Loop technique: Dynamics of metal/melt equilibration

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Summary

I report here the experimental results on the dynamics of equilibration of silicate melts suspended from Ni loops of different diameters at $1400\,°C$ and at constant oxygen fugacity. It is found that saturation of silicate melt of anorthite-diopside eutectic composition with Ni is reached during the first few hours because the nickel ions in the melt diffuse extremely rapidly. Fast convection usually results in relatively homogeneous Ni content throughout the sample for loops with diameters $3.2–4.0\,mm$. Hence, glass homogeneity with respect to an element of interest may not be sufficient evidence that metal/melt equilibrium is reached. It is demonstrated that central parts of Ni diffusion profiles in samples with diameter as low as $2.6\,mm$ are also "flattened" by convection. Possible driving forces of convection in a loop sample are discussed.

Zusammenfassung

Die Loop-Technik: Dynamik der Metall/Schmelze Äquilibrierung

Hier werden die experimentellen Ergebnisse zur Äquilibrierungs-Dynamik von Silikatschmelzen vorgelegt. Diese wurden bei konstanter Sauerstoff-Fugazität von Ni-loops verschiedener Durchmesser bei $1400\,°C$ suspendiert. Es zeigt sich, dass Ni-Sättigung von Silikatschmelzen von eutektischer Anorthit-Diopsid-Zusammensetzung schon während der ersten Stunden erreicht wird, da die Ni-Jonen ausserordentlich rasch in die Schmelze diffundieren. Rasche Konvektion führt zu relativ homogener Nickel-Verteilung in der Probe wenn loops mit $3.2–4.0\,mm$ Durchmesser verwendet werden. Homogene Verteilung eines Elementes im Glas bedeutet nicht notwendigerweise, dass Gleichgewicht zwischen Metall und Schmelze erreicht wurde. Es wird gezeigt, dass zentrale Teile von Nickeldiffusions-Profilen in Proben von bis zu $2.6\,mm$ Durchmesser auch durch Konvektion "abgeflacht" sein können. Mögliche Kräfte die zur Konvektion in loop-Proben führen können werden diskutiert.

Introduction

Convection in experimental liquids is known to be a major problem in the investigation of the physico-chemical properties of silicate melts, such as density, viscosity, and diffusion. In the latter case misinterpretation of the concentration profiles, affected by convection, may result in erroneous conclusions. For example, *Kress* and *Ghiorso* (1993) studied multicomponent diffusion in the MAS and CMAS systems and concluded that an n−1 dimensional diffusion matrix was not sufficient to explain some features of the experimental profiles. Later, *Richter* et al. (1998) conducted similar experiments with MAS liquids and found that, in some cases, convective fingering took place in capsules as narrow as 0.8 mm. They also suggested that ''some of the diffusion profiles used by *Kress* and *Ghiorso* (1993) to obtain their diffusion matrix might have been affected by double-diffusive convection''. *Kress* and *Ghiorso* (1993) themselves were aware of possible fingering and applied the criteria of *Vitagliano* et al. (1992) to prove the stability. Convection was not predicted in any of their experiments.

Here I present the results on the melt convection in metallic loops of small diameters, which are widely used in 1-atm experiments. The difference of experimental profiles of a trace element (Ni on low percentage level was chosen as an example) from profiles predicted by the appropriate diffusion model was used to recognize convection. Actually, the present experimental design (melt in a loop) is much simpler than the one usually used in experiments on the diffusion in silicate melts (two adjoining melts of different compositions in one capsule) and seems to provide no reasonable driving force for convection. The convection found under such conditions results in the conclusion that the stability tests based on calculations should probably be applied with caution.

Additionally, the present experiments provide an insight into the dynamics of metal/melt equilibration in the loop technique, which has become the predominant method for measuring solubilities and activities of iron group and noble metals in silicate melts (e.g., *Holzheid* et al., 1994; *Borisov* et al., 1994; *Borisov* and *Walker*, 2000).

Experimental procedures

The experiments were conducted in a Deltech vertical-tube one-atmosphere furnace, where fO_2 was controlled by CO/CO_2 gas mixtures. A $PtRh_6/PtRh_{30}$ thermocouple in the working furnace and a ZrO_2 solid electrolyte oxygen sensor were employed for measuring temperature ($\pm 2\,°C$) and fO_2 (± 0.1 log unit) during experimental runs.

