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# $H_2O$ loss during piston-cylinder experiments

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## ABSTRACT

The capsule materials Au, $Ag_{75}Pd_{25}$, and Pt, were tested for permeability to C-H-O fluids in a piston-cylinder apparatus at 10 kbar and 900–1100 °C. The capsules were embedded in boron nitride. After the experiments, the C-H-O fluids were analyzed by gas chromatography to determine the oxygen content of the capsules.

No significant loss of oxygen was observed in any capsule material at temperatures $\leq$1050 °C. At 1100 °C, however, which is above the melting point of Au and $Ag_{75}Pd_{25}$ at 10 kbar, oxygen loss from Pt capsules amounted to between 12 and 80%, over a period of 6 days. These results were confirmed by experiments performed using pure $H_2O$ as the fluid.

Water loss during piston-cylinder experiments is a serious problem. A temperature of about 1050 °C represents the upper thermal limit for constant $H_2O$-containing systems.

## INTRODUCTION

Among experimentalists, there are many unpublished reports and much hearsay concerning the properties of noble metals and alloys commonly used as capsule materials in high-pressure experiments. Sealed metal capsules have been used in many volatile-bearing experiments at high pressures and temperatures to study the influence of volatiles (e.g., C-H-O fluids) on geological systems. However, it is perhaps surprising that no mention is made in the experimental literature of the problems that may arise due to unexpected changes in the properties of capsule materials, except those reported by Patiño Douce and Beard (1994, 1995) and Brooker et al. (1998). Patiño Douce and Beard (1994, 1995) performed experiments in a piston-cylinder apparatus in the range 925–1000 °C and 7–15 kbar with durations of 5–31 days. The pressure medium was NaCl in all experiments except at 1000 °C and 10 kbar, where $BaCl_2$ was used. At 1000 °C and 10 kbar, $H_2O$ loss up to 57%, relative to the initial $H_2O$ content, was documented after a run duration of 5 days during dehydration-melting experiments of an amphibolite gneiss. The samples were contained in gold capsules 1.4 mm in outer diameter with a wall 0.2 mm thick. Because the total $H_2O$ content of the samples studied by Patiño Douce and Beard (1994) was <50 μg, documentation of $H_2O$ loss by gravimetric or manometric means was not feasible. Therefore, the oxygen contents of glasses were determined with an electron microprobe to estimate the $H_2O$ contents of the experimental products using the procedures of Nash (1992). The $H_2O$ contents of the glasses were calculated from excess O in the glass analysis, with the assumption that all excess oxygen is held in $H_2O$ and all Fe is $Fe^{2+}$.

Brooker et al. (1998) performed experiments in a piston-cylinder apparatus in the range 1600–1650 °C and 15–25 kbar with durations of 10–30 min. The capsules were surrounded by Pyrex powder. Additional pressure-transmitting materials were crushable alumina and NaCl. At 1600 °C and 20 kbar, no $^{18}O$ transfer through Pt was detected after a run duration of 30 min. They used a double-capsule technique. A 3 mm pre-annealed inner capsule containing a jadeite + $^{13}CO_2$ mixture ($^{18}O$ enriched) was crimp welded and then surrounded by a jadeite + $^{12}CO_2$ mixture. The inner capsule and the outer material were then sealed in a 5 mm pre-annealed platinum capsule of the "ash can" design (Sneeringer and Watson 1985). The $^{18}O$ contents of the inner and outer capsule were determined using an ion microprobe.

To check the important results of Patiño Douce and Beard (1994, 1995), which seem to differ from the results of Brooker et al. (1998), we performed our own experiments. We present the results of a systematic investigation of the efficacy of three commonly used precious metals in volatile encapsulation. Although our observations of volatile loss may not be transferable directly to other specific experimental situations, we nevertheless feel that it is opportune to warn others of the potential problems identified in this study.

## STARTING MATERIALS AND SAMPLE PREPARATION

Four different kinds of solid compounds, stored in a desiccator, were used as starting materials to generate volatiles at the experimental conditions: (1) silver oxalate ($Ag_2C_2O_4$); synthesized from oxalic acid dihydrate ($H_2C_2O_4 \cdot 2\ H_2O$; Merck no. 495) and silver nitrate ($AgNO_3$; Merck no. 1512); (2) 3-(2-Furyl)-acrylic-acid ($C_7H_6O_3$; Merck no. 814022); (3) fumaric acid ($C_4H_4O_4$; Merck no. 800269); and (4) 4´-Methoxy-acetophenone ($C_9H_{10}O_2$; Merck no. 805795).

