

PARTITIONING OF Co AND Ni BETWEEN Fe-METAL AND OXIDE OR OLIVINE

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The siderophile element abundance patterns of the earth's mantle not only provide insight into the processes involved in core formation but also provide critical information concerning the question of core-mantle equilibrium. The partition behavior of Ni and Co are of particular interest in this context, since these elements appear to be uniformly distributed throughout the upper mantle and their abundances in upper mantle rocks and minerals are well established.

The partitioning of Ni and Co between oxides and Fe-metal, and between olivine and Fe-metal in both magnesian "model mantle" and Mg-free systems is currently being determined experimentally over temperatures ranging from 1000 to $\geq 1500^{\circ}\text{C}$ and pressures ranging from 0 to approximately 80 kbar.

The following equilibria have been studied: $\text{Ni}_2\text{SiO}_4 + 2\text{Fe} = \text{Fe}_2\text{SiO}_4 + 2\text{Ni}$; $\text{Co}_2\text{SiO}_4 + 2\text{Fe} = \text{Fe}_2\text{SiO}_4 + 2\text{Co}$; $5(\text{Mg}_{0.8}\text{Ni}_{0.2})_2\text{SiO}_4 + 2\text{Fe} = 5(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4 + 2\text{Ni}$; $5(\text{Mg}_{0.8}\text{Co}_{0.2})_2\text{SiO}_4 + 2\text{Fe} = 5(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4 + 2\text{Co}$; $\text{NiO} + \text{Fe} = \text{FeO} + \text{Ni}$; $\text{CoO} + \text{Fe} = \text{FeO} + \text{Co}$.

Experimental investigations of the following proved unsatisfactory due to kinetic problems: $5(\text{Mg}_{0.8}\text{Ni}_{0.2}\text{O}) + \text{Fe} = 5(\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}) + \text{Ni}$; $5(\text{Mg}_{0.8}\text{Co}_{0.2}\text{O}) + \text{Fe} = 5(\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}) + \text{Co}$. Experiments were carried out in evacuated SiO_2 -glass tubes and in piston-cylinder and "squeezer" high-pressure apparatus. Either Ni or Co together with Pt capsules were used. Minimal reaction was observed between the subsolidus charges and capsule materials below 1500°C . Experimental conditions and results are summarised in Tables 1 and 2.

The K values for the reaction $\text{CoO} + \text{Fe} = \text{FeO} + \text{Co}$ appear to decrease slightly with an increase in either temperature or pressure. A similar conclusion probably holds for the Ni-bearing system. These K values agree well with data from previous experimental studies, e.g. Schenk et al. (1968) and also with equilibrium constants derived from thermodynamic data, indicating essentially ideal behavior in metal and oxide solid solutions.

The K values for Co or Ni olivine-metal equilibria do not show a clear correlation with either temperature or pressure. The similarity between the K values for (CoFe) olivine and (CoFeMg) olivine equilibria indicate that there is only minor preferential distribution of cations in the olivine structure.

The K values for Ni-olivine equilibria are in accord with the experimental data of Irvine and Kushiro (1976) but differ significantly from K values for co-existing olivine and metal in lunar low-Ti mare basalts (Hewens and Goldstein, 1974) and in pallasites (Buseck and Goldstein, 1969). This suggests that site distribution phenomena are significant at high Ni concentration levels.

Olivine-metal and oxide-metal partition equilibria are particularly relevant to the question of core-mantle equilibrium, and will be evaluated in terms of the recent hypothesis of Ringwood (1977) that oxygen (as FeO) is an important light element in the earth's core.

Table 1. Co and Ni partitioning between metal and oxide in simple systems

P	T°C	K ¹	K	K _{mean}
		CoO+Fe ²	FeO+Co	
vacuum	1000	41	42	42
	1100	27	28	28
	1200	23	27	25
	1300	20	19	20
	1400	17	18	18
30 kbar	1200	17	19	18
	1300	16	16	16
	1400	—	13	13
75 kbar	1300	14	—	14
		NiO+Fe	FeO+Ni	
vacuum	1000	201	(83)	142
	1100	94	123	104
	1200	76	74	75
	1300	(98)	(102)	(100)
	1400	61	65	63
30 kbar	1200	—	69	69
	1300	61	61	61
	1400	78	—	(78)
60 kbar	1200	34	50	45

Dubious values in parentheses.

¹K is the equilibrium constant obtained using mole percent (n) values, e.g.

$$K = \frac{n_{\text{FeO}}^{\text{ox}}}{n_{\text{CoO}}^{\text{ox}}} \times \frac{n_{\text{Co}}^{\text{m}}}{n_{\text{Fe}}^{\text{m}}} \text{ where ox = oxide, m = metal.}$$

²Starting assemblage.

Table 2. Co and Ni partitioning between metal and olivine

P	T °C	K ¹	K	K _{mean}
		Co ₂ SiO ₄ +2Fe ²	Fe ₂ SiO ₄ +2Co	
30 kbar	1200	11	19	15
	1300	13	16	15
		5 (Mg _{0.8} Co _{0.2}) ₂ SiO ₄ +2Fe	5 (Mg _{0.8} Fe _{0.2}) ₂ SiO ₄ +2Co	
vacuum	1200	12	13	13
	1300	—	12	12
	1400	11	11	11
	1500	13	9	11
30 kbar	1200	did not equilibrate	10	10
	1300	"	8	8
	1400	"	7	7
	1500	"	10	10
		Ni ₂ SiO ₄ +2Fe	Fe ₂ SiO ₄ +2Ni	
30 kbar	1200	52	44	48
	1300	46	42	44
		5 (Mg _{0.8} Ni _{0.2}) ₂ SiO ₄ +2Fe	5 (Mg _{0.8} Fe _{0.2}) ₂ SiO ₄ +2Ni	
vacuum	1200	21	22	22
	1300	23	33	28
	1400	22	29	25
	1500	16	27	22
30 kbar	1200	—	46	—
	1300	15	42	—
	1400	14	37	—
	1500	19	36	—

¹K = $n_{\text{FeO}}^{\text{ol}}/n_{\text{NiO}}^{\text{ol}} \times n_{\text{Ni}}^{\text{m}}/n_{\text{Fe}}^{\text{m}}$; FeO + MgO + NiO in olivine = 100; n = mole percent; ol = olivine; m = metal.

²Starting assemblage.

References

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