PRESSURE AND TEMPERATURE DEPENDENT PARTITIONING OF COPPER: IMPLICATIONS FOR TERRESTRIAL CORE FORMATION. Ph. Kegler[1], A. Holzheid[1], C. McCammon[2], D.C. Rubie[2] and H. Palme[3], [1]Universität Kiel, Institut für Geowissenschaften, [2]Universität Bayreuth, Bayerisches Geoinstitut, [3]Senckenberg Frankfurt am Main, Forschungsinstitut und Naturmuseum.

Introduction: The abundance of Cu in the Earth's mantle normalized to C1 and Mg is similar to the abundances of Ni and Co [1, 2]. This is surprising as Cu is much less siderophile [2] than Ni and Co. Although a lower bulk Earth abundance of Cu is expected because of its lower condensation temperature, this is not sufficient to compensate for the much lower one bar siderophility of Cu when compared to Ni [2]. Either the strongly chalcophile nature of Cu [3] or a pressure and temperature dependence of the metal/silicate partition coefficient that is different from those of Ni and Co accidentially produces a similar depletion. To better understand the abundance of Cu in the Earth's mantle we studied the metal - silicate partition behaviour of Cu as function of P, T, silicate composition, and alloy composition (Cu, Fe, Ni, and C contents). The first results are presented here.

Experimental methodology: Piston-cylinder experiments (BGI Bayreuth, Universität Kiel) were performed at pressures between 0.5 and 2.5 GPa and temperatures between 1350 and 1700°C. Different experimental setups were used to determine the dependence of the metal-silicate partition coefficient of Cu ($D^{met/sil}$Cu = wt.% Cu in metal / wt.% Cu in silicate) on oxygen fugacity, alloy composition, temperature and pressure.

Oxygen fugacity dependence: To determine the dependence of $D^{met-sil}$Cu on fO_2, basaltic melts with FeO contents between 0 and 20 wt. % were equilibrated with an $Fe_{97}Cu_3$ alloy at constant pressure and temperature (0.5 GPa, 1350°C).

Dependence on alloy composition: The influence of alloy composition was determined by using FeCu-alloys with Cu contents between 100 ppm and 12wt. %. To test the influence of Ni, three experiments with Ni bearing FeCu-alloys were performed ($Fe_{94}Ni_5Cu_1$, $Fe_{90}Ni_9Cu_1$, $Fe_{84}Ni_{15}Cu_1$) at 0.5 GPa and 1350°C.

Temperature and pressure dependence: A silicate melt of basaltic composition was equilibrated with an $Fe_{97}Cu_3$ alloy at different pressures and temperatures. Silicate powder was placed into an FeCu-alloy crucible at temperatures below the melting temperature of the metal phase. At temperatures above the melting point of the metal phase, both silicate and metal phases were placed into a graphite crucible.

Analyses: Major and trace element concentrations of all post run charges were analyzed using EMP (metal and silicate glass; Universität zu Köln) and LA-ICP MS (only silicate glass; Universität Münster).

Results and discussion: Fig. 1 shows the results of the oxygen fugacity dependence of $D^{met/sil}$Cu at 1350°C and 0.5 GPa compared to the 1 atm. data of [3]. The observed slope of 0.19 ± 0.02 (R^2 = 0.99) yields a valence of 0.76 ± 0.08. This is in good agreement with the data of [3]. The difference between the absolute values of $D^{met/sil}$Cu of this work and of [3] is the result of different alloy compositions.

The influence of $D^{met/sil}$Cu on alloy composition is illustrated in Fig. 2. All experiments were performed at 1350°C and 0.5 GPa. $D^{met/sil}$Cu values are recalculated to an oxygen fugacity of 2.3 log units below the iron-wüstite buffer (IW) using the fO_2-dependence of Fig.1. The nonideal behavior of Cu in FeCu-alloys is obvious. Experiments with Ni–bearing FeCu alloys show that Ni (0-15 wt.%) increases the lithophility of Cu (Fig. 2). This is an important observation as meteoritic metal contains significant quantities of Ni (2 to 25 wt.%). The composition of the core-forming alloy is therefore crucial for the interpretation of Cu concentrations in the Earth's mantle.

Fig. 3 shows the dependence of $D^{met/sil}$Cu on temperature at 1.5 GPa compared to data from [3] performed at 1 atm. All data are recalculated to an oxygen fugacity of ΔIW-2.3. The lithophility of Cu increases with increasing temperature. This is in good agreement with [3]. In addition, Fig. 2 shows that the influence of carbon on $D^{met/sil}$Cu can only be minor. Graphite capsules were used for experiments at tempertures above 1500°C. The carbon contents of alloys range from 5.3 to 6.5 wt.%.

Fig. 4 shows the pressure dependence of $D^{met/sil}$Cu. All experiments were performed at 1450°C and are recalculated to IW-2.3. The data show a weak increase of lithophility with increasing pressure.

	Core/mantle	Required P [GPa]	at T [°C]
Cu	6.3	14	2390
Ni	29.6	82	3930
Co	28.6	65	3530

Table 1: Pressure and temperature required to produce equalities between experimentally determined metal-silicate partition coefficients and core-mantle ratios along the temperature of the peridotite liquidus.

Conclusions: Table 1 shows the pressures and temperatures along the peridotite liquidus required to reach the core/mantle ratio for Cu, Ni, and Co by metal-silicate equilibration using the data of this work and of [4].

