

ACCRETION AND CORE FORMATION OF TERRESTRIAL PLANETS: INSIGHTS FROM EXPERIMENTALLY DETERMINED SOLUBILITY BEHAVIOR OF SIDEROPHILE ELEMENTS IN SILICATE LIQUIDS. Ph. Kegler^{1,2}, A. Holzheid² and H. Palme¹, ¹Universität Köln, Institut für Geologie und Mineralogie, 50674 Köln, Germany, philip.kegler@uni-koeln.de, herbert.palme@uni-koeln.de, ²Universität Münster, Institut für Mineralogie, 48149 Münster, Germany, holzheid@uni-muenster.de.

Introduction: In common models of core formation in the terrestrial planets the proto-planet is covered with a deep, hot and turbulent convecting magma ocean [e.g., 1]. Molten metal droplets of the accreted material sink through the partially or completely molten silicates to the bottom of the magma ocean, where the final equilibration with the mantle-silicates occur. 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 unstable and rapidly sink down to the centre of the planet contributing to the growth of the core [e.g.,2]. This leads to a strong partitioning of siderophile elements (e.g., Fe, Ni, Co, Ge, noble metals) as well as the chalcophile elements (e.g., Cu, Pb, Zn) into the core and a corresponding depletion in the mantle [3]. The trace amounts of siderophile and chalcophile elements that are retained in mantle silicates record the conditions of metal segregation. Moreover, if metal and/or metal sulfide segregation was an equilibrium process, the relative depletions of siderophile and chalcophile elements give important clues for deducing the conditions of differentiation and core formation processes in the Earth and other planetary bodies. The concentrations of many siderophile elements (e.g., Ni, Co, Ge, highly siderophile elements) are overabundant in the Earth's mantle compared to expected concentrations based on experimentally determined metal-silicate partition coefficients at one atmosphere. To explain this poor match between the experimentally determined metal-silicate partition coefficients and observed abundances of the siderophile as well as some chalcophile elements in today's mantle, a strong temperature and pressure dependence is assumed for these elements and has been experimentally verified for some elements (summarized in [1]). According to [4-9] metal-silicate partition coefficients of Ni and Co converge at high pressure. Based on the convergence, the relative abundances of Ni and Co would be consistent with metal-silicate equilibrium at the base of a single stage magma ocean at a depth of about 800 km. The results of recent experiments showed a more complex behavior of Ni and Co metal-silicate partition coefficients with increasing pressure that does not support the single stage magma ocean model [10,11]. In addition kinetic constraints on metal-silicate separation scenar-

ios, proposed by [12], question the model of metal-silicate equilibrium at the base of a magma ocean. To better understand possible metal-silicate equilibration within the magma ocean (and not limited to the base of 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 methodology: 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 apparatus at the Universität Münster and at the Bayerisches Geoinstitut (0.3-3.5 GPa) and by using multi anvil presses at the Bayerisches Geoinstitut (3.5-10 GPa). In all experiments either Fe₅₄Ni₂₉Co₁₇, Fe₉₇Ge₃, or Fe₉₇Cu₃ alloys were equilibrated with a synthetic basaltic melt (SiO₂: 49.1 wt.%; Al₂O₃: 14.1%; CaO: 24.9 %; MgO: 10.6 %; FeO: 7.0 %). The 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 LaCrO₃ 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). Meas-

ured isotopes were Ge73, Cu63, and – as internal standard - Ca44. The following conditions were used: energy density $\sim 8.5 \text{ J/cm}^2$, 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, $D^{\text{met/sil}}$, are plotted as function of pressure. All partition coefficients are recalculated to equilibrium with pure metals, (see [13] for more details). Appropriate activity coefficients of [14] (Ni, Co), [15] (Cu), and [16] (Ge) are used for calculation of $D^{\text{met/sil}}$. For better comparison, all plotted $D^{\text{met/sil}}$ values were additionally 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 Cu₂O as stable species in the silicate phases. Due to the lack of precise knowledge of temperature dependences of Cu and Ge $D^{\text{met/sil}}$ at elevated pressure, Ni and Co $D^{\text{met/sil}}$ were recalculated to 1450°C, i.e., run temperature of all Cu and Ge high pressure experiments. The main results of our study on metal-silicate partition coefficients can be summarized as follows: (1) $D^{\text{met/sil}}$ of Ni, Co, Ge, and Cu decrease with increasing pressure at constant temperature and IW-2.3. (2) Ni and Co $D^{\text{met/sil}}$ values change their pressure dependence from a strong dependence at pressures below 5 GPa to a weaker dependence at higher pressures. Identical values of $D^{\text{met/sil}}$ 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. (3) Co $D^{\text{met/sil}}$ is in agreement with the core-mantle ratio of Co at about 40 GPa. However, $D^{\text{met/sil}}$ values of Ni, Ge, and Cu at 40 GPa differ by factors of about 2, 5, and 7, respectively. Although the absolute abundance of Co in the Earth mantle could be the result of metal-silicate equilibration at the bottom of a 1200 km deep magma ocean, expected mantle contents of the other studied siderophile elements at 40 GPa would have reached only 15 % (Cu), 20 % (Ge), and 50 % (Ni) of the observed mantle abundances. Our observations question the hypothesis of a simple single stage magma ocean. Alternative hypotheses to explain the siderophile element abundances in the Earth mantle could be inefficient core formation [17], heterogeneous accretion [18,19], or self oxidation of the Earth mantle with a multiple stage magma ocean [20,21].

