HIGH CONCENTRATIONS OF HIGHLY SIDEROPHILE ELEMENTS WERE STRIPPED FROM EARTH’S MANTLE BY THE SEGREGATION OF EXSOLVED IRON SULFIDE MELT. D. C. Rubie1, V. Laurent2, S. A. Jacobson1,2, A. Morbidelli3, H. Palme3, A. K. Vogel1, and D. J. Frost1, 1Bayerisches Geoinstitut, University of Bayreuth, D-95490 Bayreuth, Germany (dave.rubie@uni-bayreuth.de), 2Observatoire de la Cote d’Azur, Nice, France (seth.jacobson@oca.eu, morby@oca.eu), 3Forschungsinstitut und Naturmuseum Senckenberg, Frankfurt, Germany (palmeherbert@gmail.com).

Introduction: Moderately siderophile elements, such as Ni, Co, W and Mo, are variably depleted in the bulk silicate Earth (BSE), relative to chondritic meteorite abundances, as a consequence of metal-silicate equilibration and segregation during formation of Earth’s core. This is because the metal-silicate partition coefficients are different for each element. In contrast, highly siderophile elements (HSEs: Re, Os, Ir, Ru, Rh, Pt, Pd and Au) are present in Earth’s mantle in near-chondritic relative abundances [1-4]. The conventional explanation is that the HSEs were stripped from the mantle by metal-silicate segregation during core formation but were added back to near-chondritic proportions by the late accretion of chondritic material after core formation had ceased. Here we test this hypothesis using a combined accretion/core formation model. Because of the possible importance of sulfur [5], the model is based on new experimental high-pressure partitioning data for Pt, Pd, Ru and Ir.

Methods: In order to investigate the effect of S on the behaviour of the HSEs during core formation, we performed two sets of high P-T experiments using multianvil apparatus. (1) We studied the effect of S on HSE metal-silicate partitioning by equilibrating a peridotite melt with a range of compositions along the Fe-FeS join at constant P (11 GPa) and T (2200°C). (2) The P-T dependence of HSE sulfide-silicate partitioning was investigated by equilibrating FeS melt with molten peridotite at pressures of 7-21 GPa and temperatures of 2100-2400°C. Major element compositions of the run products were analyzed by electron microprobe, whereas HSE and S abundances in the silicates were determined using LA-ICP-MS.

Results: The metal-silicate partitioning experiments show that the HSEs become less siderophile with increasing S-concentrations in the metal. This effect is strongest for Ir, while the influence of S on Pd metal-silicate partitioning is moderate. Thus, if S is present, the core-forming metal will be less efficient in removing the HSEs from the Earth’s mantle. Our second set of experiments confirms that the HSEs are strongly chalcophile at high P and T. \(K_{DS}^{\text{sulfide-silicate}}\) for all HSEs decrease with increasing T although the effect for Pd is weak (Fig. 1). With increasing P, \(K_{DS}^{\text{sulfide-silicate}}\) of Ru, Pd and Ir decrease very weakly while that of Pt increases. The overall result is that at high P-T conditions Ru and Pd are less chalcophile than Pt and Ir. From these sulfide-silicate partitioning experiments, we also determined the sulfur content at sulfide saturation (SCSS) for peridotite melt. As expected from previous studies, S-solubility in the melt decreases strongly with increasing pressure. However, SCSS in peridotite melt is higher than in basaltic and chondritic (CV3) melts due to the strong effect of melt composition.

Accretion/Core formation model: We have previously modelled the evolution of moderately siderophile element concentrations in Earth’s mantle and core by combining a geochemical model of multistage core formation with the results of astrophysical N-body models of planetary accretion [6]. The latter models start with around a hundred embryos (~Mars-size) embedded in a protoplanetary disc consisting of few thousand much smaller planetesimals that extends from 0.7 to 10 astronomical units (AU). The compositions of all starting bodies are defined by assuming chondritic relative abundances of non-volatile elements and a variable oxygen content that causes bodies to be more oxidized with increasing distance from the Sun. The planets accrete through embryo-embryo and embryo-planetesimal collisions. Each collision is considered to result in extensive melting, magma ocean formation and an episode of core formation that involves chemical equilibration between liquid metal and silicate. The compositions of the latter are determined by mass bal-
ance combined with element partitioning models for Si, Ni and FeO. Several parameters are refined in order to produce a model Earth with a final mantle composition close to that of Earth’s mantle.

