Fluid-Mineral Interactions: A Tribute to H. P. Eugster
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A new hydrothermal technique for redox sensing using buffer capsules

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Abstract—A reversal of the usual double capsule technique pioneered by Eugster was used in this study: various buffer assemblages contained in small thin-walled (0.02 mm) palladium capsules were included with the more massive amounts of water and solids loaded in the gold bag of a rocking autoclave, not to control the redox potential, but to measure it. In this manner the reacting palladium capsules could be used to estimate redox conditions within the much larger gold cell of Dickson autoclaves. Experiments involving basalt-simulated groundwater mixtures were conducted at 200° and 300°C at 30 MPa for 4000 hours. The following buffers were used: Cu-Cu_2O, Cu-CuO, Fe_3O_4-Fe_2O_3, Ni-NiO, Co-CoO, Fe_2SiO_4-Fe_3O_4-SiO_2. The reacting buffers fix the $\log fO_2$ between -23 and -35 at 300°C and -40 and -43 at 200°C. These ranges are consistent with fO_2 values obtained from SO_4-H_2S and fH_2 measurements for the same experiments. This technique holds promise for redox estimates at lower temperatures than has been previously thought possible in using such buffering assemblages.

INTRODUCTION

THE GEOCHEMICAL CHARACTERIZATION of hydrothermal systems involves the determination of all pertinent equilibria. However, in experiments it is often difficult to measure or control the redox state. This paper presents results of hydrothermal experiments conducted to determine the redox conditions developed during basalt-water reactions (MOORE *et al.*, 1985).

Historically, the double buffer capsule technique of EUGSTER (1957), and later of EUGSTER and WONES (1962), utilized a gold outer capsule containing a buffer assemblage with a platinum inner capsule containing a small amount of material to be equilibrated. In this arrangement the mass of the buffer was much larger than that of the material to be equilibrated and the diffusivity of hydrogen through platinum together with the buffer thus controlled the resulting redox state of the system.

By contrast, in this technique we have added six or seven palladium capsules, each containing small amounts of buffer materials (*ca.* 25 mg) and water, into the gold cell of a Dickson autoclave. This cell contained at least 15 g of basalt and 150 mL of solution. Because the relative masses involved are so different, reaction of only a small amount of the basalt could control the system redox, if allowed by reaction, permeation, or diffusion kinetics. These buffer capsules would then act to sense the redox state and not control it.

Previous investigations (reviews by HUEBNER, 1971; or by CHOU, 1987) suggest that equilibration might not take place in reasonable periods (inferred to be days to weeks) at temperatures even as low as *ca.* 400°C. Within our experiments which were designed for other reasons to last 3000–5000 hours at 200° and 300°C it was possible to see if equilibration would occur and, if so, to determine the redox conditions arising from basalt-water reactions under conditions simulating those which might occur in a nuclear waste repository or in a geothermal field.

EXPERIMENTAL TECHNIQUES AND MATERIALS

The hydrothermal experiments were conducted using a Dickson rocking autoclave. The design and operation of the autoclave are described in DICKSON *et al.* (1963), SAKAI and DICKSON (1978), SEYFRIED *et al.* (1979 and 1987), and MOORE *et al.* (1985). This apparatus consists of a flexible gold sample cell (approx. volume 250 mL) with a titanium lid connected by a gold-lined titanium capillary tube to an external sampling valve. The gold cell is contained within a pressurized steel autoclave which is heated in a furnace. Aqueous samples of 5–10 mL may be removed periodically through the external sampling valve by squeezing the gold cell with a small over-pressure within the autoclave. This can be done at any time during the experiment without seriously perturbing the pressure and temperature of the experiment. The solution aliquots were analyzed for major dissolved species including sulfate, sulfide, and pH (MOORE *et al.*, 1985), and dissolved hydrogen using the method of KISHIMA and SAKAI (1984a and b), GRANDSTAFF *et al.* (1985) and ULMER *et al.* (1985).

The basalt used throughout the experiments was collected from the entablature of the Umtanum flow, in the Pasco Basin northwest of Hanford, WA. It is a fairly typical low-magnesium Columbia Plateau Miocene tholeiite, with 47% mesostasis (more than half of which is true glass (AL-

LEN *et al.*, 1985)). The composition and mineralogy are given in MOORE *et al.* (1985).

