

PARTITIONING OF Cr, Mn, Co AND Ni BETWEEN OLIVINE AND
BASALTIC LIQUID: AN EXPERIMENTAL STUDY

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Heikki Mäkipää

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ABSTRACT

The distribution of Cr^{3+} , Mn^{2+} , Co^{2+} and Ni^{2+} among olivine and mafic silicate liquid has been studied between 1120 and 1250°C under unhydrous conditions at 1 bar total pressure. The distribution of Co was concluded to be dependent only on temperature according to the following equation:

$$\ln D_{\text{Co}}^{\text{ol/l}} = 14556/T(^{\circ}\text{K}) - 8.766$$

All other distribution coefficients are dependent on oxygen fugacity or composition or both. With controlled oxygen fugacity and the similar composition the following equations can be described for the distribution of Cr, Mn and Ni.

$$\ln D_{\text{Ni}}^{\text{ol/l}} = 10863/T(^{\circ}\text{K}) - 4.738$$

$$\ln D_{\text{Mn}}^{\text{ol/l}} = 6050/T(^{\circ}\text{K}) - 3.841 \quad (\text{Si/O} = 0.305 \text{ in glass})$$

$$\ln D_{\text{Mn}}^{\text{ol/l}} = 5600/T(^{\circ}\text{K}) - 3.596 \quad (\text{Si/O} = 0.295 \text{ in glass})$$

$$\ln D_{\text{Cr}}^{\text{ol/l}} = -22545/T(^{\circ}\text{K}) + 15.656$$

Because of the strong compositional influence to the partitioning, all equations presented are only valid for rocks similar to those of the present study.

INTRODUCTION

The partitioning of trace elements between crystals and liquid is of interest because of petrogenetic history of melts. The partitioning is dependent on different parameters, and may therefore, if properly calibrated, be used in geothermometry and geobarometry.

Lack of pertinent thermodynamic data, and ignorance about the compositional influence on the partitioning, caused the present study to be undertaken, in which the distribution was studied between olivine and liquid for Cr, Mn, Co and Ni.

All distribution coefficients are presented in form ppm element in olivine/ppm element in glass.

EXPERIMENTAL PROCEDURES

Composition of starting material

The bulk compositions of the glasses used as starting materials are given in Table 1. Two of them are lavas from 1975 and 1977 eruptions in N-Iceland, and four of them are older pleistocene tholeiites. The composition varies from quartz normative to olivine normative tholeiites. The starting glasses were prepared from the powdered lavas by keeping them in Pt-loop in a furnace at 1315°C and controlled f_{O_2} close to that of the FMQ buffer for two hours. No transition metal or other oxides were added to the original materials, except for Co, of which a few hundred ppm were adopted from the crushing systems.

Sample No.	RE-5	TH-10	HE-32	HE-35	KRA-503	KRA-731
No. of anal.	15	15	15	15	20	20
SiO ₂	48.98	49.26	48.49	50.22	50.20	49.93
TiO ₂	1.78	1.44	1.25	1.13	2.11	1.70
Al ₂ O ₃	14.93	14.24	15.11	15.19	13.50	13.84
FeO ^t	12.14	11.85	10.89	11.01	14.80	12.27
MnO	0.16	0.14	0.16	0.18	0.24	0.22
MgO	7.39	7.09	9.63	10.50	5.47	7.23
CaO	11.38	10.66	11.15	10.60	10.30	11.63
Na ₂ O	2.39	1.99	1.49	1.41	2.36	2.26
K ₂ O	0.20	0.18	0.08	0.10	0.33	0.26
P ₂ O ₅	0.19	0.19	0.08	0.09	0.22	0.17
CIPW norms (with Fe ₂ O ₃ /FeO = 0.15 and recalculated to 100 %)						
Qz		1.80		0.69	2.09	0.56
Or	1.19	1.09	0.48	0.59	1.96	1.54
Ab	20.28	17.32	12.80	11.92	20.02	19.17
An	29.51	30.24	34.84	34.79	25.34	26.89
Di	21.29	18.87	16.94	13.93	20.48	24.49
Hy	15.71	25.07	28.16	33.72	22.74	20.19
Ol	5.85		2.06			
Il	3.39	2.81	2.41	2.14	4.02	3.24
Mt	2.33	2.34	2.12	2.02	2.84	3.52
Ap	0.44	0.45	0.19	0.21	0.51	0.39
Transition metals (except Sc and Fe) in ppm						
Ti	9765	8030	6365	5825	15995	9750
V	270	240	270	315	380	320
Cr	160	75	265	290	50	190
Mn	1550	1450	1455	1460	2230	2010
Co	65	105	45	40	180	390
Ni	200	165	305	270	80	125
Cu	90	145	135	120	160	65
Zn	45	55	40	45	110	75

