

# Sulphur and selenium partitioning between silicate and metallic melts at core-mantle boundary conditions

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The Earth's core is dominantly composed of a metallic Fe-Ni mixture. However, seismic observations show that the density is about 5-10% lower than expected for an Fe-Ni alloy under pressure and temperature conditions of the Earth's core (e.g., Birch, 1952; McQueen and Marsh, 1960, 1966; Anderson and Isaak, 2002; McDonough, 2003). The discovery of this density discrepancy initiated numerous studies aimed to identify and quantify the alloying light elements in the Earth's core. Sulphur has been suggested to be a most likely candidate to alloy with the metallic core because of its depletion in the crust and the mantle relative to other volatile elements by several orders of magnitude (e.g., Rama Murthy and Hall, 1970; Dreibus and Palme, 1996). However, experimental data on sulphur partitioning between silicate and metallic liquids at pressures and temperatures relevant for core-mantle boundary conditions are missing for several reasons. On one hand, conventional experimental approaches limit pressure and temperature conditions up to 25 GPa and 2200 K. And on the other hand, chemical analyses of sulphur, e.g., by electron microprobe (EMP) or X-ray fluorescence (XRF) analyses, are restricted because of high detection limits and the required large amount of sample material. New approaches and developments in the past decade, like laser-heated diamond-anvil cells (LDAC), allow studies at core-mantle boundary conditions. Unfortunately, in-situ chemical analysis in LDACs is impossible due to the high absorption of sulphur fluorescence in the diamonds. The approach used here is based on the fact that sulphur and selenium can be considered as geochemical twins (Jenner et al., 2009; Wykes et al., 2010). The excitation energy of selenium is significantly higher than that of S, which makes Se accessible by in-situ XRF analysis in LDACs. Therefore, Se can probably be used as a model to set constraints on the sulphur partitioning between silicate and metallic melts at elevated PT conditions.

Here, we report partitioning data of Se between silicate and metallic liquids at very high pressures and high temperatures. Experiments have been performed in double-sided laser-heated LDACs at the high pressure beamline P02.2 as described in Petitgirard et al. (2012) using an excitation energy of 25.6 keV. Micro-XRF mappings are used to visualize changes of the Se distribution before and after laser heating. Micro-XRD is used to determine the experimental pressure, the onset of melting and also provides information on distribution of high-pressure / high temperature phases. Samples, sandwiched between thin layers of NaCl, are composed of a thin Fe<sub>90</sub>Ni<sub>10</sub> metal foil that partly overlaps with a very small Se and S doped chondritic glass piece. The salt acts as pressure media and insulating material. Laser heating was performed at the interface of metal foil and chondritic glass. Nine experiments have been carried out within a pressure range of 20 to 80 GPa. Figure 1 shows element distribution maps of Fe and Se after laser heating of three experiments at different pressures.

In order to clarify if Se can be used as geochemical analog to sulphur, additional analyses using the JEOL Superprobe JXA 8230 at Helmholtz Centre Potsdam (GFZ) were carried out on recovered samples. These data show a similar distribution pattern of S and Se in all studied samples, and a solubility of ~1-2 wt.% S and ~2-2.5 wt.% Se in the metallic melt at ~45 GPa. To sum up, Se can be considered as an analog to sulphur at pressure and temperature conditions of the Earth's core formation. Therefore, using Se or other suitable geochemical twins of light elements that are accessible by in-situ XRF analysis in LDAC can significantly help to decipher the Earth's core composition.

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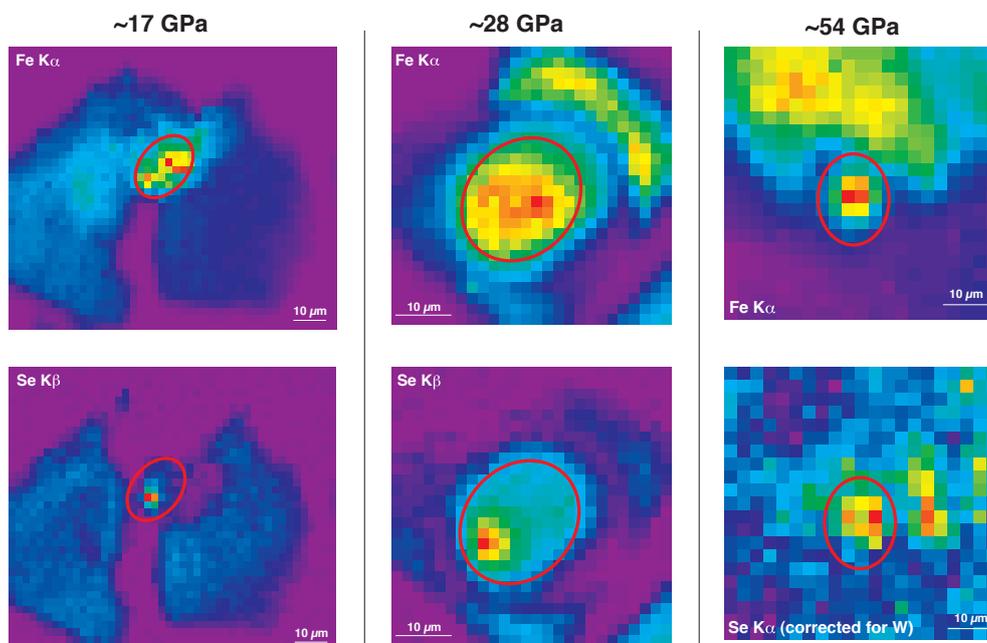


Figure 1: Iron and selenium distribution maps measured after laser heating at three different pressures. Images clearly show a distinct preference of Se for the metallic melt. Red circles mark laser heated areas.

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