**Letter**

**HP-PdF$_2$-type FeCl$_2$ as a potential Cl-carrier in the deep Earth**

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**Abstract**

We report for the first time the formation of a HP-PdF$_2$-type FeCl$_2$ phase (space group Pa$ar{3}$), through high pressure-temperature ($P-T$) reactions in the hydrous systems ($\text{Mg}_0.6\text{Fe}_{0.4} \text{Si}_2\text{O}_7 + \text{H}_2\text{O} - \text{NaCl}$ and $\text{FeO}_2\text{H} - \text{NaCl}$) in a laser-heated diamond-anvil cell up to 108 GPa and 2000 K. Applying single-crystal X-ray diffraction (XRD) analysis to individual submicrometer-sized grains, we have successfully determined the crystal structure of the as-synthesized FeCl$_2$ phase, in agreement with our theoretical structure search results. In situ high $P-T$ XRD data revealed the substitution of Cl for OH(O) in such a cubic Pa3 structure, demonstrating that this topology is a potential host for both H and Cl in the deep Earth. The chemical analysis of the recovered sample showed that the post-perovskite phase contains considerable amounts of Na$_2$O and FeO$_2$. The coexistence of the cubic FeCl$_2$ phase and post-perovskite suggests that the lowermost mantle could be a potential reservoir of Cl. The possible presence of volatiles such as H and Cl in the deep lower mantle would impact the composition and iron valence state of the post-perovskite phase.

**Keywords:** Iron chloride, multigrain X-ray diffraction, lower mantle, hydrogen and chlorine cycle, post-perovskite; Physics and Chemistry of Earth’s Deep Mantle and Core

**Introduction**

Chlorine (Cl) is abundant in seawater and most geological fluids. Owing to its hydrophilic behavior, Cl abundances and isotopic data provide important information on geological processes (Bonifacie et al. 2008; Sharp et al. 2010). Hydrous minerals have been shown to be major Cl carriers from oceanic to deep subduction environments (Kendrick et al. 2017). Serpentinites act as the major carriers of H (or H$_2$O) and Cl, and subducting serpentinites play an important role in the recycling of Cl (Scambelluri and Philippot 2001). Mass balance calculations suggest that Cl inputs exceed outputs at certain subduction zones (Barnes and Straub 2010; John et al. 2011). This is consistent with the observations of Mg$_2$-, Fe$_2$-, and alkali-rich saline fluids containing up to 50 wt% Cl, Na, K, Mg, and Fe trapped as inclusions inside high-pressure vein minerals in many eclogite terranes, suggesting that Cl is recycling back into the mantle by subduction (Scambelluri et al. 1997).

There is a growing body of research that focuses on the storage potential of halogens and hydrogen in the mantle. Roberge et al. (2017) showed that the Cl contents in hydrous wadsleyite and ringwoodite ranging from 60 ± 60 to 200 ± 48 ppm are much lower than their F contents that range from 186 ± 19 to 850 ± 85 ppm, but that the substitution correlations of Cl with OH remain unclear. Yoshino and Jaseem (2018) found that incorporation of water and alumina greatly enhances F solubility in bridgmanite, exceeding 1 wt%, showing a sufficient capacity to store the whole F budget. The ionic radius of Cl$^-$ is significantly larger than that of F$^-$, so that the Cl solubility in the mantle silicates is expected to be very low. The major host for Cl in the deep mantle remains unknown. Du et al. (2018) predict a series of stable structures of iron chlorides, including Fe$_2$Cl$_4$, FeCl$_2$, FeCl$_3$, FeCl$_4$, and FeCl$_6$ in the pressure range of Earth’s mantle and core.

Recent studies showed that the pyrite-structured FeO$_2$ and FeO$_2$H$_x$ ($x \leq 1$) phases were observed under $P-T$ conditions representative of the deep lower mantle (DLM) (Hu et al. 2016; Liu et al. 2017; Mao et al. 2017; Nishi et al. 2017; Yuan et al. 2018). The latest study by E. Koemets et al. (2021) argued that FeO$_2$ and FeO$_2$H$_x$ adopt HP-PdF$_2$-type other than pyrite-type structure due to the absence of the O–O covalent bonds. In spite of the controversy, we termed this cubic FeO$_2$H$_x$ as “py-phase” in this work. As an important hydrogen carrier, the py-phase has been experimentally confirmed to be stable in the DLM along average mantle geotherm. Koemets et al. (2020) reported a novel Na$_2$FeCl$_3$OH$_2$ phase through chemical reactions between FeO$_2$H and NaCl under high $P-T$ conditions. It is intriguing to explore the potential relation of hydrogen and chlorine in the Fe-bearing system in the DLM. Here we report the first experimental discovery of a cubic FeCl$_2$ phase, referred to as “c-FeCl$_2$,” coexisting with a post-perovskite (pPv) phase in the system (Mg,Fe)$_2$SiO$_4$–H$_2$O–NaCl. We demonstrated replacement of OH(O) by Cl in the cubic Pa3 structure, providing a new hydrogen-chlorine relation under the $P-T$ conditions of the DLM.

**Methods**

We used goethite ($\alpha$-FeOH) powder (99+% purity, Alfa Aesar) and synthesized Mg$_{0.6}$Fe$_{0.4}$Si$_2$O$_7$ orthopyroxene (En60) as the starting samples. Three hydrous sample assemblies ($\text{Mg}_0.6\text{Fe}_{0.4} \text{Si}_2\text{O}_7 + \text{H}_2\text{O} - \text{NaCl}$–H$_2$O–NaCl) and $\alpha$-FeO$_2$H$-\text{NaCl}$ (Run ETR3) were designed for this study. In situ synchrotron XRD experiments were performed at HPCAT (Sector 16) (Meng et al. 2018; Meng et al. 2019).