Table 1. Microprobe analyses and CIPW-norms of basalts used as starting material for the experiments.

Experimental techniques

The experiments were carried out in a Pt wound vertical tube quench furnace. The run temperatures were measured using Pt/Pt 10% Rh thermocouple before and after each run. The temperature fluctuation during each run were within 1°C so that the reported temperatures are accurate to within $\pm 2^\circ\text{C}$. The thermocouple was calibrated at the melting point of gold (1063°C). The total pressure in the runs was the atmospheric pressure of the laboratory and the furnace atmosphere was a mixture of carbon dioxide and hydrogen (close FMQ buffer) which was passed upwards through the furnace with constant rate. In some runs the oxygen fugacity was controlled following the FMQ buffer and in some runs the oxygen fugacity was kept constant (constant gas mixture and flowing rate).

The glasses which were melted at 1315°C were suspended directly into the furnace at the desired temperature. The samples were held in a pure Pt loop in the hottest zone of the furnace, where no temperature gradient was detectable over a 4 cm length of the furnace.

After approximately 24 hours the platinum wire was melted with an electric current so that the sample fell down into the water where it quenched to room temperature within seconds. The run duration of 24 hours appears to be sufficient for the attainment of equilibrium (e.g. Kennedy 1948, Yoder & Tilley 1962, Seward 1971, Sun et al. 1974, Duke 1976). However, Drake & Weill (1975) and Watson (1977) used much longer times to equilibrate their samples. Experiments conducted at the same temperature using longer duration times gave identical results and in the present study some 3 and 5 day runs were made without a noticeable gain. Equilibrium is also indicated by the homogeneity of the product phases in the present study.

Oxidation state during the runs

In the early melting experiments (e.g. Bowen & Schairer 1932, Kennedy 1948) the oxidation state was controlled by the container. It is well known that all metals that can be used successfully for high-temperature studies take part in the reaction removing some iron from the sample as well as affecting its oxidation state. This iron loss is, however, "not extensive enough to change results significantly" (Muan 1958).

Because the oxidation state is a function of oxygen fugacity many authors (e.g. Yoder & Tilley 1962, Fudali 1965, Hill & Roeder 1974) started with experiments on the basis of different oxygen fugacity.

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 the oxygen fugacity and temperature, but is also influenced by bulk composition (Seward 1971, Duke 1976).

In natural rocks it appears that Co, Ni and Mn (Watson 1977) are dominantly in the divalent state but Cr in the trivalent state.

Analytical methods

In geochemistry the elements are generally classified as either major or trace elements. In phase equilibrium studies the most important problems of major elements are associated with the determination of thermodynamic activities. For trace elements, which might be expected to obey dilute solution laws, the major problem is the limitation of existing analytical techniques (Drake 1972).

The use of techniques such as neutron activation, isotope dilution, X-ray fluorescence and others, which permit the high-precision analysis of element present in

trace amounts, suffer from the serious limitation, that it is impossible to analyze the phases in situ in the sample. This problem is evaded the electron microprobe X-ray analyzer. Major element analyses can easily be made, but trace elements cannot be determined with acceptable counting precision. The detection limits vary depending on the element and the matrix but 100 ppm detection limit is typical but using special operating conditions lower levels can be reached.

All mineral and glass analyses were carried out on an automatic ARL-SEMQ microprobe. Major element analyses were obtained by operating the electron probe at an accelerating potential of 15 kV and 25 nA sample current. Counting time of 20 seconds on peak and 4 seconds on background was used. The correction procedures of Bence & Albee (1968) was used and the correction factors of Albee & Ray (1970). Data for all the standards used for standardization are available at the Nordic Volcanological Institute (Imslund 1977).

