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# Noble Gas Reactivity in Planetary Interiors

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While the field of noble gas reactivity essentially belongs to chemistry, Earth and planetary sciences have brought a different perspective to the field. Indeed, planetary interiors are natural high pressure ( $P$ ) and high temperature ( $T$ ) laboratories, where conditions exist where bonding of the heaviest noble gases may be induced thermodynamically through volume reduction (Le Châtelier's principle). Earth and planetary sciences besides generate numerous and precise observations such as the depletion of the terrestrial and martian atmospheres in xenon, pointing to the potential for Xe to be sequestered at depth, potentially induced by its reactivity. More generally, this paper will review the advances on noble gas reactivity at the extreme  $P$ - $T$  conditions found within planetary interiors from experiments and theoretical investigations. This review will cover the synthesis of cage compounds, stoichiometric oxides and metals, and non-stoichiometric compounds where noble gases are only minor or trace elements but could be essential in solving some Earth and planetary puzzles. An apparent trend in noble gas reactivity with  $P$  emerges. In the case of Xe which is the most documented, metals are synthesized above 150 GPa, i.e., at terrestrial core conditions, stoichiometric Xe-oxides between 50 and 100 GPa, i.e., in the  $P$ - $T$  range of the Earth's lower mantle, but Xe-O high energy bonds may also form under the modest pressures of the Earth's crust ( $<1$  GPa) in non-stoichiometric compounds. Most planetary relevant noble gas compounds found are with xenon, with only a few predicted helium compounds, the latter having no or very little charge transfer between helium and neighboring atoms.

**Keywords:** xenon, krypton, argon, neon, helium, planetary interiors, high pressure

## 1. INTRODUCTION

The inertness of noble gases is the cornerstone of noble gas geochemistry. Helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe) are all important markers of a variety of planetary processes, ranging from Earth's accretion, degassing of the atmosphere, vigor of mantle convection, to tracking underground nuclear tests. Noble gas abundances and isotopic ratios have thus been measured in a large variety of samples (atmosphere, fluids, rocks) and from different geological contexts, from Archean rocks over 2.5 Gy old [1, 2] to Martian meteorites [3] and comets [4]. Besides the Earth and Mars, the only other planetary atmosphere probed so far is that of Jupiter [5]. Future missions are targeted at measuring noble gases in other atmospheres with pre-selected NASA DAVINCI+ mission to Venus and SPRITE mission to Saturn, noble gases being presented as critical to understanding the formation and evolution of giant planets.

From these measurements, planetary accretion reservoirs and processes may be traced. Only Ne has preserved a solar signature in some terrestrial samples, a signature interpreted as a proof for the existence of a deep magma ocean (i.e., partially or fully molten Earth in equilibrium with a primary solar-like atmosphere) within the first hundred My of the Earth's formation [6, 7]. Heavier Kr and Xe noble gases overall have a chondritic signature in terrestrial and martian samples, with a minor cometary contribution [4, 8]. Jupiter is the only other planet whose atmosphere has been studied in detail. It is slightly depleted in He, strongly in Ne [5], and enriched by a factor of 2.5–2.7 in heavy noble gases (Ar, Kr, Xe) compared to solar abundances [9], as expected from trapping in amorphous ice and pointing to a major cometary contribution to Jupiter.

Noble gases are also widely used to trace planetary processes. For instance, the iodine-plutonium-xenon system is used to date the formation of the atmosphere [10, 11] due to the very short half-lives of  $^{129}\text{I}$  (17 My) and  $^{244}\text{Pu}$  (82 My). Helium and Ar isotopes constrain mantle degassing and convection over much longer time scales [12–14] owing to the longer half-life of their parent isotopes (for instance 1.25 Ga for  $^{40}\text{K}$ ). None of Kr stable isotopes is purely radiogenic, preventing its use to constrain chronology of the atmosphere evolution. It was pointed out as early as 1970 that Xe is under abundant in the atmospheres of the Earth and Mars relative to the chondritic abundance pattern [15], a depletion of up to 90% [10] and known as the “missing Xe” problem. Atmospheric Xe is furthermore strongly depleted in light isotopes [16], and this depletion in light Xe isotopes was progressive throughout the Archean [17]. The case is more debated for Ar, but the classical double-layered convection model [12] precisely required two separated layers in the mantle on the basis that an unsampled reservoir, such as the lower mantle, must be enriched in Ar to satisfy radiogenic  $^{40}\text{Ar}$  mass balance. Seismic tomography later showed that there is a mass flow from the upper to the lower mantle, but the need for an Ar-rich reservoir remains.

