Crystal structures and motifs in the Fe-Mg-O system under extreme conditions

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Fe, Mg, and O are among the most abundant elements in terrestrial planets. Understanding the Fe-Mg-O system's behavior and properties under extreme conditions can help us identify a plethora of new phases and states possible in planetary interiors. By using the crystal structure prediction, we explore the polymorphs of Fe-Mg [1], Fe-O [2] and Fe-Mg-O [3,4] compounds under Earth's and exoplanetary interior pressures from 300 GPa to 3 TPa. Motif analyses show octahedral clusters are energetically favored for Fe-Mg-O compounds at Earth's interior pressure. Meanwhile, under exoplanetary interior conditions, low-enthalpy phases in all binary and ternary FeMgO compounds prefer BCC-like packing motifs. Our findings on the Fe-Mg-O system at core pressures appear to have some straightforward geophysical consequences. The Fe-rich side (right corner) of the ternary phase diagram suggests that Fe_2Mg and Fe_2O can form a continuous isomorphic solid $Fe_2(Mg_{1-x}O_x)$ solution. Both end-members are BCC-like structures at 350 GPa. BCC-like Fe_2Mg and hcp ε-Fe are likely to inter-alloy and form a eutectic system, with two coexisting solid phases for some composition-temperature ranges. Small Mg concentrations might produce hcp-like $Fe_{1-x}Mg_x$ alloys, but a BCC-like $Fe_{2+x}Mg_{1-x}$ might precipitate and coexist beyond a certain concentration threshold. The situation is very similar for the Fe_2O-Fe system. Therefore, the Fe-Mg-O system might contain Mg and O dissolved substitutionally in ε-Fe for small Mg and O concentrations, but beyond a certain concentration threshold BCC-like $Fe_{2+x+y}(Mg_{1/2-x}O_{1/2-y})$ might precipitate. BCC-Fe can be stabilized at inner core pressures by alloying with S, and it has been argued, but not confirmed, that BCC iron could be stabilized at inner core conditions. Therefore, the precipitation of BCC-like $Fe_{2+x+y}(Mg_{1/2-x}O_{1/2-y})$ for non-negligible amounts of Mg, O, or both is possible. The ternary phases discovered in the O-rich side of the phase diagram are relevant for the mantle of some Super-Earths. The absence of stable ternary phases at pressures lower than ~228 GPa suggests that stable phases involving all three elements are solid-solutions of end-member phases with a small concentration of inter-alloying metals. For example, we found that at 200 GPa, the low-energy structures are dominated by structures with octahedral

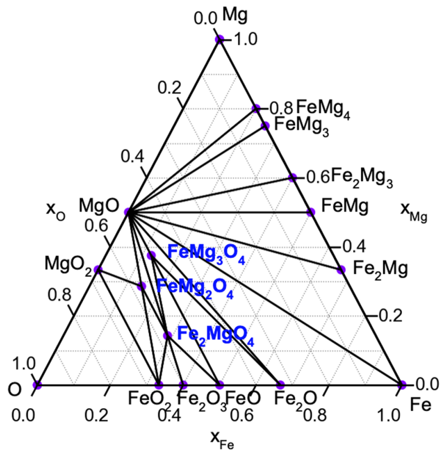

Figure 1. The phase diagram of Fe-Mg-O system under 350 GPa.

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coordination, with more Mg than Fe, and approximately 50% O, i.e., ferropericlase or B1-type $(Mg_{1-x}Fe_x)O$. At 350 GPa, the oxygen-rich ternary phases $FeMgO_3$, Fe_2MgO_4, $FeMg_2O_4$, and $FeMg_3O_4$ emerge as ground states or low-enthalpy phases, besides the B1-type phase. One of them, *I-42d* $FeMg_2O_4$, has the same structure as *I-42d* Mg_2SiO_4, the stable silicate phase predicted to exist in the mantle of Super-Earths above ~500 GPa. Here emerges the possibility of an *I-42d*-type $Mg_2(Si_{1-x}Fe_x)O_4$ phase, with Fe substitutional in the Si site, or vice-versa, an unusual type of substitution in the Earth's mantle, unless as a coupled Mg-Si substitution. Finally, O's greater intermixing with the metallic elements at 350 GPa suggests that Mg and O abundances might be non-negligible in the Earth's inner core. Also, core formation by Fe exsolution from the oxides might be a more complicated process during Super-Earths' core formation, or O and Mg might be more abundant light elements in Super-Earths' cores. We also identify a few ultra-high-pressure effects in these systems at the TPa regime. With increasing pressure, Mg becomes more compressible than Fe, leading to miscibility and Fe-Mg compounds' formation. In the Fe-O system, high pressures enhance the overlap of atomic wave functions, which broadens the Fe *d* bands. This lowers the density of states at the Fermi level, i.e. carrier density. These studies provide comprehensive structure databases to support future investigations of the high-pressure behavior of Fe-Mg-O compounds and to understand the interior of terrestrial planets.

Keywords: Crystal structure prediction; Exoplanet; High-pressure.

REFERENCES

[1] Y. Fang, Y. Sun, R. Wang, F. Zheng, S.Q. Wu, C.-Z. Wang, R.M. Wentzcovitch, and K.-M. Ho, *Phys. Rev. B* **104** (2021) 144109.

[2] F. Zheng, Y. Sun, R. Wang, Y. Fang, Feng Zhang, S.Q. Wu, C.-Z. Wang, R.M. Wentzcovitch, and K.-M. Ho, *Phys. Rev. Materials* **6** (2022) 043602.

[3] R. Wang, Y. Sun, R.M. Wentzcovitch, F. Zheng, Y. Fang, S.Q. Wu, Z. Lin, C.-Z. Wang, and K.-M. Ho, *New J. Phys.* 23 (2021) 063050.

[4] Y. Fang, Y. Sun, R. Wang, F. Zheng, F. Zhang, S. Wu, C.-Z. Wang, R. M. Wentzcovitch, K.-M. Ho Phys. Rev. Materials **7** (2023) 113602

BIOGRAPHY

Yang Sun completed his Ph.D. in 2016 from the University of Science and Technology of China and Postdoctoral Studies at Ames National Laboratory, US DOE in 2016-2019, and Columbia University in 2019-2020. He was an associate research scientist at Columbia University from 2020 to 2022 and a research scientist at Iowa State University from 2022 to 2023. He currently works as an Associate Professor at Xiamen University. He works on the structure and phase transition of matters under extreme conditions and computational material discovery. He has published more than 90 papers in reputed journals.