The trace element analyses were carried out using 25 kV accelerating potential and 60 nA - 0.6 uA sample current. Counting times used were 100 seconds and 10 seconds on peak and background, respectively. The X-ray peak intensities were corrected only for background intensity.

The chemical effects on X-ray spectra is common knowledge among microprobe users. It is observed in the form of changes in line position, shape and relative intensity. The wavelength shift is strongest for the light element K-lines. Because the K-line peak shifts are often quite large they must be taken into account. For this reason special conditions were employed for the trace element determination and the line position was checked in each case. Standards employed for the various elements were as follows: augite and hornblende (Mason & Allen 1973) for all transition metals in low concentrations. In high concentrations the standards were 99.99 per cent pure metals for Co and Ni, rhodonite for Mn.

RESULTS

Chromium

Partitioning values of chromium between olivine and liquid are greater than unity above about 1160°C, indicating that chromium enters the olivine lattice (Fig. 1). This can easily be explained by chromium camouflage by Fe^{3+} . Below 1160°C chromium seems discriminate against olivine.

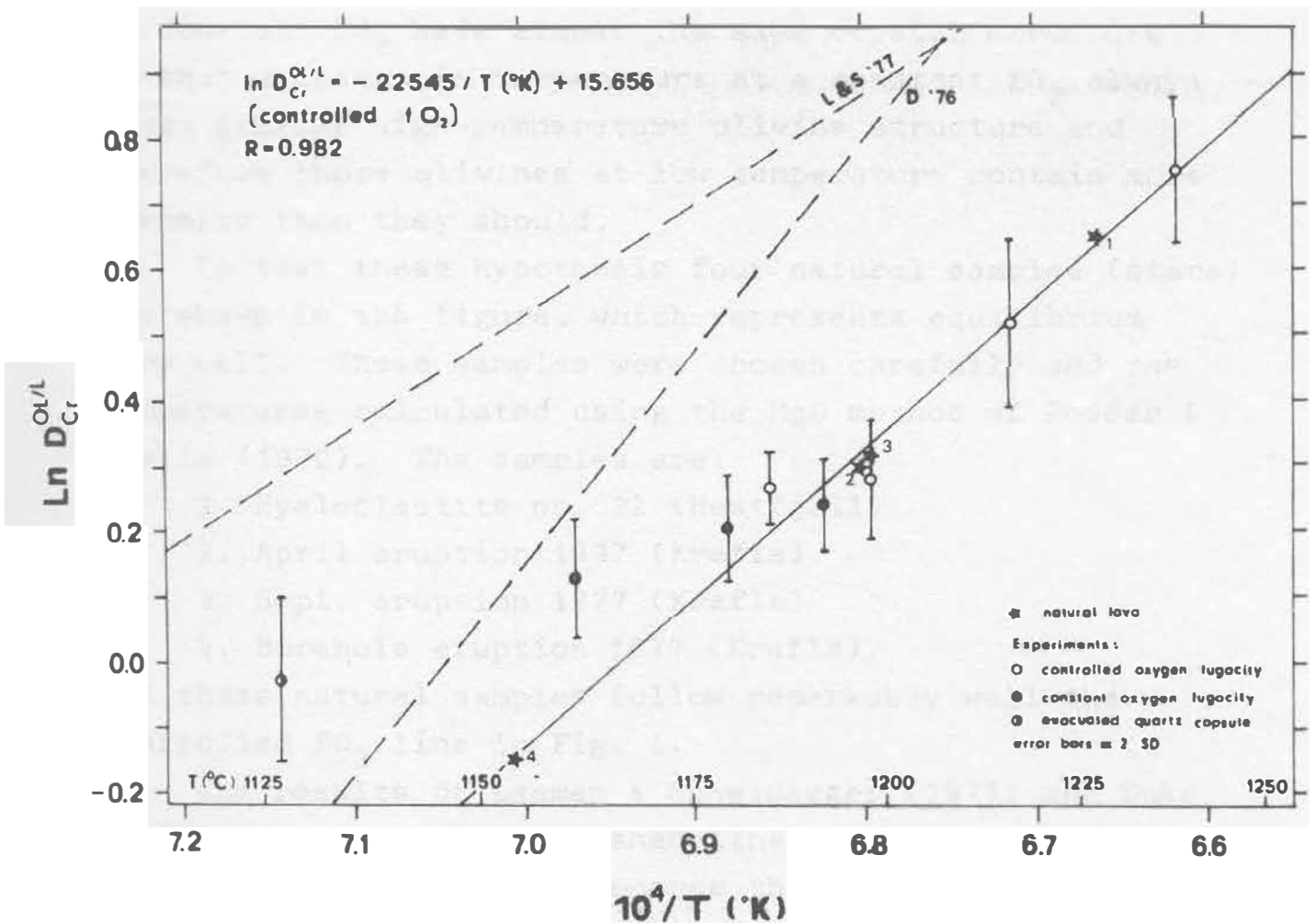


Fig. 1. Distribution of chromium between olivine and liquid. Equation and solid line were fitted by method of least-squares to present data only. L & S '77 (Leeman & Scheidegger 1977) D '76 (Duke 1976). Numbers 1, 2, 3 and 4 see text.

The solid circles with constant oxygen fugacity show very clearly that the distribution coefficient decreases with decreasing temperature, but this effect is weak. The measured strong correlation between distribution coefficient and temperature is mainly caused by the buffered oxygen fugacity and temperature together.

