PARTITIONING OF CHROMIUM, MANGANESE, COBALT AND NICKEL BETWEEN OLIVINE AND BASALTIC LIQUID: AN EXPERIMENTAL STUDY

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The partitioning of Cr³⁺, Mn²⁺, Co²⁺ and Ni²⁺ between olivine and mafic silicate liquid has been studied under anhydrous conditions at 1 bar total pressure and temperatures of 1120° to 1270°C. The results suggest that 1) the partition coefficients for Cr, Mn, Co and Ni are strongly temperature dependent, 2) at constant temperature D_{C0} is independent but D_{Cr}, D_{Mn} and D_{Ni} are dependent upon melt composition, 3) the partition cofficients are greater than one at these temperatrue ranges and the preference sequenc is Ni \geq Co > Mn > Cr, 4) the partition cofficients do not vary as a function of element content in the melt, 5) all partition coefficients can be used in geothermometry, the relative temperature accuracy being within \pm 20°C.

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Introduction

The partitioning of trace elements between the common rock-forming minerals and liquid is interesting because of the petrogenetic history of melts. The partitioning depends of different parameters and may therefore, if properly calibrated, be used in geothermometry.

The transition metal partitioning is of particular interest because the elements are strongly concentrated in ferro-magnesian silicates. As a result of olivine and pyroxene fractionation the residual magma is rapidly depleted in the transition metals.

A number of papers have recently been

published on transition metal partitioning between olivine and silicate melt, especially that of nickel (e.g. Duke, 1976; Hart and Davis, 1978; Leeman and Lindstrom, 1978). Partition coefficients for cobalt have been determined by several workers, e.g. Leeman, (1974) and Duke (1976). Watson (1977) worked with Mn, and Schreiber and Haskin (1976) with Cr.

Some workers have assumed that trace element partition is independent of total composition, whereas others have emphasized the possibility of this relationship. The present account is an attempt to evaluate the compositional effect.

Many of the workers added spikes of the elements in question to the starting materials to get the experimental products

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Compo- nents	No	N-5031	TH-10 ²	K-7311	RE-5 ²	N-216 ³	NAL-134	HE-30 ²	HE-35 ²
SiOa		50.25	49.26	49.93	48.98	47.5	47.60	50.22	50.22
TiO		2.13	1.34	1.70	1.63	0.75	1.09	1.07	0.97
A1202		13.42	14.24	13.83	14.93	15.8	16.66	14.47	15.19
Fe ₂ O ₃		4.15	2.20	2.54	2.49	0.74	0.88	1.15	1.13
FeO		11.14	9.87	9.98	9.90	8.51	8.77	9.98	9.99
MnO		0.24	0.19	0.22	0.20	0.16	0.13	0.18	0.19
MgO		5.43	7.09	7.23	7.39	9.8	9.56	10.23	10.50
CaO		10.30	10.66	11.63	11.38	13.2	12.76	10.15	10.60
NagO		2.38	1.99	2.20	2.39	1.7	2.14	1.26	1.41
K ₂ O		0.33	0.18	0.26	0.20	0.09	0.11	0.10	0.10
P_2O_5		0.23	0.19	0.11	0.19	-	0.09	0.09	0.08
Total		100.00	97.21	99.63	99.68	98.23	99.79	98.90	100.38
Comp. N	0.	5	6	7	8	9	10	11	12

Table 1. Composition of starting material.

¹ Grönvold and Mäkipää (1978)

² Mäkipää (1978 a)

³ Unpublished XRF analysis by Dr. K. Grönvold

within the analytical range of the microprobe. It is, however, questionable whether Henry's law is valid at higher concentrations. Some workers have avoided the issue by using beta-track mapping, which can be used at lower concentrations.

In many common basaltic rocks the transition metal concentration, particularly that of Cr, Mn and also Ni, exceeds the present analytical limit of the microprobe (40 ppm \pm 5 ppm). With such rocks it is possible to work with realistic compositions experimentally; the behaviour at lower concentrations is then less important.

In the present study the olivine/liquid partition coefficients for Cr, Mn, Co and Ni in basaltic systems were determined experimentally. The bulk composition of the glasses used as starting materials (before doping) are given in Table 1. Two of them are lavas from the 1975 and 1977 eruptions in northern Iceland (Grönvold and Mäkipää, 1978), four are older pleistocene tholeiites (Mäkipää, 1978 a) and two more MgO-rich lavas from northern Iceland. The composition varies from quartz normative to olivine normative tholeiites. The temperature varied ⁴ Mäkipää (1978 b)

Fe₂O₃/FeO calculation Mäkipää (1979) — not determined

from 1270° to $1100 {}^{\circ}C$ at atmospheric pressure and the oxygen fugacity from 10^{-6} to 10^{-10} . The validity of Henry's law at higher concentrations ($\sim 1 {}^{0}/{0}$) is demonstrated.

Experimental procedures

Analytical methods

In phase-equilibrium studies the most important problems of major elements are associated with the determination of thermodynamic activities. For trace elements expected to obey dilute solution laws the major problem is the limitation of existing analytical techniques (Drake, 1972).

