

First-principles exploration of crystal structures of pure iron and iron-silicon alloy at Earth's inner core pressures

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Recent experimental and theoretical studies have revealed that many simple elements have complex crystal structures with low symmetry at high pressures [1]. One of the examples is calcium, which is the alkali earth metal bordering the 3d-transition metal on the periodic table. It was found that the electrons of 4s-character decrease with pressure, while those of 3d- increase. Then calcium behaves like the 3d-transition metal under high pressure. In the condition, calcium takes very complex crystal structures. It has a face-centered cubic (fcc) structure (Ca-I) at ambient condition and transforms to a body-centered cubic (bcc) structure (Ca-II) at 20 GPa, then to a simple cubic structure (Ca-III) at 32 GPa. By further compression, Ca-IV (113-137 GPa) and Ca-V (137 GPa) emerge [2], each of which has a complex crystal structure. Both Ca-IV and Ca-V have a coordination number of 7. The structure of Ca-IV is a four-fold helical structure and that of Ca-V a zigzag structure [3,4]. These facts suggest a possibility that iron, which is a 3d-transition metal and a primary constituent of the Earth's inner core, would also have the complex crystal structures in high pressure conditions.

In this study, we investigate the validity of this hypothesis by applying the complex crystal structures of calcium to iron and examining the relative energy differences among the candidate structures. In addition to the calculations of pure iron, we also investigate the effect of silicon incorporation on the appearance of complex crystal structures in highly compressed iron.

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Metals in oxidized and metasomatized peridotite xenoliths derived from the mantle wedge

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Relatively high oxidation state has been well known as one of the main character of mantle-wedge peridotites [1, 2], and interpreted as a result of the supply of slab derived materials (fluids and melts) [2]. Residual mantle peridotite xenoliths from Avacha volcano, on the volcanic front of southern Kamchatka arc, are characterized by SiO₂-addition through the reaction with slab derived fluids and melts. Most of the Avacha peridotites show highly oxidized conditions ($\Delta\text{FMQ} = -0.2$ to $+2.0$). But we found several native metals and alloys, i.e. native Ni, native Fe, Fe silicide (Fe-Si-Ti alloy) and possible native Ti, as inclusions in such oxidized and metasomatized peridotite xenoliths (samples #159, #166 and #679). In addition, #159 also contains several grains of FeAs₂ (löllingite) [3] and a large amount of sulfides [4] as inclusions, and sulfides are not altered to any secondary minerals [4]. Three grains of Fe-Si-Ti alloys are found in #159 and #166, and the grain in #166 show an inhomogeneous element distribution as a kind of sector zoning although other grains in #159 are homogeneous in chemistry. The two Fe-Si-Ti alloys in #159 show Fe₅₄Si₄₀Ti₆ and Fe₃₀Si₇₀ in chemistry, and the former is almost the same as the most Fe-rich part of the grain in #166.

The metals and alloys form inclusion trails with other minute inclusions (probably fluid(s)) in relatively coarse mantle minerals. The Fe-rich silicide in sample #159 forms an inclusion trail with pyroxenes in olivine. This possibly indicates the transportation of Si and Ti by an extremely reduced fluid or melt (but not sulfide melt) within relatively oxidized mantle wedge. Our finding implies the possibility of solubility of Ti to aqueous fluid although not indicated theoretically or experimentally.

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