Influence of volatiles on the chemistry of Fe-O system

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Abstract

Being the only geochemically abundant element in Earth's interior with multiple stable oxidation states, iron plays a key role in controlling oxygen fugacity and, consequently, in regulating redox equilibria, phase relations, and volatile cycles in the deep Earth. Numerous mixed-valence iron oxides with unexpected compositions have recently been identified under high-pressure and high-temperature conditions, revealing rich crystal chemistry and intriguing physical properties, including pressure-induced spin transitions, charge ordering, and the emergence or collapse of magnetic order [1–4]. The chemical behaviour of iron-bearing compounds is particularly sensitive to the presence of volatiles such as H_2O and CO_2, which are continuously recycled into Earth's interior through subduction processes. In recent years, novel iron carbonates [5–7] and hydroxide/oxyhydroxide phases [8,9] have been synthesized at high pressures and high temperatures. Hydrous phases such as pyrite-type FeO_2H_x ($x \leq 1$) are considered possible carriers of water and hydrogen to the lowermost mantle [8,9] and have been proposed as a potential origin of ultralow-velocity zones and seismic anomalies near the core–mantle boundary [10]. Despite intensive research, the role of volatiles in controlling the chemistry of Fe-bearing compounds at extreme conditions remains insufficiently understood.

In this study, we applied single-crystal X-ray diffraction in laser-heated diamond anvil cells (DACs) to investigate the high-pressure behaviour, chemical reactivity, and thermal stability of Fe-bearing compounds, including oxides and carbonates, in the presence of H_2O and CO_2 at pressures up to 75 GPa and temperatures up to 3000 K. Recent advances in multi-grain single-crystal XRD enable the detection of minor phases and reliable determination of their crystal structures, thereby significantly improving the accuracy of phase identification in complex high-pressure assemblages. We compare the chemical reactions between iron compounds and volatiles with those occurring in inert pressure media under conditions relevant to Earth's deep interior. Our results show that volatiles can substantially alter reaction pathways at extreme conditions, even when they are not incorporated into the final crystalline products.

References

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