

Neutral Nickel in Silicate Melts: Characterization of experimental results. T. Nesheim¹, R. O. Colson², A. Cota, A. Larson, J. Rock, and C. Johnson, ¹Minnesota State University Moorhead, ²Minnesota State University Moorhead, Dept of Anthropology and Earth Science, colson@mnstate.edu.

Introduction: We have equilibrated Ni metal with silicate melt at 1 atmosphere pressure under reducing conditions (C-CO buffer) in an effort to better understand the significance of small metal beads often found in metal-melt equilibration experiments subsequent to quench [1, 2]. If the metal beads form during the quench and were present as dissolved Ni⁰ during the experiment, then the presence of neutral nickel in solution is likely to influence nickel partitioning. Alternatively, metal beads that occur naturally in suspension might also have important implications for petrogenesis in the presence of a metal phase. We examine the concentration, density, and size of Ni metal beads in the melt as a function of cooling rate and the form in which the Ni is added to the experiment. For all experiments, nickel metal beads occur throughout quenched silicate glass in sizes ranging from <0.07 microns radius to 5 microns. Results are consistent with the interpretation that most of the metal beads formed during the quench and were present in solution during the experiment. Our observations have significant implications for metal-silicate and silicate-silicate partitioning of Ni under reduced conditions such as may have existed during early core formation on Earth or during some magmatic processes on the Moon (e.g. 3, 4).

Experimental Methods: Five experiments were done in a 1-atm gas mixing furnace at temperatures ranging from 1477 to 1562°C. Oxygen activity was maintained at a low value by running experiments in graphite capsules in a CO atmosphere. The target composition of four experiments (VesNiWire 1, 2, and 3 and VesNiPowder 2) was: 57.5wt% SiO₂, 7.2% Al₂O₃, 31.3%MgO, and 4%CaO. One experiment (ggNi1) had a composition of 48.4%SiO₂, 8% Al₂O₃, 25.7%MgO, and 16.1%CaO. Experiments contained no reducible FeO or NiO. In an effort to determine the origin of small metal beads, we examined the effects of the following variables: Slow quench vs. fast quench and Ni added as a single large chunk (wire) vs. Ni added as a disseminated powder in the glass (40-90µm dia.). Subsequent to quench, the silicate glass was separated from the main Ni metal bead (to prevent x-rays from nearby metal producing errant microprobe results), and mounted in epoxy. Samples were cut, polished and carbon coated for examination under an electron microprobe. Submicron-sized metal beads were found and mapped using backscattered electron imaging (BEI). The size of beads was deter-

mined by measuring the apparent Ni concentration over a known area of the sample that contained a single bead. We also measured Ni concentration in areas where no beads were observed. Beam currents of 30-50nA and long counting times on both peak and background positions were used to achieve microprobe sensitivities down to about 20ppm Ni. One sample was analyzed by SIMS at Washington University in St. Louis.

Experimental Results: Electron microprobe analyses (EMP) were done in regions in which no metal beads were observed in the silicate glass. EMP results (averaging values from three experiments which were identical within analytical uncertainty), are comparable to SIMS results (Fig. 1). In all cases, Ni concentrations in the silicate glass far exceed values attributable to NiO at the fO₂ values of these experiments. Ni concentrations reach their highest values where silicate glass was in contact with Ni metal, and decrease to near zero at the far edge of the glass. Intermediate concentrations appear constant at about 0.002% (based on EMP and SIMS analyses not shown in Fig. 1). Each EMP point plotted in Fig. 1 is the average of 14-26 points. Standard deviation of these analyses exceeded the standard deviation attributable to analytical uncertainty, suggesting that Ni may be heterogeneously distributed (such as due to presence of metal beads too small to be detected under BEI). However, the consistency of concentrations among the four different experiments in Fig. 1 suggests either a thermochemical control of the concentration (the Ni was present in solution prior to quench), or a dynamic control of the Ni beads such that an equilibrium-like concentration is achieved.

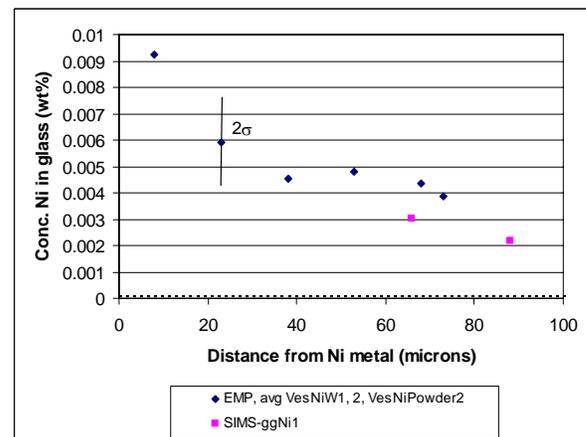


Fig. 1 EMP and SIMS analyses of regions where no metal beads are seen. Dashed line represents expected NiO concentration. Ni metal source was removed prior to analyses so that it would not influence results.

The sharp decrease in Ni concentration going away from the Ni metal source toward the edge of the silicate glass is also seen when considering density of metal beads (Fig. 2). This decrease indicates that the edge of the melt is acting as a Ni sink, suggesting that Ni is being lost as a volatile species. This observation is consistent with the interpretations of [5].