References: [1] Walter, M. J., et al. (2000) In: *Origin of the Earth and Moon*, pp 265-290. [2] Stevenson, D. J. (1990) In: *Origin of the Earth*, pp 231-249. [3] O'Neill, H. St. C. and Palme, H. (1997) In: *The Earth's mantle: Structure, composition and evolution* pp 3-126. [4] Li, J. & Agee, C. (1996) *Nature*, **381**, 686-689. [5] Li, J. & Agee, C. B. (2001). *GCA*, **65**, 1821-1832. [6] Bouhifd, M. A. & Jephcoat, A. P. (2003) *EPSL*, **209**, 245-255. [7] Tschauner, O. et al. (1999) *Nature*, **398**, 604-607. [8] Righter, K. & Drake, M. J. (2004) In: *Geochemistry of the mantle and core*, pp 425-449. [9] Chabot, N. L. et al. (2005) *GCA*, **69**, 2141-2151. [10] Kegler, Ph. et al. (2004) *LPSC XXXV*, 1632. [11] Kegler, Ph. et al. (2005) *LPSC XXXVI*, 2030. [12] Rubie, D. C., et al. (2003) *EPSL*, **205**, 239-255 [13] Holzheid, A. & Palme, H. (1996) *GCA*, **60**, 1181-1193. [14] Guillermet A.F. (1989) *Calphad* **13**, 1-22 [15] Maruyama, N. & Banya, S. (1980) *J. Jpn. Inst. Metals*, **44**, 1422-1431. [16] de Boer, F. R. et al. (1989) *Cohesion and Structure*. [17] Jones, J. H. & Drake, M. J. (1986) *Nature*, **322**, 221-228. [18] Ringwood, A. E. (1984) *Proc. R. Soc. London*, **A395**, 1-46. [19] Wänke, H. et al. (1984) In: *Archean geochemistry*, pp 1-24. [20] Frost, D. J. et al. (2004) *Nature*, **428**, 409-412. [21] Wade, J. & Wood, B. (2005) *EPSL*, **236**, 78-95.

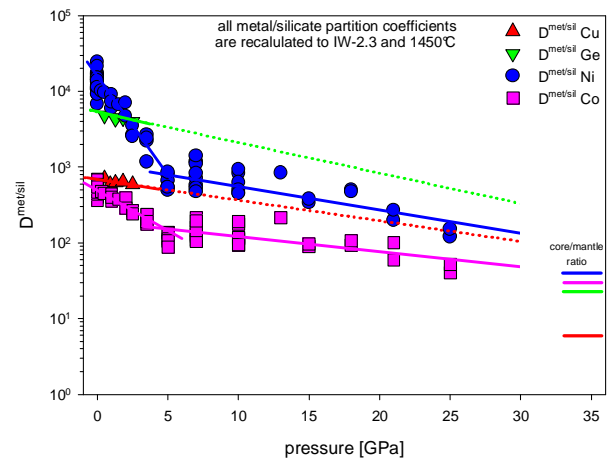


Figure 1: Metal-silicate partition coefficients of Cu, Ge, Ni, and Co vs. pressure. All data are recalculated to an oxygen fugacity 2.3 log units below the iron-wüstite buffer and 1450°C. The horizontal bars represent the core/mantle ratios in today's Earth (blue = Ni (39); pink = Co (31); green = Ge (26); red = Cu (6)).