Approximately 3–5 mg of each of these compounds were loaded into capsules. Two experiments were performed with capsules filled with 1.5 μL pure $H_2O$ and 30 mg powdered quartz (Riedel de Haën no. 18643). The capsule material was Au, Pt, or $Ag_{75}Pd_{25}$ (capsule dimensions: Au 3.2 mm outer diameter, 0.2 mm wall; Pt 3.4 mm outer diameter, 0.2 mm wall;

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$Ag_{75}Pd_{25}$ 3.2 mm outer diameter, 0.1 mm wall; length of all capsules: 10 mm). The capsules were then flattened and welded shut. Efficient cooling during welding was achieved by dipping the sample capsules into water. No weight loss was observed after welding.

## EXPERIMENTAL PROCEDURES

A piston-cylinder apparatus of the type described by Johannes (1973) was used throughout this study. The different capsule materials were tested for oxygen loss at 900 and 1000 °C. Moreover, experiments using platinum capsules were performed at 1050 and 1100 °C. All experiments were done at 10 kbar with a duration of 6 days. The cell assembly consisted of an NaCl outer sleeve with a graphite furnace and boron nitride surrounding the sample capsules. This experimental setup is described in detail by Truckenbrodt et al. (1997). At temperatures ≥1000 °C, an additional Pyrex tube separated the graphite furnace from the NaCl sleeve. The temperature was controlled and measured using an Inconel-sheathed type K thermocouple (DIN IEC 584-1). No correction for pressure effects on EMF was applied. The thermal gradient over the sample position is presumed to be <5 °C (Johannes 1973). Temperature stability throughout all runs was better than ±5 °C. The temperature was controlled either by an Eurotherm-820 controller or a PCS-controller I. The "piston-in" method was applied (Johannes et al. 1971). The cold sample was exposed to a pressure of about 2 kbar below the final pressure. After the temperature of the experiment had been attained, the pressure was raised 0.5 kbar above the given experimental pressure to compensate friction. The pressure is believed to be accurate to within ±0.5 kbar (Johannes 1973). The runs were terminated by turning off the current (initial quenching rate > 100 °C/s).

## ANALYTICAL PROCEDURES

The C-H-O fluid in the sample capsules was analyzed by gas chromatography. The system was calibrated for a quantitative analysis of $H_2$, CO, and $C_2H_6$ with a minimum weight of 2 μg, and for analysis of $CO_2$, $CH_4$, and $H_2O$ with a minimum weight of 10 μg. The analytical procedure is described in detail by Truckenbrodt et al. (1997). From the analytical data (masses of the different gas species), the molar oxygen content of the fluid was calculated directly using the molar mass of each gas species. This calculated oxygen content was compared to the initial oxygen content of the starting material. The $H_2O$ content of the capsules filled with pure $H_2O$ was determined gravimetrically. The starting $H_2O$ content was corrected by the amount of $H_2O$ evaporated during sample preparation (while filling with $SiO_2$). This $H_2O$ amounts to 0.110 ± 0.010 mg (mean value of ten different measurements).

## RESULTS

For all Au capsules used up to 1000 °C, no remarkable oxygen loss was observed. The comparison of the oxygen contents before and after the experiment revealed a maximum decrease of 6% in one 1000 °C experiment (Fig. 1). In some experiments, an increase of up to 8% was observed. The oxygen contents of $Ag_{75}Pd_{25}$ capsules remained practically constant during the experiment at 1000 °C (Fig. 1).