Techniques such as neutron activation, isotope dilution, X-ray fluorescence and others, which permit the high-precision analysis of elements present in trace amounts, suffer from the serious limitation that they do not permit the phases *in situ* in the sample to be analysed. This problem is avoided by using an electron microprobe X-ray analyzer. Major elements are easily analysed, but trace elements are somewhat problematic. The detection limits vary, depending on the element and the matrix, but a 100-ppm detection limit is typical; using special operating conditions, however, substantially lower levels can be reached.

The mineral and glass analyses were all carried out on an automatic ARL-SEMQ microprobe. The major elements were analysed by operating the electron probe at an accelerating voltage of 15 kV and a sample current of 25 nA. The counting time was 20 seconds on peak and 4 seconds on background.

The trace elements were analysed using a 25-kV accelerating voltage and a $0.6-\mu A$ sample current. The counting times were usually 100 seconds on peak and 40 seconds on background.

During the measurements, changes in the line position, shape and relative intensity of the X-ray spectra were observed. The wavelength shift is strongest for the light element K-lines. The K-line peak shifts are often rather large and must therefore be taken into account (Häkli 1963). Hence, the trace elements were determined under special conditions, and the line position was checked for each element. The standards employed for the various elements were: augite and hornblende for all transition metals in low concentrations; synthetic chalcopyrite for Ni and Co (1 0 /o Ni, 1 0 /o Co) and rhodonite for Mn. In addition a glass standard with Co and Ni spike was used. To test the accuracy of analyses a number of spot analyses were performed on the doped materials. So far the results indicate that all the analyses discussed here can be used quantitatively.

Experimental techniques

The experiments were conducted in a Ptwound vertical quench furnace at the University of Iceland. The run temperatures were measured using a Pt/Pt—10 %—Rh thermocouple before and after each run. The thermocouple was calibrated at the melting point of gold (1064.4 °C). The temperature fluctuation during each run was within 1 °C; thus the reported temperatures are considered to be accurate to ± 2 °C or better.

The runs were made at atmospheric pressure. The fo_2 in the furnace was controlled by a mixture of carbon dioxide and hydrogen passed upwards through the furnace at a constant rate (~ 4 cc/s).

Glasses were produced by heating the samples for about 20 minutes at 1320 $^{\circ}$ C and then suspending them directly into the furnace at the desired temperature. This procedure has been found to produce the most homogeneous and euhedral crystals. The samples were held in a pure Pt loop in the hottest zone of the furnace, where no tem-

Fig. 1. Ni partitioning between olivine and liquid at constant temperature (1206 $^{\circ}$ C) as a function of run duration showing the run duration required to the equilibrium. The individual dots with the same run duration indicate different Ni concentrations in sample.





Fig. 2. Loss of elements during the run as a function of run duration using unsaturated platinum wires as containers.

perature gradient was detectable for a length of 4 cm.

Major element equilibrium can be attained with a run duration of 24 hours (e.g. Duke, 1976). This time may, however, be substantially too low for trace element equilibration. The attainment of trace element equilibrium depends on run duration, the element in question and the temperature. These parameters were established by a number of experiments.

The runs at constant temperature with different durations (Fig. 1) indicate that the equilibrium partitioning of Ni between olivine and liquid requires a run lasting at least 30 hours. Shorter runs suffice to attain equilibrium partitioning of Cr and Mn between olivine and liquid. These results agree well with the experiments of Leeman and Lindstrom (1978).

It must be pointed out, however, that at lower temperatures $(1100^{\circ}-1150^{\circ} \text{ C})$ the run

must last much longer (>70 h) before the trace elements equilibrate.

Drake (1972) reported that about $30 \ 0/0$ of all the experimental-run products are lost owing to kinetic problems during the attainment of equilibrium between plagioclase and liquid. To avoid this with olivine some duplicate experiments were performed without any significant gain. Note that all the D values reported here are based on at least two separate experiments.

Oxidation state and oxygen fugacity during the runs

Each of the transition metals can occur in at least two different oxidation states. The relative amount in the various oxidation states depends mainly on oxygen fugacity and temperature and is also influenced by bulk composition (Duke, 1976).

Under natural conditions Co, Ni and Mn (Watson, 1977) appear to be dominantly in the divalent state, whereas Cr is in the trivalent state.

In most of the runs the oxygen fugacity was kept close to the FMQ-buffer, in accordance with the FMQ-buffer equation of Wones and Gilbert (1969):

 $\log fo_2 = -25738/T(^{\circ}K) + 9.00$

The composition of the gas mixture at a given temperature was calibrated by Mr. Sigurdur Jakobsson using the O_2 probe. The reported oxygen fugacities are accurate to within \pm 0.2 log units or better.

The FMQ-buffer gives a slightly more oxidizing atmosphere than the Co—CoO buffer, so that Co was in the divalent state in all the experiments.

To ensure that NiO is not significantly reduced some of the runs were conducted at an oxygen fugacity that was slightly more oxidizing than the Ni—NiO buffer. In this oxygen fugacity range Mn is always in the divalent state and Cr in the trivalent state (Watson, 1977).

However, according to Schreiber and Haskin (1976), some Cr might be in the divalent state at these oxygen fugacities. Thus Mn, Co and Ni were in the divalent state and Cr predominantly in the trivalent state in all the present experiments.

The Pt wire loops used in the experiments should give the best oxygen fugacity control, because with them the samples are completely exposed to the gas mixture.