Another explanation could be that all olivines at lower temperatures have invisible Cr-rich spinel inclusions, that cannot be separated mechanically from the olivine. However, this is very unlikely.

The third possibility is that olivines crystallized at constant fO_2 have almost the same crystal structure so that a change in temperature at a constant fO_2 always gives similar high-temperature olivine structure and therefore those olivines at low temperature contain more chromium than they should.

To test these hypotheses four natural samples (stars) are shown in the figure, which represents equilibrium very well. These samples were chosen carefully and the temperatures calculated using the MgO method of Roeder & Emslie (1970). The samples are:

1. Hyaloclastite no. 32 (Hestfjall)
2. April eruption 1977 (Krafla)
3. Sept. eruption 1977 (Krafla)
4. Borehole eruption 1977 (Krafla).

All these natural samples follow remarkably well the controlled fO_2 line in Fig. 1.

The results of Leeman & Scheidegger (1977) and Duke (1976) are shown as two dashed lines. The agreement with L & S's data is better, because the lines are almost parallel. Authors suggested that their distribution values could be systematically over-estimated because they are used total analysis of separated olivine grains, which contain Cr-rich spinel inclusions.

Manganese

The distribution of manganese between olivine and liquid is more complicated (Fig. 2). As seen in the figure, the distribution coefficients are greater than unity and the values increase with decreasing temperature.

It is important to separate how the fO_2 and bulk composition affect the distribution coefficient. Immediately reject a question, which is such parameter which indicate best the bulk compositional variation. Of course there are many possibilities to adopt, but the silicon-oxygen ration seems to be most widely accepted.

