NEW RESULTS OF METAL/SILICATE PARTITIONING OF NI AND CO AT ELEVATED PRESSURES AND TEMPERATURES. Ph. Kegler[1], A. Holzheid[2], D.C. Rubie[3], D. Frost[3] and H. Palme[1], [1]Universität zu Köln, Institut für Geologie und Mineralogie, 50674 Köln, Germany, philip.kegler@uni-koeln.de, [2]Universität Münster, Institut für Mineralogie, 48149 Münster, Germany. [3]Universität Bayreuth, Bayerisches Geoinstitut, 95440 Bayreuth, Germany

Introduction: What is the reason for the comparatively high Ni and Co abundances and the chondritic Ni/Co ratio in the Earth's mantle? Many workers have studied this question (e.g. [1-4]) and most of them conclude that metal/silicate equilibration in a deep magma ocean covering the surface of the early Earth has produced the high Ni and Co concentrations in the Earth's mantle. In these models estimated pressures and temperatures at the bottom of the magma ocean vary from 24 to 59 GPa and from 2200 to >4000K. These variations reflect uncertainties in P and T dependencies of Ni and Co metal-silicate partition coefficients.

Partitioning of an element (el) between metal and silicate can be described by the exchange metal-silicate partition coefficient, $K_D^{el\text{-}Fe}$,

$$K_D^{el\text{-}Fe} = D_{met/sil}^{el} / D_{met/sil}^{Fe}$$

with $D_{met/sil}^{el} = C_{met}^{el} / C_{sil}^{el}$ (C=concentration by weight). The advantage of using the K_Ds is its independence on oxygen fugacity allowing easy comparison of different data sets. The purpose of this work is to extend the present data basis by new experimental determinations of $K_D^{Ni\text{-}Fe}$ and $K_D^{Co\text{-}Fe}$ at a wider range of pressures and temperatures. Since K_Ds depend on P and T it is important to disentangle the effects of temperature and pressure.

Experiments: The metal/silicate partition behavior of Ni and Co has been investigated with additional experiments at pressures from 10^{-5} GPa (1 atm.) to 25 GPa and temperatures ranging from 1300 to 2300°C. At 10^{-5}, 5, 7 and 10 GPa isobaric experiments were performed at several temperatures to study the temperature dependence of the partition coefficients. An $Fe_{54}Ni_{29}Co_{17}$ alloy was equilibrated with a silicate melt of basaltic composition using crucibles made of MgO single crystals to enable liquid metal – liquid silicate equilibration. The detailed experimental setup and analytical procedures are as described in [5].

Results: A so far neglegted consequence of using a MgO crucible is the formation of ferropericlase during the experiments by the reaction of MgO (crucible), FeO (basaltic melt) and Fe (metal alloy), respectively (Figs. 1&2). Ferropericlase covers the metal blob in Fig. 1 and also forms at the MgO-melt interface. The presence of ferropericlase allows to control the experimental conditions by using high p and T data for ferropericlase-metal equilibria from the literature [e.g. 6]. Fig.2 shows the results of the EMP-analyses along a line leading from metal into the MgO capsule, marked in Fig. 1. Although there are some variations in absolute concentrations of Fe, Ni and Co in single phases, ratios of Fe/Ni/Co are essentially constant and allow the precise determination of exchange partition coefficients between metal, ferropericlase and basaltic melt. The results of metal-ferropericlase partition coefficients are in excellent agreement with data from [6], strengthening the reliabilty of the metal - basaltic melt exchange partition coefficients.

A comparison of the temperature dependence at 10^{-5} GPa (1 atm.) of [2] with the temperature dependence at pressures above 5 GPa shows a dramatic change of the temperature dependences of $K_D^{Ni\text{-}Fe}$ and $K_D^{Co\text{-}Fe}$, from a strong T-dependence at low pressures to a weak dependence at pressures above 5 GPa. New data from [7] at 7 GPa give the same temperature dependence as determined here. It is now clear that there is a very large difference in the temperature dependence of Ni and to lesser extent of Co partition coefficients between metal and melt at 10^{-5} GPa and at pressures > 5 GPa.

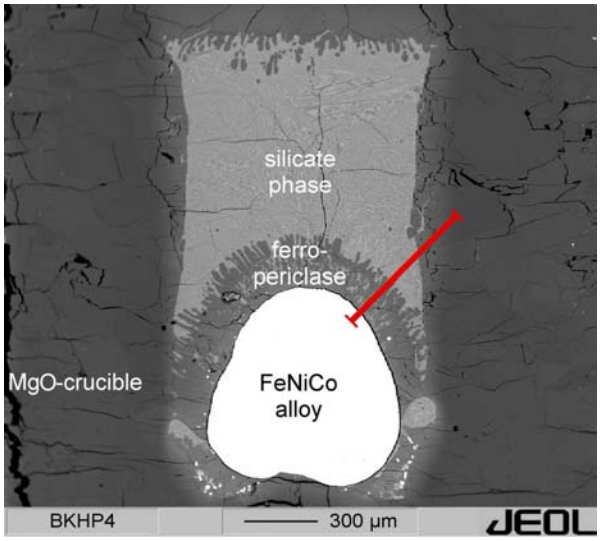

Fig. 1: Run product of a high pressure experiment: T=1900°C, P=10 GPa, duration 40 min. Between the alloy and the silicate phase a rim of ferropericlase formed during the experiment. Analytical results shown in Fig. 2 were obtained along the red line.