The most striking fact emerging from the current data set of noble gas analyses in natural samples remains the “missing Xe.” This paradox has launched a search for either ways to lose Xe to space [17–20] or to trap Xe at depth. The interiors of the Earth are indeed characterized by extreme  $P$ - $T$  conditions, with a six-order magnitude increase in  $P$  and 3-order magnitude increase in  $T$  between the surface ( $10^5$  Pa–287 K) and the core of the planet (365 GPa–5,000 K). Such conditions may induce chemical reactivity as negative reaction volume change under increased  $P$  may overcome enthalpic effects of otherwise prohibited reactions at ambient  $P$ . Natural samples do indicate higher Xe retention in particular contexts. Xe concentrations in near surface rocks are  $\sim 0.05$  ppt (part per trillion) in basalts [21] and up to 0.2 ppb (part per billion) in deep sea siliceous fossils [22]. The latter samples have  $^{132}\text{Xe}/^{36}\text{Ar}$  ratios of up to 0.05, i.e., about thirty times higher than in mid-ocean ridge basalts [23, 24]. Xe enrichment over other noble gases is also reported in high  $P$  contexts such as mantle xenoliths exhumed by volcanism [25–28] and impact craters [29] by two orders of magnitude with the highest excess ( $^{132}\text{Xe}/^{36}\text{Ar} = 0.170$ ) being reported in excavated lunar crustal rocks [30].

The initiation of high  $P$  solid-state chemistry of Xe was triggered by the discovery of its metallization at 135 GPa [31], yet the potential link to the missing Xe paradox took a decade to be established. Since then, there has been a continuous feedback between high  $P$  mineral physics and condensed matter physics in the search for new noble gas compounds. Foreseen as promising by Grochala [32] but then still experimentally unexplored, the high  $P$  chemistry of noble gases now extends to several atoms, an effort largely led by the perspective to understand noble gas reactivity at deep Earth's conditions. Interestingly, noble gases are archetypical pressure-transmitting media used in laser heated diamond-anvil cell experiments to reproduce hydrostatic deep Earth's conditions in an otherwise rather uniaxial compression apparatus, and thermally insulate the sample from the diamond anvils. This technical aspect has doubtless been a positive factor in elucidating some of the high  $P$  noble gas reactivity reviewed here, and that covers first retention of noble gases in rings, channels and cage structures, second noble gas oxides, third noble gas compounds with metals, and finally other types of high  $P$  noble gas compounds relevant of planetary interiors.

## 2. RETENTION OF NOBLE GASES IN RING, CHANNEL, AND CAGE STRUCTURES

### 2.1. Clathrates and Other Cage Compounds

Water ice is one of the most prevalent substances in the Solar System, with the majority of it existing at high  $P$  and  $T$  conditions in the interiors of giant planets. While clathrate hydrates have long been considered as carriers of noble gases to the giant planets, a consensus emerges now for simple adsorption on amorphous ice [9]. On Earth, clathrate hydrates are found in pergelisols and oceanic margins. Noble gases are among the gases that stabilize clathrate hydrate structures through van der Waals interactions.  $\text{Ar}_6 \cdot \text{H}_2\text{O}$  was actually the first compound of a noble gas discovered in Villard [33]. All noble gases form clathrates by combination with water, with  $P$ - $T$  stability field extending from He to Xe [34]. However, even Xe hydrates are stable only up to 2.5 GPa [35].

Cyclo-silicates can host large amount of noble gases in the channels and ring sites of their crystal structures. These minerals are not occurrences of noble gas reactivity at depth, but are essential carriers of noble gas recycling via subduction of lithospheric plates [36, 37], from the surface reservoirs (atmosphere, oceans) to the deep Earth where reactions may take place. Natural occurrences of He and Ar in cyclo-silicates are abnormally high [38]. He, Ne and Ar occupy ring sites in amphibole [37], a mineral formed in the altered oceanic crust, and experimentally measured solubilities are up to four orders of magnitude higher than for other silicates at similar run  $P$  (0.17 GPa). Ring sites are formed by a pair of opposing six-membered  $(\text{Si,Al})\text{O}_4^{4-}$  tetrahedra rings, with a ring inner diameter circa 5 Å. Noble gases sitting in these sites are thus surrounded by 12 neighboring oxygens at approximately 2.5 Å. Kr and Xe solubilities have not been investigated in amphibole, but are even higher than Ar solubility in serpentine ( $\times 2$  for Kr,  $\times 10$

for Xe), another important mineral from the altered oceanic crust [39].

The very first attempts at testing Xe reactivity with silica [40] were guided by the fact that SiO<sub>2</sub> high *T* phase cristobalite has large cages that could trap Xe atoms and favor chemical reactivity. However, when SiO<sub>2</sub> was loaded as cristobalite, it systematically transformed to quartz, with the latter efficiently trapping Xe (cf. section 3). Xenon, far from stabilizing cristobalite, in fact destabilizes it. Instead, He proved much more interesting in this respect as cristobalite loaded in He as a diamond-anvil cell *P*-transmitting medium was shown to convert to He-cristobalite at 8 GPa instead of transforming to cristobalite-II at 1.6 GPa [41], its structure and stoichiometry (SiO<sub>2</sub>He) were solved (Figure 2).