Approximately 14 GPa and 2390°C are needed to achieve the core/mantle ratio of Cu, although extrapolations to such high pressures and temperatures are very uncertain, as demonstrated by Ni and Co metal/silicate partition coefficients which show very different trends at low and high pressures and temperatures. The calculated pressures and temperatures needed to produce core/mantle ratios of Ni and Co are considerably higher. Furthermore we have neglected the strongly chalcophile nature of Cu, which could increase the partitioning into core-forming metal and/or sulphide.

The results of this work show that metal/silicate equilibration at the bottom of a single deep magma ocean seems unlikely to produce the abundances of these elements in the Earth's mantle.

A possible explanation for today's concentration of moderately siderophile elements in Earth's mantle might be a stepwise and incomplete equilibration between core-forming metal and mantle silicate under increasingly more oxidizing conditions as described by [5].

References: [1] McDonough W.F. (2001): *in: Earthquake Thermodynamics and Phase Transformations the Earth's Interior* (eds. R. Teisseyre and E. Majewski) pp. 3–23. [2] Schmitt, W. et al. (1989): *GCA 53, 173-185*. [3] Holzheid, A. and Lodders, K. (2001): *GCA*, 65, 1933-1951. [4] Kegler, Ph. et al. (2008): *EPSL*, 268, 28-40. [5] Rubie, D.C. et al. (2008): *Origin and Evolution of Planets 2008, Ascona 29.06.-04.07.*2008.

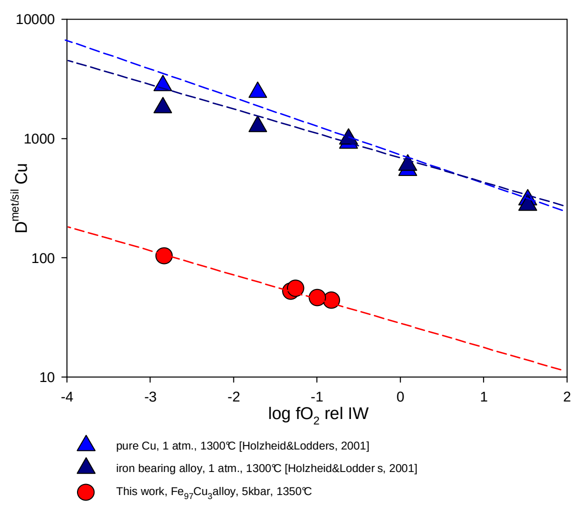

Fig.1: Dependence of $D^{met/sil}$ Cu on fO_2.

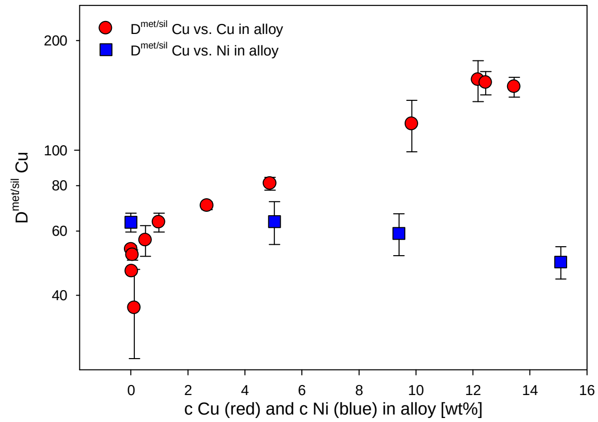

Fig. 2: Dependence of $D^{met/sil}$ Cu on alloy composition recalculated to ΔIW-2.3. All experiments are performed at 1350°C and 0.5 GPa. Red dots represent experiments with different Cu concentration in FeCu alloy, blue squares represent experiments made with different Ni and Fe but constant Cu (1 wt.%) concentration in alloy.

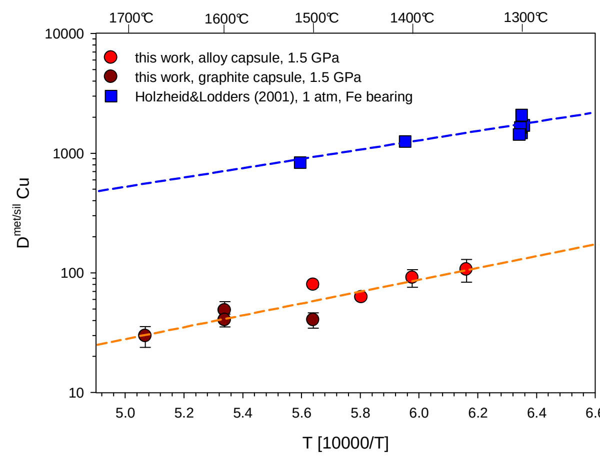

Fig. 3: T-dependence of $D^{met/sil}$ Cu recalculated to ΔIW -2.3

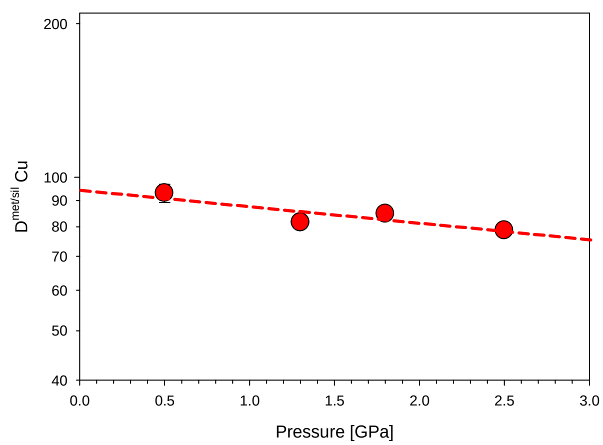

Fig. 4: P-dependence of $D^{met/sil}$ Cu (1450°C, recalculated to ΔIW-2.3)