Solubilities of nickel and cobalt in silicate melts in the presence of graphite and (CO,CO_2) fluid at 1350–1400°C and 7–15 kbar

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Theories of the formation of the Earth strongly suggest that the Earth should have been substantially molten during and immediately after accretion, when molten alloy and molten silicate underwent gravitational separation. It is expected hat during large-scale melting of the carbon-bearing mantle carbon-bearing liquids would be less effective at depleting silicate liquids in siderophile elements than C-free liquids. Nickel and cobalt show a modest reduction in siderophility at graphite saturation determined at 50–80 kbar and 2000–2300°C (Jana and Walker, 1997). This study was undertaken to exam the effect of pressure and elemental carbon and (CO,CO_2) fluid on equilibria between coexisting silicate and (Ni, Co) metallic carbon- bearing liquids at 7–15 kbar and 1350–1400°C. Recently it has been proposed that carbon's volatility is strongly pressure-dependent (Wood, 1993). It is expected that addition of free carbon and CO,CO_2 to the system will effect the apparent partition coefficient by diluting the liquid metal with carbon and possible formation of metallic carbon- bearing species in the melt and the CO-CO_2 varpor phase (Kadik and Holloway, 1997).

Experiment

The high pressure experiments were performed with a non-end-loaded piston-cylinder apparatus using NaCl-pyrex solid medium assemblies. The capsule assemble consisted of two capsules (an outer welded Pt -capsule and inner graphite capsule) was used throughout experiments. The silver oxalate isolated from samples was used as the CO_2 and O_2 source. Details of the experimental technique are given in Jakobsson and Holloway (1985). Experimental conditions, electron microprobe analyses and results are presented in Table 1. Both silicate and carbon - bearing metal liquids, on quenching, formed discrete, relative large masses of metal intergrowth and glass with a few clinopyroxene crystals in some runs. The 15 kbar experiment was about 90% crystalline. Graphite occurred both as stable crystals in contact with silicate and metal melts and as quench crystals in the metal phases. The Ni and Co carbon -bearing alloys consisted of a quench texture of two metals (Fig. 1). One metal phase was enriched in Pt (5–10 wt.%) and low in carbon (0.5 wt.%), while the other phase was low in Pt (0.1– 2 wt.%) and high in carbon (1.5 wt.%). Either Ni or Co made up the remainder of the metal phases the carbon contents are minimum estimates because a significant amount of quench graphite exsolved from the metal.

Discussion.

The transition of a neutral metal atom from metal into silicate melt is accompanied by oxidation according to the following equation:

$$M \text{ (solid or liquid metal)} + (n/4) \times O_2 = MeO_{n/2} \text{ (liquid silicate)} \quad (1)$$

where n is the valence of the metal ion. The equilibrium constant of reaction (1) is given by

$$K = [(X(MeO_{n/2}) \times \gamma(MeO_{n/2})]/[a(Me) \times (f_{O_2})^{n/4}] \quad (2)$$

where X_i, a_i and γ_i denote mole fraction, activity, and activity coefficient ($a_i = \gamma_i \times X_i$) (liquid silicate).
To evaluate the importance of the carbon and the pressure effect on element partitioning we compare our data with D(metal/silicate) of Ni and Co at normal pressure. For 7 and 10 kbar and 1350–1400°C in the presence graphite and (CO, CO_2) fluid and the given f_{O_2} metal partitions less strongly into the silicate melts then at atmospheric pressure in the absent of carbon (Table 1). At constant f_{O_2} the effect of pressure on the equilibrium (1) is given by: = $\bar{V}(MeO_{n/2}$, liquid silicate) - $\bar{V}$ (Me, liquid metal) > 0. The positive value of ΔV will cause the reaction (1) to shift to the left with increasing pressure, which effect we observe. However, the apparent partition coefficient will also be lowered if the activity of Me is lowered in the metal phase. The metal phase in our runs is 90–98 wt.% of either Ni or Co which translates into a mole fraction range of 0.90 to 0.96. Unless Ni or Co exhibit a strong

TABLE 1. Electron microprobe analysis of experimental products in the Ni and Co partitioning experiments and calculated Ni, Co- metal/silicate partition coefficients at P = 7–15 kbar, T = 1350–1400°C in the presence of graphite and at P = 1 bar, T = 1350°C for the carbon-free Ab-An-Di system

Metal	P, bar	t, °C	$-\log f_{O_2}$	NiO, CoO in melt, wt.%	Ni, Co in metal, wt.%	C in metal, wt.%	*D*(met/sil)
Ni	10000	1350	8.18	1.01± 0.09	90.1± 0.05 (L) 99.4± 0.05 (D)	0.69± 0.05 (L) 1.46± 0.05 (D)	95.8 ± 7.5
Ni	10000	1400	7.85	0.92± 0.08	93.7± 0.05 (L) 97.1± 0.05 (D)	1.43± 0.05 (L) 1.74± 0.05 (D)	109.5± 9.5
Ni	15000	1350	7.64	n.d.	95.9± 0.05 (L)	1.54± 0.05 (L)	n.d.
Ni	1	1350	8.18	3.41± 0.015	99.9± 0.01		29.3± 0.1
Co	7000	1350	8.59	11.2 ± 0.3	95.2± 0.05 (L) 97.7± 0.05 (D)	n.d. n.d.	8.9± 0.2
Co	1	1350	8.59	18.1± 0.06	99.9± 0.01		5.4± 0.1
Co	10000	1350	8.59	12.7± 0.2	n.d	n.d	7.9± 0.2
Co	10000	1400	7.85	14.1± 0.9	92.7± 0.05 (L) 86.5± 0.05 (D)	0.00 6.25± 0.05	7.0± 0.6
Co	1	1350	8.18	28.1± 0.1	99.9± 0.01		3.6± 0.1

negative deviation from ideality in metallic liquid the dilution effect will be much smaller than the effect observed. Another interpretation is to consider the effect of carbon species formation in melt or vapour phases on Ni and Co solubility in melt. The value of D_{Ni} and D_{Co} does not show a strong composition dependence. We conclude that partitioning of Ni and Co between metal and silicate phase at pressures of 10–15 kbar is not sensitive to the carbon content and most of the effect is due to pressure. However, during metal separation during large-scale melting of a carbon-bearing mantle at high carbon activity the amount of carbon dissolved in the metal phase may be similar to that in our experiments (Table 1). It could effect on a carbon depletion of the outer mantle, when molten carbon - bearing alloy and molten silicate underwent gravitational separation. By measuring partition coefficients between Fe- alloy and silicate melt (Allende CI chondrite as a starting material) Li and Agee (1996) show that Ni and Co become less siderophile with pressure. Our experimental results on solubilities of nickel and cobalt in silicate melts in the presence of graphite and (CO,CO_2) fluid at 1350–1400°C and 7–15 kbar show that those elements become more siderophile with increasing pressure. These data show that pressure and composition are key variables in the resolution the mantle siderophile element problem.

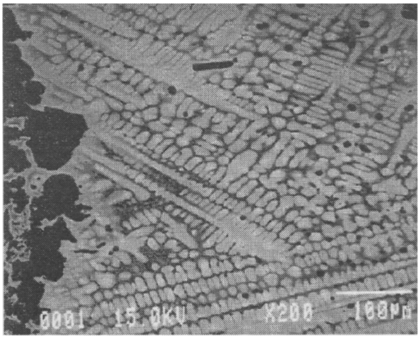

FIG. 1. Backscattering electron image of run product: quench Ni metallic phase and graphite (black), P = 10 kbar, T = 1350°C.

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