## 2.2. Stuffed Amorphous Silicates

Noble gas solubility in molten silicates depend on their composition. In fact, noble gas solubility in vitreous silica has been used to characterize glass network geometry [44]. Noble gas retention in silicate melts has long been postulated as occurring by insertion in the interstitial voids [45], with the abundance depending on the melt's polymerization, itself constrained by the SiO<sub>2</sub> content as SiO<sub>4</sub><sup>4-</sup> tetrahedra polymerize as rings (see below). Silicate melts may accommodate larger amounts of dissolved noble gases under increased *P* until solubility reaches a plateau circa 5 GPa with for instance a maximum of 3 mol% Ar in silica-rich melts [46, 47]. Note that solubility drops at higher *P* were reported [48, 49] but these results were not reproduced [50], possibly due to incomplete melting of the samples at higher *P* in the first studies.

Noble gases affect the behavior of non-crystalline silicates under pressure. Up to 1–2 mol% He may dissolve into the interstitial voids in SiO<sub>2</sub> glass under pressure [51, 52], resulting in a much less compressible glass [52], with a spatial scale of the medium-range order almost independent on *P* compared to SiO<sub>2</sub> glass compressed in solid *P*-medium or compressed in H<sub>2</sub>. Similarly to He in compressed SiO<sub>2</sub> glass, Xe was also found to affect the medium-range order with a sharpening of the first sharp diffraction peak on x-ray diffraction data, indicative of a stronger medium-range order [53]. More importantly, Xe-O bonds with a bond length of 2.05–2.10 Å and a coordination number of 12 were reported, indicative of the Xe insertion in six-membered rings (i.e., rings formed of six SiO<sub>4</sub><sup>4-</sup> tetrahedra) rather than in interstitial voids. This ring structure of molten and glassy silicates is similar to that of cyclo-silicates, except that there is a statistical distribution of ring sizes, mostly from 4 to 10 tetrahedra depending on melt composition [54]. This distribution has been recently quantified in vitreous silica by neutron diffraction [55], the six-membered ring being the most prominent and having an inner diameter of 4.30 Å, consistent with the Xe-O bond length reported above. Krypton local environment in compressed melts, as investigated using x-ray absorption spectroscopy [56], is a shell of oxygen atoms located at 2.49 Å. This relatively short distance indicates some degree of covalency albeit less than for Xe-O bonds. It is however difficult to reach further conclusions, as the coordination number could not be calculated due to the lack of Kr oxide references that are necessary to process x-ray absorption spectroscopy data.

## 3. NOBLE GAS OXIDES

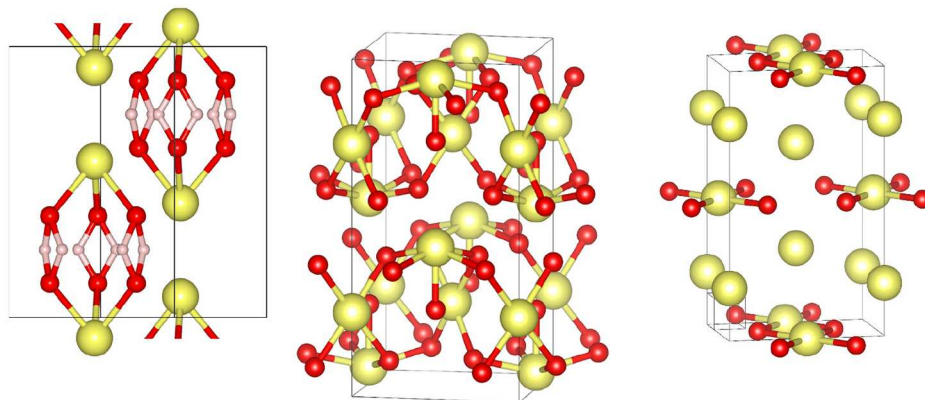
The mineralogical constituents of the crust and mantle of terrestrial planets are silicates, with a predominance of framework silicates in the continental crust such as quartz and feldspars, and a predominance of olivine in the mantle that undergo phase transitions at depth, and decomposes into bridgmanite and magnesiowustite below 660 km. First steps toward establishing noble gas reactivity in planetary crust and mantle have been the synthesis of noble gas oxides, keeping in mind that it can only be firmly established between silicates and noble gases as trace elements for realistic implications to planetary interiors.

### 3.1. Stoichiometric Oxides

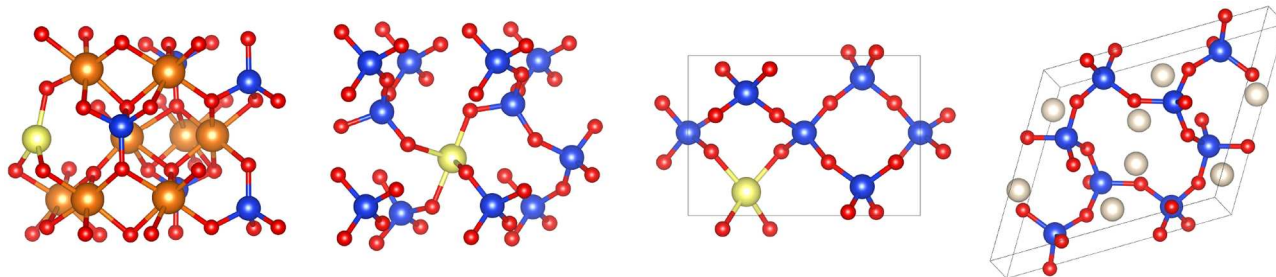
Xenon oxides have been known since the sixties with the synthesis of tetrahedral forms (XeO<sub>3</sub> by Templeton et al. [57], XeO<sub>4</sub> by Huston et al. [58]) by hydrolysis of xenon fluorides at cryogenic *T*, and more recently with the synthesis of XeO<sub>2</sub> that has a different geometry with local square planar oxygen environment [59]. Although the local structure of XeO<sub>2</sub> is square planar, Xe being bonded to four oxygens, its full crystallographic structure has not yet been resolved.