The bands for loops were cut from Ni foil (0.125 mm thick, 99.9+% purity, Heraeus, Hanau), and loops with nominal diameters 2.0, 2.6, 3.2 and 4.0 mm were prepared, designated 20ii, 26ii, 32ii and 40ii, respectively. All experiments are conducted in two steps. First, the initial silicate powder of anorthite-diopside eutectic composition was mixed with an organic glue and inserted into the loops that were then suspended on a ceramic disk and transferred into the furnace. They were melted for about 1 hour at $1420\,°C$ and $10^{-10.2}$ atm fO_2. Under these conditions, Ni solubility is expected to be below 700 ppm (*Holzheid* et al., 1994)

Table 1. *Annealing time (t hours) of experimental samples with nominal loop diameter (d mm)*

Sample	d	t
4008	4.0	3.0
3208	3.2	3.0
2008	2.0	3.0
4010	4.0	2.0
3210	3.2	2.0
3211	3.2	1.0
2611	2.6	1.0
4009	4.0	0.5
3209	3.2	0.5
2609	2.6	0.5

All samples were annealed at $1400\,°C$ and $10^{-7.65}$ atm fO_2

and the melt may be effectively considered to be "Ni-free", provided that annealing then continues under conditions where solubility is in the percentage level. Anticipating that the mathematical treatment of the diffusion might use the model of a circular cylinder, the main purpose of this stage was to produce perfect cylindrical loops with bubble-free glasses. Ten of the best loops were chosen for the second step. Two or three loops of different diameters were simultaneously annealed at $1400\,°C$ and $10^{-7.65}$ atm fO_2 for 0.5, 1.0, 2.0 and 3.0 hours (Table 1), then quenched by quickly withdrawing the ceramic disk from the hot zone to the top of the furnace. The whole samples (glass cylinders in Ni loops) were then mounted in epoxy and polished. At least 1/3 of the loop's thickness was polished away to minimize edge effects and to make the model of an infinite cylinder more suitable.

The Ni profiles across the glasses were determined using a Cameca Camebax electron microprobe (JSC/NASA, metallic Ni as a standard). Operating conditions were 15 kV accelerating voltage, a beam current of 20 nA, a beam spot of about 6–8 μm, and 20 sec counting times. Analytical error was always below 3 percent. The Ni profiles through the centers of the cylinders were measured every 20 μm, thus about 100 to 200 points were analyzed in every sample.

Results and discussion

Annealing for three hours at $1400\,°C$ was found to be sufficient to reach complete saturation of silicate glass with Ni. Indeed, the samples 4008, 3208 and 2008 all demonstrate homogeneous and very similar Ni contents, almost within the error limits: 1.36 ± 0.07, 1.41 ± 0.07 and 1.52 ± 0.07 wt.%, respectively. The equation on Ni solubility in the same melt composition at $1400\,°C$ (*Borisov* and *Walker*, 2000) obtained by equilibrating pure Ni and Ni-rich Ni-Os loops with silicate liquid in an fO_2 range between 10^{-12} and 10^{-6} atm (log Ni, ppm $= 0.48 \cdot \log fO_2 = 7.80$), gives essentially the same results: 1.34 ± 0.15 wt.% (in this case the error is equivalent to an experimental $\log fO_2$ error of ±0.1 log-bars). The equation from *Holzheid* et al.
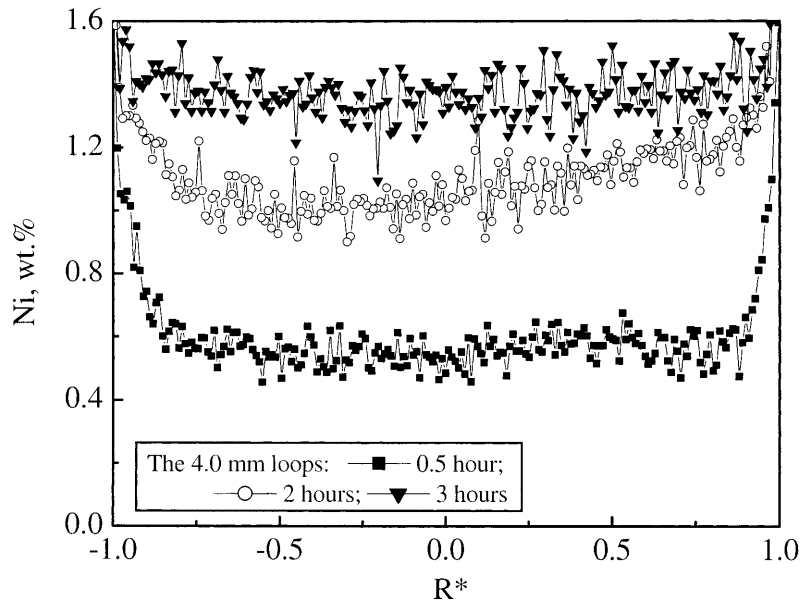
Fig. 1. Ni content (wt.%) across the samples of 4.0 mm diameter for three different annealing times. $R^* = R/R_0$ is a dimension-less parameter, where R_0 is a loop radius

