氏名・(本籍)	ひらおなおひさ 平尾直久
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論文審査委員	(主査) 教授 大谷栄治 教授 藤本博巳（地球物理学専攻） 藤巻宏和，吉田武義 教授 中沢弘基，工藤康弘，谷口宏充 助教授 近藤忠

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Abstract

High pressure and high temperature in situ X-ray diffraction experiments for iron-silicon, iron-hydrogen, and iron-water, and iron-nickel-water systems have been carried out in order to reveal the identity and abundance of light element(s) in the Earth's core.

First, in situ X-ray diffraction experiments were performed in order to examine the stability and pressure-volume equation of state of iron-silicon alloys, Fe-4 wt.% Si ($Fe_{92}Si_8$), Fe-8.7 wt.% Si ($Fe_{84}Si_{16}$), and Fe-17.8 wt.% Si ($Fe_{70}Si_{30}$), with diamond-anvil cell techniques up to 181 GPa, 196 GPa, and 124 GPa, respectively. A body-centered cubic (bcc) to a hexagonal close packing (hcp) phase transformation in Fe-4 wt.% Si began at 17 GPa and was completed by 23 GPa, and in Fe-8.7 wt.% Si at 16 GPa and by 36 GPa. The high-pressure phases of Fe-4 wt.% Si and Fe-8.7 wt.% Si with the hcp structure were found to be stable up to 181 GPa and 196 GPa, respectively. No phase transition of Fe-17.8 wt.% Si was observed up to 124 GPa. The equation of state parameters for iron-silicon alloys were obtained from fitting the pressure-volume data to a third-order Birch-Murnaghan equation of state: V_0 = 22.6(2) Å^3, K_0 = 185(7) GPa, and K'_0 = 4.6(2) for hcp Fe-4 wt.% Si; V_0 = 22.2(8) Å^3, K_0 = 198(9) GPa, and K'_0 = 4.7(3) for hcp Fe-8.7 wt.% Si; V_0 = 179.41(45) Å^3, K_0 = 207(15) GPa and K'_0 = 5.1(6) for Fe-17.8 wt.% Si. The bulk moduli of iron-silicon alloys obtained in this work are higher than that of the other iron compounds.

Secondly, high pressure in situ X-ray diffraction experiments were performed on the Fe-H system up to 80 GPa using diamond-anvil cells and synchrotron radiation in order to determine the stability field and equation of state of iron hydride. No phase transformation of iron hydride with double hexagonal close packing (dhcp) structure was observed up to 80 GPa and at room temperature. Anomalous compression behavior at 30 to 50 GPa was observed, and iron hydride might be less compressible above 50 GPa than at lower pressures. The bulk modulus above 50 GPa is larger than that of pure hcp-iron. The present data support the *ab initio* calculation suggesting a magnetic transition of iron hydride at around 60 GPa. High pressure and temperature experiments yield a melting temperature of iron hydride at 38 GPa and 1400-1500 K, based on the disappearance of X-ray diffraction peaks from solid phase and the texture change indicative of fluid flow associated with melting. This result shows that the melting temperature of pure iron is reduced by 800-1000 K, which is consistent with the previous works on the Fe-H system.

Thirdly, high pressure and temperature experiments on iron-nickel-water system have been studied up to 23 GPa and 1220 K by a combined laser-heated diamond-anvil cell and X-ray diffraction technique in order to understand the effect of nickel on the iron-water reaction under high P-T conditions. Iron-nickel alloys react water to form iron-nickel hydride at low temperatures below 1220 K, which is similar to the Fe-H_2O system. The reaction of iron-nickel alloys with water indicates that the amount of metal hydride produced by the reaction with water is smaller in the Fe-Ni-H_2O system than in the Fe-H_2O system, suggesting that it might be possible that this has influenced on the hydrogen concentration in the Earth's core.

Fourthly, in situ synchrotron X-ray diffraction experiments were carried out at around 24 GPa and to 1200 K with Kawai-type multi-anvil high-pressure apparatus in order to investigate the reaction of iron with water at high pressures and temperatures. Wüstite (FeO) was formed by the reaction of iron with water, but no iron hydride was observed. The present results suggest that iron hydride be not produced in excess of iron and the amount of hydrogen dissolved into hcp-Fe might be smaller than 6 at.%.

These experimental results propose that the seismic observation of the Earth's inner core could be explained by the

addition of silicon or hydrogen into iron. Upon the Preliminary Reference Earth Model (PREM), the calculated density and bulk sound velocity of iron-silicon alloys indicate that the inner core containing the silicon contents of 4-6 wt.% (8-11 at.%) could satisfy the seismological constraints. If only a small amount of hydrogen (0.18-0.32 wt.% or 9-15 at.%) was dissolved into iron, the density of iron with hydrogen could be consistent with the observed density of the inner core and the addition of hydrogen into iron would depress the melting temperature of iron significantly.

論文審査の結果の要旨

平尾直久の博士論文は核内にどのような軽元素がどの程度含まれているか明らかにするために，鉄-シリコン系，鉄-水素系，鉄-水系，鉄-ニッケル-水系の高圧実験を行ったものである。

鉄シリコン系の研究では，3種類の鉄シリコン合金Fe-4 wt.% Si, Fe-8.7 wt.% SiおよびFe-17.8 wt.% Siについて，高圧X線その場回折実験を実施した。Fe-4 wt.% Si においては17 GPaから23GPaまでの圧力でbcc相とhcp相が共存するが，それ以上の圧力ではhcp相のみになり，この相は少なくとも181 GPaまで安定に存在する。Fe-8.7 wt.% Siについては，16 GPaから36 GPaまでbcc相とhcp相が共存し，それ以上の圧力では完全にhcp相に転移し，196GPaにおいてもhcp相が安定に存在する。Fe-17.8 wt.% Siでは124 GPaまでbcc相のままであった。さらに，鉄シリコン合金のBirch-Murnaghan状態方程式のパラメーターを決定し，鉄シリコン合金の体積弾性率は，純鉄やほかの鉄軽元素系合金よりも大きいことを明らかにした。

鉄-水素系では，最高圧力である80 GPaまで高圧X線その場観察実験を行い，鉄水素化物はdouble hexagonal close packing (dhcp)構造が安定であること，50 GPa以上では鉄水素化物が硬くなり，50GPa以上における体積弾性率は純鉄のそれよりも大きくなることを示した。この結果は，60 GPa付近で鉄水素化物が磁気崩壊を起こすとするAbinitio計算の結果に一致する。

さらに，鉄-ニッケル-水の反応実験を5-23 GPa，1070-1220 Kで行い，鉄-水系と同様に低い温度で反応するが，水との反応により生成される水素化物の量は，鉄-ニッケル-水系が鉄-水系よりも少ないことを明らかにした。このことは地球核へ運ばれる水素量に影響する。

これらの実験にもとづいて，地球の内核にシリコンや水素が存在する可能性を議論した。以上の平尾直久提出の博士論文は，高圧実験にもとづいて，地球核を構成する物質を解明し，地球核の理解に大きく貢献した。以上のように，本博士論文は自立して研究活動を行うために十分な研究能力と学識を有することを示している。従って，平尾直久提出の博士論文は，博士（理学）の学位論文として合格と認める。