The first Xe oxide experimentally synthesized by use of high *P* was Xe<sub>2</sub>O<sub>6</sub>H<sub>6</sub> (Figure 1), obtained by reaction between superionic ice and Xe above 50 GPa and 1,500 K upon laser heating in diamond-anvil cells [60], with platinum used as a laser coupler. Superionic ice is a high *P*-*T* phase forming at 50 GPa and characterized by a full mobility of the hydrogen atoms [62], while the oxygen lattice is identical to that of lower *T* phase X. Xe<sub>2</sub>O<sub>6</sub>H<sub>6</sub> is metallic due to the Xe and O atoms, however the diffusivity of hydrogen atoms is similar to that of superionic ice. Pure Xe oxides were predicted to be stable against decomposition above 83 GPa by *ab initio* calculations: XeO, XeO<sub>2</sub>, and XeO<sub>3</sub> [63], followed by Xe<sub>2</sub>O<sub>3</sub> and more Xe-rich phases at even higher *P* [64]. Only Xe<sub>2</sub>O<sub>3</sub> was observed experimentally albeit at slightly higher *P* (87 GPa instead of the predicted 75 GPa), along with Xe<sub>2</sub>O<sub>5</sub> at 83 GPa [61]. Interesting fact: Xe may exist at different oxidation states in the same structure. That Xe oxidation is induced at significantly lower *P* with superionic ice compared to pure oxygen could be due to the reactivity of the very diffusive hydrogen with platinum, the formation of platinum hydride contributing to a larger volume reduction of the global reaction. In addition, the oxygen and xenon sublattices in Xe<sub>2</sub>O<sub>6</sub>H<sub>6</sub> bears remarkable resemblance to those of η-O<sub>2</sub> [65] and pure Xe, both having hexagonal closed-packed structures and the η-O<sub>2</sub> being characterized by a high degree of charge transfer.

For krypton, only KrO has been predicted to be stable against decomposition above 300 GPa [66], and no Kr-compound has been synthesized experimentally. No argon oxide nor neon oxide have yet been documented to form at the conditions of planetary interiors, despite the visionary editorial by Abelson [67] citing ArH<sub>4</sub> and ArO<sub>6</sub> as examples of *P*-induced chemistry. But surprisingly, one helium oxide has been reported. On the basis of *ab initio* calculations, FeO<sub>2</sub>He, is predicted to be stable at core-mantle boundary conditions [68]. Unlike Xe-oxides and KrO discussed above, there is almost no charge transfer



**FIGURE 1** | Experimentally observed and theoretically predicted xenon oxides. From left to right:  $\text{Xe}_2\text{O}_6\text{H}_6$  [60],  $\text{Xe}_2\text{O}_5$ ,  $\text{Xe}_2\text{O}_3$  [61]. Color code for atoms: xenon (yellow), oxygen (red), hydrogen atoms (light pink).



**FIGURE 2** | Experimentally synthesized noble gas-silicates. From left to right: Xe-doped olivine  $\text{Mg}_2\text{SiO}_4$  [42], Xe-doped  $\beta$ -quartz [43],  $(\text{Xe},\text{Si})\text{O}_2$  phase for which Xe site occupancy is unknown [43], cristobalite-He [41]. Color code for atoms: magnesium (orange), xenon (yellow), oxygen (red), silicon (dark blue), helium (white).