We have extended the accretion/core formation model to include the highly siderophile elements Pt, Pd, Ru and Ir, based on our new HSE partitioning data and the Grand Tack N-body accretion simulation 4:1-0.5-8 [6]. The volatile element sulfur has a significant effect on metal-silicate partitioning of HSEs, by making them less siderophile, and is therefore included in the bulk compositions of starting bodies, with bulk S concentrations increasing with distance from the Sun. The S compositional gradient is adjusted to result in 1.7-2 wt% S in Earth’s core. We consider first the effects of metal-silicate equilibration and segregation on evolving Pt, Ru, Pd and Ir abundances in Earth’s mantle as a function of time (Fig. 2).

Figure 2: Evolution of mantle abundances of HSEs with time, based on metal-silicate equilibration, during Earth’s accretion. Each symbol represents an impact and “mass accreted” is the total mass after each impact normalized to Earth’s current mass (M_e). The final giant impact, at 113 My, increases Earth’s mass from 0.872M_e to 0.997 M_e. Mantle HSE abundances are shown by horizontal dashed lines.

HSE concentrations become high at an early stage of accretion and increase to exceed Earth mantle concentrations by an order of magnitude by the end of accretion (Fig. 2). The main reason is that most impacting bodies had undergone early core-mantle differentiation as a result of heating caused by the decay of 26Al. HSE partition coefficients are extremely high (10^6-10^11 [4]) at the low P-T conditions of planetesimal differentiation (≤0.3 GPa and ≤1900 K), which means that the HSEs partitioned almost entirely into their metallic cores during differentiation. Earth mantle increases result mainly from the accretion of differentiated planetesimals: at the high P-T conditions of metal-silicate equilibration in Earth, partition coefficients are lower, by 2-5 orders of magnitude, than under the conditions of planetesimal differentiation. HSEs are therefore transferred from the metal of impactors’ cores to Earth’s mantle. This is the case provided at least some fraction (e.g. >10%) of accreted metal equilibrates in the magma ocean. Thus, contrary to conventional wisdom, accreted metal actually adds HSEs to the mantle rather than removing them. In addition, the HSE concentrations are highly fractionated because each has a different metal-silicate partition coefficient, so that final relative abundances are strongly non-chondritic.

Based on metal-silicate segregation alone, the final mantle sulfur content also exceeds the BSE concentration by a factor of 5-6. The evolving S concentrations greatly exceed sulfur solubilities in crystallizing magma oceans at high pressure. Thus, exsolution of FeS liquid and its segregation to the core must have occurred in cooling magma oceans. We model this as a pervasive process that also strips HSEs from the magma ocean(s). Using our new HSE sulfide-silicate liquid partitioning data, Pt and Ir concentrations are reduced to <1 ppb by this process (prior to late accretion) whereas concentrations of Pd and Ru are 5-10 ppb because these elements are less chalcophile than Pt and Ir. Finally, when a late veneer accretes, with a mass 0.3% of Earth’s current mass, the final HSE concentrations become close to BSE values (Fig. 3). In particular, calculated Pd/Ir and Ru/Ir are suprachondritic in agreement with BSE values [2]. Previous explanations for these suprachondritic ratios have relied mainly on postulating the accretion of meteoritic material that is not present in existing meteorite collections [2, 3]. Here we show that a planetary differentiation process could have been responsible.

Figure 3: Evolution of mantle concentrations of HSEs with time based on both metal-silicate and sulfide segregation. The vertical dashed lines show the time of the final giant impact (GI) at 113 My and the start of late veneer accretion (LV) at 119 My after sulfide segregation has ceased.