Loss of elements during runs

Some of the iron in a sample is absorbed by the platinum container. The same would be expected for Ni and Co, too. At an early stage the iron loss was believed to be »not extensive enough to change results significantly and destroy the normative chemistry of basalts» (e.g. Green and Ringwood, 1967). Mysen et al. (1975) reported that with $Pt_{95}Au_5$ capsules the iron loss to the container was considerably lower than with pure Pt capsules.

However, according to Johannes an Bode (1978), the loss of iron from basalts to Pt capsules is highly significant and increases with increasing temperature, run duration and hydrogen fugacity. Further, they pointed out that $Pt_{95}Au_5$ containers do not eliminate the drawback. They reported about 40—70 % loss of iron at 1200 °C even in 8-hour runs.

Platinum wire loops can be used in experiments at one-atm pressure, and the loss of the elements is less significant. To minimize the element loss in the present experiments the weight ratio Pt/basalt was kept as low as possible. The average Pt-wire/ basalt weight ratio in the experiments was 1:8 compared with the Pt-capsule/basalt weight ratio 4:1.

To establish the extent of Fe, Co and Ni loss to the container some experiments were conducted at different run durations, oxygen fugacities and temperatures. At high temperature the run duration is the most serious factor in removing elements from the liquid. As shown in Fig. 2, the loss of Ni is up to about 40 % during a 16-hour run. In experiments performed with very MgO-rich magmas the samples lose a highly significant amount of their original transition metal contents during the runs (which usually last for several days). The loss of the elements decreases rapidly with decreasing temperature and at 1200 °C the loss of Ni is about 10 % within 7 days.

The loss of iron is noticeable, especially at higher temperatures, though it is not so significant as reported by Johannes and Bode (1978). At 1200 °C the loss is only a few percentages of the starting compositions. The loss of iron and other elements can be reduced by presaturating the Pt wire with the same material for several hours at high temperature. After presaturation of 170 hours at 1250 °C the loss of all elements (except alkalies) is insignificant.

Run products and the homogeneity of the phases

The samples were quenched either by dropping them into water or by pulling them rapidly out of the furnace. The absence of any overgrowth or quench crystals suggests rapid quenching.

The glasses produced were very homogeneous and contained varying amounts of olivine and plagioclase as the primary liquidus phases. The maximum degree of crystallization was visually estimated to be less than $20 \ 0/0$ and to contain both olivine and plagioclase.

The olivines were usually small euhedral crystals (Fig. 3). Subhedral or skeletal olivine were rare. Some olivines occasionally contained small chromium spinels.



Fig. 3. Run product (KRA 731/16) showing the morphology of plagioclase and olivine crystals. T = 1162 °C, log fo₂ = -9.06, run duration 25 hours.

In all experiments plagioclase was the second or first crystallization phase and the crystals were usually euhedral laths (Fig. 3). Sometimes, however, they also showed swallow-tailed morphology, especially after short runs. At high oxygen fugacities chromiumspinel crystallization played an important role. In some cases the spinel was the first phase to appear and formed large octahedral crystals.



Fig. 4. The growth of olivine crystal in experiment as a function of run duration.

The size of the olivine crystals correlates well with the run duration (Fig. 4). Some workers have reported difficulties, especially at higher pressures, to get crystals large enough for microprobe analysis. The problem is not so serious in experiments at 1-atm pressure because even during the 8-hour runs the crystals reached the size required.

The equilibrium partitioning of Fe, Co and Ni was studied as a function of run duration by approaching the equilibrium from two directions.

First, both samples were melted for about ten minutes at 1320 °C. One glassy sample was suspended directly at the desired temperature (1200 °C) and equilibrated for 8 and 40 hours. Another sample was first equilibrated for 30 hours at 1150 °C and then reequilibrated for 8 and 40 hours at 1200 °C. The results clearly reveal that although reequilibration takes much longer, after 40 hours the results are identical.

This test indicates that the partition data reported here well represent the equilibrium values.

Results

Henry's law behaviour

Ni partitioning in olivine appears to follow Henry's law over a range from $0.1 \, {}^{0}/_{0}$ to at least 5 ${}^{0}/_{0}$ NiO (Hart and Davis, 1978). In contrast, Mysen (1978) reported very large changes in partition coefficients as a function of Ni content.

To test the feasibility of Henry's law at higher concentrations CoO and NiO were added as oxides to a selected sample in the following concentrations (ppm): 200 to 11000 for Co, and 300 to 12000 for Ni.

Natural concentrations 50-290 ppm Cr and 1450-2230 ppm Mn were used.

The results (Fig. 5) indicate that the parti-





tion coefficient for Ni does not vary as a function of the element content of the melt, i.e. it obeys Henry's law. Partition coefficients

The partition coefficients are here defined as $D_{i}^{ol/liq} = \frac{C_{i}^{ol}}{C_{i}^{liq}}$

where C $_{i}^{ol}$ is the concentration of element i (ppm) in olivine and C $_{i}^{liq}$ in liquid.

A summary of run conditions and the averaged Cr, Mn, Co and Ni partition coefficients are given in Table 2.

Dependence of D on oxygen fugacity, temperature and composition

Chromium

The data available for Cr partitioning as a function of oxygen fugacity are very limited. Huebner and Lipin (1976) reported that the partition of chromium between olivine and silicate liquid is independent of the redox state, temperature and Mg/(Mg + Fe). They did find out, however, that D_{Cr} tends to increase with decreasing oxygen fugacity.