VesNiWire2 did not start out with any metal beads or reducible metal oxides. Therefore, the presence of small metal beads in this experiment argues either that the zero-valent Ni is soluble in the melt prior to quench, or that small metal beads are produced, rather than consumed, at the melt-metal interface. Experiment VesNiPowder2 started with Ni metal powder dispersed in the sample, yet the concentration of beads on quench is actually lower than for VesNiWire2, again inconsistent with a model in which dispersed metal beads gradually decrease toward zero as equilibrium is approached. VesNiPowder2 was roughly 82 degrees cooler and run without a cap on the graphite capsule, which may explain the difference in metal bead concentration.

If the metal beads form during the quench by exsolution of Ni dissolved in the melt (as opposed to the metal beads being in suspension in the melt prior to quench), then the size and density of the metal beads should be dependent on quench rate. Experiment VesNiWire 2 was air quenched at a rate of several tens of degrees per second. VesNiWire3 was allowed to cool in the furnace at an average rate of 100 degrees per minute for the first minute, then 44 degrees per minute thereafter. If the Ni were dissolved in the melt prior to quench, a slower cooling rate might be expected to produce an increase in Ni bead size and a decrease in Ni bead density while leaving the overall Ni concentration the same. This relationship was observed, as shown in Fig. 3, arguing that the reduced Ni is actually in solution prior to quench. One particularly large metal bead (10 μ m in diameter) observed in VesNiWire3 was not included in the calculation of average bead size because it was so much larger than other observed beads.

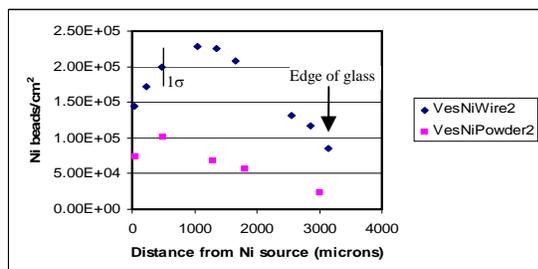


Fig. 2 Density of metal beads observed by BEI. No beads were initially present in VesNiWire2. Ni was added as powder in VesNiPowder2.

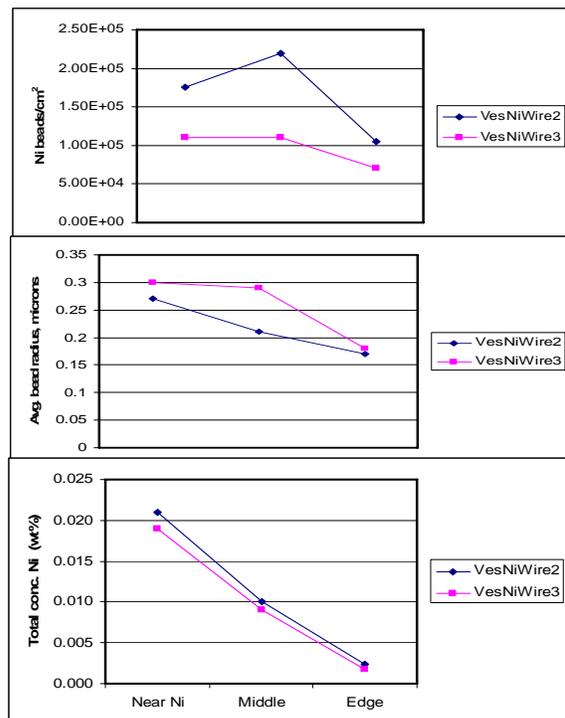


Fig. 3 Density of beads is lower and size larger in VesNiWire3 which was quenched at a much slower cooling rate. Total concentration of Ni (calculated from bead size and density and the EMP analyses above) is roughly the same.

VesNiWire1 was run at 1477°C, and olivine crystallized prior to quench. If Ni metal beads were present in suspension prior to quench, some of these should have been incorporated into the olivine as inclusions. However, Ni metal beads are very rare in the olivine, and, where they do occur, they are exclusively in the very outermost rim of the olivine, consistent with formation during the quench (Fig. 4).

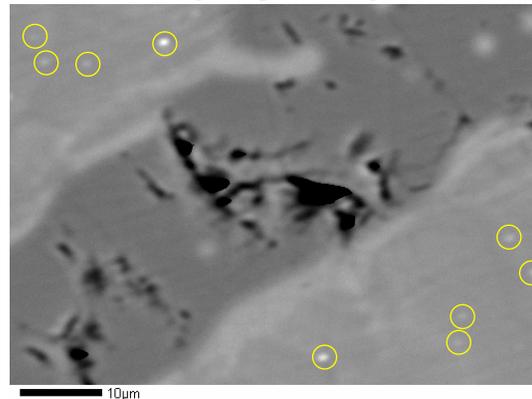


Fig. 4. Metal beads (circled bright specks) are dispersed in the quench crystals and glass, but do not occur in the olivine crystals formed prior to quench (darker in this BEI image).

References: [1] Brenan J M, McDonough W F, and Ash R (2005), *Earth Planet. Sci. Let.* 237, 855-872, [2] Borisov A and Walker R J (2000) *Am Mineral.* 85, 912-917. [3] Steele A M, Colson R O, Korotev K L, and Haskin L A (1992), *Geochim Cosmochim Acta* 56, 4075-4090. [4] Ehlers K E, Sisson T W., Recca S I, and Grove T L (1992). *Geochim. Cosmochim. Acta*, 56, p. 3733 - 3743. [5] Colson, R. O. (1992), *Nature* 357, 65-68.