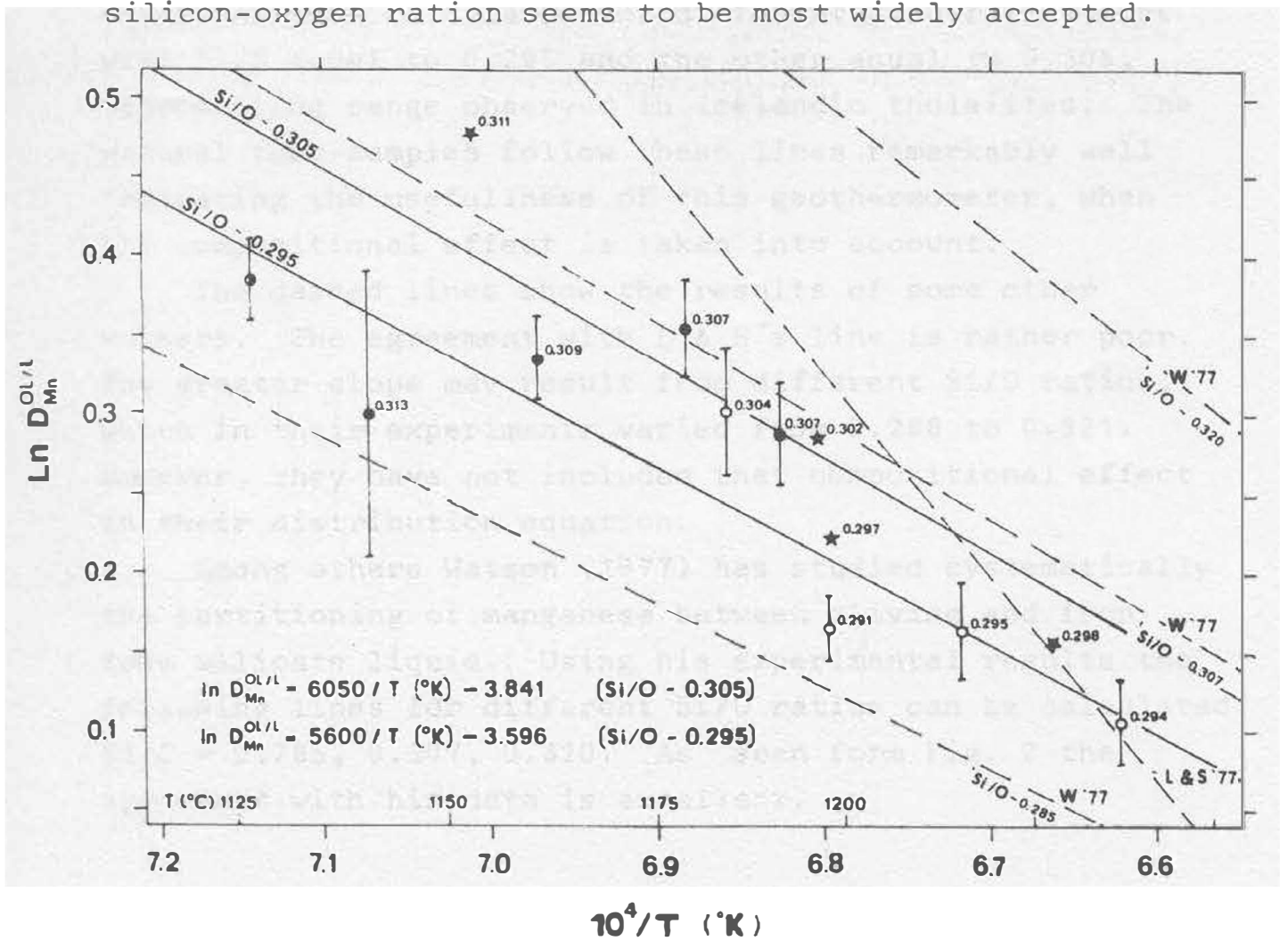


Fig. 2. Distribution of manganese between olivine and liquid, symbolism as in Fig. 1. Equations and solid lines with different Si/O ratios were fitted by method of least-squares to present data only. W '77 (Watson 1977).

The controlled fO_2 experiments show systematic variation against distribution coefficient with different Si/O ratios, so that the higher Si/O ratio the greater distribution coefficient.

The constant fO_2 experiments show very clearly that fO_2 affects the distribution coefficient seriously. Because manganese is almost always in the divalent state, the only way to explain this is in terms of the olivine crystal structure which, as explained in Cr-case, depends markedly on fO_2 .

On the basis of this data two Mn-distribution equations were calculated for different Si/O ratios, one with Si/O equal to 0.295 and the other equal to 0.305, representing range observed in Icelandic tholeiites. The natural test-samples follow these lines remarkably well indicating the usefulness of this geothermometer, when the compositional effect is taken into account.

The dashed lines show the results of some other workers. The agreement with L & S's line is rather poor. The greater slope may result from different Si/O ratios, which in their experiments varied from 0.288 to 0.321. However, they have not included that compositional effect in their distribution equation.

