

Mineral-physics constraints on core–mantle equilibrium

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Recent models of core chemistry (e.g. Allegre *et al.*, 1995) argue for Si as a component of the Earth's core. Allegre *et al.*'s proposal is based on the assumption that the Earth has a chondritic Mg/Si ratio. Sherman (1997) showed from the equations of state of core components that a core composition of 2.3 wt.% S and 7.3 wt.% Si would be in agreement with PREM, estimates of the Gruneisen parameter of iron, and the plausible temperature range of the core. However, the existence of Si in the core implies extremely reducing conditions that are incompatible with any Fe^{2+} in the Earth's mantle. This, in turn, implies core-mantle disequilibrium and heterogeneous accretion during the formation of the Earth.

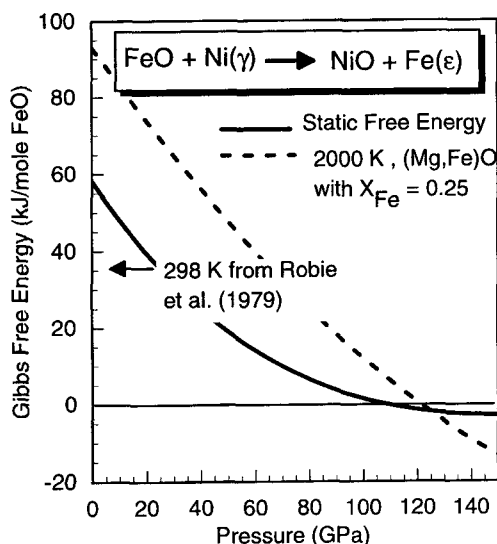
Failure of siderophile constraints

Based on the inferred concentrations of siderophile elements in the mantle, it has long been argued that the Earth's core and mantle are not in chemical equilibrium (Ringwood, 1972). Siderophile elements partition into metallic iron over coexisting oxides and silicates. In stony-iron meteorites, the metal/silicate partition coefficient for Ni is 1700 (Ringwood, 1972). Assuming that the Earth's core contains 5 weight percent Ni (as found in the metallic phase of meteorites) we would expect the average Ni content of the Earth's mantle+crust to be 29 ppm. Although the concentration of Ni in the Earth's crust is this low, the concentration of Ni in the mantle is nearly 100 times higher. Ultramafic rocks, for example, have Ni contents near 2700 ppm. Anderson (1983) infers the Ni content of the upper and lower mantle to be 1610 and 2110 ppm, respectively.

Before we can use the high siderophile content of the mantle to argue for core-mantle disequilibrium, we must know the partitioning of such elements at high pressure. In recent years, experimental studies have suggested that the siderophile behaviour of Ni decreases with pressure. To extrapolate these results and to understand the chemistry of Ni in the Earth's deep interior, first-principles quantum mechanical calculations (using density functional theory with the generalized gradient approximation for the exchange

correlation functional) were done of the electronic heat capacity and equations of state of Ni, NiO, Ni_3S , Fe, FeO and Fe_3S . The total energies and equations of state were then used to predict the pressure and temperature dependence of the reactions $\text{Ni} + \text{FeO} = \text{Fe} + \text{NiO}$ and $\text{Ni}_3\text{S} + \text{FeO} = \text{Fe}_3\text{S} + \text{NiO}$ up to 150 GPa. The electronic structures and equations of state of each phase are in very good agreement with experiment at low pressure. The static free energy of the reaction $\text{Ni} + \text{FeO} = \text{Fe} + \text{NiO}$ decreases with pressure and, assuming ideal solid solution along the Fe-Ni and FeO-NiO binaries, the static partition coefficient for nickel between Fe and FeO will be close to unity under lower-mantle pressures.

At high temperature, we must consider the change in electronic entropy associated with the Ni and Fe d-electrons. The greater electronic entropy of Ni in the metallic phase and electronic configurational entropy of Fe^{2+} in the oxide phase means that mantle temperatures will partially offset the static pressure effect. Still, in the Earth's lower mantle Ni will be less siderophile than at low pressure. Regardless of what composition we wish to impose on the core, the



high Ni abundance of the mantle cannot be used to argue for core-mantle disequilibrium nor for heterogeneous accretion during the Earth's formation.

References

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