(1994) gives an even lower solubility (0.95±0.10%), perhaps because of considerable extrapolation beyond the experimental range where the equation was obtained. For further calculations I will assume for these experimental conditions $C_S = 1.52$ wt.%.

Fast equilibration of Ni loop with silicate melt of anorthite-diopside eutectic composition is not very surprising. *O'Neill* and *Eggins* (1999) also reported that at the same temperature (1400 °C), equilibrium of Fe, Ni, Co, Mo, and W loops with silicate melts in the system CaO-MgO-Al_2O_3-SiO_2-TiO_2 may be reached within 4 hours.

Another interesting result is the presence of unequivocal convection in loops of large diameter. Figure 1 displays Ni profiles in 4.0 mm loops annealed for 0.5, 2 and 3 hours. These profiles are relatively flat (excluding the outermost 5 percent of the sample diameter) but reveal very different levels of Ni content ranging from 0.56±0.10 wt.% for the 0.5-hour experimental glass up to 1.36±0.07 wt.% for the 3-hour experiment. The diffusion rate apparently is the limiting factor but, being supplied by diffusion, Ni thoroughly mixes by convection through most of the sample.

Figure 2 displays Ni profiles for 3.2 mm loops annealed for 0.5, 1, 2, and 3 hours. It also exhibits evidence for convection, which normally results in relatively flat profiles. Occasionally, however, profiles may be irregular such as the one of sample 3209 (0.5 hour), with a more diffusion-like left half and a more convection-like, relatively flat, right half. Figure 3 presents the Ni profiles for 2.6 mm loops with 0.5 and 1 hour experimental durations. For samples with such small diameter, it was anticipated that the diffusion profiles were not complicated by convection.
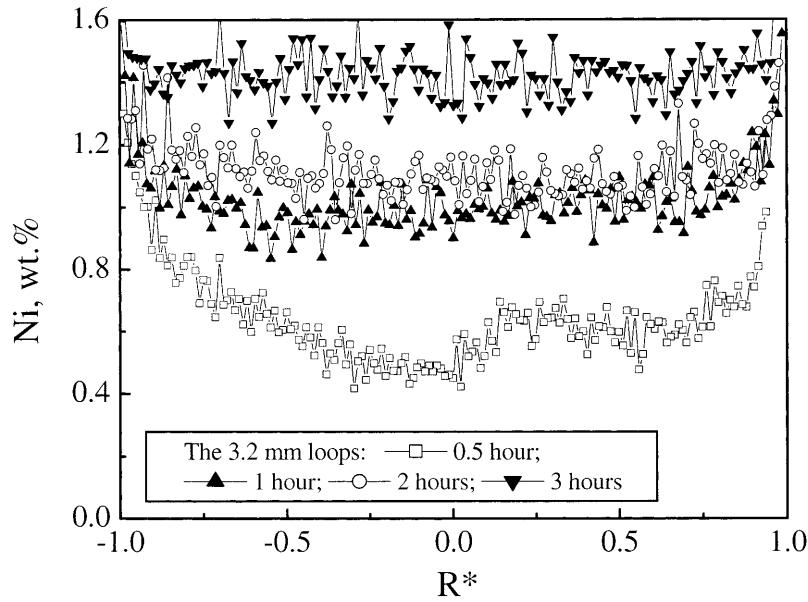
Fig. 2. Ni content (wt.%) across the samples of 3.2 mm diameter for four different annealing times
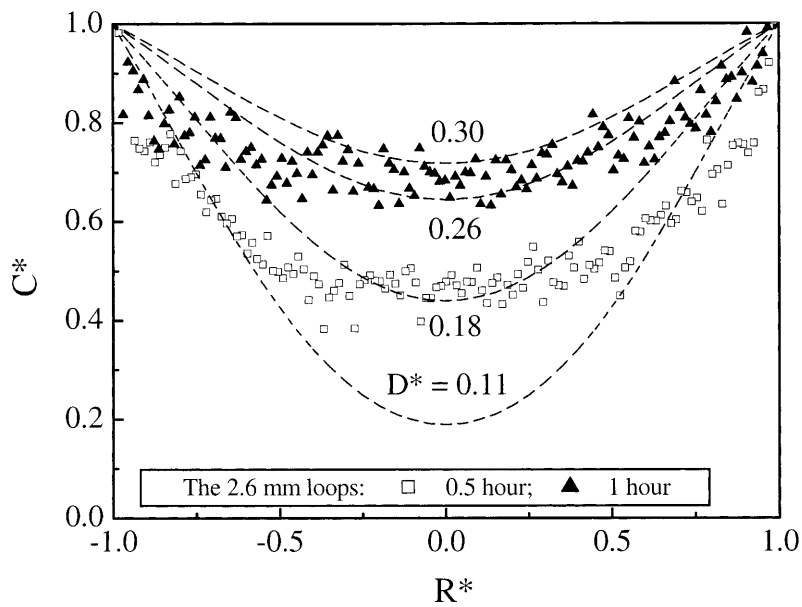

