# Measuring the solubility of neutral nickel in silicate melts: Another experimental problem.

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**Introduction:** Presence of sub-micron nuggets of metal in suspension in silicate melts has hampered efforts to measure solubilities of nickel and platinum group elements in silicate melts. New experiments show that even when Ni nuggets are absent during an experiment, they can be introduced into the silicate melt during the quench when gas bubbles from the metal phase exsolve and "spew" sub-micron nuggets into the silicate melt phase. Under some conditions, this can produce effects that mimic those expected for quench-exsolution of neutral nickel soluble in the silicate melt.

**Background:** Formation of soluble neutral nickel in a silicate melt can be expressed according to the reaction $Ni^0$(melt) + $1/2O_2 \leftrightarrow$ NiO (melt), $K=[NiO]/[Ni^0][O_2]^{1/2}$, suggesting that neutral nickel must be soluble at some concentration in silicate melts [1, 2], perhaps occupying sites similar to those occupied by noble gases. If neutral nickel is sufficiently soluble, it has implications for magma evolution in systems at low $fO_2$ [3].

Attempts to measure neutral nickel in silicate melts have had a checkered history, with measurements complicated by presence of "nuggets" of metal in suspension in the melt [4-8], or in some cases inferred incorrectly based on electrochemical measurements, as shown by [1].

We have proposed previously that some of the metal nuggets observed in experiments may not have been in suspension during the experiment, but rather may have formed by exsolution during the quench [3, 9, 10].

If the nuggets form from soluble neutral nickel during quenching, then nugget size and density (but not total Ni concentration) should depend on quench rate. Such a case requires that solubility increases with increasing temperature (to accomplish the exsolution during quench).

[11] observe these conditions for Pt solubility in silicate melts at high pressure, and we have shown a similar effect for Ni solubility at 1 atm [3, 9, 10]. These observations appear to suggest that at least some of the metal nuggets observed in melt represent metal that exsolved from the melt during the quench.

Additional observations consistent with this interpretation include lack of nuggets in crystalline phases (suggesting the nuggets were not present during crystal growth, but formed during the quench) [9], observed $Ni^0$ in melts that began with no nickel present (failure of metal to settle out cannot account for its presence) [3, 9, 10], and presence of $Ni^0$ in crystalline phases even when nuggets are not observed [3, 10].

Observations less consistent with this interpretation include persistently heterogeneous distribution of nickel in the melt [3], and an increase in nugget size with increasing Al in the melt, at constant quench rate [3].

**New Experiments:** Samples were run in a 1-atm gas mixing furnace in graphite capsules in CO atmosphere to ensure absence of measurable $Ni^{2+}$. Ni was added to the experiment as Ni wire. Compositions were chosen with a high liquidus T for two purposes: 1) at higher T we expect higher solubility of neutral nickel (required if the nuggets are forming during the quench) and 2) we wanted a crystal mush at the experimental temperature to limit mobility of Ni nuggets.

Compositions were the following: For experiment Fo-Ni-1: 49.5 wt% $SiO_2$, 13.5% $Al_2O_3$, 19.3% CaO, 18.2% MgO + excess Fo grown in absence of any Ni (experimental T=1563ºC). For experiment SMA-1-P3redo: 34.5wt%$SiO_2$, 18.5% $Al_2O_3$, 47.0% MgO + excess spinel (experimental T =1645ºC). For VesBubble demo experiments, composition was 52.7 wt% $SiO_2$, 10% $Al_2O_3$, 2.0 CaO, 35.3% MgO (liquidus T~1575ºC, experimental T=1498ºC). Ni metal was added to the Vesbubble demo #1 experiment, but not to Vesbubble demo 2.

In experiment Fo-Ni-1, olivine crystals were pregrown in the absence of Ni to ensure an Ni-free starting condition. This ensured that any Nickel found in the olivine crystals must be due to soluble neutral nickel diffusing into the crystals during the experiment.

Experiments were quenched by dropping the capsules into water, yielding cooling rates near 170ºC/sec.

**Results:** With olivine or olivine plus spinel present as a crystal mush, nickel in the olivine is below our detection limit (Fig. 1). In addition, we reanalyzed experiment SCMA10-5-Niwire#1--which also had a crystal mush-- after applying Ag paint to mask surrounding metal stringers (Ni metal was removed before analysis, but in that experiment, metal stringers remained between the silicate sample and the graphite capsule). Concentration of Ni in the glass (in experiment Fo-Ni-1) was also below detection limit (3ppm±52 ppm 1$\sigma$ ).

No diffusion gradient of Ni into the pre-grown Ni-free Fo crystals of Fo-Ni-1 was observed.

