PARTITIONING BEHAVIOUR OF COPPER AND GERMANIUM: IMPLICATIONS FOR TERRESTRIAL CORE FORMATION SCENARIOS.

A. Holzheid[1], Ph. Kegler[2,3], D. Frost[4], D.C. Rubie[4], and H. Palme[2], [1]Universität Kiel, Institut für Geowissenschaften, [2]Universität Köln, Institut für Geologie und Mineralogie, [3]Universität Münster, Institut für Mineralogie, [3]Universität Bayreuth, Bayerisches Geoinstitut.

Introduction: A widely accepted model to explain the abundances of moderately siderophile (metal-seeking) elements (e.g., Fe, Ni, Co, W, Mo) in the Earth's mantle, is to assume chemical equilibrium between core forming metal and silicate at the bottom of a deep global magma ocean, which extends to the upper region of the lower mantle [1-9]. Molten metal droplets of the accreted material sink through the partially or completely molten silicate phases to the bottom of the magma ocean, where the final equilibration with the mantle-silicates occurs. Increasing amounts of accumulated metal at the bottom of the magma ocean leads to the formation of large metal diapirs, which will eventually become gravitationally instable and rapidly sink down to the centre of the planet contributing to the growth of the core [e.g.,10]. This leads to a strong partitioning of siderophile elements (e.g., Fe, Ni, Co, Ge, noble metals) as well as chalcophile elements (e.g., Cu, Pb, Zn) into the core and a corresponding depletion in the mantle [11]. The trace amounts of siderophile and chalcophile elements that are retained in mantle silicates record the conditions of metal segregation when compared to expected abundances based on experimentally determined metal-silicate and metal-sulfide partitioning behavior. To better understand possible metal-silicate equilibration within the magma ocean we have expanded our study to Ge and Cu by experimentally determining the metal-silicate partitioning of the two elements at elevated pressure.

Experimental and analytical techniques: Experiments were done within the range of 1 atm to 25 GPa at temperatures between 1300 and 2300°C. The experiments were performed with vertical gas mixing furnaces at the Universität Köln (1 atm), by using piston cylinder apparati at the Universität Münster and at the Bayerisches Geoinstitut (0.3-3.5 GPa) and by using multi anvil presses at the Bayerisches Geoinstitut (1.5-25 GPa). In all experiments either $Fe_{54}Ni_{29}Co_{17}$, $Fe_{97}Ge_3$, or $Fe_{97}Cu_3$ alloys were equilibrated with a synthetic basaltic melt (SiO_2 49.1 wt.%; Al_2O_3 14.1%; CaO 24.9 %; MgO 10.6 %; FeO 7.0 %). Experiments with even lower Ge- and Cu-concentrations in the FeGe- and FeCu-alloys (only up to 0.5 wt.% Ge and Cu, respectively) are in progress. All experiments were terminated by withdrawing the samples from the hot spot position into the cooling jacket position of the vertical gas mixing furnaces (1 atm experiments). The high pressure experiments were terminated by turning-off the power to the graphite heater (piston cylinder experiments) or $LaCrO_3$ heater (multi anvil experiments). All experimental charges were mounted in epoxy, cut longitudinally through the center of the assemblies and polished as microprobe sections. Metal phases and major

elements of the silicate phases of the post-run charges were analyzed using a Jeol 8900RL electron microprobe (Universität Köln). Operating conditions for metal phases were 20 kV and 25 nA and a focused beam. Counting times were 60 sec. Major elements of the silicate phases were analyzed with 20 kV, 50 nA and a defocused beam (raster size 20 µm). Counting times were 60 sec. Trace elements, such as Ni and Co in the silicate phases were determined by electron microprobe with 20 kV, 400 nA and a defocused beam (raster size 20 µm). Counting times were up to 600 sec, giving detection limits of 50 ppm for NiO and CoO. Trace elements of Ge and Cu in the silicate phases were analyzed using a laser ablation ICP mass spectrometer (UP193HE - New Wave Research, Element 2 MS - Finnigan, Universität Münster). Measured isotopes were Ge73, Cu63, and - as internal standard - Ca44. The following conditions were used: energy density ~8.5 J/cm^2, pulse rate: 5 Hz, number of shots per single analysis: 100, spot size: 180 µm. The minimum detection limits (99% confidence) were 0.03 ppm for Ge and 0.01 ppm for Cu.