The solution used in experiments is a chemically prepared synthetic equivalent of groundwater found in contact with the Umtanum flow at a depth of 1 km under the Pasco Basin. This synthetic groundwater contained about 300 mg/L dissolved chloride and 30 mg/L fluoride. The need to quantitatively conserve the halide ions to satisfy the water-rock interaction aspects of this research made us cautious about introducing silver-palladium alloys which would have had higher permeability rates than pure palladium (CHOU, 1987 and 1989). The groundwater composite used is given in SMITH (1980, 1981).

The capsules were made from 3.0 mm diameter, thin-walled (0.20 mm) palladium tubing by arc welding the "ash can" shape in a technique similar to that of SNEERINGER and WATSON (1985). This capsule shape was selected to avoid scoring of the inner wall of the gold bag during the rocking of the autoclave. The 0.20 mm wall thickness did endure the abrasion of 3000–4000 hours of rocking in the basalt powder (60–125 μm size range)-water slurry. The capsules were 12 to 18 mm long. They each contained *ca.* 25 mg of the buffer assemblages: Cu-Cu_2O, Cu-CuO, Fe_3O_4-Fe_2O_3, Fe_2SiO_4-Fe_3O_4-SiO_2, Ni-NiO and Co-CoO all prepared from reagent grade chemicals. Sufficient water (5 to 12 mg) was added to allow complete redox equilibration. Comparison of the before- and after-weights to judge reaction of the buffers was pointless due to abrasion losses of the palladium capsules.

After the experiments the capsules were visually examined for possible holes. The capsules were cut open and the contents were qualitatively examined and characterized with binocular microscope, X-ray diffraction, and electron microprobe.

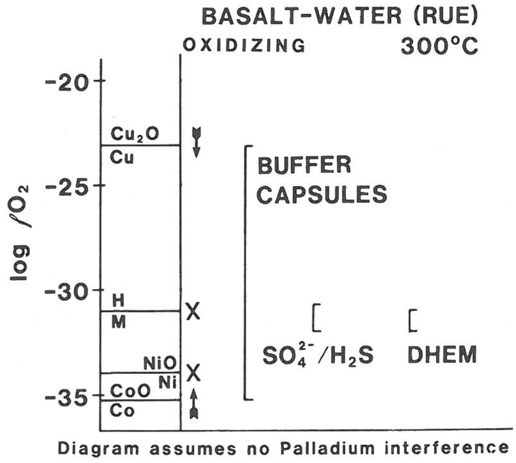

FIG. 1. Columbia River Plateau Reference Umtanum Entablature (RUE) Basalt Redox Data for 300°C. Various buffer assemblages used in palladium capsules as explained in the text are summarized: arrows point in the direction of change recorded by the buffer assemblage; no major change in the buffer assemblage is recorded as an "X". Brackets to the right show the ranges determined by the three different techniques. DHEM stands for direct hydrogen evolution measurement.

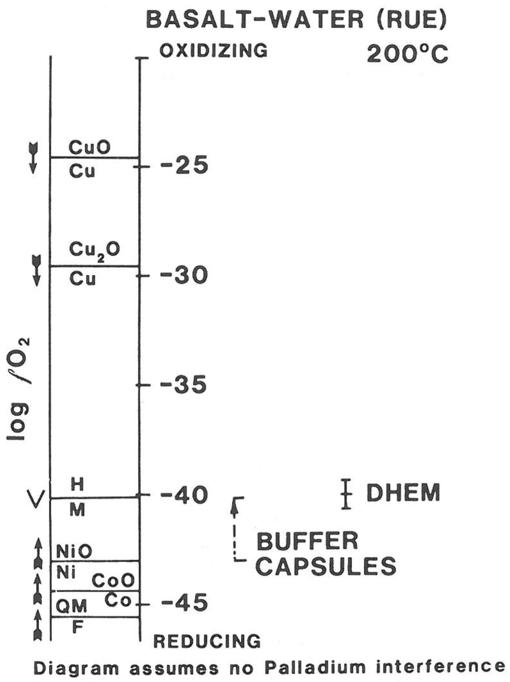

FIG. 2. Columbia River Plateau Reference Umtanum Entablature (RUE) Basalt Redox Data for 200°. Various buffer assemblages used in palladium capsules as explained in the text are summarized: arrows point in the direction of change recorded by the buffer assemblage; a recrystallization and change in the starting proportions of a buffer is recorded as a "V". Brackets to the right indicate the ranges measured by two techniques. DHEM stands for direct hydrogen evolution measurement.