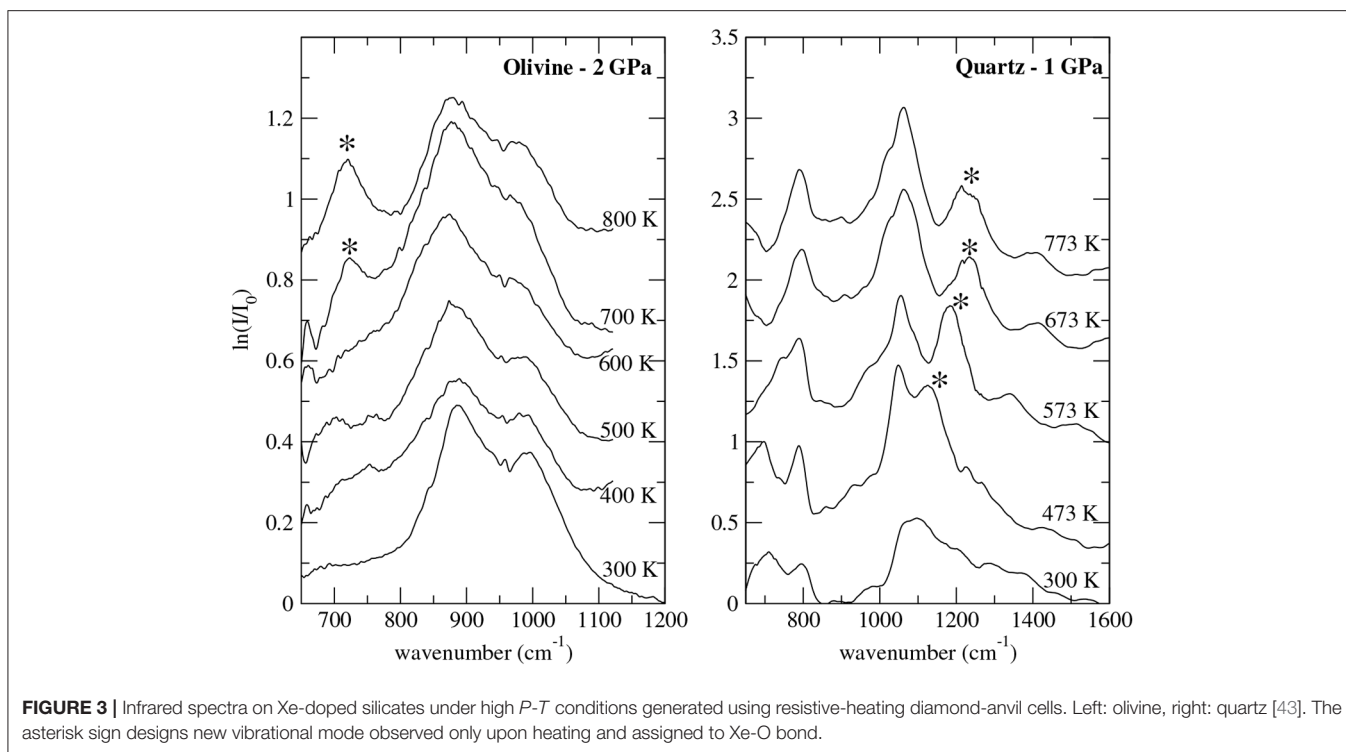
from He to surrounding atoms. Excess primordial He (i.e.,  $^3\text{He}$ , while  $^4\text{He}$  has been produced throughout Earth's history by radioactive decay) are found in some basalts which rock source is identified as originating from very deep in the mantle [69]. Thermochemical piles are domes of both thermal and chemical origin in the deep mantle, rooted above the core-mantle boundary below central Pacific and south Atlantic-Africa [70], with locally partially molten zones (ultra-low velocity zones) at their very base. These piles might have been preserved during a large part if not all of Earth's history and could indeed be He-rich, providing a reasonable context for the formation of  $\text{FeO}_2\text{He}$ . Besides, hydrogen bearing iron peroxide  $\text{FeO}_2\text{H}$  [71] is also stable at the corresponding  $P$ - $T$  conditions, or as partially dehydrogenated  $\text{FeOOH}_x$  postulated as an important component of the ultra-low velocity zones [72]. Both  $\text{FeO}_2\text{He}$  and  $\text{FeO}_2\text{H}$  have a cubic structure with identical cell parameter of, respectively 4.32 Å at 135 GPa [68] and 4.33 Å at 133.5 GPa [73], but with different symmetries, Fm-3m vs. Pa-3.

### 3.2. Xenon as a Minor/Trace Element in Oxides

That Xe reacts with oxides at the conditions of the deep crust and mantle is a strong indication that it can be stored at depth. However, Xe is a trace element in planetary interiors (cf. section 1), therefore the relevant reactions are not those producing

stoichiometric compounds but those where Xe retention occurs as a trace or minor element. This aspect considerably changes the energetics of the reaction, and consequently the  $P$ - $T$  conditions at which they may occur. Xe trapping in the deep crust and mantle could solve the Xe paradox, and this occurs by Xe substitution to Si (cf. **Figure 2**) whereby Xe gets oxidized such as in hot compressed  $\text{SiO}_2$  quartz [74] or  $(\text{Mg},\text{Fe})_2\text{SiO}_4$  olivine [75]. Xe-O bonds are best evidenced by new Raman and infra-red vibrational modes (cf. **Figure 3**) that appear under  $P$  upon heating above the melting curve of Xe, the reaction being thermodynamically favored by the volume reduction between reactants (i.e., liquid Xe and quartz or olivine) and products (i.e., Xe-doped quartz or Xe-doped olivine). Theoretical calculations have confirmed this mechanism for quartz [43, 76, 77] and olivine [42], and helped refine the crystal-chemistry of Xe in these minerals. Volume and cell-parameters vs.  $P$  relationships as well as Raman signature of Xe-doped silicates could be theoretically reproduced by substituting Xe to Si albeit in different geometries depending on the mineral: quasi-planar three-fold in olivine vs. linear two-fold (2 nearest O atoms at 1.99 Å) with 2 next nearest O neighbors in orthogonal plan at 2.27 Å in quartz [43]. Theoretically-derived solubility is up to 0.4 at% Xe in both phases [42, 43].