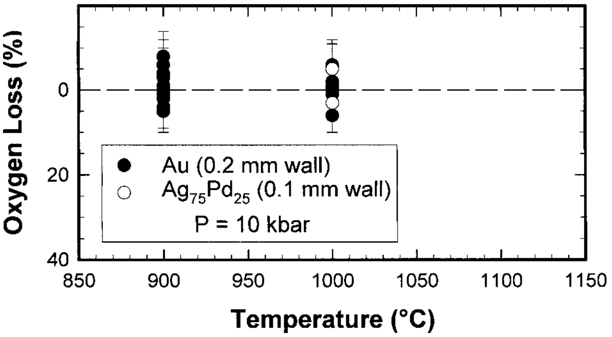

**FIGURE 1.** Oxygen balance for gold and $Ag_{75}Pd_{25}$ capsules and its dependence on temperature. Shown are the changes in oxygen contents relative to the initial oxygen contents. The oxygen contents of the fluids were measured by gas chromatography. All experiments were performed at 10 kbar with a duration of 6 days. Different kinds of starting materials were used (starting H/O = 0, 1, or 5). No distinct oxygen loss could be observed.

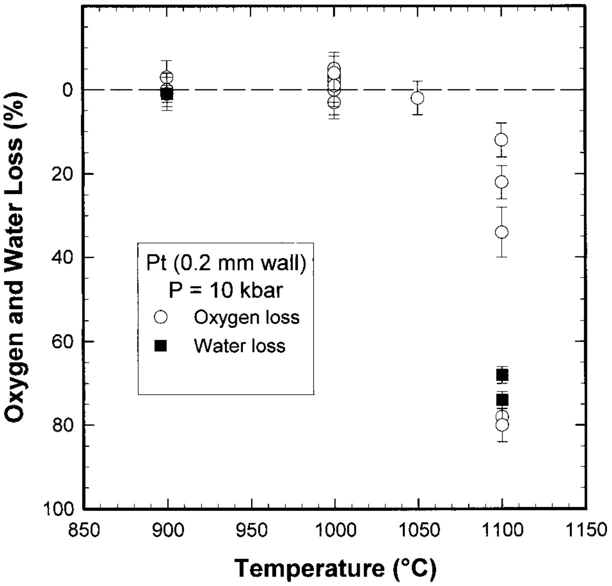

**FIGURE 2.** Oxygen balance and $H_2O$ balance, respectively, for platinum capsules and their dependence on temperature. Shown are the changes in oxygen (and $H_2O$, respectively) contents relative to the initial oxygen (and $H_2O$, respectively) contents. The oxygen contents of the fluids were measured by gas chromatography. The $H_2O$ contents were measured gravimetrically. All experiments were performed at 10 kbar with a duration of 6 days. At 1100 °C, a massive oxygen and $H_2O$ loss could be observed.

For Pt capsules, no measureable oxygen loss was observed up to 1050 °C. At 1100 °C, however, a distinct oxygen loss occurs. In all capsules, the oxygen loss amounts to ≥ 12%. Two capsules lost about 79% of the initial oxygen (Fig. 2, Table 1). To confirm these results, two experiments (with two capsules per experiment) were performed with pure $H_2O$ sealed in platinum capsules. At 900 °C, the comparison of the $H_2O$ content before and after the experiment reveals a decrease of 1% in both capsules, whereas at 1100 °C the $H_2O$ loss from each capsule amounts to 71 ± 3% (Fig. 2, Table 2).

**TABLE 1.** Oxygen balance in platinum capsules

| Starting H/O | Sample no. | *T* (°C) | Starting O content* (mmol) | Measured O content† (mmol) | Change in O content‡ (%) |
|---|---|---|---|---|---|
| 0 | 56 | 900 | 0.047 | 0.047 | 0 (3) |
| 1 | 58 | 900 | 0.069 | 0.071 | 3 (2) |
| 2 | 60 | 900 | 0.067 | 0.066 | –1 (2) |
| 0 | 143 | 1000 | 0.059 | 0.06 | 2 (3) |
| 0 | 147 | 1000 | 0.06 | 0.06 | 0 (3) |
| 0 | 146 | 1000 | 0.059 | 0.06 | 1 (3) |
| 1 | 158 | 1000 | 0.064 | 0.063 | –3 (2) |
| 1 | 163 | 1000 | 0.065 | 0.065 | 0 (2) |
| 1 | 162 | 1000 | 0.065 | 0.069 | 5 (2) |
| 1 | 144 | 1000 | 0.064 | 0.065 | 1 (2) |
| 1 | 171 | 1000 | 0.066 | 0.069 | 4 (2) |
| 5 | 165 | 1000 | 0.040 | 0.041 | 3 (4) |
| 5 | 164 | 1000 | 0.041 | 0.041 | 0 (4) |
| 5 | 161 | 1000 | 0.040 | 0.040 | 0 (4) |
| 0 | 152 | 1050 | 0.059 | 0.058 | –2 (3) |
| 0 | 150 | 1100 | 0.059 | 0.046 | –22 (3) |
| 0 | 149 | 1100 | 0.059 | 0.012 | –80 (3) |
| 1 | 160 | 1100 | 0.066 | 0.051 | –22 (2) |
| 1 | 166 | 1100 | 0.064 | 0.056 | –12 (2) |
| 5 | 168 | 1100 | 0.041 | 0.009 | –78 (4) |
| 5 | 169 | 1100 | 0.041 | 0.027 | –34 (4) |