Results and discussion: In Figure 1 metal-silicate partition coefficients, $D^{met/sil}$, are plotted as function of pressure. All partition coefficients are recalculated to reflect equilibrium distribution between silicate and metal of core forming metal composition (Fe 85 wt.%, Ni 5.5 wt.%, Co 0.3 wt.%, Ge 1.1 ppm, Cu 29 ppm, difference to 100% = light element). Appropriate activity coefficients of [12] (Ni, Co), [13] (Cu), and [14] (Ge) are used for calculation of $D^{met/sil}$. For better comparison, all plotted $D^{met/sil}$ values were recalculated to an oxygen fugacity relevant for metal/silicate separation during core formation (2.3 log units below the iron-wüstite buffer) by assuming NiO, CoO, GeO and Cu_2O as stable species in the silicate phases and a temperature of 1600°C. For Cu and Ge pressure and temperature ranges are comparatively small. More experiments are in progress. So far the main results can be summarized as follows: (1) $D^{met/sil}$ of Ni, Co, Ge, and Cu decrease with increasing pressure at constant temperature and IW-2.3. (2) Ni and Co $D^{met/sil}$ values change their pressure dependence from a strong dependence at pressures below 5 GPa to a weaker dependence at higher pressures. (3) $D^{met/sil}$ of Ge and Cu do not change their pressure dependences within the investigated pressure range (1 atm–2.5 GPa). However, changes in pressure dependence of $D^{met/sil}$ of Ge and Cu at ~5 GPa in analogy to the observed changes for $D^{met/sil}$ of Ni and Co, cannot be ruled out, especially as changes in pressure dependences of solubilities of other siderophile and chalcophile element oxides were also recently observed (WO_2 and SO_2, personal communications of M. Walter and L. Rose-Weston). (4) Identical values of

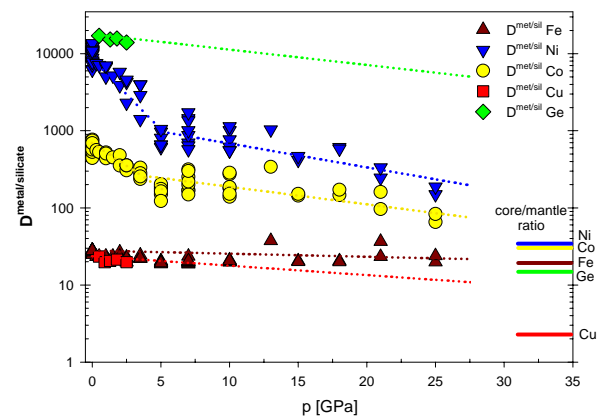$D^{met/sil}$ of Ni and Co, required to explain the chondritic Ni/Co ratio in the Earth mantle, are extremely unlikely within the pressure range of the upper mantle. Extrapolation to high pressure and temperature leads to the conclusion that none of the abundances of Ni, Co, Ge, and Cu in the Earth mantle could be the result of metal-silicate equilibration at the bottom of a 750 km deep global magma ocean (corresponding pressure at the bottom of the magma ocean = 25 GPa). Expected mantle contents of the four elements would have reached only 21% (Cu), 0.2% (Ge), 36% (Ni), and 83% (Co) of the observed mantle abundances.

Does any pressure and temperature condition exist that would account for the siderophile and chalcophile element abundances in the Earth's mantle as a result of a single-stage equilibrium? In Table 1 pressure values are listed. At these pressures today's core-mantle ratios would be identical to metal-silicate partition coefficients. These equalities are required to account for the element abundances in the Earth's mantle as a result of a single-stage equilibrium. An iteration method was used to derive the required pressures. $D^{met/sil}$ values (IW-2.3 was kept constant) converge to the core-mantle ratios by stepwise refinement of pressure and temperature. The temperature was always at least 100°C above the peridotite liquidus at the selected pressure. The pressures at core/mantle ratio - $D^{met/sil}$ equality range from 6.7 to 82 GPa at T ~ 3700°C. No single pressure and temperature condition exist. Based on the $D^{met/sil}$ values of our study the hypothesis of a simple single stage magma ocean that account for the siderophile and chalcophile element abundances in the Earth's mantle [1,2] has to be questioned. Advanced models, based on computational modelling, with metal-silicate fractionation in a convecting magma ocean [15], or other hypotheses (i.e., inefficient core formation [16], heterogeneous accretion [17,18], self oxidation of the Earth mantle with a multiple stage magma ocean [8,9,19]) are alternative explanations for the present siderophile element abundances in the Earth mantle.

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Figure 1: Metal-silicate partition coefficients of Cu, Ge, Ni, and Co vs. pressure.

All data are recalculated to a metal phase appropriate to the composition of the Earth core, an oxygen fugacity 2.3 log units below the iron-wüstite buffer, and 1600°C. The horizontal bars represent the core/mantle ratios in today's Earth (blue = Ni (30); pink = Co (29); green = Ge (12); red = Cu (2.3)).

Table 1: Pressure required to produce equalities between experimentally determined metal-silicate partition coefficients and core-mantle ratios

	core/mantle ratio	required p [GPa]	at T [°C]
Ni	29.6	82	3930
Co	28.6	65	3530
Ge	12.1	6.7	3700 (1)
Cu	2.3	(2)	

All metal-silicate partition coefficients were recalculated to IW-2.3 and the composition of core forming metal. Temperatures were at least 100°C above the peridotite liquidus. (1) T dependence (only 1-atm T dependences are available) taken from [20]. (2) unrealistic low pressure due to imprecise determinations of T dependences.