⁴⁺, Al³⁺, Ca²⁺, Na⁺ and H⁺. *Chemical Geology*, 57, 303–331.
- Nash, W.P. (1992) Analysis of oxygen with the electron microprobe: Applications to hydrated glasses and minerals. *American Mineralogist*, 77, 453–456.
- Newman, S., Stolper, E.M., and Epstein, S. (1986) Measurement of water in rhyolitic glasses: Calibration of an infrared spectroscopic technique. *American Mineralogist*, 71, 1527–1541.
- Sack, R.O., and Ghiorso, M.S. (1989) Importance of considerations of mixing properties in establishing an internally consistent database: Thermochemistry of minerals in the system Mg₂SiO₄-Fe₂SiO₄-SiO₂. *Contributions to Mineralogy and Petrology*, 102, 41–68.
- Silver, L., and Stolper, E.M. (1989) Water in albitic glasses. *Journal of Petrology*, 30, 667–709.
- Smithells, C.J. (1967) *Metals reference book*, vol. II, 683 p. Plenum, New York.
- Stolper, E.M. (1982) The speciation of water in silicate melts. *Geochimica et Cosmochimica Acta*, 46, 2609–2620.
- Volkl, J., and Alefeld, G. (1978) Diffusion of hydrogen in metals. In G. Alefeld and J. Volkl, Eds., *Hydrogen in metals I: Basic properties*, p. 321–348. Springer-Verlag, Berlin.
- Zhang, Y., Stolper, E.M., and Wasserburg, G.J. (1991) Diffusion of water in rhyolitic glasses. *Geochimica et Cosmochimica Acta*, 55, 441–456.