Xe-doped quartz transforms into a new  $(\text{Xe},\text{Si})\text{O}_2$  phase upon increased heating above 1,700 K at 1 GPa [43].  $(\text{Xe},\text{Si})\text{O}_2$  structure bears similarities to the predicted  $\text{XeO}_2$  structure [64]



that is not stable at any of the  $P$  investigated but admittedly the best candidate for the ambient  $P$   $\text{XeO}_2$  phase [59] as characterized by Raman spectroscopy. Both phases are orthorhombic with cell parameters within 10% difference, and have a square planar Xe local environment.

Xe reactivity with lower mantle minerals such as bridgmanite and ferropericlase has not been tested yet. At lower mantle conditions, silicon bonds to six nearest oxygen atoms in an octahedral geometry. It is therefore a promising area of research as Xe substitution to six-fold Si could lead to structures similar to ambient  $P$  Xe perovskites whereby Xe bonds to oxygens in octahedral sites [78].

## 4. OTHER HIGH $P$ NOBLE GAS COMPOUNDS RELEVANT OF PLANETARY INTERIORS

### 4.1. Noble Gas Compounds Relevant to Planetary Fe Cores

The search for Xe reactivity with metals was initiated by the report of Xe metallization at 135 GPa [31], later refined to 155 GPa by means of electrical resistivity measurements [79]. Iron-xenon reactivity received most attention since the first paper by Caldwell et al. [80], showing no tendency from Xe to form a metal with Fe up to 150 GPa. Xe-metals reactivity was later shown to occur at higher  $P$  with Fe and Ni, first by alloying with Fe with up to 0.8 mol% Xe at the conditions of the terrestrial inner core [81]. Later, Xe-metal compounds were predicted from theoretical predictions [82] and observed in experiments with

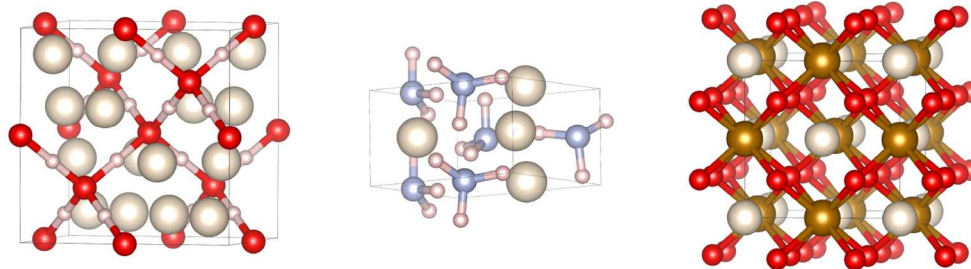
$\text{XeFe}_3$  stable above 200 GPa and 2,000 K [83], conditions that are significantly reduced for  $\text{XeNi}_3$  to 150 GPa and 1,500 K [83, 84]. In these compounds, Fe and Ni act as oxidants, gaining electrons, and forming anions. This is yet another illustration of pressure-induced noble gas chemistry. Implications for Xe sequestration at depth within planetary cores are less convincing however, as Xe is missing from both martian and terrestrial atmospheres while the martian core extends to <40 GPa [85], i.e., far below the  $P$ -threshold required to induce Xe-Fe chemistry.

The latest development in this direction is the  $\text{ArNi}$  compound synthesized above 140 GPa upon laser heating ( $T > 1,500$  K) [86]. If such reaction extends to Fe, the Earth's core could be a deep Ar reservoir.  $\text{ArNi}$  is an intermetallic Laves phase, so there is no bonding but significant electron transfer between Ar and Ni atoms.

### 4.2. Noble Gas Compounds Relevant to Giant Planets Interiors

The range of applications in this subsection covers giant planets, which main constituents are H and He for Jupiter and Saturn, and planetary ices for Uranus and Neptune [87].  $P$ - $T$  conditions reach up to 4,000 GPa–20,000 K inside Jupiter [87], and 510 GPa–5,800 K inside smaller Uranus [88].

Helium is depleted from the atmosphere of Jupiter, and more importantly from that of Saturn, a depletion due to heavier He sedimenting inside the planets at  $P$ - $T$  conditions where  $\text{H}_2$  and He are immiscible. Helium sedimentation may have sequestered Ne, which dissolves preferentially in He rather than in  $\text{H}_2$  [89]. Going beyond simple noble gas solubility in giant planets materials, other processes might sequester noble gases



**FIGURE 4** | Noble gas compounds potentially relevant for giant planets interiors. From left to right:  $\text{He}_2\text{H}_2\text{O}$  [94],  $\text{NH}_3\text{He}$  [95], and  $\text{FeOOHe}$  [68]. Color code for atoms: helium (white), oxygen (red), nitrogen (light blue), iron (gold), hydrogen (light pink).

at depth. Van der Waals noble gas compounds with hydrogen have been synthesized:  $\text{Ar}(\text{H}_2)_2$  [90] at 4.3 GPa and stable to at least 358 GPa [91],  $\text{Kr}(\text{H}_2)_4$  at 5.3 GPa and stable to at least 50 GPa [92], and  $\text{Xe}(\text{H}_2)_8$  at 4.8 GPa and stable to at least 255 GPa [93]. Raman and/or infra-red spectroscopies have shown that hydrogen is molecular ( $\text{H}_2$ ) in these compounds, freely rotating, with no indication of H-noble gas bonding.

