Synthesis of an eight-coordinated Fe$_3$O$_4$ high-pressure phase: Implications for the mantle structure of super-Earths. C. C. Zurkowski$^1$, J. Yang$^1$, S. Chariton$^2$, V. B. Prakapenka$^3$, Y. Fei$^1$. $^1$Earth and Planets Laboratory, Carnegie Institution for Science, 5241 Broad Branch Road NW, Washington D.C. 20015. $^2$Center for Advanced Radiation Sources, The University of Chicago, 9700 South Cass Avenue, Building 434A, Argonne, IL 60439 (czurkowski@carnegiescience.edu)

**Introduction:** The high pressure-temperature behavior of Fe$_3$O$_4$ captures broad planetary interest owing to its mixed valence properties and potential as an indicator of mantle oxidation state. Post-spinel transitions in Fe$_3$O$_4$(Fe$^{2+}$Fe$^{3+}$O$_4$) may also serve as low pressure analogs for Mg$_2$SiO$_4$ in exoplanetary interiors.$^{1,2,3,4}$ Recent computational studies report that Mg$_2$SiO$_4$ dominates the mantles of exoplanets greater than 4-Earth masses and may adopt 8-fold coordination at these conditions.$^{5,6}$ These results highlight the importance for further assessment of post-spinel transitions in the context of exoplanetary density structures. We examined the crystal chemistry of Fe$_3$O$_4$ using powder and single crystal X-ray diffraction and characterize the stability of an 8-fold coordinated, charge-ordered tetragonal Fe$_3$O$_4$ stable above 70 GPa at high temperatures with important implications for understanding the mantle structure and densification of super-Earths.

**Methods:** We performed in-situ X-ray diffraction measurements of Fe$_3$O$_4$ in the laser-heated diamond anvil cell (DAC). BX-90-type DACs (Kantor et al., 2012) equipped with Boehler-Almax conical diamonds (200 μm culet diameter) and seats were used for pressure generation. Sample chambers were loaded with single crystals of Fe$_3$O$_4$ (97%, Alfa Aesar) and filled with neon gas as a pressure transmitting medium.

Samples compressed to target pressures were probed with angular dispersive X-ray diffraction at Argonne National Laboratory, Sector 13 ID-D, of the Advanced Photon Source. A 42 KeV monochromatic X-ray beam tuned to 2.5 μm x 3.5 μm full width, half maximum was used. At target pressures, double sided laser heating was employed, and X-ray diffraction was collected *in-situ*. Samples were quenched once suitable grain growth of the target phases was achieved. Diffraction patterns were processed using Dioptas$^7$ and GSAS-II.$^8$

Upon temperature quenching, diffraction maps of the heated spot were collected. At locations of target phase growth, the sample was rotated +/- 30° in the path of the X-ray beam and diffraction images were collected every 0.5° with 2-5 s exposure times. Using CrysAlis Pro,$^9$ the detected reflections were mapped in the reciprocal space, lattices were identified and indexed, and the intensities of the reflections were integrated and corrected. The reduced structure factors and lattice parameters for each lattice were then used to determine a starting structure model,$^{10}$ from which, the atomic coordinates and displacement parameters were refined.$^{11}$

**Results:** With pressurization and heating up to 65.9(1) GPa and 1820(120) K, grains of previously known CaTi$_2$O$_4$-type h-Fe$_3$O$_4$ (Bbmm) were observed. With further pressurization to 78 GPa and heating above 1200 K, a new set of diffraction peaks and a change in texture of the diffraction images was readily identified, suggesting a phase transition in Fe$_3$O$_4$ at these conditions. No further transitions were observed with continued heating to 78.5(1) GPa and 2580(210) K.

![Figure 1. Diffraction reflections satisfying the hk1 condition for the Fe$_3$O$_4$ polymorph synthesized at 80 GPa. The cell is pseudo-cubic, but peak splitting at high diffraction angles indicates a tetragonal distortion.](https://example.com/fig1.png)

The new diffraction peaks were initially indexed in the reciprocal space to a cubic lattice, but peak splitting at high diffraction angles reveals a tetragonal cell with geometry: $a = 5.847(3)$ Å, $c = 5.966(5)$ Å (Figure 1), in agreement with recent studies.$^3$ Structure model refinement of this new Fe$_3$O$_4$ phase converged on the Eu$_3$S$_2$-structure type (I-42d) (Figure 2).$^{12}$ This structure can be described as an ordered Th$_3$P$_2$ structure, where the presence of distinct cation sites decreases the symmetry from I-43d to the tetragonal subset I-42d.$^{11,13}$ The details of the refined Fe$_3$O$_4$ atomic coordinates and displacement parameters are provided in Table 1.
observations of a Th$_3$P$_2$-like cell with tetragonal symmetry are in good agreement with the structure predicted for Mg$_3$SiO$_4$ and Mg$_3$GeO$_4$.	extsuperscript{5,14} The Eu$_3$Si$_4$-type Fe$_3$O$_4$ is composed of two FeO$_6$ sites in a ratio of 1:1 with face sharing between polyhedra, establishing the onset of 8-fold coordination at these pressures in the Fe-oxide system. Previous characterizations of the Eu$_3$Si$_4$ architype suggest that the Fe1 site is occupied by both Fe$^{2+}$ and Fe$^{3+}$ and the Fe2 site is occupied by only Fe$^{3+}$ (Figure 2).	extsuperscript{12}

**Implications:** The mantle structures of the terrestrial planets are characterized by phase transitions in silicates associated with increases in Si coordination number from 4 to 6. At the extreme pressure conditions in super-Earth mantles, further increases in coordination number are expected.	extsuperscript{4,6} An exciting result of this work is the synthesis and further characterization of an 8-fold coordinated FeO$_6$, a post-spinel phase. An outstanding uncertainty across the studies of the Mg-silicates and germanates is the P-T boundary between the low temperature site-ordered I-42d (Eu$_3$Si$_4$-type) and high temperature site-disordered I-43d (Th$_3$P$_2$-type) structures.	extsuperscript{4,5,6} As recent calculations of Mg$_3$GeO$_4$ suggest the persistence of cation ordering to high temperatures,	extsuperscript{14} Our observations of a site ordered I-42d FeO$_6$ to 2600 K at 80 GPa experimentally support these calculations	extsuperscript{14} and suggest some degree of ordering at high temperatures in the analog Mg$_3$SiO$_4$. Furthermore, the predicted stability of this 8-fold coordinated Mg$_3$SiO$_4$ in super-Earth interiors ranging from ~0.5-3 TPa	extsuperscript{5} would mark a critical densification transition from 6- to 8-fold coordinated silicates and likely coincide with profound changes in the thermodynamic properties of the mantle material (e.g., heat capacity, elemental partitioning, water content, thermal conductivity). Based on this work, further examination into the properties of this 8-fold coordinated Fe$_3$O$_4$ analog will likely provide important insight into the silicates that dominate the mantles of >4M$_E$ super-Earths.