Among others Watson (1977) has studied systematically the partitioning of manganese between olivine and iron free silicate liquid. Using his experimental results the following lines for different Si/O ratios can be calculated: Si/O = 0.285, 0.307, 0.320. As seen from Fig. 2 the agreement with his data is excellent.

Cobalt

The cobalt content in the rocks studied is very low, down to 30 ppm. However, the accuracy of the analyses is good, as can easily be seen from the standard deviations.

Co decreases rapidly with differentiation and enters mainly olivines and pyroxenes.

All experiments with constant fO_2 as well as controlled fO_2 show linear correlation between distribution coefficient and temperature (Fig. 3).

The amount of cobalt does not affect the distribution, at least up to 3000 ppm in the olivine. Also all the natural test samples fall on the correlation line.

Leeman (1977) is about the only one who has systematically studied cobalt partitioning. The agreement with his data is relatively good. Roeder (1974) collected available experimental data from the literature, and calculated best fit equations. The resulting equation is almost identical to the one presented here.

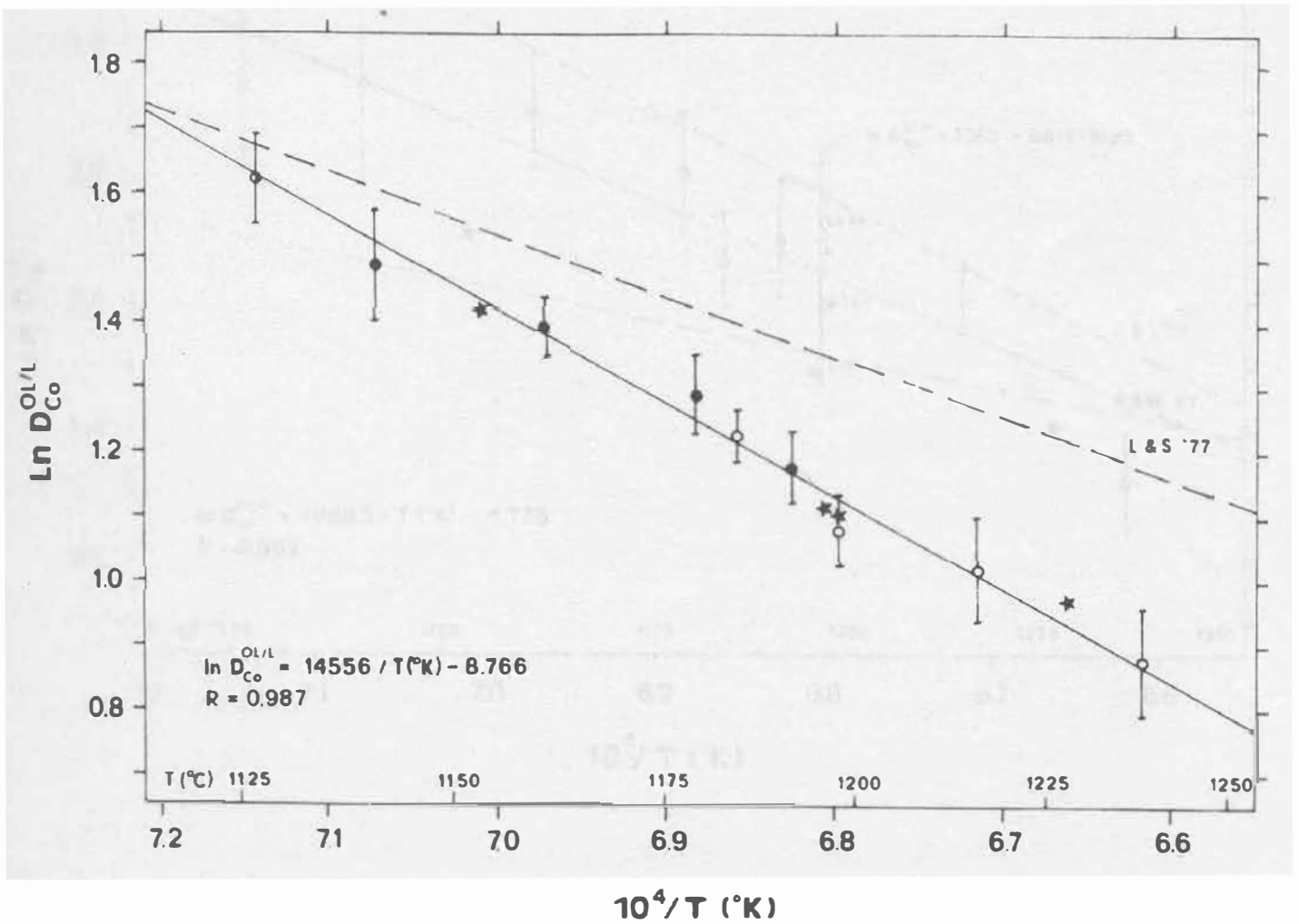


Fig. 3. Distribution of cobalt between olivine and liquid, symbolism as in Fig. 1. Equation and solid line were fitted by method of least-squares to present data only.

Nickel

The distribution coefficients for nickel has frequently been used as a geothermometer. However, the warning of Häkli & Wright (1966) tends to be forgotten that the use of their geothermometer for other kind rocks is limited by at least three factors: First, they did not know the effect of total pressure; secondly, the effect of water pressure and thirdly, the effect of chemical activities, particularly SiO₂ and FeO.

