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Solubility of Germanium in Silicate Melts and its Significance for Core Formation in the Earth

Astrid Holzheid[1] & **Herbert Palme** (palme@min.uni-koeln.de)[2]

[1] Universität Münster, Institut für Mineralogie, Corrensstr. 24, Münster, 48149, F.R. of Germany
[2] Universität zu Köln, Institut für Mineralogie und Geochemie, Zülpicherstr. 49b, 50674 Köln, F.R. of Germany

Germanium is a compatible, moderately siderophile and volatile element. The approximately constant Ge/Si ratio in various types of terrestrial rocks reflects the diadochic relationship between Ge and Si as Ge^{4+} substitutes for Si^{4+} in silicates. The crustal Ge abundance (1.4 ppm) is about 40% higher than the Ge content of the primitive upper mantle with 1.1±0.1 ppm (McDonough & Sun, 1995). This is the same crust/mantle ratio as for SiO_2. Compared to CI-chondritic abundances, Ge is depleted in the Earth's mantle by a factor of 0.02, reflecting the combined effects of core formation in the Earth and volatility related depletion in the material from which the Earth is made. When corrected for volatility, the Ge core/mantle ratio is with 25 about the same as Ni (Kargel & Lewis, 1993).

Experimentally determined metal/silicate partition coefficients of both elements, Ni and Ge, at an oxygen fugacity appropriate for core formation and at 1 bar pressure are much higher than the core/mantle ratio of 25. Earlier claims that this reflects the absence of equilibrium between core and mantle were questioned by Li and Agee (1996) who found that Ni and Co become more lithophile with increasing pressure and temperature, allowing for separation of core forming metal in a homogeneously accreting Earth at a depth of 800-1000 km. In order to be consistent with this picture the Ge metal/silicate partition coefficient $D_{Ge}^{met/sil}$ must also decrease with pressure and/or temperature. Contrary to Ni, Schmitt et al. (1989) found an increase of $D_{Ge}^{met/sil}$ with temperature, between 1300 and 1600ºC. This would require a very strong decrease of $D_{Ge}^{met/sil}$ with pressure, i.e. a decrease of the siderophility with pressure. In an attempt to determine the pressure dependence of $D_{Ge}^{met/sil}$, Holzapfel et al. (2000) determined the partial molar volume of GeO_2 in silicate liquids. The result indicates an increase of the siderophility with pressure, leading to even stronger depletions of Ge at higher pressure, a distinctive inconsistency with the observed upper mantle abundances, and clearly supporting a heterogeneous accretion model. Holzapfel et al. determined the partial molar volume of quadrivalent Ge oxide (GeO_2). The stable Ge species at the conditions of core formation is, however, unclear. Schmitt et al. obtained divalent Ge cations dissolved in a silicate liquid, while Capobianco et al. (1999) provided evidence for Ge^{4+} as dominant Ge species in liquid silicate. We therefore decided to experimentally determine the valence of Ge in silicate melts by equilibrating pure Ge metal with silicate melts at various oxygen fugacities and constant temperature.

All experiments were conducted in a vertical tube furnace at one atmosphere. The oxygen fugacity was controlled by gas mixtures of CO and CO_2. A $PtRh_6/PtRh_{30}$ thermocouple and a $CaO\text{-}Y_2O_3$-stabilized ZrO_2 solid electrolyte sensor were employed for measuring temperature and oxygen fugacity during the experimental runs. In all experiments powdered silicates of anorthite-diopside eutectic composition were inserted on top of pure Ge metal powder into small Al_2O_3 or ZrO_2 crucibles with ratios of approximately 1:2.5 (by weight). Crucibles were equilibrated at different fugacities, isothermal conditions (1329±3ºC), and run durations of about 2 hours. Samples were quenched to glass by withdrawing them from the hot zone to the top of the furnace. Glass samples were separated by crushing the glass-containing crucible and handpicking individual glass fragments. Fragments adhering to the crucible were avoided. Germanium concentrations in glasses were analysed by instrumental neutron activation analysis (INAA) and/or by electron microprobe (EMP). A beam current of 20 nA, an accelerating voltage of 15 kV and counting times of 300 seconds for Ge were employed (EMP-analysis).

The experiments show a decrease of the Ge solubility in the silicate at reducing conditions. The decrease is compatible with Ge^{4+}. However, the present data are not sufficiently accurate to exclude Ge^{2+} at oxygen fugacities slightly above the Fe-FeO (IW) buffer. Further experiments to clarify the situation are in progress.

If Ge^{4+} were the stable Ge species at the conditions of core formation, Germanium would become more siderophile with increasing depth (Holzapfel et al., 2000) and the homogeneous accretion model would predict much higher Ge depletions in the Earth's mantle than observed in today's mantle.

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