Fig. 6. The partitioning of Cr between olivine and liquid as a function of temperature. L & S — Leeman & Scheidegger (1977), D — Duke (1976), open circles test samples (natural lava).

Run No.	Comp.	T (°C)	log fo ₂	Run duration (hours)	\mathbf{D}_{Cr}	Cr	\mathbf{D}_{Mn}	Mn	\mathbf{D}_{Co}	Co	$D_{ m Ni}$	Ni	182
				(nours)									Hei
11	5	1125	_	64	0.97	123	1.46	1670	5.05	90	18.82	96	kk
2	6	1198	- 83	2.4	1 32	200	1.42	2009	2.94	82	15.25	128	1
3	6	1155	- 8.5	48	0.69	220	1.50	1899	4.90	62	18.59	91	
4	7	1192	- 8.9	23	1.24	290	1.26	2010	3.28	390	16.96	125	M
5	7	1187	- 8.7	24	1.03	286	1.35	1981	3.85	393	16.96	90	äk
6	7	1186	- 9.0	23	1.23	188	1.47	1862	3.78	478	16.67	81	ip
7	7	1183	- 8.8	42	1.06	228	1.41	1821	3.88	444	16.82	92	ää
8	7	1180	- 91	23	1 23	184	1.34	2085	3.59	380	17.60	125	
9	7	1168	- 8.9	21	0.90	221	1.47	1861	4.01	480	17.40	98	
10	7	1166	- 9.3	24	1.02	188	1.41	1816	4.59	407	19.62	104	
11	7	1162	- 91	25	1.05	271	1.62	1671	3.87	420	19.74	86	
12	7	1161	- 9.3	24	1.23	175	1.35	1690	3.75	360	18.38	80	
13	7	1158	- 9.0	24	0.80	269	1.52	1772	4.66	480	19.91	96	
14	7	1155	- 8.6	24	0.61	184	1.54	1810	4.53	420	18.71	77	
15 2	7	1153	- 91	22	0.87	262	1.68	1587	3.89	497	16.62	89	
162	7	1147	- 9.3	22	0.78	261	1 73	1508	4.22	448	16.88	105	
17 2	7	1142	- 9.5	32	0.66	2.2.4	1.35	1507	4.34	445	18.92	99	
18	7	1140	- 96	67	0.62	151	1.59	1636	5.13	420	22.63	95	
10	8	1185	- 8.4	24	1 31	251	1 43	2102	3.41	69	15.15	93	
20	8	1155	8 5	48	0.83	235	1 46	2062	4.82	60	19.63	80	
20	0	1934	- 8 1	26	1.83	375	1.09	1490	2 59	301	11.82	162	
21	0	1218	- 84	44	1.85	360	1.15	1459	2.75	209	13,55	143	
22	9	1210	- 8.2	28	1.08	362	1.12	1438	3.02	231	12.94	120	
23	9	1202	- 8.5	49	1.50	358	1.15	1470	3.30	269	14.63	125	
25 1	10	1263	- 7.8	38	1.86	332	1.09	1446	2. 4.2	125	11.00	198	
26 1. 2	10	1200	- 7 9	9	1.81	340	1 21	1420	2.06	180	8.81	200	
20	10	1244	- 8 1	15	1 69	388	1 11	1506	2 90	148	12.22	125	
20	10	1108	- 8.5	48	0.86	160	1 29	1450	3.20	177	16.63	111	
20	10	1190	- 9.5	120	1.11	150	1.25	1631	3.40	182	15.35	134	
30	11	1238	- 7.8	24	1.90	260	1 22	1621	2.41	107	12.62	211	
31	12	1216	8.0	24	1.69	321	1.31	1741	2.78	97	13.60	180	
39	12	1208	- 7 9	137	1.69	158	1.14	1610	3.03	139	15.59	3709	
22	12	1208	- 7 9	137	2.33	151	1 16	1680	2.94	141	15.03	1715	
34	12	1208	- 79	137	1.00	101	1 14	1585	2.64	154	14.61	1319	
35	12	1200	-73	137	1.34	160	1.22	1599	3.17	144	15.78	867	
26	12	1208	- 7 9	137	1.01	100	1.12	1551	2.91	156	14.78	676	
37	12	1208	- 7 9	137	_		1 23	1519	2.90	157	14.85	548	
20	12	1200	- 7 9	137	1 62	94	1.17	1578	2.80	191	15.61	341	
30 2	12	1200	- 7 9	17	1.02	78	1 10	1569	3.11	128	15.52	3670	
39 -	12	1207	- 7 9	17	0.76	80	1.01	1578	2.77	150	15.49	1660	
40 -	12	1207	- 7.9	17	0.97	81	1.01	1562	2.47	146	14.32	1220	
49 2	12	1207	70	17	1.01	92	0.99	1520	2.36	160	13.82	812	
432	12	1207	- 7 9	17			1.03	1530	2.35	150	12.99	627	
14.2	12	1207	- 7 9	17	_		1.01	1560	2.20	122	10.12	483	
45 2	12	1207	- 7.9	17	1.38	109	1.04	1559	2.08	150	7.86	121	
46 2	12	1206	- 7.9	8	0.65	113	0.99	1648	1.75	231	11.04	4540	
10 -	14	1200	1.0	0	0.00							and the second second	

Table 2. Experimental conditions and results.