Fig. 3. Ni profiles across the samples of 2.6 mm diameter for two different annealing times. $C^* = C/C_S$ is a dimension-less parameter, where C_S is a saturation concentration (see text for details). Theoretical profiles for the model of infinite circular cylinder (a few different D^* values) are shown with dashed lines for comparison

Mathematical treatment of Ni profiles in 26ii samples

The most suitable mathematical treatment for melts in a round loop is to assume an infinite circular cylinder in which diffusion is everywhere radial. In practice, however, the loops have a finite thickness. Nevertheless, all loops were prepared from Ni ribbons (not wire) up to 1.2 mm wide and the glasses had the shape of cylinders with flat to only slightly spherical surfaces, so one can expect this model to be valid as a first approximation. The equation is less complicated when written in terms of three dimension-less parameters: $D^* = Dt/R_0^2$, $R^* = R/R_0$ and $C^* = (C - C_0)/(C_S - C_0)$, where D is the diffusion coefficient, t is the duration of the experiment, R_0 is the radius of the loop, R is distance in the cylindrical coordinate system, and C_0, C_S, and C are the initial concentration, saturation concentration, and the concentration in the cylinder at a distance R from the loop, respectively. When $C_0 \approx 0$, $C^* = C/C_S$. For the conditions $C = C_S$ at $R = R_0$ for $t \geq 0$, $C = C_0$ at $0 < R < R_0$ for $t = 0$, one obtains

$$C^* = 1 - 2 \Sigma_{n=1}^{\infty} \ \exp(-D^* \beta_n^2) \cdot J_0(\beta_n R^*)/\beta_n J_1(\beta_n)$$

where $J_0(x)$ is the Bessel function of the first kind of order zero, β_n are the positive roots of the equation $J_0(\beta) = 0$, and $J_1(x)$ is the Bessel function of the first order. The suggested formula is a slightly modified version of equations from *Crank* (1975) or from *Carslaw* and *Jaeger* (1959, section 7.6). I used in my calculations $n = 20$ but found that even the first 10 terms would be sufficient for any reasonable accuracy.

I normalized the Ni content to C_S and compared the experimental data with a few theoretical profiles for different D^* values. One can see that there is no such theoretical profile that will match the whole range of experimental data, and the central parts of the experimental profiles look as if they are "flattened" by convection.