RESULTS

Results of the experiments are given in Figs. 1 and 2. In each figure log fO_2 (oxygen fugacity) is plotted as a vertical nomograph. The value of fO_2 for each buffer assemblage (as calculated from thermochemical data of HELGESON *et al.*, 1978) is plotted on this vertical axis. Buffers used varied with the experiment but included the following: the fayalite-magnetite-quartz (FMQ) buffer, the magnetite-hematite buffer (MH), the Ni-NiO buffer and the Co-CoO buffer. Oxidation of the buffer assemblage is indicated by an upward pointing arrow. Reduction is indicated by a downward pointing arrow. Buffers in which no reaction occurred are indicated by (X). Also plotted on the diagrams are other redox values of pertinent buffers such as Cu-Cu_2O and/or Cu-CuO. The oxygen fugacity of the parent basalt, as extrapolated down from 900°C from our own ZrO_2 cell measurements falls approx. 1.3 log units below the (FMQ) buffer, *i.e.* −34.7 at 300°C.

Fig. 1 summarized the results of a basalt/water experiment (BR-14) conducted at 300°C. The copper buffer (Cu-Cu_2O) is very likely disproportionated to the CuO-Cu buffer in that Cu_2O is reported to be unstable below 375°C (Hansen, 1958). Nevertheless, the inferred CuO was totally reduced while the (Co-CoO) buffer was totally oxidized (as indicated by the arrows). There was little or no reaction in the iron (Fe_3O_4-Fe_2O_3) and nickel (Ni-NiO) buffers. These results bracket the value of log fO_2 between -23 and -35. The results indicate that hydrogen diffusion across the palladium membrane was fast enough in 3000–4000 hours to have had reaction of at least some of the buffer solids.

Values of log fO_2 calculated from high-temperature sulfate-sulfide speciation (labeled SO_4^{2-}/H_2S; MOORE *et al.*, 1985) and from measured values of dissolved hydrogen (labeled DHEM) (GRANDSTAFF *et al.*, 1985; ULMER *et al.*, 1985) indicated that, assuming equilibrium, the oxygen fugacity had attained values near that defined by the magnetite-hematite (MH) equilibrium. Therefore, the results are not inconsistent over the three techniques, *i.e.*, SO_4^{2-}/H_2S, DHEM, and the current capsule technique. The iron and nickel buffers may not have reacted because the redox state of the experiment may have been close to the equilibrium boundary and therefore, there was little thermodynamic driving force for their reaction. While KISHIMA and SAKAI (1984a) have shown that (FMQ) is quite reactive at 300°C, results from experiments (*e.g.* BARTON and SKINNER, 1979) suggest that Cu-bearing phases should react faster than Ni- or Fe-bearing phases.

Results of an experiment at 200°C are shown in Fig. 2. Buffer reactions in that experiment constrain values of log fO_2 between -40 and -43. Most of the buffers showed complete or virtually complete reaction at 200°C and 5000 hours. Again, the Cu_2O may have disproportionated to CuO and Cu, but both buffers showed the disappearance of all copper oxides. Moreover, the magnetite-hematite (MH) buffer showed a dramatic octahedral recrystallization of the magnetite along with an XRD-noticeable depletion (but not annihilation) of the amount of hematite present. These observations taken together with the compelling mass of the water-rock charge, both suggest that the redox conditions were not in violation of the (MH) buffer value, but were rather close to it. Again the bracketed redox values from the redox buffers are not inconsistent with the log fO_2 value calculated from measured dissolved hydrogen concentrations (indicated by "DHEM").

DISCUSSION

Ideally, a sensor should be inert and not react with the system materials (except for hydrogen diffusion in the present experiments). This may not have been the case. The outside of one capsule from the 300°C experiment was examined using scanning electron microscopy with element discrimination. The palladium capsule had reacted with dissolved sulfide in solution [the synthetic groundwater has an initial concentration of 2.9 mg/L and some sulfur may be contributed from the natural basalt used] and produced palladium sulfide. Solution aliquots from this experiment contained less sulfide than had aliquots from previous experiments without the palladium capsules. This suggests that the palladium capsule reacted with and removed sulfur from solution. This may have gently perturbed the redox state of the system to slightly more oxidized values as evidenced by the production of traces of hematite as a run-by-product within the gold cell. Nevertheless, in sulfur-free systems this complication would not occur.

