

APPENDIX I

Determination of f_{O_2} using NiPd and CoPd sensors

In order to validate the relative oxidation (f_{O_2}) of the experiments presented in this study, several tests were conducted in tandem with the primary partitioning experiments. The sensors rely on measuring the relative oxidation of Ni and Co within NiPd and CoPd respectively. These sensors operate under the principle that the Ni and Co will oxidize out of the metal alloy thus reducing the a_{Ni} and a_{Co} in the metal alloys. Thus, it requires an increasingly higher f_{O_2} to oxidize the remaining Ni and Co in the alloys. The relationship between the f_{O_2} of the system and the a_{Ni} and a_{Co} in the alloys has been quantified by several experimental studies covering the conditions relevant to the experiments presented (Pownceby and O'Neil 1994, Taylor et al. 1992). This allows for correlating the final metal composition from the sensors with the equilibrium f_{O_2} of the experiment design.

The sensor capsules described were run in both “normal” Ni-alloy Nimonic vessels and those with hematite added to the pressure fluid. These represent the same conditions used to create “reduce” and “oxidized” conditions for the partitioning experiments presented. The tests involved using Au capsules similar in size to the experimental capsules to contain two small pellets of metal mixtures of Ni-Pd and Co-Pd. The capsules were also loaded with sufficient water to oxidize the Ni and Co and alumina (Al_2O_3) powder to fill the capsule and isolate the two metal pellets. The sensors were run for the same duration

as the partitioning experiments at the same magmatic conditions (800 °C and 100–200 MPa). After quench the capsules were opened and the pellets of metal alloy and oxides were removed and mounted in 1” epoxy mounts. Polished mounts were carbon coated and the compositions of the remaining metal alloys were determined by WDS-EPMA analysis. The results of these analyses for all 4 experimental vessels are shown in Table 6. The analytical uncertainty for the sensor tests at reduced conditions was almost always below the inherent 0.2 log unit uncertainty for the sensor calibrations (Pownceby and O'Neil 1994; Taylor et al. 1992). The uncertainty for the sensors at oxidized conditions was greater due to the much smaller fraction of Ni and Co remaining in the alloy at equilibrium. These tests show that the average f_{O_2} for the vessels is measured at $\log f_{\text{O}_2}$ (ΔNNO) = 0.64 ± 0.18 and 1.98 ± 0.43 for reduced and oxidized conditions respectively. We believe that the consistency of these results shows the “steady state reached by the buffering assemblage at reduced and oxidized conditions. Most importantly, these results are consistent with the reduced (sulfide) and oxidized (sulfate) run products observed in the partitioning experiments run under the same conditions.

References cited

- Pownceby, M.I., and O'Neil, H. S. (1994) Thermodynamic data from redox reactions at high temperatures. III. Activity-composition relations in Ni-Pd alloys from EMF measurements at 850-1250 K, and calibration of the NiO + Ni-Pd assemblage as a redox sensor, *Contributions to Mineralogy and Petrology*, 116, 327-339
- Taylor, J.R., Wall, V.J., Pownceby, M.I. (1992) The calibration and application of accurate redox sensors. *American Mineralogist*, 77, 284-295

TABLE 6. Ni-Pd and Co-Pd f_{O_2} sensor measurements for reduced and oxidized experimental designs

| Ni/Co Sensors | $\Delta\text{NNO-Reduced } (\pm 2\sigma)$ | | $\Delta\text{NNO-Oxidized } (\pm 2\sigma)$ | |
|--|---|-------------|--|-------------|
| | Ni-Pd | Co-Pd | Ni-Pd | Co-Pd |
| VESSEL 1 | 0.53 (0.2*) | 0.48 (0.2*) | 2.27 (0.44) | 1.95 (0.25) |
| VESSEL 2 | 0.73 (0.2*) | 0.64(0.2*) | 1.94 (0.25) | 1.83 (0.49) |
| VESSEL 3 | 0.64 (0.2*) | 0.67 (0.2*) | 1.69 (0.2*) | 1.88 (0.21) |
| VESSEL 4 | 0.72 (0.2*) | 0.73 (0.22) | 2.34 (0.34) | 1.96 (0.31) |
| AVERAGE f_{O_2} | 0.64 (0.18) | | 1.98 (0.43) | |

* Analytical uncertainty is below calibration uncertainty of the sensor, ~0.2 log units

APPENDIX II

Comparison of quartz-hosted and glass hosted saline fluid inclusions

In order to better examine equilibrium in the Cu-Mo partitioning runs we have also characterized the trace metal content of several fluid inclusions from each experiments hosted in the run product glass. These analyses were conducted using the same general analytical procedures discussed in the Methods section but posses several features that make complete characterization more unreliable or impossible. First, fluid trapping in the host glass does not generate the same well-defined populations of inclusion types observed in quartz-hosted inclusions due to much more abundant fluid mixing. A significant amount of filtering was required to separate out inclusions that fall within the same salinity range as those hosted in quartz and contain roughly the same daughter mineral assemblage. As a result, roughly 2/3 of the inclusions observed were discarded due to obvious mixing (in the case of brine/vapor), co-entrapment of other phases (such as oxides/sulfides) or insufficient Na signal for standardization. Second, the glass host contains significant amounts of the major elements normally used to monitor homogeneity and total salinity across fluid inclusion assemblages. The poor signal to background ratio for most the major elements (K, Ca, Fe) meant that characterizing overall

average fluid compositions was not possible. Finally, a host correction has to be made to subtract out the contribution of the glass based on the signal prior to analyzing the inclusions. This is done using the protocols within the AMS software (Mutchler et al. 2009) used to reduce all the LA-ICPMS data for these experiments. As a result of the challenges limiting full characterization, the glass-hosted inclusions have not been included in the overall averages presented to calculated partition coefficients.

However, the glass-hosted saline inclusions do offer an additional assesment of experiment equilibrium. While in-situ fracturing does provide much more time for equilibration prior to fluid trapping, the quartz-hosted inclusions begin trapping on day 3 while the glass-hosted inclusions are trapped upon quench. By comparing the Cu and Mo concentration of these inclusions from all but one of the runs (CMA406 did not have any successful glass hosted inclusion analyses), we can look for any discrepancy that would indicate disequilibrium between the time of trapping the quartz-hosted inclusions and the quench. The concentrations of Cu and Mo for both quartz-hosted and glass-hosted inclusions are shown in Figure 7. The data clearly shows excellent agreement between the two types of inclusions across all experiments types and is a strong indication that indeed the experiments equilibrate prior to in-situ fracturing and remain equilibrated until quench.