Possible driving forces of convection in a loop sample

One of the main problems in the technique of interdiffusion of two liquids is known to be the suppression of convection, especially if the two melts have different densities (e.g., *Richter* et al., 1998). That should not be the case here: there is only one melt in a loop with only a small gradient in Ni concentration/density from the outermost layers to the center. Using the partial molar volume data of the melt-forming oxides (*Lange* and *Carmichael*, 1987; *Bottinga* et al., 1982) I calculated that a Ni-saturated melt (1.5 wt%) will be only 0.5 percent denser than a Ni-free melt of the same major element composition, so it is unlikely that convection is driven by such a small density difference. Two alternative explanations of existing convection may be suggested.

In the present experiments, fO_2 was controlled by a CO/CO_2 gas mixture flowing from the bottom to the top of the furnace with an average linear velocity of about 0.8 cm/sec. This flow rate is believed to be close to the optimum rate for fO_2 buffering (*Darken* and *Gurry*, 1945). However, it does not mean that the gas flow should be completely laminar. The thermal gradient in the working zone of a Deltech 1-atm furnace does not exceed 1 °C/cm. Nevertheless, at the 1400 °C level, the temperature in the furnaces only 3 cm below the hot spot is about 10 °C

lower. One may suggest that fluctuations in gas temperature due to turbulent flow might be too fast to be recorded by the thermocouple, but sufficient to trigger convection.

Another possibility is related to the deviation of the loop geometry from that of an ideal cylinder. As mentioned above, some experimental glasses had the shape of cylinders with slightly spherical surfaces. Although the loops themselves appeared ideally rounded, these spherical surfaces were asymmetric with the highest spots dislocated relative to the axis of the cylinder. The surface tension on the free surface of the melt in such a sample must also be asymmetric, so convection driven by a surface tension gradient (*Scriven* and *Sternling*, 1964) may not be excluded.

Thus, independent of the cause, convection in silicate loops of even relatively small diameters appears to be a reality.

Glass homogeneity as a criterion of equilibrium: a revision

Most experimentalists working with metal/melt systems, using either the loop technique or other containers, consider glass homogeneity with respect to the element of interest as a criterion for a close approach to equilibrium (e.g., *Borisov* et al., 1994; *Holzheid* et al., 1994; *Jana* and *Walker*, 1997). Figures 1 and 2 clearly demonstrate that homogeneity alone is not sufficient proof that equilibrium between a metal and a silicate melt at given P-T-fO$_2$ conditions was reached. At very high temperatures in the presence of a high thermal gradient, e.g. in piston-cylinder or multi-anvil apparatuses, convection may homogenize much smaller volumes of melt than in loop experiments. One can argue that even in the example shown in Fig. 1, the outermost 100 to 150 μm of the samples still reveal some kind of concentration gradients. To analyse Ni on a percentage level in experimental glass equilibrated at 1 atm is rather straightforward. The problem is obviously more severe when the element of interest is present only in trace element concentrations. For example, *Borisov* et al. (1994) and *Holzheid* et al. (1994) investigated metal solubilities at ppb- and ppm concentration levels and used a bulk technique such as instrumental neutron activation analysis. (e.g., *Borisov* et al., 1994; *Holzheid* et al., 1994). For such experiments, it is common practice to simply remove the outermost 100 to 300 μm of the glass cylinders (i.e. the previous loop/melt boundary layers) to exclude any surface contamination. Researchers working with laser ablation ICP-MS (with beam diameters around 50 to 100 μm) or microprobe in scanning mode also endeavour to avoid analyses close to the metal loop. The microprobe scanning mode is often used to integrate poorly quenched products of high-pressure experiments (e.g., *Jana* and *Walker*, 1997). And at last, it is well known that microprobe analysis can be biased by secondary fluorescence, especially at low concentration levels, shallow takeoff angles, and/or high accelerating voltages (e.g., *Heinrich*, 1981). I do not challenge the results of the work cited above. *Borisov* et al. (1994) and *Holzheid* et al. (1994) proved equilibrium by reversal with Pd, Ni and Co, and *Jana* and *Walker* (1997) demonstrated the lack of variation in metal/silicate partitioning in experiments with different run duration. Nonetheless, I emphasize that glass homogeneity alone should not be taken as a criterion for attainment of equilibrium.

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