47 2	12	1206	- 79	8	0.91	110	0.99	1653	2.05	247	8.56	2918
48 2	12	1206	- 7.9	8			0.90	1612	2.10	259	7.22	1403
49 2	12	1/2/06	-7.9	8			1.01	1630	2.22	248	6.40	864
50 2	12	1206	-7.9	8	0.56	73	0.95	1676	2.06	280	6.56	422
51 2	12	1206	-7.9	8	2.32	106	1.05	1616	2.19	181	6.01	425
52 2	12	1206	-79	8		_	1.05	1636	2.20	160	5.92	208
53	12	1206	- 7 9	31	-		1.04	1612	2.51	221	15.62	5207
54	12	1206	- 7.9	31	-	_	1.07	1716	2.51	199	14.76	2434
55	12	1206	- 7 9	31	_		1.04	1698	2.94	178	15.40	1801
56	12	1206	- 7.9	31	-		1.08	1712	2.62	210	14.17	1648
57	12	1206	- 7.9	31	_		1.10	1744	2.87	171	12.16	1075
58	12	1206	- 7.9	31			1.02	1790	2.77	241	12.92	898
50	12	1206	- 7.0	31	_		1 01	1860	2.81	2.52	11.71	411
60	12	1206	- 8 3	41	1 97	117	1.14	1635	2.80	517	14.61	1040
61	12	1200	- 8 3	41	1 18	184	1.08	1584	2.86	139	15.01	1115
62	12	1200	- 8.3	41	1 13	186	1 10	1562	3.07	6297	15.46	94
62	12	1200	- 8.0	70	1.10	100	1 15	1585	3.23	242	15.07	3080
64	12	1205	- 8.0	70	_		1 12	1518	3 53	163	15.95	1207
65	12	1205	- 0.0	70	1 37	183	1 17	1545	3 10	205	15.58	1029
66	12	1205	- 8.0	70	1 10	180	1 18	1589	3 14	109	15.97	621
67	12	1205	- 0.0	70	1.10	100	1.10	1540	3 33	146	15.20	486
01	12	1205	- 0.0	70	1 35	160	1.10	1521	3 93	132	14 90	412
00	12	1205	- 0.0	70	1.55	103	1 10	1521	3 40	102	15.00	188
09	12	1205	- 0.0	07	1 02	71	1.10	1506	3.62	10611	16 10	180
70	12	1205	- 0.0	07	1.03	11	1.20	1552	3 82	7170	15.54	100
71	12	1205		07			1.20	1560	3.40	5200	16 35	170
72	12	1205	- 8.0	07	_		1.30	1561	2 72	2020	15.40	101
73	12	1205	- 8.0	07	_		1.29	1490	3.15	1042	15.20	171
74	12	1205	- 8.0	07	1 46	74	1.10	1400	2.59	075	15.50	190
75	12	1205	8.0	81	1.40	242	1.20	1400	2.50	102	16.00	160
76	12	1200	- 8.0	09	1.10	240	1.10	1760	3.50	5120	16.30	547
77	12	1197	- 8.5	40	0.90	349	1.20	1960	3.00	159	17.91	1260
78	12	1192	- 9.4	58	1.27	270	1.30	1720	4.17	150	17.21	1300
79	12	1192	- 9.4	50	1.15	330	1.41	1045	2.00	179	17.94	200
80	12	1192	- 9.4	50	1.20	196	1.10	1045	3.90	166	17.03	105
81	12	1192	- 9.4	50	1.59	100	1.21	1910	2.00	19627	16.00	105
82	12	1192	- 9.4	50	1.09	209	1.01	102	2.70	5200	17.75	104
83	12	1192	- 9.4	58	1.02	231	1.00	1074	3.10	1679	16.01	104
84	12	1192	- 9.4	28	1.40	241	1.42	1620	3.00	1072	16.91	270
85	12	1183	- 8.8	42	0.91	304	1.27	1572	4.00	6152	15.02	160
86	12	1183	- 8.8	42	1.05	540	1.50	1075	2.10	120	10.90	100
872	12	1168	- 8.9	17	1 01	971	1.10	1005	3.10	159	12.40	202
88 2	12	1168	- 8.9	17	1.01	271	1.10	1720	5.00	10256	12.02	204
89	12	1162	- 9.1	20	1.10	202	1.00	1000	4.20	10250	10.90	610
90	12	1162	- 9.1	25	1.20	329	1.42	1479	4.09	110	19.10	010
91	12	1158	- 9.0	24	0.93	304	1.40	1740	4.24	100	10.00	2600
92	12	1155	- 8.5	48	0.77	100	1.47	1720	5.01	144	10.70	3020

² not in equilibrium
 — not determined

Comp. refers to the starting material composition in Table 1.

Partitioning of Cr, Mn, Co and Ni

183

184 Heikki T. Mäkipää

In their study on the synthetic system forsterite-anorthite-silica, Schreiber and Haskin (1976) noted that chromium redox equilibrium is strongly dependent on temperature and oxygen fugacity. They also reported that $D_{\rm Cr}$ increases with decreasing oxygen fugacity. A similar trend is demonstrated by the present data.