Additionally, the reactivity of the buffers with palladium must also be considered. With the electron microprobe, we specifically checked for any alloying of buffer materials with palladium and detected only the anticipated Cu-Pd alloy reaction as shown in the sketched version of the electron-backscatter image in Fig. 3. Note the diffusion of copper into the palladium did produce both an alpha and a beta alloy phase, qualitatively matching the anticipated alloys shown in the Cu-Pd phase diagram (HANSEN, 1958), as shown in the inset of Fig. 3. Since the activity of copper was diminished by this alloy-formation, some adjustment is necessary to the fO_2 values plotted in Figs. 2 and 3 which are those of the copper-copper oxide systems without palladium. No activity data for the Cu-Pd-O system could be found with which to estimate the necessary corrections to the fO_2 values for the Cu buffers in palladium tubes.

Despite the reactivity of palladium with some buffers and with sulfur, the conclusion is that reaction rates of the buffers in the palladium capsules were such, that by running a group of buffers in this fO_2-sensing-mode, useful redox approximations were/are still possible at temperatures as low as 200° and 300°C. With our choices of specific buffers, we could only narrow down the water-rock interaction redox range to about 14 log units of oxygen fugacity. The AgPd-AgCl-Ag technique subsequently reported by CHOU (1989) allows the determination of the specific redox value in such autoclave studies. Our times for redox equilibration were defined by the experimental design to be in the order of thousands of hours, as is often the case in autoclave experiments, but shorter times are also likely to work as indicated by KISHIMA and SAKAI

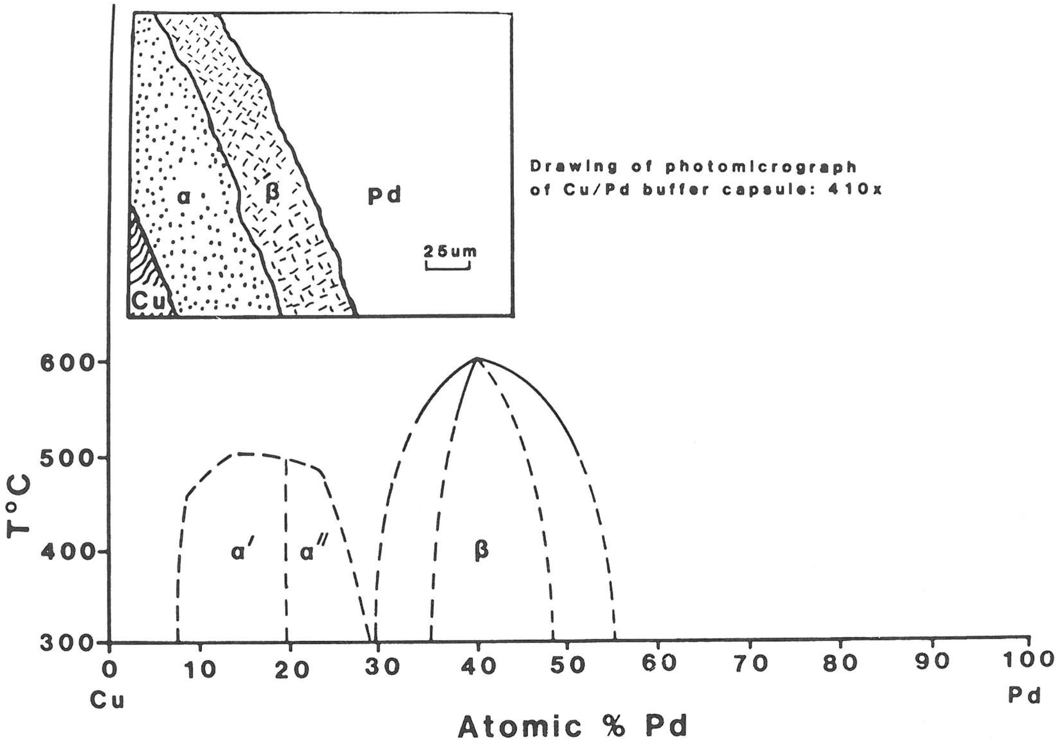

FIG. 3. The Cu-Pd Binary Phase Diagram and a Sketch of a Scanning Electron Microscope Image of the Palladium Tube Wall. The phase diagram (after HANSEN, 1958) predicts the exact phases found by the reaction of copper containing buffers with the palladium of the capsules. Further discussion is given in the text.

(1984a) and CHOU (1987, 1989). In our study the buffering capsules, the sulfate/sulfide equilibria and the hydrogen evolution methods are consistent and as has been shown in the review by ULMER *et al.* (1986), the fO_2 values obtained in this study do overlap those measured for basalt geothermal wells by others (ARNÓRSSON *et al.*, 1983; and GISLASON and EUGSTER, 1984).

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