*Note:* All experiments were performed at 10 kbar with a duration of 6 days.

* Calculated from the composition and amount of the starting material.

† Oxygen content of the C-H-O fluid measured by gas chromatography.

‡ Relative difference between starting O content and measured O content (with analytical error).

**TABLE 2.** Water balance in platinum capsules

| *T* (°C) | Starting $H_2O$ content* (mg) | Final $H_2O$ content† (mg) | Water loss‡ (%) |
|---|---|---|---|
| 900 | 1.336(14) | 1.324(4) | 1(2) |
| 900 | 1.390(14) | 1.380(4) | 1(2) |
| 1100 | 1.265(14) | 0.336(4) | 74(2) |
| 1100 | 1.528(14) | 0.482(4) | 68(2) |

*Note:* All experiments were performed at 10 kbar with a duration of 6 days.

* Corrected because of water evaporation during sample preparation (with analytical error; for details, see text).

† With analytical error.

‡ Relative difference between starting $H_2O$ content and final $H_2O$ content (with analytical error).

## DISCUSSION AND CONCLUSION

During experiments with all three investigated capsule materials, no oxygen loss (and, consequently, no $H_2O$ loss) occurred at temperatures up to 1000 °C (Figs. 1 and 2). Moreover, capsules made of Pt showed no oxygen loss at 1050 °C. At temperatures $\geq 1100$ °C, however, oxygen losses of 22–80% occurred in platinum capsules. Additional experiments with capsules containing pure $H_2O$ show $H_2O$ losses of 71 and 76% at 1100 °C. Consequently, the $H_2O$ loss observed by Patiño Douce and Beard (1994, 1995) was confirmed by our investigation. Nevertheless, the lowest temperature at which oxygen loss occurred is 100 °C higher than reported by those authors. The reason for this difference is not yet clear. Some capsules show an increase of oxygen content during the experiment. This increase mainly occurs in capsules with a starting H/O of 5. The starting material in these cases ($C_9H_{10}O_2$) is very hygroscopic. The increase in oxygen content may therefore be due to the $H_2O$ absorbed during sample preparation.

Water loss during high-temperature piston-cylinder experiments is a serious problem. A temperature of about 1050 °C (±50 °C) represents the upper thermal limit for constant $H_2O$-containing systems. Patiño Douce and Beard (1994) concluded from their experiments that most $H_2O$ loss apparently occurred via diffusion of $H_2O$ and, to a lesser extent, via diffusion of hydrogen. They could not explain adequately why the diffusive loss of $H_2O$ accelerated markedly over a narrow temperature interval, but they speculated that it may be related to annealing or some other temperature-sensitive change in the Au capsule material. Similar processes are plausible for oxygen loss detected during our investigations. This temperature-sensitive change must be reversible. During preparation of the samples for gas chromatography, the unpierced capsules were heated at 150 °C in a vacuum with no additional oxygen loss. Consequently, the capsules were gas tight at low temperatures again.

The results of Patiño Douce and Beard (1994, 1995) and our results appear to be in contrast with the study of Brooker et al. (1998). One possible factor is that the experiments of Brooker et al. (1998) were performed at higher temperatures with shorter run durations. Therefore, the results are not directly comparable. Nevertheless, run durations of 30 min at 1600 °C were sufficient to detect carbon migration through the Pt wall. Oxygen migration was not observed.

Perhaps the properties of the Pt depend on the manufacturing method of the supplier, are related to impurities in the Pt, or depend on the material surrounding the capsule. In future studies of fluid-bearing systems, experimentalists may be well advised to check that their proposed capsule material is sufficiently impermeable to the fluid phase.

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