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MATERIAL WITNESS

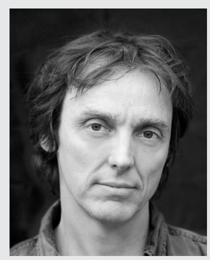
Helium's deep mystery

The first compound of the noble gases, $XePtF_6$, was first reported by Neil Bartlett in 1962[1]. Others followed, but not until the past few years has the lightest of the noble gases, helium, begun to shed its reputation for total inertness. At high temperature and pressure it appears able to form relatively weak bonds with other atoms and molecules. Although inert and hydrophobic species like helium can occupy cavities in hydrate clathrates[2], the interactions it experiences there are merely van der Waals forces, not genuine bonds. But under high pressures of around 300 GPa, water molecules do seem able to form bonds to He with a strength comparable to a hydrogen bond[3]. What's more, helium will form an insulating electride with sodium at 113 GPa (ref. [4]) and, according to first-principles calculations, a compound with iron above 4 TPa (ref. [5]). Perhaps the most exotic helium compound predicted so far is a nitride containing polymeric nitrogen channels in which the helium atoms are encapsulated[6].

The last of these predictions was made by Yanming Ma of Jilin University in China and his co-workers. Ma and colleagues have also investigated high-pressure phases of other noble gases with potential geochemical relevance, such as the possibility of xenon reacting with iron and nickel in the Earth's inner core[7]. They say that the intermetallic phases $XeFe_3$ and $XeNi_3$ could potentially serve as reservoirs of Xe that could explain its relative paucity — less than 10% of expected primordial amounts — in the Earth's atmosphere.

Now Ma and his collaborators have turned to another geochemical puzzle involving the noble gases. Lavas from volcanic hotspots, which carry material in rising convective plumes from the deep mantle, may have high ratios of ^3He to radiogenic ^4He, compared to those in the atmosphere[8]. This supports the longstanding idea that there exists within the deep Earth a reservoir of primordial helium — but then where is it? First-principles calculations by Zhang et al. have now identified a helium-containing iron oxide FeO_2He at pressures and temperatures comparable to those of the core–mantle boundary (CMB), which they present as a candidate for this helium source[9].

The idea builds on the discovery of the unusual oxide phase FeO_2, a peroxide that was observed experimentally to be stable under these conditions[10] and which could form solid solutions with lower-mantle minerals. Zhang et al. carried out a global optimization of the free energies for FeO_2He phases, which converged on a cubic structure stable above 120 GPa at 0 K, this boundary rising to 135 GPa at 3,000 K — the conditions obtaining at the CMB. The helium atoms receive only a very small degree of electron donation from the iron atoms, but serve mainly to stabilize the compound through electrostatic shielding.



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After decades of seeming like something of a curiosity, noble-gas chemistry is thus now proving to be of considerable potential relevance to the composition of planetary interiors. It's a reminder that our chemical intuitions developed from experience under ambient conditions might not always be appropriate for understanding the chemistry of the cosmos. ❐

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