The partitioning values of chromium between olivine and liquid as a function of temperature are shown in Fig. 6 at fo_2 close to FMQ. Above about 1160 °C the values are greater than one, indicating that chromium prefers the olivine lattice. In terms of the crystal chemistry this means the substitution of chromium ion for iron and magnesium in the octahedral site. This will be discussed later. However, below 1160 °C olivine seems to repel chromium.

The experiments at constant oxygen fugacity show clearly that the partititon coefficient decreases with decreasing temperature. There is, however, no apparent change in olivine composition within a large temperature interval (Roeder and Emslie, 1970). This means that at lower temperatures olivine almost retains the high temperature composition that offers more octahedral sites for Cr than does low-temperature olivine. Especially Cr^{3+} , which has the highest octahedral site preference energy of the elements studied, will be enriched relatively more than other elements.

To test this hypothesis the data of four natural samples are shown in Fig. 6. One of these has chromium spinel inclusions as described by Mäkipää (1978 a); all of them are slightly crystalline and the olivine crystals observed represent equilibrium (Mäkipää, 1978 b; Grönvold and Mäkipää, 1978).

The equilibrium temperatures for the natural samples were calculated using the partitioning of MgO (Roeder and Emslie, 1970); in melting experiments at 1-atm pressure the temperatures differed no more than about 5 $^{\circ}$ C from the calculated values. All these natural samples are remarkably consistent with the controlled (QMF) oxygen fugacity line.



Fig. 7. The partitioning of Mn between olivine and liquid as a function of temperature. W 0.29 etc. Watson (1977) with different Si/O ratios. Solid lines 0.295 and 0.305 (Si/O ratio) were fitted to present data by method of least-squares.

The only serious effect on partitioning is oxygen fugacity, which changes the composition of olivine and affects the amount of chromium in olivine. The strong correlation observed between $D_{\rm Cr}$ and temperature is thus mainly due to the joint effect of buffered oxygen fugacity and temperature.

Manganese

The control of the partition of manganese between olivine and liquid is complicated. Leeman (1974), Duke (1976) and Watson (1977) have determined experimentally the partition coefficients for Mn as a function of temperature. The data available for $D_{\rm Mn}$ show a relatively large scatter, mostly caused by the variation in magma composition.

As seen in Fig. 7, the main trend is for partition coefficients to increase with decreasing temperature. All the values in this temperature range (1125-1250 °C) are greater than one indicating that Mn prefers the olivine lattice.

It is important to discriminate between the effects of fo_2 and bulk composition on the partition coefficient. The experiments at constant oxygen fugacity show very clearly that fo_2 markedly affects the partition coefficient. It is well known that at this oxygen fugacity manganese is always divalent. Probably the only way to explain this is by the relatively constant olivine composition, which as with Cr, is conspicuously dependent on fo_2 . This problem was avoided by Watson (1977), who used iron-free compositions in his experiments. In the system with a persistent forsterite structure fo_2 has no apparent effect.

The experiments at controlled fo_2 show systematic variation in the partition coefficients in relation to temperature: the lower the temperature the higher the partition coefficient. The relatively large scatter in the plot is due to the difference in composition. Although the FeO/(FeO + MgO) ratio only varies from about 0.51 to 0.73 and the Si/O ratio from 0.290 to 0.311, this narrow composition range has a considerable influence on partition coefficients.

On the basis of the present data, two Mn partition equations were calculated for different Si/O ratios, one with a Si/O ratio equal to 0.295 and the other equal to 0.305, representing the range observed in the most common Icelandic tholeiites.

Watson (1977) has discussed the suitability of the Si/O ratio in reflecting the melt composition. With his experimental results the following lines can be calculated for different Si/O ratios: Si/O = 0.285, 0.307 and 0.320. The consistency with Watson's data (Fig. 7) supports the validity of the Si/O ratio as a general structural parameter, even though Watson (op.cit.) used iron-free materials.

The natural test samples follow these lines remarkably well, indicating the usefulness of this geothermometer when the compositional effect is taken into account.

Cobalt

The natural cobalt content of the rocks studied was very low, down to about 30 ppm. The amount of Co usually decreases rapidly with crystallization and Co mainly enters olivines and pyroxenes.

Assuming that the octahedral site preference energy is one of the most important factors controlling the partition of transition metals between olivine and liquid, the partitioning of Co should not be so sensitive to compositional differences as that of Ni.

On this basis, behaviour of Co partitioning at constant oxygen fugacity is easily understood. Although under these conditions the structure of olivine offers more octahedral sites, Co, unlike Cr, does not show any such preference.

All the experiments at constant fo_2 and at buffered fo_2 show a linear correlation be-



Fig. 8. The partitioning of Co between olivine and liquid as a function of temperature. L & S — Leeman & Scheidegger (1977), solid line (without index) was fitted to present data by method of least-squares, open circles — test samples (natural lava).

tween partition coefficient and temperature (Fig. 8), the partition coefficient increasing with decreasing temperature. Owing to the rather good correlation the Co partition between olivine and liquid is readily applicable to natural rocks.