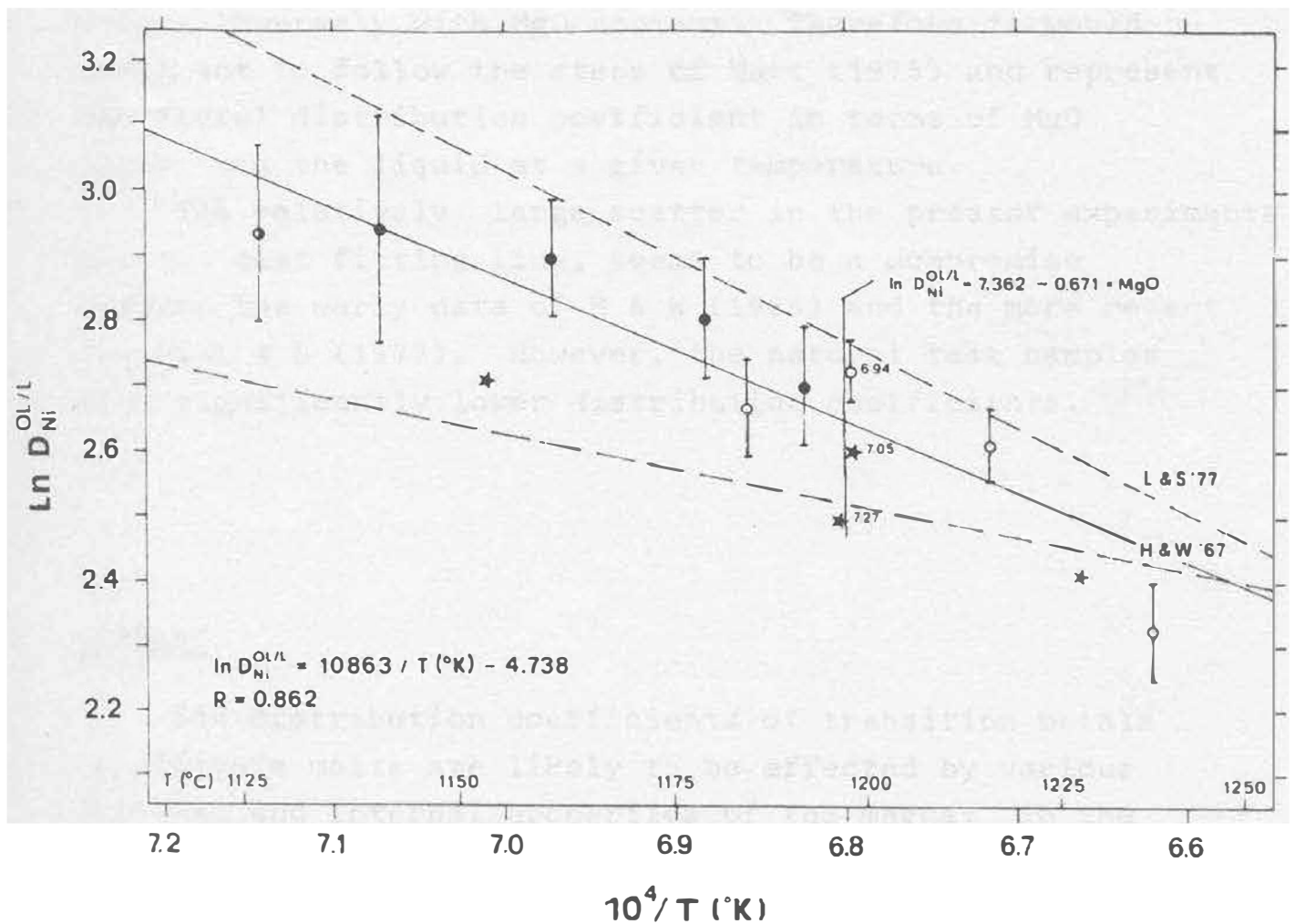


Fig. 4. Distribution of nickel between olivine and liquid, symbolism as in Fig. 1. Equation and solid line were fitted by method of least-squares to present data only. H & W '67 (Häkli & Wright 1967).

Mysen (1976) has pointed out the dependence of the distribution coefficient on bulk composition and also on the total amount of Ni. Up to about 1000 ppm (glass 60 ppm) Ni in olivine the distribution coefficient is linear at a constant temperature, but decreases rapidly at higher contents. This affects seriously the use of this distribution coefficient because the nickel content of many basaltic rocks exceeds this range.

However, the distribution coefficient seems to decrease with increasing temperature (Fig. 4). How strong this temperature effect is, is not yet known because D_{Ni} varies inversely with MgO content. Therefore it would be pertinent to follow the steps of Hart (1975) and represent the nickel distribution coefficient in terms of MgO content in the liquid at a given temperature.

The relatively large scatter in the present experiments, and the best fitting line, seems to be a compromise between the early data of H & W (1966) and the more recent one of L & S (1977). However, the natural test samples show significantly lower distribution coefficients.

SUMMARY

The distribution coefficients of 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 for experiments to try to evaluate the effects of some of these variable properties.

The distribution coefficients for Co, Cr, Mn and Ni are strongly temperature dependent and the other main results are briefly summarized below.

- (1) Co. The distribution coefficient for Co between olivine and liquid appears to be the only dependent on temperature. Varying the composition

and the fO_2 has no apparent effect. Measurements of Co could therefore be used as a geothermometer and indicator of fractionation of volcanic suites.

- (2) Cr. The distribution coefficient between olivine and liquid is dependent on temperature and fO_2 . Better knowledge of the fO_2 effect is needed before D_{Cr} can be used quantitatively.
