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

ALBERTO E. PATINO 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 f₀₂, that is attributable to H loss, the low abundance of Fe³⁺ and the low f₀₂ (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 f₀₂, 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 W₁₇Re₂₃-W₁₅Re₂₅ thermocouples. Minerals and glasses were analyzed for
TABLE 1. H$_2$O contents of the high-temperature experiments

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (kbar)</th>
<th>H$_2$O$^*$ contents (wt%)</th>
<th>Total$^*$ contents (wt%)</th>
<th>%Melt</th>
<th>Bulk H$_2$O$^*$ contents (wt%)</th>
<th>Corr. factor‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-92-1 (biotite gneiss, glass rhyolitic)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>950</td>
<td>10</td>
<td>15</td>
<td>3.2</td>
<td>100.3</td>
<td>50</td>
<td>1.2-2.0</td>
</tr>
<tr>
<td>950</td>
<td>10</td>
<td>31</td>
<td>3.2</td>
<td>99.9</td>
<td>46</td>
<td>1.1-1.9</td>
</tr>
<tr>
<td>975</td>
<td>10</td>
<td>11</td>
<td>3.6</td>
<td>100.1</td>
<td>48</td>
<td>1.3-2.2</td>
</tr>
<tr>
<td>1000</td>
<td>10</td>
<td>5</td>
<td>1.8</td>
<td>99.8</td>
<td>57</td>
<td>0.78-1.3</td>
</tr>
<tr>
<td>PB-92-2 (amphibole gneiss, glass rhyodacitic to dacitic)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>925</td>
<td>7</td>
<td>15</td>
<td>4.5</td>
<td>100.4</td>
<td>23</td>
<td>0.79-1.3</td>
</tr>
<tr>
<td>950</td>
<td>7</td>
<td>15</td>
<td>4.5</td>
<td>99.9</td>
<td>16</td>
<td>0.55-0.92</td>
</tr>
<tr>
<td>950</td>
<td>10</td>
<td>7</td>
<td>5.8</td>
<td>99.7</td>
<td>26</td>
<td>1.1-1.9</td>
</tr>
<tr>
<td>950</td>
<td>10</td>
<td>15</td>
<td>5.1</td>
<td>100.2</td>
<td>29</td>
<td>1.1-1.9</td>
</tr>
<tr>
<td>975</td>
<td>10</td>
<td>31</td>
<td>4.3</td>
<td>98.9</td>
<td>28</td>
<td>0.85-1.4</td>
</tr>
<tr>
<td>975</td>
<td>10</td>
<td>11</td>
<td>5.1</td>
<td>99.5</td>
<td>33</td>
<td>1.3-2.2</td>
</tr>
<tr>
<td>1000</td>
<td>10</td>
<td>5</td>
<td>4.4</td>
<td>100.1</td>
<td>15</td>
<td>0.48-0.82</td>
</tr>
<tr>
<td>950</td>
<td>15</td>
<td>15</td>
<td>5.5</td>
<td>100.0</td>
<td>22</td>
<td>0.92-1.5</td>
</tr>
<tr>
<td>975</td>
<td>15</td>
<td>15</td>
<td>5.1</td>
<td>100.0</td>
<td>21</td>
<td>0.82-1.4</td>
</tr>
<tr>
<td>1000</td>
<td>15</td>
<td>15</td>
<td>5.0</td>
<td>100.1</td>
<td>16</td>
<td>0.64-1.1</td>
</tr>
</tbody>
</table>

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

* H$_2$O$^*$ = H$_2$O content of the glass calculated from excess O in the glass analysis, with the assumption that all excess O is held in H$_2$O and all Fe is Fe$^{2+}$.

$^*$ Total of probe analysis including H$_2$O.$^*$.

† Bulk sample H$_2$O calculated from H$_2$O.$^*$ and the melt fraction. Range of values reflects 20% relative error in H$_2$O.$^*$ and 67% relative error in melt fraction. Oxidation of all Fe in the glass to Fe$^{3+}$ 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.

