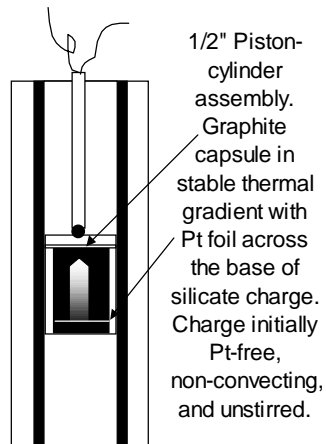


**A NEW LOOK AT PT SOLUBILITY IN SILICATE LIQUID.** E. A. Cottrell<sup>1</sup> and D. Walker<sup>1</sup>, <sup>1</sup>Lamont-Doherty Earth Observatory and Department of Earth and Environmental Sciences, Columbia University, Palisades NY 10964  
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**Introduction:** Pt nuggets found in the silicate glass of solubility experiments at low  $fO_2$  may be the quench products of Pt in solution in silicate liquid, not mechanical contaminants. Pt solubilities measured in the range of geologically interesting  $fO_2$  would then be several orders of magnitude higher than conventionally assumed. Such a finding may remove the perception of "excess" Pt in Earth's mantle.

**Experimental procedure:** We performed experiments on Pt solubility in silicate liquid at 10kb and 1350-1500°C in a piston-cylinder apparatus. The charge was composed of natural basalt or Pt-free



CMASN packed into a graphite container of low  $fO_2$  appropriate to Earth's interior. The charge was placed in the thermal gradient of the heater with the top of the charge about 20°C hotter than the bottom. A sheet of Pt foil was placed across the base of the charge. After annealing at 800°C and 10kbar to close porosity, the temperature was raised to 1350-1500°C and held for up to a couple of hours before quenching, recovery, sectioning and polishing.

**Results and Discussion:** The quenched silicate contains an emulsion of Pt nuggets (or Pt-Fe alloy in experiments containing Fe). The nuggets are optically visible (1–10  $\mu\text{m}$  in cross-section) and are dispersed throughout the charge in runs as short as 1/2 hour. Using image analysis of the Pt alloy nuggets' area we estimate the abundance of Pt in the silicate to be 5-10 ppm Pt. This is much higher than the conventionally-accepted Pt solubility of <1 ppb at the experimental  $fO_2$  of these experiments [1,2]. We interpret the nuggets as having been in solution in the silicate liquid at the P-T of the experiment and to have exsolved during sample quench. We explain why below.

Similar particle dispersions have been reported previously for Pt [1,2], Ir [3], and Re [4] and have been interpreted differently. In those cases the nuggets may be present in the silicate because of incomplete segregation of initially-mixed metal and silicate starting materials, or because of dispersive redistribution of crucible or paddle pieces mechanically or via convective stirring at the P-T of the experiment. The nuggets may also be the result of evaporative processes at melt/gas interfaces [1]. They would therefore have nothing to do with the true solubility of the noble metal in silicate liquid. This interpretation dictates the selection of the nugget-free spaces in the silicate as representative of the real solubility.

We eliminated all three of these potential mechanisms of Pt redistribution in our experiments. To eliminate incomplete segregation of metal/silicate mixtures, or Pt redistribution by any form of stirring, we start with Pt-free silicate in a thermal gradient with the hot side up. In contrast to the experiments of others, our Pt starts entirely in a single sheet of foil at the bottom of a non-convecting, non-stirred charge. Most of the initial Pt foil remains intact as the basal foil layer; however, some Pt also winds up as an emulsion of nuggets in the silicate. Because our experiments have no free gas phase with the silicate melt at 10 kbar, evaporative mechanisms operating at 1 bar across melt/gas interfaces are not viable. Pt is redistributed in the charge independent of these mechanisms.

We also considered Pt redistribution through a vapor phase that might initially permeate the interstices between solid silicate particles during the sintering stage at 800°C before compaction and melting. That vapor phase should diminish during the pre-anneal and disappear almost immediately into solution when the charge is melted. To evaluate this transport route, we processed a CMASN (An-Di eutectic) charge in the normal manner but quenched it to glass after only ~ 20 sec at 1500°C. If the Pt transport was through the interstitial vapor early on, then the nuggets should already have been in place. This experiment showed no redistribution of Pt from the basal foil sheet – no nuggets!

This "null experiment" is also important because it confirms that the dispersion of Pt nuggets observed throughout the charges after times as short as 1/2 hour is not an artifact of the sample preparation procedure. Sample cutting, grinding, and polishing could conceivably redistribute the Pt on the surface of the

specimen in a manner that is of no relevance to the solubility of Pt in silicate. Recovery of a “clean” silicate charge at  $t = 0$  not only removes this concern but also underlines the significance of finding Pt nuggets throughout the charge at  $t = 1/2$  hour.