Potential planetary He-compounds were predicted (**Figure 4**):  $\text{NH}_3\text{He}$  above 45 GPa [95],  $\text{HeH}_2\text{O}$ , and  $\text{He}_2\text{H}_2\text{O}$  [94] stable against decomposition at 2–8 and 8–92 GPa, respectively, and  $(\text{H}_2\text{O})_2\text{He}$  above 296 GPa [96]. In none of these compounds does He form bond with other atoms. The propensity of He to form compounds under high  $P$  without forming chemical bonds is explained by its insertion with ionic compounds and consequent stabilization of Coulomb interactions [94], besides the volume reduction associated with the reaction. Interestingly, like  $\text{Xe}_2\text{O}_6\text{H}_6$ ,  $\text{He}_2\text{H}_2\text{O}$  is superionic at high  $T$  above 40 GPa [94], with free mobility of He and protons. However, this occurs at 40 GPa only, 10 GPa lower than for pure ice. The presence of He therefore lowers the  $P$  at which superionicity occurs compared to pure water. This effect should be considered in modeling Uranus and Neptune interiors, superionic ices being the most likely candidates as the carriers of the internal planetary magnetic field.

## 5. LIMITATIONS AND FUTURE DIRECTIONS IN INVESTIGATING NOBLE GAS REACTIVITY IN PLANETARY PROCESSES

### 5.1. Current Limitations

Two important limitations of the study of noble gas retention mechanisms in minerals are conceptual. First, most measurements are carried out on samples synthesized at high  $P$ - $T$  conditions but quenched to ambient conditions, i.e., far from thermodynamic equilibrium, potentially causing noble gases to exsolve. Second, solubility studies still assume neutral speciation and propose retention in defects with similar size as zero charge noble gas radii [97] such as oxygen vacancies [98, 99]. This is however unrealistic for noble gas solubilities above 1 at% as reported at lower mantle conditions for Ar in bridgmanite [98] and Kr in ferropericlase [99], oxygen defects

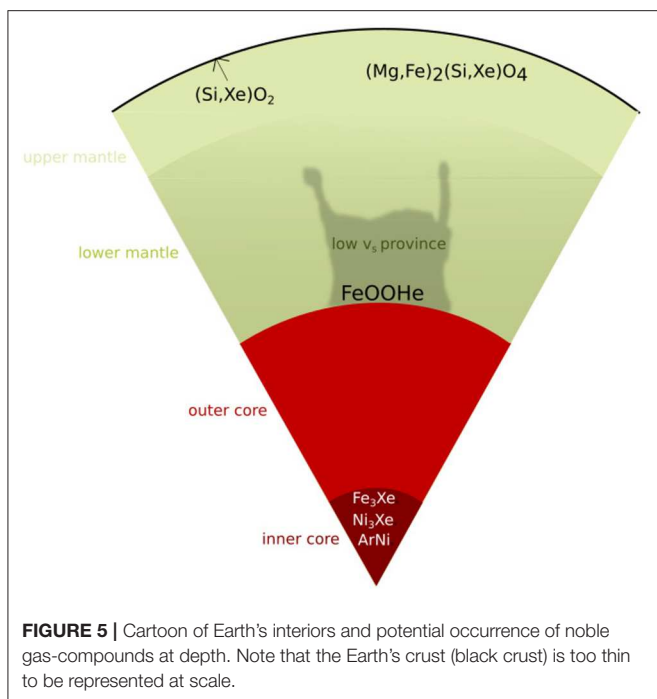
concentrations being at least two orders of magnitude smaller [100, 101].

Even if these conceptual biases are lifted, technical limitations remain. For a chondritic Earth including 1.5% of volatile-rich late veneer [102], 90% of missing Xe [10] represents roughly  $7.10^{13}$  kg of Xe. This translates into concentrations of 10 ppb if all that Xe is stored in the lower continental crust, and 0.05 ppb if stored in the upper mantle. These values are much smaller than the 0.4 at% Xe solubility in olivine and quartz [42, 43], which means that the missing Xe problem is easily solved by storage in silicates at depth. But these values are also much smaller than the detection limit of 0.1 at% for both x-ray diffraction and Raman spectroscopy [42], which is also the minimum concentration that can be handled by theoretical *ab initio* calculations. Neither experimental nor theoretical approaches can therefore be applied to natural levels of concentrations. Henry's law might nonetheless still be obeyed as *ab initio* study on Xe incorporation mechanisms in olivine [42] shows no change in the configuration of Xe with dilution ranging from 0.9 at% down to 0.1 at%; the presence of Xe is only felt locally as expected for a diluted defect and Xe atoms do not interact with each other. This argument justifies the relevance of theoretical calculations and experiments done with 0.1–1 wt% noble gas content to natural abundances.