Sample SCMA10-5-Niwire#1 was examined with XANES to see if neutral nickel with a signature different from metallic nuggets could be observed,which might indicate some neutral nickel in true solution in glass or olivine. The signature of the nickel did indeed suggest neutral nickel rather than divalent nickel, but it matched the signature of the Ni-C-Si alloy present in the nuggets, providing no indication of any neutral nickel in true solution. In addition, the concentration of nickel from the XANES analysis were much higher than expected from the EMP analysis, consistent with the interpretation that the x-ray beam sampled a larger volume than the electron beam and thus resulted in more fluorescence from metal surrounding the analysis spot (despite the presence of the Ag paint) or perhaps fluorescence from metal hidden beneath the surface.

These new results mean that concentration is not observed to increase with increasing T, as expected for quench-grown Ni nuggets (Fig. 1).

**Discussion:** The correlation between nugget size and quench rate suggests that these nuggets are introduced during the quench, as we previously said [3, 9, 10]. However, we now believe that this occurs when gases, exsolved from the metal phase during the quench, spew metal particles into the melt.

Gas bubbles are typically seen in all of our metal-silicate experiments after quenching. That the bubbles formed during the quench is suggested by bubbles being suspended in the middle of the metal and the silicate. That the bubbles are associated with the metal phase is suggested by the typical concentration of more or larger bubbles at the metal-melt interface. Figure 2 shows that the bubbles are less abundant in the absence of a metal phase, again suggesting that at least most of the gas phase is generated in the metal. Bubbles transport Ni nuggets on their inside surface (Fig. 3).

Spewing into the melt during quench accounts for the sharp drop in nuggets and apparent Ni concentration in experiments done in a crystal "mush" in which mobility of nuggets is limited. It accounts for the heterogeneous distribution of nuggets [3, 12, 13]. It accounts for the absence of metal nuggets in the crystalline phase except in quench rims [9]. It is consistent with the Ni nuggets observed on the inside surface of gas bubbles (Fig. 3), and with the observed generation of gas bubbles from the metal phase during quench (Fig. 2). It can account for the dependence of nugget size on quench rate, presuming that the rate of quenching affects the manner in which exolved gases at the metal-melt interface transport nuggets into the melt. To some extent it accounts for the dependence of nuggets on melt composition, presuming that the size of the spewed nuggets depends on the viscosity and surface tension of the melt. It does not account for the correlation of apparent melt concentration to Ni activity--rather than Ni concentration--as reported in [2].

**Summary:** Although we continue to maintain that neutral nickel must be present in silicate melts at some concentration, the "spewing" of metal particles into the melt, due to gas exsolution from the metal phase during the quench, means that we have not measured it.

**References:**

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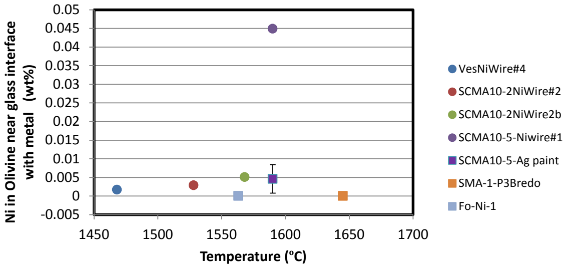

Figure 1 . Data from [3] are shown as circles. New data are shown as squares. 2σ uncertainty for new data are smaller than the symbol or as shown.

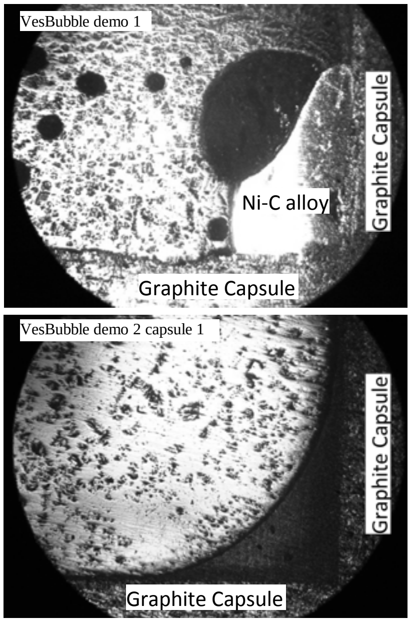

Figure 2 Bubbles formed in experiment with Ni metal but much less common (not observed in the image) in experiments without metal. Up during the quench was toward the top of each image.

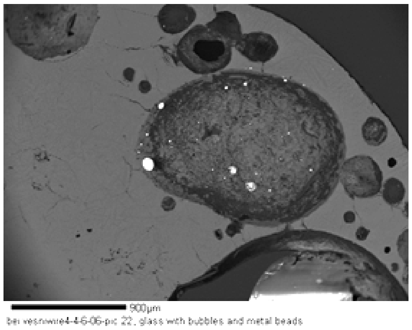

Figure 3 Ni nuggets on the inside surface of bubbles in the silicate glass.