Nickel

Since the classic paper by Häkli and Wright (1967) the partition coefficients for nickel have often been used as a geothermometer. On the basis of octahedral site preferency energy, Ni should show by far the strongest enrichment in olivine. Unfortunately this also means that the partitioning of Ni is strongly dependent on the composition of the melt, because in more silica-rich melt the degree of polymerization of SiO₄ tetrahedras increases.

If the Si/O ratio is related to the melt structure then the compositional dependence of the partitioning of Ni may be partially resolved. In the present experiments the Si/O ratio varied from 0.29 to 0.31 and all the partition coefficients displayed a significant temperature dependence (Fig. 9). To distinguish between compositional effcet and temperature dependence some experimental results (Si/O = 0.27 - 0.37) by Hart and Davis (1978) are shown on the same diagram. For melts with Si/O ratios of about 0.30, the close agreement with the present experiments indicates that the composition dependence of the Ni-partition coefficient is very small over the range of melt compositions considered. Leeman's data (1974) with an Si/O ratio \sim 0.300 also plot very close to the line presented, which is a combination of data from Leeman and Lindstrom (1978) and Hart et al. (1976), with Si/O close to 0.300.

Hart and Davis (1978) suggested that $D_{\rm Ni}$ varies inversely with the MgO content of liquid at a given temperature, even at a constant value of Si/O. The same was true in the present study. This NiO-MgO relationship possibly gives an exchange constant (Ni/Mg) olivine/(Ni/Mg) melt that is more convenient



Fig. 9. The partitioning of Ni between olivine and liquid as a function of temperature. L & L — Leeman & Lindstrom (1978), H & W — Häkli & Wright (1967), open circles — test samples (natural lava), triangles — Leeman (1974) Si/O ratio 0.300, crosses — Hart & Davis (1978) with different Si/O ratios.

than the partition coefficient, but, as discussed by Hart and Davis (1978), the results do not agree as well with temperature as do the D values. For further discussion, see Leeman (1974) and Hart and Davis (1978).

As mentioned above, Häkli and Wright (1967) collected and studied five samples from the Makaopuhi lava lake in Hawaii and based their geothermometer on the fractionation of nickel between olivine and glass. The composition of the lava is rather similar to that used here.

Their data, however, show a smaller temperature dependence than that given here. This small but significant divergence might be due to inaccuracies in their sample collection (especially temperature determinations) or to the disequilibrium between olivine and liquid. Nonetheless, their data are well suited to natural samples under conditions that are difficult to duplicate in experimental laboratories. In fact all the natural test samples used here are consistent with the line presented by Häkli and Wright (1967) (Fig. 9).

Takahasi (1978) proposed $K^{MgO} = (MgO)^{ol}/(MgO)^{liq}$ (mole ratios) as a quantitative pa-

rameter for comparing different liquid compositions. With this ratio as a parameter the precision of the geothermometer is not better (in some cases even poorer) than with the Si/O ratio as a compositional parameter.

Summary of experimental results

The partition coefficients for transition metals in silicate melts are likely to be affected by various external and internal properties of the magma. In the present study natural rocks were used in the experiments in the attempt to evaluate the effects of some of these variables.

The concentration of the element in question does not affect the partition coefficients up to at least 1 wt. 0/0, i.e. all the elements studied obeyed Henry's law.

At these temperatures the partition coefficients (except for that of Cr) are greater than one indicating that these elements prefer the olivine lattice and will thus be rapidly depleted from liquid during crystallization.

The strong temperature-dependence of the partition coefficients for Cr, Mn, Co and Ni has been used to calculate temperatures for



Fig. 10. The difference between the calculated (T_c) and observed (T_o) temperatures of present experiments.

the experimental data incorporated in the regression analyses. Fig. 10 shows the difference between the calculated (T_o) and observed (T_o) temperatures for each element. The present data suggest that the precision of these geothermometers in terms of the relative temperatures is generally within \pm 20 °C (see below).

The main results are briefly:

(1) Cr. The partition coefficient between olivine and liquid is dependent on temperature and fo_2 . The D varies slightly with temperature but increases rapidly with decreasing oxygen fugacity. By combining these two features the temperature can be estimated reasonably to within about \pm 30 °C.

- (2) Mn. The partition coefficient between olivine and liquid is strongly dependent on bulk composition. With the Si/O ratio as an index of the liquid structure, a good correlation between D_{Mn} and temperature is obtained at constant Si/O ratio.
- (3) Co. The partition coefficient for Co between olivine and liquid appears to be dependent on temperature alone. The variation in composition and fo_2 has no apparent effect. Concentrations of Co could therefore be used as a geothermometer within a precision of about ± 20 °C or better. More experimental data could improve the geothermometer still further.
- (4) Ni. The partition coefficient for Ni is very strongly dependent on temperature, but at constant temperature the D is also strongly dependent on melt composition and varies inversely with the MgO content of the melt. For basaltic melts (Si/O ratio close to 0.30), however, the precision of this geothermometer is within ± 20 °C.

Discussion and comparison with other studies

The partition coefficients of Cr, Mn, Co and Ni between the olivine and liquid studied vary rather widely. To explain this behaviour, their dependence on the composition of the basaltic melts and the influence of the variation on the activity coefficients of the elements must be established.

