**Incompatibility of Ni in Olivine at Low fO$_2$ and Consideration of Solubility of Neutral Nickel.** R. O. Colson, Dept of Anthropology and Earth Science, Minnesota State University Moorhead, Moorhead MN 56563, colson@mnstate.edu.

**Introduction:** New experiments show partition coefficients for Ni between olivine and melt to be less than 1 (incompatible) at temperatures above 1500°C and at low fO$_2$. These low partition coefficients are likely related to neutral Ni (Ni$^0$) in the melt, either in solution or as nano-particles that are mimicking equilibrium in some ways (such as by partitioning into olivine and producing a coherent dependence on T). However, experimental complexities continue to complicate the interpretation of these results. Even so, disentangling the experimental complexities is worthwhile both for application to petrogenesis and for improved understanding of fundamental melt chemistry.

**Experimental:** Experiments were done in 1-atm gas mixing furnaces at fO$_2$ values low enough that Ni$^{2+}$ concentrations in all phases are expected to be below detection limits (run in graphite capsules in a CO atmosphere with fO$_2$ values from 1.4 to 5.6 x 10$^{-16}$, depending on T). Experimental compositions were FeO-free (SiO$_2$-Al$_2$O$_3$-MgO-CaO) to avoid complexities due to variable concentration and valence of Fe. Melt compositions are given in Table 1. Silicate samples were initially Ni-free but were equilibrated with Ni wire (forming a molten Ni-C-Si alloy, 88.2wt%-10.2wt%-1.5wt% by EMP, 1500°C). Experimental temperatures ranged from about 1470°C to 1630°C. Samples were air or water quenched, with quench rates ranging from a few degrees C per second to about 170 °C per second. Ni analyses done by EMP involved careful determination of background concentrations and long counting times to achieve sensitivities down to about 20ppm. The Ni alloy was removed from the sample prior to analyses to avoid excessive fluorescence of Ni metal when nearby glass or olivine samples were analyzed.

Table 1: EMP analyses.

|  | Ves-NiWire | Ves-NiWire#4 | SCMA-10-2-Ni-wire#2b | SCMA-10-5-NiWire#1 | An90 Di10-8 Niwire#2 |
|---|---|---|---|---|---|
| SiO2 | 56.2 | 58.5 | 49 | 35.4 | 35 |
| Al2O3 | 7.8 | 8.2 | 17 | 16.3 | 40 |
| MgO | 31.2 | 28.7 | 30 | 31 | 2.2 |
| CaO | 4.5 | 4.5 | 3.5 | 17.3 | 24.8 |

**Nickel Partitioning:** Measured Ni partition coefficients were significantly below values expected from experiments done at higher fO$_2$ (e.g. [1]) and in most cases less than 1 (Fig 1). Incompatible Ni partitioning at low fO$_2$ has been reported before [2] and used to interpret Apollo 15 Green glass [3]. Low D values are presumed to be due to presence of neutral Nickel in
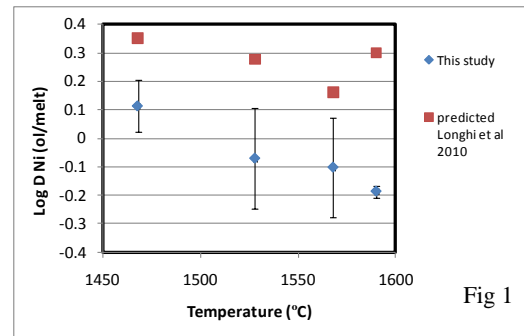


Fig 1

both melt and olivine, affecting the partitioning coefficient at low fO$_2$ regardless of the state of the neutral Ni. The importance of these low D values in natural petrogenesis depends on whether the amount of Ni$^0$ in the melt (as either small metal nuggets that become incorporated into silicate phases or as Ni$^0$ in true solution) is significant in comparison to Ni$^{2+}$ present. Although the experiments reported here were at low fO$_2$, the effect on systems at higher fO$_2$ can be predicted by taking into account contributions from both Ni$^{2+}$ and Ni$^0$ in the system according the expression:

D=(Ni$^{2+}$olivine + Ni$^0$olivine)/(Ni$^{2+}$melt + Ni$^0$melt)

Concentrations of both Ni$^{2+}$ and Ni$^0$ in melt and olivine for any particular Ni activity can be calculated from data given here and in [1, 4, 5, 6]. Results are shown in Fig. 2. The two curves derive from differences in apparent Ni$^0$ solubilities reported in [5] and [6]. Vertical bars show an fO$_2$ range from IW+1 to IW-2. A sharp change in D value is predicted, suggesting the effects observed in this report may be important at fO$_2$ values below IW+1.
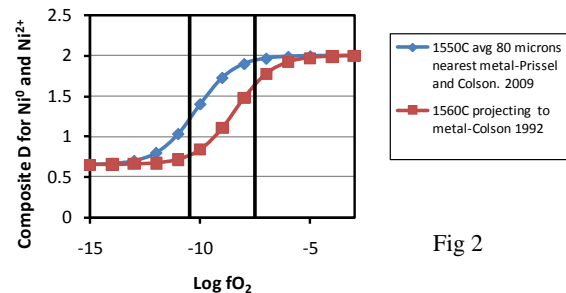


Fig 2

**Observations consistent with solubility of Ni$^0$ in silicate phases:** "Nuggets" of nickel metal are observed in most of these experiments ranging from hundreds of nanometers to a few microns in size. Several observations suggest that at least some of these nuggets form during the quench by exsolution from the melt.

1) The size and spacing of the nuggets are correlated to the quench rate in a way consistent with formation during the

quench [5, 7, present study].  Similar observations have been made for Pt nuggets [8].