### 5.2. Future Directions

Much more efforts have been devoted to understand Xe retention at depth than for lighter noble gases. However, the “missing Xe problem” requires a solution that only applies to Xe. Kr retention mechanism as a minor element has so far only been elucidated in compressed silicate melts [56], with the detection of Kr-O bonds having a lower degree of covalency than Xe-O bonds. Ar and Ne retention mechanisms will be very challenging to solve experimentally due to their lighter mass and consequent weak contribution to x-ray based signals. This could explain why these topics were so far never covered despite Ar and Ne being widely used  $P$ -transmitting media for x-ray diffraction measurements using laser-heated diamond anvil cells. Spectroscopic methods might be more straightforward to probe any noble gas induced vibration, although their use at combined high  $P$  and high  $T$  is still difficult.

Major x-ray synchrotron facilities are undergoing upgrades in this decade in order to build extremely brilliant sources



with improved coherence by a factor of hundred. That should prove highly beneficial to the study of noble gas reactivity with planetary materials at more realistic conditions. This will for instance open the prospect of x-ray absorption spectroscopy measurements at below 0.1 at% concentrations. Increased photon flux will furthermore considerably shorten data collection times, allowing count-limited measurements (e.g., local structure by x-ray absorption or pdf analyses) on these diluted systems for smaller samples at lower mantle conditions using laser heated diamond-anvil cell experiments.

Last but not least, it will be crucial to evaluate the consequences of noble gas chemical reactivity at depth on isotopic fractionation during planetary differentiation processes in order to properly interpret the wealth of high precision isotopic data on natural samples.

## 6. CONCLUSION

A variety of noble gas compounds may form inside planets, and those potentially found in the Earth are summarized in **Figure 5**. If most of them are with Xe, even the most inert element of the periodic table, He, reacts at the extreme  $P$ - $T$  conditions found in planetary interiors. While He-compounds do not involve He bonding to other atoms, different types of bonding are found in Xe-compounds, from covalent with Xe as an oxidizing agent (i.e., electron donner), to metallic with Xe as a reducing agent (i.e., electron taker). The main take-away message of this review is therefore that noble gas abundances measured in planetary atmospheres and rocks are certainly a very rich source

of information, but they reflect not only planetary formation processes, origins and dynamics, but also  $P$ -induced noble gas chemistry at depth.

As detailed in section 3, Xe trapping in the deep crust and upper mantle could solve the “missing Xe” problem in the atmospheres of the Earth and Mars, and this occurs by Xe substitution to Si whereby Xe gets oxidized such as in compressed  $\text{SiO}_2$  quartz [74]. This report stimulated further work in noble gas chemistry including the synthesis of the Graal compound  $\text{XeO}_2$  [59]. Earth sciences have thus brought a different perspective to the field, as Xe-O high energy bonds can be formed under the modest pressures of the Earth’s crust in natural minerals. Reciprocally, the synthesis of Xe-water compounds by UV radiation [103] has motivated the investigation of Xe reactivity with water at extreme conditions [60], and the discovery of the  $\text{Xe}_2\text{O}_6\text{H}_6$  oxide stable at the conditions of the interiors of Uranus and Neptune. The search for new noble-gases compounds at high  $P$ - $T$  conditions has also been fueled by the search for high energy compounds in condensed matter physics. The synergy between Earth and planetary sciences, high  $P$  condensed matter physics, and chemistry has been fruitful and should be pursued, in the perspective to discover new synthesis pathways and new types of noble gas compounds, with the wealth of potential societal benefits that follow such as storage of energy or better anesthetics in medicine [104]. A main effort will be to find ways to preserve the newly found compounds metastably back to room conditions, as none of these high  $P$  compounds is yet recoverable.

Future research perspectives could be directed at pursuing the synthesis of noble gas-doped phases instead of stoichiometric compounds, which proved to considerably lower the  $P$ -threshold of Xe bonding to O from 83 GPa in pure Xe-O system [61] down to 1 GPa in more complex silicate systems [43, 74]. Not only is this the mandatory way to adequately reproduce the chemistry of naturally very weakly abundant noble gases in terrestrial planets, but this is also a potential solution to recover metastable phases back to room  $P$ . In the opposite direction, the discovery of very large exoplanets (super Earths, super Neptunes, super Jupiters) opens the perspective to expand the exploratory  $P$ -range for noble gas chemistry at depth, as illustrated by the FeHe compound stable above 4,000 GPa, i.e.,  $P$  greater than at the center of Jupiter [105].

## AUTHOR CONTRIBUTIONS

The author confirms being the sole contributor of this work and has approved it for publication.

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**Conflict of Interest:** The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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