Very little is known, however, about the structure of basaltic melts. It has been argued (Whittaker, 1967) that tetrahedral sites dominate in the liquid studied and the number of octahedral sites available for transition metals decreases with decreasing basicity of the melt. All transition metal ions enter both normal octahedral and tetrahedral sites. In addition, a number of defect sites occur in crystals and melt as a result of temperature and pressure history of crystallization. The transfer between the sites depends on various factors, e.g. the octahedral site preference energy (OSPE) of the element. In short, during crystallization the number of octahedral sites decreases and therefore the ions with strong OSPE enter the crystal lattice, which offers numerous octahedral sites, rather than become enriched in »more tetrahedral» liquid.

 Cr^{3+} has the strongest OSPE (38 kcal) of the elements studied and therefore occurs in octahedral coordination. The Cr^{3+} ions show the greatest early enrichment in transition metals. Curtis (1964) reported that early fractionation in the Skaergaard intrusion had removed most of the Cr^{3+} from the magma. Cr^{3+} , however, mainly enters the pyroxene lattice in excellent agreement with the present experiments, because Cr^{3+} seems to disfavour olivine at lower temperatures during crystallization. This is conspicuous when pyroxene starts to crystallize.

Because of its relatively strong OSPE (21 kcal), Ni²⁺ should be expected, on the basis of the crystal field theory, to show the strongest early enrichment of divalent transition metals. In fact this is easily seen if we compare the OSPE and partition coefficients of divalent cations (e.g. Henderson and Dale, 1970). Leeman and Scheidegger (1977) noted that the relation lnD vs. OSPE is not linear for all the elements (especially Co has a higher D value) and argued that ionic size and OSPE are not the sole controls of partitioning. Co^{2+} , however, has a very weak OSPE (7 kcal) and hence might be one of the most promising transition metals for partition studies; the weaker the OSPE the more independent the partition coefficient is of total composition.

The change in the partition behaviour of the transition metals studied might be largely influenced by the variation in the activity coefficients of Cr_2O_3 , MnO, CoO and NiO in the magma. Little is, however, known about their activities. Some approximations can be made for some major elements. The activity of the element is a function of temperature, oxygen fugacity and total composition. Roeder (1974) showed that the activity coefficient of iron in basaltic melts is a function of alkalies and alumina. Developing his model further, we can establish also the silica activity.

Leeman and Lindstrom (1978) described a method for estimating NiO activity in liquid and argued that the activity coefficient depends strongly on temperature but less on melt composition. Nonethelses, it should be pointed out that the activity coefficient of NiO is dependent on the concentration of Ni in liquid.

A more convenient method for approximating the activities is to use mole fractions. These approximations are clearly far from the true values, but until more thermodynamic data are available, they give the best results. Further, in the present study, there should not be any significant difference between the activities because of the small range in temperature and melt composition.

As mentioned earlier, the present experiments show clearly that Henry's law is valid for all the elements studied from natural levels (about 30 ppm) to about $1 \, ^{0}/_{0}$. However, much more experimental data are needed at higher pressures and in the presence of volatiles before the final word can be said.

Schreiber and Hanskin (1976) reported a highly significant dependence of $D_{\rm Cr}$ on temperature at low fugacity ($\sim 10^{-9}$); at higher fugacities ($\sim 10^{-3}$), however, the effect is very weak. Akella (1975) investigated the partitioning of Cr between silicates and liquid at 1-atm pressure as a function of temperature, partial pressure of oxygen and cooling rate. In summarizing his results he noted that $D_{\rm Cr}$

190 Heikki T. Mäkipää

decreases as temperature decreases and that at constant temperature $D_{\rm Cr}$ increases with decreasing oxygen fugacity.

The results of the present study are consistent with the studies cited above. If the effects of oxygen fugacity and temperature are combined, it is easy to understand the relatively high correlation observed between partition coefficient (D_{Cr}) and temperature at buffered oxygen fugacity.

Duke (1976) studied experimentally the partitioning of some transition metals but some doubt has been cast on his results in the literature because of the converse apparent variation with temperature compared with the data of other workers. Lindstrom and Weill (1978) pointed out that the oxygen fugacity $(10^{-9.7}-10^{-10.4})$ in Duke's experiments should cause the reverse but, as shown in this study, an oxygen fugacity of up to $10^{-9.5}$ has no such an effect.

In his study on manganese partitioning Watson (1977) maintained that the disagreements regarding Leeman's (1974) data are the result of differences in the thermodynamics of iron-bearing (Leeman) and iron-free (Watson) systems.

The present study, however, does not support this. If this were the case, then Duke's data should show apparent deviation as well. The agreement between Duke's and Watson's data is, however, adequate. In general, for temperature measurement applications, the agreement for Mn between the data of Leeman (1974), Duke (1976), Watson (1977) and the present study is adequate if the compositional effect is taken into account.

The overall close agreement between the present results and those of, say, Leeman (1974) and Leeman and Lindstrom (1978) for basalts warrants the use of transition metal partitioning as geothermometry. The experimental technique and the starting materials were rather similar to those used by Leeman & Lindström. The fact that they had markedly wider compositional and temperature ranges gives a good basis for detailed studies such as the present one.

No attempt was made, however, in the present study to evaluate the possible effects of pressure and volatiles (e.g. H_2O , CO_2 , F, Cl) on the partition coefficients. Pressure might have a tendency to change the structural coordination of melt and to increase the solubility of divalent cations but this has not yet been established.

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