2)  Nuggets are not observed to occur in crystalline phases except as incorporated into quench growth [7, present study].  If nuggets existed in suspension prior to quench, they should have become entrained in olivine grains.

3)  The measured concentration of $Ni^0$ (whether in solution or not) increases with increasing temperature [5, 6].  This relationship is prerequisite to nuggets forming during the quench, but also suggests a behavior more consistent with solution than with simple suspension of nuggets prior to quench.

4)  A dependence on temperature of $Ni^0$ solubility in olivine was observed in the present study (Fig. 3).  Nuggets are not observed in the olivine, and so presence of $Ni^0$ there, and it's dependence on temperature, is strongly indicative of solution rather than suspension of nuggets.  The concentration of $Ni^{2+}$ expected for the experiments reported in Fig. 3 is two and a half orders of magnitude below the observed concentrations (calculated from activity and partitioning values from [1, 4, 9]).



Fig 3
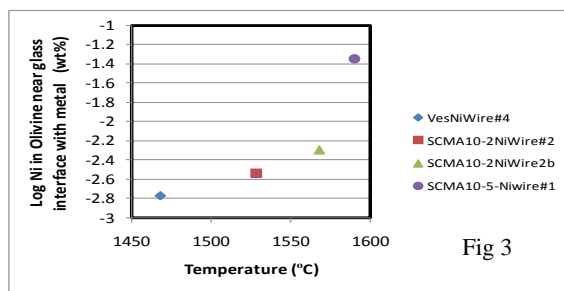
5)  There was no nickel added directly to the silicate phases of these experiments or the experiments of [5] and [7].  Nickel was added by equilibrating with Ni wire.  Thus, high Ni concentrations cannot be rationalized as resulting from nuggets that don't have time to settle out.  [6] reports that bracketing reversal experiments from both low and high initial Ni concentrations converge toward a common value.

6)  [6] shows that the concentration of Ni in the melt is correlated to activity of Ni in the metal phase and not to its concentration.  Suspended metal nuggets should result in correlation to concentration.

**Experimental complexities that need to be addressed before greater confidence in $Ni^0$ solubility can be acheived:**

1)  The distribution of observed nuggets is highly heterogeneous.  Highest concentrations are often in central areas distant from both the Ni-C alloy and from the edges of the silicate sample in contact with a gas phase.  Sometimes the distribution suggests either settling or movement by convection.

2)  The EMP-determined concentrations of $Ni^0$ not obviously associated with nuggets, including in olivine, are highly heterogenous.  In general, concentrations decrease away from the metal phase toward the glass-gas phase contact.  This has been interpreted as resulting from volatile loss of the $Ni^0$ from the melt [5, 6, 7] either during the experiment or during the quench.  However the nature of this volatile phase isn't known and the volatile loss hasn't been demonstrated.   In the present experiments, $Ni^0$ concentrations in melt inclusions in Ol are significantly higher than in other areas of the melt, perhaps preserving a pre-quench concentration.  Concentrations are also higher on the side of olivine grains away from the metal phase, suggesting the metal phase may also act as a $Ni^0$ sink during the quench.  This heterogeneity and complexity introduces signficant doubts and questions about the experimental results.

3)  Although the size of beads is generally correlated with quench rate, the bead size also appears to depend on sample composition in unexpected ways.  Fig. 4 shows correlations for different compositions.  In general, the bead size at any particular quench rate increases as the concentration of $Al_2O_3$ increases.



Fig 4
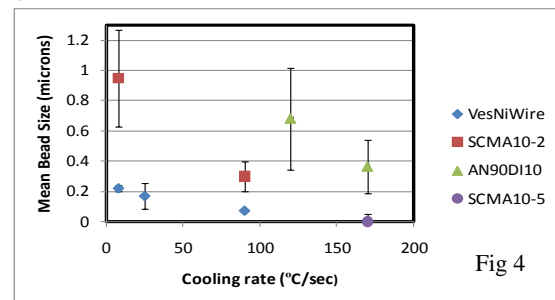
4)  Vesiculation occurs in the melt on quenching [5, 10].  This vesiculation causes significant turbulence during quench.   The origin of the quench gas is not known, but understanding the gas and its origins probably bears on understanding of the $Ni^0$ in silicate phases.

5)  $Ni^0$ concentrations reported in [6] are significantly higher than more recent measurements [5, 7].  Concentrations measured more recently often depend on quench rate (concentrations are a facter of 3-4 higher for the highest quench rates) or how nickel was added (adding Ni as NiO increases observed size and number of Ni nuggets).

**Conclusions:**  $Ni^0$ is measured in olivine and silicate melts equilibrated with Ni metal, producing Ol/melt D values that are less than 1.  Although presence of $Ni^0$ in olivine is not easily attributed to metal nuggets in suspension in the melt, experimental complexities continue to hinder a clean interpretation of the nature of the $Ni^0$ species in melt or olivine.

**References:** [1] Longhi et al (2010) GCA 74, 784-798. [2] Steele et al (1991) LPS XXII 1317-1318.  [3] Steele et al (1992) GCA 56, 4075-4080. [4] Ertel et al (1997) GCA 61, 4707-4721. [5] Prissel and Colson (2009) LPS XL 1172. [6] Colson (1992) Nature 357, 65-68.  [7]  Nesheim et al (2007) LPS XXXIIX 1719. [8] Cottrell and Walker (2006) GCA 70, 1565-1580. [9] Hultgren et al (1972) Selected Values of the Thermodynamic Properties of binary alloys. [10] Colson (1993) LPS XXIV 321-322.