- (3) Mn. The distribution coefficient between olivine and liquid is strongly dependent on bulk composition. Using the Si/O ratio as an index of the liquid structure a reasonable correlation between D_{Mn} and temperature is obtained at constant Si/O ratio.
- (4) Ni. The distribution coefficient for Ni appears to be strongly dependent on composition and varies inversely with MgO content.

The fact that trace element distribution coefficients are seriously affected by various properties of the magma makes their use as indicators of magma properties more uncertain than sometimes previously. But at the same time with increased experimental and thermodynamic knowledge their potential can be even greater.

The present study was intended as a preliminary exploration. For the next steps in the evaluation of the distribution coefficients the following points need to be kept in mind.

- (a) The oxygen fugacity seriously affects some of the distribution coefficients. In the present study the actual fO_2 values could not be measured directly so the effects could not be evaluated quantitatively. This facility has now been developed and experiments can be performed.
- (b) The compositional independence needs to be tested on more extreme compositions and worked out in greater detail particularly for Ni.
- (c) The amount of transition metal present may affect the distribution coefficient. This is known for

D_{Ni} which is linear only at low concentrations. In the present study only natural concentrations were used except for Co where some Co was added accidentally during the crushing process. This had no apparent effect on the D_{Co} .

- (d) No attempt has been made in the present study to evaluate possible effects of pressure and water content on the distribution coefficients. These effects could seriously affect the use of particularly Cr and Mn as geothermometers or indicators of fractionation.

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