We have eliminated left-over starting materials, mechanical mixing, convective stirring, melt-gas transfer, vapor transport during sintering, and sample preparation as possible agents to explain the presence of Pt nuggets in the silicate. We are left with dissolution and diffusion as the supply and transport mechanisms for putting enough Pt into the silicate part of the charge to result in the growth of the Pt nuggets upon quench. Our conclusion challenges conventional wisdom for the following reasons. The first and foremost is that Pt must be at least  $10^3$  more soluble than expected [1,2] to produce the loading of Pt nuggets observed. The second reason is that the diffusivity of Pt through the silicate must be very high ( $D \sim 10^{-4} - 10^{-5} \text{ cm}^2/\text{sec}$ ) if 3 mm charges are traversed in 1/2 hour. And third, the temperature dependence of the solubility must be prodigious to render most of the Pt in solution into Pt nuggets upon cooling. The diffusion kinetics required to create the nuggets upon quench alone boost the needed Pt diffusivity another order of magnitude or so, well beyond plausible values.

The high solubility of Pt is only implausible when compared to an extrapolation to low  $f\text{O}_2$  of results well established by [1] at  $f\text{O}_2 > 10^{-5}$  atm. These data and their extrapolation are given in the figure below. The extrapolation predicts the solubility of Pt to be less than 1ppb at  $<10^{-5} f\text{O}_2$ ; however, the data fall well above predicted values and show significant scatter. [1] conclude that Pt solubility at low  $f\text{O}_2$  cannot be interpreted from the data due to nugget contamination. The LA-ICPMS studies of Pt [2] and Re [4] choose the nugget-free portions of the time-dependent signal to interpret as the solubility (which corresponds to the lower bound of the scatter in the low- $f\text{O}_2$  data of [1]) and infer that bulk analysis is compromised by the inclusion of the nuggets. Our values for Pt solubility form an upper bound for the scatter observed in the data of [1] at  $f\text{O}_2 < 10^{-5}$  atm. Therefore, there is no large discrepancy between our results and prior observations, only a difference of interpretation. Our experiments suggest that the Pt nuggets were in solution at the P and T of the experiments and that the solubility of Pt is high.

The second challenge to conventional wisdom is that our experiments require diffusivities as rapid as  $10^{-4} - 10^{-5} \text{ cm}^2/\text{sec}$ . Because the scatter in [1] at  $<10^{-5}$  atm has no  $f\text{O}_2$  dependence, neutral Pt is possible as the species in solution at this very high abundance. Pt diffusivity may not be constrained by normal ex-

pectations for cations if neutrally speciated. For instance [5] has reported a diffusivity for neutral Ne of  $\sim 3 \cdot 10^5 \text{ cm}^2/\text{sec}$  in basaltic liquid at a temperature  $100^\circ\text{C}$  below ours. Ne has a larger effective atomic size ( $1.6 \text{ \AA}$ ) than neutral Pt ( $1.4 \text{ \AA}$ ) so that the diffusivities required to rationalize our observations are not extraordinary. By the precedent of Ne they could easily be considerably faster.

If our observations and inferences for Pt are correct then the implications for the mantle’s HSE budget are very important. Specifically, if the solubility and partitioning of Pt into the silicate is  $\sim 10^3$  or  $10^4$  higher than previously thought, then the “excess” Pt problem simply disappears. The equilibration of metal alloy with liquid silicate during core formation would not have depleted the mantle of Pt as much as previously believed. The analogous quandary of having to scavenge Pt from unreasonably large volumes of silicate magma to create many terrestrial magmatic Pt deposits would also be diminished if Pt is more soluble than is conventionally assumed. This potential resolution to the “excess” Pt problem may be too much of a good thing in that Pt may actually be “depleted” in the mantle with this new yardstick for core formation’s expected impact. This would not be so terrible as it is much easier to understand extra depletion of the mantle Pt from a multistage core formation process than it is to understand any mantle excesses.

**References:** [1] Borisov A. and Palme H. (1997) *GCA*, **61**, 4349-4357. [2] Ertel et al. (1999) *GCA*, **63**, 2439-2449. [3] Lindstrom D.J. and Jones J. H. (1996) *GCA*, **60**, 1195-1203. [4] Ertel et al. (2001) *GCA*, **65**, 2161-2170. [5] Lux G. (1987) *GCA*, **51**, 1549-1560.

