Synthesis of an eight-coordinated Fe_3O_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[2], 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_3O_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_3O_4 ($Fe^{2+}Fe_2^{3+}O_4$) may also serve as low pressure analogs for Mg_2SiO_4 in exoplanetary interiors.[1,2,3,4] Recent computational studies report that Mg_2SiO_4 dominates the mantles of exoplanets greater than 4-Earth masses and may adopt 8-fold coordination at these conditions.[4,5,6] These results highlight the importance for further assessment of post-post spinel transitions in the context of exoplanetary density structures. We examined the crystal chemistry of Fe_3O_4 using powder and single crystal X-ray diffraction and characterize the stability of an 8-fold coordinated, charge-ordered tetragonal Fe_3O_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_3O_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_3O_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 $CaTi_2O_4$-type *h*-Fe_3O_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_3O_4 at these conditions. No further transitions were observed with continued heating to 78.5(1) GPa and 2580(210) K.

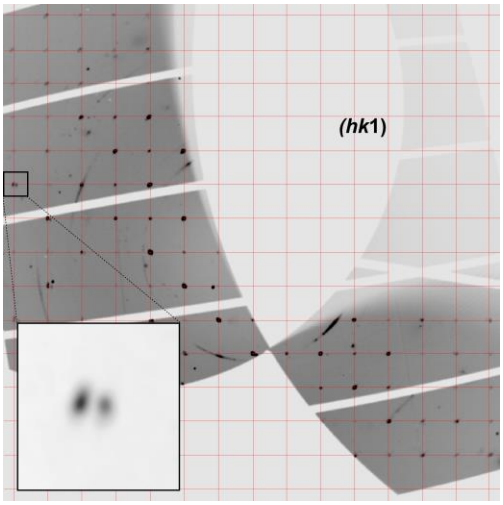

Figure 1. Diffraction reflections satisfying the *hk*1 condition for the Fe_3O_4 polymorph synthesized at 80 GPa. The cell is pseudo-cubic, but peak splitting at high diffraction angles indicates a tetragonal distortion.

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_3O_4 phase converged on the Eu_3S_4-structure type (*I*-42*d*) (Figure 2).[12] This structure can be described as an ordered Th_3P_4 structure, where the presence of distinct cation sites decreases the symmetry from *I*-43*d* to the tetragonal subset *I*-42*d*.[11,13] The details of the refined Fe_3O_4 atomic coordinates and displacement parameters are provided in Table 1. Our

Table 1. Atomic coordinates of Eu_3S_4-type Fe_3O_4 synthesized at 80 GPa and 2600 K

Atom	Wykoff Site	Sym.	x	err	y	err	z	err	sof	Uiso	err
Fe01	**8d**	**.2.**	0.378	0.002	0.75	--	0.625	--	0.5	0.025	0.002
Fe02	**4a**	**-4..**	0	--	0.5	--	0.75	--	0.25	0.010	0.001
O003	**16e**	**1**	0.329	0.003	0.445	0.003	0.686	0.007	1	0.018	0.006

observations of a Th_3P_4-like cell with tetragonal symmetry are in good agreement with the structure predicted for Mg_2SiO_4 and Mg_2GeO_4.[5,14] The Eu_3S_4-type Fe_3O_4 is composed of two FeO_8 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_3S_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).[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.[4-6] An exciting result of this work is the synthesis and further characterization[3] of an 8-fold coordinated Fe_3O_4, a post-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*-42*d* (Eu_3S_4-type) and high temperature site-disordered *I*-43*d* (Th_3P_4-type) structures,[4,5,6] as recent calculations of Mg_2GeO_4 suggest the persistence of cation ordering to high temperatures.[14] Our observations of a site ordered *I*-42*d* Fe_3O_4 to 2600 K at 80 GPa experimentally support these calculations[14] and suggest some degree of ordering at high temperatures in the analog Mg_2SiO_4. Furthermore, the predicted stability of this 8-fold coordinated Mg_2SiO_4 in super-Earth interiors ranging from ~0.5-3 TPa[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_3O_4 analog will likely provide important insight into the silicates that dominate the mantles of >4M_E super-Earths.

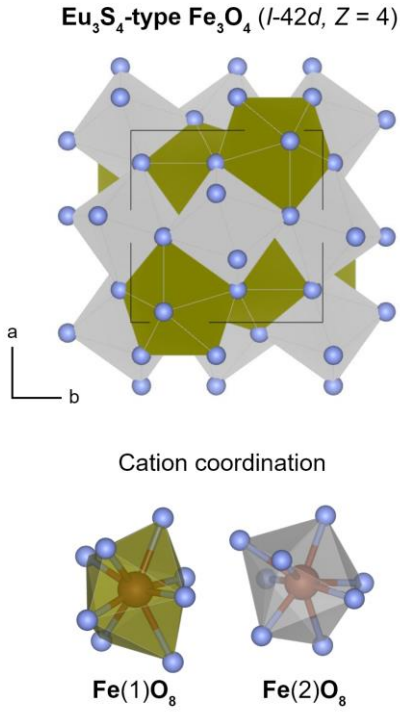

Figure 2. Crystal structure and cation coordination environments of the Eu_3S_4-type Fe_3O_4.

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