ANOMALOUS BEHAVIOUR OF NOBLE METAL AT THE REDUCING CONDITIONS: THEORETIC AND EXPERIMENTAL INVESTIGATIONS AND THE IMPLICATIONS TO THE GEOCHEMICAL AND COSMOCHEMICAL PROBLEMS

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It is well known that noble metals at high temperatures can easily react with certain substances (sulfur, selenium, tellurium, phosphorus, arsenic, antimony, molten lead, zinc, tin, bismuth, etc.). At low oxygen fugacity noble metals can react not only with such "exotic" substances, but even with silica, the main component of silicate melts. For example, Borisov with coworkers, making experiments with a loop technique to determine Pd and Au solubilities in silicate melts [1, 2] revealed that slightly below IW buffer conditions all experiments failed because of the destruction of the Pd- and PdAu loops. The reason was found to be Pd alloying with silica of the melt [1]. Indeed, the eutectic temperature in Pd-Si binary is only 760°C and the eutectic composition is about 16 at.% Si. It is obvious, that at "normal working" temperatures (1300°C or higher) a much smaller fraction of silicon would be enough to destroy a capsule or a loop.

In the following discussion I will designate a noble metal as *metal* (Me) and the alloying partner, that is usually stable as oxide at redox conditions at which the noble metal is stable in metallic state, as *metalloid* (Md). The latter could be Si, Ge, As, Bi and other nonmetals, but also Fe, Co, Ni or other metals. Again, by definition, the Me/Me oxide equilibrium line in the T-fO₂ field lies in a much more oxidizing region, than Md/Md oxide one. The reaction of Me with Md oxide can be described as:

 $Me(sol.) + MdO_n(sol. or liq.) =$

=Me (liq. MeMd alloy) + Md (liq. MeMd alloy) + + $n/2 O_2$, (1)

with the reaction constant:

$$K_1 = (fO_2)^{n/2} \times a_{Me}^{alloy} \times a_{Md}^{alloy} / a_{MdOn} \times a_{Me},$$
(2)

where a_i is the activity of a component i. For pure Me the equation (2) can be rewritten as:

$$logfO_2 = 2/n log(K_1 \times a_{MdOn}) + +2/n log(a_{Me}^{alloy} \times a_{Md}^{alloy}).$$
(3)

At constant activity of Md oxide, the oxygen fugacity, at which solid Me converts in liquid MeMd alloy is a strong function of temperature. There are two ways to construct such T-fO₂ diagrams: by calculation, if thermodynamic data are known [3] or by experiments [4].

On Fig. 1 I showed the calculated melting diagram of Pt-Fe alloy in silicate melt with constant concentration (10 mol. %) of FeO (see [3] for details). Trend A-B clearly demonstrates that even at decreasing temperature one could emerge the situation with melting of an initially solid alloy. It could be a spike of very reducing H₂-containing deep fluid, or quick decompression of carbon-containing melts or any other process with temporal sharp decrease of fO₂. I would suggest a term *"redox melting"* to emphasize the process, when it is not temperature but oxygen fugacity, which is responsible for solid phase melting. If these Pt-Fe alloy droplets are small enough, they will easily reequilibrate after fO₂ "normalization" to have a composition relevant to T-fO₂ conditions in point B (see Fig. 1). An attempt to reconstruct the maximum temperature for such alloy composition by simple using solidus of Pt-Fe binary will thus result in ironically high overestimation.

On Fig. 2 I gave an example of the construction of Pd-Si melting diagram by experiment [4]. The experiments were conducted in one-atmosphere furnace with controlled fO_2 (±0.1 log unit). Short pieces of Pd wire (99.9% purity, 0.025 mm in diameter) were placed in small quartz crucible filled with SiO₂ powder (99.99% purity). This silica was first heated for about one hour at high temperature to be converted into cristobalite. The crucible was suspended in the hot zone of the furnace at given temperature and fO₂ for 30-60 minutes. The reaction of Pd with silica (melting of wire) was determined visually after removing the crucible from the furnace. At 1300°C, for example, initially solid Pd react with pure solid SiO₂ and melts at $fO_2 = 10^{-12.2}$ atm, which is only 1.6 log unit below IW buffer. Remember, 1300°C is about 250°C below the melting point of pure Pd!

Refractory metal nuggets in Ca-Al rich inclusions of carbonaceous chondrites are known to contain practically no Pd [5, 6] and this fact I would explain the next way. Recalculating experimental data it is possible to show that an alloy with a few ppm of Pd may react with a silicate phase at fO₂ assumed for a canonical solar nebula. It does not exactly mean (but it is possible) that Pd would be melted out from alloy after condensation of first silicate phase. It rather means that primary RMN composition mustn't be calculated without taking into account silicides of PGE (as solid, liquid or vapor phase). Indeed, the experiments on equilibrium of model PGE alloys with silicate melt of CAI composition [7] demonstrated that not only Pd-Si, but perhaps, even Pt-Si alloys should be normal phases at very reducing conditions.

As it was pointed out above, oxides of some other nonmetals (As, Sb, Bi, Ge, etc.) react much more easily with PGE than silica. Borisov and Palme [8] suggested such reactions to be the main reason for the formation of submicron sized nuggets (so

called "nugget problem" in experimental petrology) in melts, equilibrated with noble metals. El Goresy et al. [9] demonstrated alloying of Zn, Ga, Ge, Sn and As with noble metals in "Fremdlinge", the complex assemblages of metal grains and sulfides, found in CAI along with RMNs. So, not only silicides, but also arsenides, bismuthides, etc. should be involved in calculations of condensate composition at fO2 as low as usually assumed for the solar nebula.

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equilibrium with basaltic melt (10 % mol. FeO).

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Fig. 1. A melting diagram of Pt-Fe binary alloys in Fig. 2. A melting curve of pure Pd metal in pure silica