We measured the O contents of the glasses with the electron microprobe using a JEOL LDEI crystal (layered dispersion element) and a 3000-μm slit (see Nash, 1992) to estimate the H$_2$O contents of the experimental products. Peak position and count rates for O were calibrated to oxygen contents in quartz. This correction factor, ranging from 0.98 to 1.078, was then applied to O in the glass analyses. The corrected O contents of the glasses were combined stoichiometrically with the analyzed cation contents, and the excess O was recalculated as H$_2$O (cf. Nash, 1992). These recalculated values are shown as H$_2$O.$^*$ in Table 1. The average relative error (2 σd) for the O analyses is 2% (Table 2†). If all this error is propagated into the excess O, then the resulting relative error in H$_2$O.$^*$ is ~20%. The weight-percent totals obtained when H$_2$O.$^*$ 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 H$_2$O contents of the experimental products (Table 1) were calculated from H$_2$O.$^*$ values and the melt fraction. Initial H$_2$O 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 H$_2$O and bulk H$_2$O contents given in Table 1 were calculated assuming that all Fe is Fe$^{2+}$. For our experiments (f$_0$ < QFM), very little Fe (<5%: e.g., Kress and Carmichael, 1988) is likely to be trivalent. However, because f$_0$ increases as dehydration proceeds (see below), Fe$^{3+}$ in the melt should be highest in the most dehydrated samples. Thus, H$_2$O losses
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 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 f₆, was calculated using the equilibrium 2FeSiO₃ + ½O₂ = Fe₂O₃ + 2SiO₂. 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.

There is a strong correlation between log f₆, 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 f₆, 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 ox-
ized than in the low-temperature experiment (IIa vs. IIo), but there is no magnetite or hematite present. Gen-
erous estimates of FeO 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 com-
ponent leaving the system. This modest increase in Fe3+
is consistent with the observation that fH2O 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 composi-
tions) should be about 0.041. This corresponds to a fH2O
of 6000 bars for equilibrium between dissolved H2O
and H2O vapor (Silver and Stolper, 1989). At the fH2O
of our experiments, the corresponding fH2O is 55 bars. The
fH2O and fH2O outside the capsule are unknown, but nei-
ter 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 gas-
es (Volkil and Alefeld, 1978), and the diffusivities of larger
species converge with those of H with increasing tempera-
ture. 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
times higher than those of O2 at the same temperature (Smi-
thells, 1967; Hauke, 1965). These values bracket the ratio
of about 100 suggested by our experimental observations.

If desiccation occurred by H2O diffusion, then the dif-
ference 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 (>1-2% total dissolved H2O) 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 concen-
tration of molecular H2O, explaining the greater desic-
cation in experiments on the amphibole gneiss. The over-
all 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 ma-
terial, 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

druring fluid-absent piston cylinder experiments at 10 kb and
925-1000 °C. Eos, 74, 656.

Berman, R.G. (1988) Internally-consistent thermodynamic data for stoi-
chiometric minerals in the system Na2O-K2O-CaO-MgO-FeO-Fe2O3-

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-
gelinite solid solutions. Contributions to Mineralogy and Petrology,
104, 645-657.


Holloway, J.R., Delaney, J.D., Karsten, J.L., Lapham, K.E., and Stanton,
magnas. Geological Society of America Abstracts with Programs, 16,
543.

Kress, V.C., and Carmichael, I.S.E. (1988) Stoichiometry of the iron ox-
idation reaction in silicate melts. American Mineralogist, 73, 1267-
1274.

Mysen, B.O., and Virgo, D. (1987) Volatiles in silicate melts at high pres-
sure 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: Ap-
lications to hydrated glasses and minerals. American Mineralogist, 77,
453-456.

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 MgSiO3-FeSiO3-SiO2.
Contributions to Mineralogy and Petrology, 102, 41-68.

Petrology, 30, 667-709.

New York.

chemica et Cosmochimica Acta, 46, 2609-2620.


MANUSCRIPT RECEIVED MARCH 28, 1994
MANUSCRIPT ACCEPTED APRIL 8, 1994