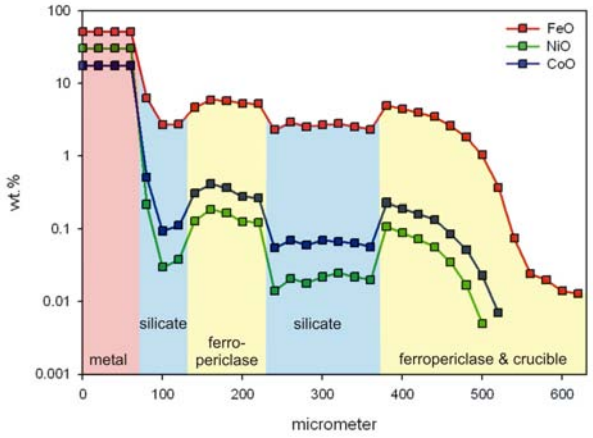

Fig. 2: Line analysis of the run product shown in Fig. 1. The FeO, NiO and CoO contents are measured from the alloy through the discontinuous ferropericlase rim and the silicate phase into the crucible.

The T-dependence between 5 and 10 GPa is the same within the accuracy of the analyses (Fig. 3). The improved accuracy of the T-dependence permits a more exact determination of the pressure dependence, as experiments performed at various pressures and temperatures can be more reliably recalculated to a single temperature. The pressure dependence of the K_Ds shows a similar behavior as the temperature dependence does. There is a low pressure regime (below 5 GPa) with high pressure dependences and a high pressure regime with weak pressure dependences. The two pressure regimes for the exchange partition coefficients of Ni and Co require a change with pressure of the molar volume of the exchange reaction

$$FeO_{sil} + Ni_{met} = NiO_{sil} + Fe_{met}$$

and the same reaction for Co. A change in the coordination number of Co^{2+} and Ni^{2+} in silicate melts with increasing pressure has been suggested by [8-10].

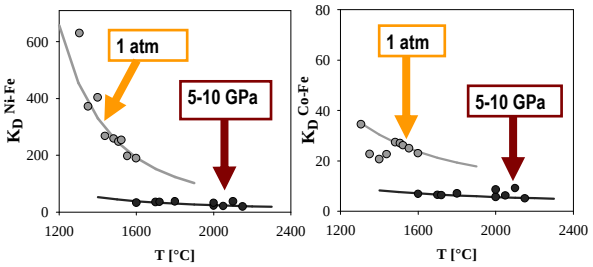

Fig. 3: Temperature dependence of K_D^{Ni-Fe} and K_D^{Co-Fe} at 10^{-5} GPa (1 atm.) and pressures from 5 to 10 GPa. Both K_Ds show a stronger T-dependence at 10^{-5} GPa than at pressures higher 5 GPa.

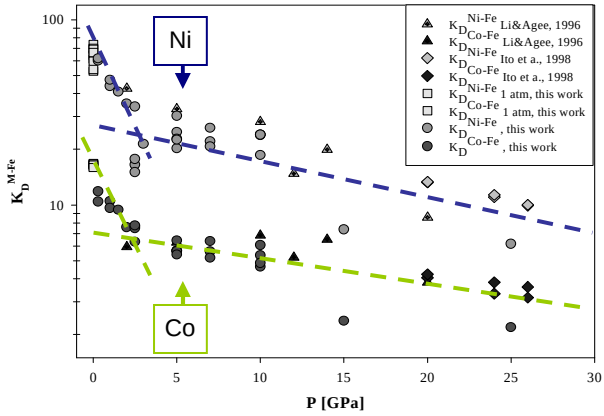

Fig. 4: Pressure dependence of K_D^{Ni-Fe} and K_D^{Co-Fe}. All data are recalculated to 2000°C using the experimentally determined T- dependence. For the high p regression all datapoints > 5 GPa are used.

Discussion: As a consequence the p- and T-dependence of K_D^{Ni-Fe} and K_D^{Co-Fe} cannot be regressed with a single linear fit as assumed by Li and Agee [3] which would produce a crossover of the K_Ds at a pressure of approximately 30 GPa. Using the pressure dependences of this work this crossover will not occur within the pressure regime of the Earth's mantle (Fig. 4). Possible explanations for the present Ni and Co concentration in the Earth mantle might be therefore inhomogeneous accretion (change of the oxidation state of accreting material) [e.g. 11-13] or inefficient core formation (later oxidized remnants of core forming metal in the mantle) [e.g. 14]. Further experiments at pressures above 15 GPa will be performed to better define the high pressure trend which presently shows some discrepancy with results of [4].

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