THE SOLUBILITY OF GOLD IN SILICATE MELTS: FIRST RESULTS. A. Borisov, H. Palme, B. Spettel. MPI für Chemie, Saarstrasse 23, 6500 Mainz, Germany

The effects of oxygen fugacity and temperature on the solubility of Au in silicate melts were determined. Pd-Au alloys were equilibrated with silicate of anorthite-diopside eutectic composition at different T-fO2 conditions. The behaviour of Au was found to be similar to that of Pd reported recently [1]. Au solubilities for alloys with 30 to 40 at. % Au decrease at 1400°C from 12 ppm in air to 160 ppb at a log fO2 = -8.7. The slope of the log(Me-solubility) vs. log(fO2) curve is close to 1/4 for Au and the simultaneously determined Pd suggesting a formal valence of Au and Pd of 1+. Near the IW buffer Pd and Au solubilities become even less dependent on fO2 perhaps reflecting the presence of some metallic Au and Pd.

Experimental. As in earlier work [1,2] liquid silicate droplets (2-3 mm diameter) were equilibrated with 0.5-1.0 mm wide metal band loops (Au45 Pd55 , at%) inside a furnace with controlled oxygen fugacity for about 50 hours. After removal of metal loops glasses were analysed for Au and Pd by INAA. By successive removal of surface layers and reanalyses of Au and Pd, profiles through the glass were obtained. From these data homogeneous Pd and Au layers and reanalyses of Au and Pd, profiles through the glass were obtained. From these data homogeneous Pd and Au distributions were found significant selective Au evaporation (typically 5-24%) of the initial Au-content) from the alloy during the experiments. Particularly severe Au-losses (61-67%) were recorded when H2/CO2 gas mixtures were used for fO2 control.

Results. Results of the experiments are graphically displayed in Figs. 1 and 2. Combined analytical uncertainties are typically in the order of 10%. The slopes of log(Me-solubility) vs. log(fO2) at 1400°C are close to 1/4 for both, Pd and Au (Fig.1), indicating the effective valence of 1+, instead of 2+ and 1+ (or perhaps 3+) for Pd and Au, respectively. This is similar to the behaviour of Ir [2] and Pd [1] recently reported. At more reducing conditions (around IW) there is a significant decrease of the slope for both metals, associated with increasing scatter of the results. A change of slope in reducing conditions was earlier found in experiments with pure Pd [1]. The existence of Pd0 was suggested as one of the possible reasons of this behaviour. The reason for the large spread in the low fO2 region in the present experiments using alloys is, however, unknown. Additional experiments will be performed to clarify this question.

At constant fO2 (air) Au and Pd solubilities increase with increasing temperature (Fig.2) opposite to the behavior of metals of the Fe group but in agreement with earlier data on Pd [1]. Extrapolation of our data to 1450°C leads to solubilities of about 197 ppm Pd and 14 ppm Au comparable to results by Capobianco [3] (Pd=290±60, Au=14±2 ppm) for silicate melts equilibrated with solid Pd66Au34 alloy in air. Both melt compositions are similar with respect to SiO2 and MgO content, but different in CaO and Al2O3 which may be responsible for the small difference in Pd solubility.

By comparing Pd solubility in equilibrium with pure Pd [1] and with Au-Pd alloys (this work), activity coefficients of Pd in Au-Pd alloys (ypd) were extracted. Their values (0.9-1.2) are compatible, within error limits, with activity coefficients calculated from thermodynamic data [4] and with values extracted from experimental data [3].

D\text{Pd}/D\text{Au} (iron metal/silicate melt). Over a wide range of oxygen fugacities the ratio of Pd to Au concentrations (weight ratio = 12±1) was found to be constant in our experiments (Fig. 1). By considering the Pd-Au alloy composition, appropriate activity coefficients [4] and normalizing to unit activities for Au and Pd, a ratio of 3.6 is obtained reflecting the difference between Au and Pd solubility in silicate melts.

Metal silicate partition coefficients, D(met/sil), were calculated from solubilities according to D(Fe/melt) = 1/(ci*yi*Bj), where ci is the solubility in equilibrium with pure Au or Pd, yi is the activity coefficient of metal i in Fe-metal and Bj is a coefficient for converting mole fractions of metal i in Fe-metal into in weight fractions. From this and from estimates of the activity coefficient ratio of Pd and Au in Fe-metal ([4, 5]: yPd/yAu in solid Fe = 0.12) a partition coefficient ratio of D\text{Pd}/D\text{Au} = 1.2 is obtained. Extrapolation to lower oxygen fugacities are made on the assumption that the dependence of Au and Pd metal/silicate partition coefficients on oxygen fugacity is the same for both metals.

Conclusions: At 1350°C and oxygen fugacities appropriate for core formation in the Earth (log fO2 = IW-2) D\text{Pd} was estimated to be about 1.6*107 [1]. From this and the results of this study a partition coefficient D\text{Au} = 2*107 is
calculated for the same conditions. The similarity of Pd and Au metal/silicate partition coefficients as well as the similar temperature dependence indicate similar behaviour of both elements during metal-silicate fractionation. Since Ir, another highly siderophile element, has a significantly higher metal-silicate partition coefficient we have concluded earlier [1] that the contents of highly siderophile elements in the upper mantle were not established by metal-silicate separation as suggested, for example, by [6] but are rather the result of accretion of a late chondrite-like veneer to the Earth. Additional arguments against a global core/mantle equilibrium are given in a companion abstract [7].


Fig.1. Effect of $f_{O_2}$ on Au and Pd solubilities. Open symbols - $H_2/CO_2/N_2$ gas mixtures, solid - air, $CO_2/N_2$ or $CO/CO_2/N_2$ gas mixtures. Alloy compositions (at.%) are indicated. Dashed line - solubility for metal dissolved as $Me^{1+}$.

Fig.2. Effect of temperature on Au and Pd solubilities in silicate melts at constant $f_{O_2}$ (air). Dashed line indicates typical slope for elements of the Fe-group.