

## Static compression of Fe<sub>4</sub>N to 77 GPa and its implications for nitrogen storage in the deep Earth

HELENE BRETON<sup>1</sup>, TETSUYA KOMABAYASHI<sup>2,\*</sup>,†, SAMUEL THOMPSON<sup>2</sup>, NICOLA POTTS<sup>2</sup>,  
CHRISTOPHER MCGUIRE<sup>2</sup>, SHO SUEHIRO<sup>3</sup>, SIMONE ANZELLINI<sup>4</sup>, AND YASUO OHISHI<sup>5</sup>

<sup>1</sup>School of GeoSciences and Centre for Science at Extreme Conditions, University of Edinburgh EH9 3FE, U.K. Orcid 0000-0002-1106-1592

<sup>2</sup>School of GeoSciences and Centre for Science at Extreme Conditions, University of Edinburgh EH9 3FE, U.K

<sup>3</sup>Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo 152-8551, Japan

<sup>4</sup>Diamond Light Source Ltd., Diamond House, Science & Innovation Campus, Didcot, OX11 0DE, U.K.

<sup>5</sup>SPring-8, Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

### ABSTRACT

Compression and decompression experiments on face-centered cubic (fcc)  $\gamma'$ -Fe<sub>4</sub>N to 77 GPa at room temperature were conducted in a diamond-anvil cell with in situ X-ray diffraction (XRD) to examine its stability under high pressure. In the investigated pressure range,  $\gamma'$ -Fe<sub>4</sub>N did not show any structural transitions. However, a peak broadening was observed in the XRD patterns above 60 GPa. The obtained pressure-volume data to 60 GPa were fitted to the third-order Birch-Murnaghan equation of state (EoS), which yielded the following elastic parameters:  $K_0 = 169$  (6) GPa,  $K' = 4.1$  (4), with a fixed  $V_0 = 54.95$  Å<sup>3</sup> at 1 bar. A quantitative Schreinemakers' web was obtained at 15–60 GPa and 300–1600 K by combining the EoS for  $\gamma'$ -Fe<sub>4</sub>N with reported phase stability data at low pressures. The web indicates the existence of an invariant point at 41 GPa and 1000 K where  $\gamma'$ -Fe<sub>4</sub>N, hexagonal closed-packed (hcp)  $\epsilon$ -Fe<sub>7</sub>N<sub>3</sub>, double hexagonal closed-packed  $\beta$ -Fe<sub>7</sub>N<sub>3</sub>, and hcp Fe phases are stable. From the invariant point, a reaction  $\gamma'$ -Fe<sub>4</sub>N =  $\beta$ -Fe<sub>7</sub>N<sub>3</sub> + hcp Fe originates toward the high-pressure side, which determines the high-pressure stability of  $\gamma'$ -Fe<sub>4</sub>N at 56 GPa and 300 K. Therefore, the  $\gamma'$ -Fe<sub>4</sub>N phase observed in the experiments beyond this pressure must be metastable. The obtained results support the existing idea that  $\beta$ -Fe<sub>7</sub>N<sub>3</sub> would be the most nitrogen-rich iron compound under core conditions. An iron carbonitride Fe<sub>7</sub>(C,N)<sub>3</sub> found as a mantle-derived diamond inclusion implies that  $\beta$ -Fe<sub>7</sub>N<sub>3</sub> and Fe<sub>7</sub>C<sub>3</sub> may form a continuous solid solution in the mantle deeper than 1000 km depth. Diamond formation may be related to the presence of fluids in the mantle, and dehydration reactions of high-pressure hydrous phase D might have supplied free fluids in the mantle at depths greater than 1000 km. As such, the existence of Fe<sub>7</sub>(C,N)<sub>3</sub> in diamond can be an indicator of water transportation to the deep mantle.

**Keywords:** Iron nitrides, Earth's core, equation of state, diamond-anvil cell, in situ X-ray diffraction, high pressure; Physics and Chemistry of Earth's Deep Mantle and Core