Until very recently, helium had remained the last naturally occurring element that was known not to form stable solid compounds. Here we propose and demonstrate that there is a general driving force for helium to react with ionic compounds that contain an unequal number of cations and anions. The corresponding reaction products are stabilized not by local chemical bonds but by long-range Coulomb interactions that are significantly modified by the insertion of helium atoms, especially under high pressure. This mechanism also explains the recently discovered reactivity of He and Na under pressure. Our work reveals that helium has the propensity to react with a broad range of ionic compounds at pressures as low as 30 GPa. Since most of the Earth’s minerals contain unequal numbers of positively and negatively charged atoms, our work suggests that large quantities of He might be stored in the Earth’s lower mantle.
The noble gas (NG) elements, such as He, Ne, Ar, Kr, and Xe, were believed not to react with other elements for decades, due to their stable closed shell electron configuration. Pauling predicted that Kr and Xe may react with F and O, which was proved by Bartlett who found the first NG compound, the ionic XeF₆⁻. Since then, numerous NG compounds have been synthesized, both in molecular and solid form. Electronic structure calculations have predicted many more. Meanwhile, the modification of external conditions such as pressure has led to the successful formation of yet different classes of NG compounds.

In most of these compounds, NG elements are oxidized and form chemical bonds by sharing their closed shell electrons. It is no coincidence that much of the recent progress on NG chemistry has been made in the area of high pressure, especially regarding unusual bonding features. This is due to the fact that high external pressure can drastically alter the chemical properties of elements. Recent theoretical studies showed that Xe becomes easier to oxidize under high pressure; for example, Xe can form stable compounds with oxygen. Even though these compounds have been found at ambient conditions, they are only metastable. Under pressures as high as those in the Earth’s core, Xe can even be oxidized by Fe and form stable Fe-Xe compounds. In contrast to the above studies, a recent investigation reported: notably diatomic gases like Xe-H₂ is 0 fi first NG compounds under high pressure. A detailed electronic structure analysis of the resulting compounds Na₂He and Na₂OHe showed that He does not lose electrons nor form any chemical bonds. It is important to notice that the Na₂He compound can be regarded as a high-pressure electrode of the form Na⁺⁺E⁻²He, where E represent the interstitial sites (quasi-atom) hosting a pair of electrons. Note that Sun et al. proposed from calculations that He can react with many ionic alkali oxide or sulfide compounds under high pressure. A very recent work by Liu et al. noticed the ability of He to form stable compounds with water molecules at high pressures. The origin of the stability of all the He-containing compounds above is not well understood.

Here we propose that helium has a general propensity to react with ionic compounds that contain an unequal number of cations and anions, e.g., A₂B or AB₃. Such compounds have large Coulomb repulsive interactions between the majority ions (cations or anions), which leads to two effects that favor reaction with helium. First, in the lower pressure range, these repulsive interactions prevent the formation of close-packed structures, thus leaving room for the insertion of helium atoms; this means that the reaction with helium can potentially be stabilized due to the large gain in PV term (compression work). More importantly, with increased pressure, the Coulomb repulsion becomes even stronger. The presence of He can then, second, keep the majority ions farther apart and therefore lower the Madelung energy. We will examine a series of example systems and show that the

Fig. 1 The enthalpy difference between A+B+He and A-BHe. Calculations, between helium and a MgF₂ + He → MgF₂He, MgO + He → MgOHe, Li₂O + He → Li₂OHe, LIF + He → LIFHe, and Na₂ + He → Na₂He, are plotted as a function of pressure. The pressure range in a–e is 0–300 GPa, and in f is 0–400 GPa. The dashed lines refer to the enthalpy of the He-inserted compounds. When a solid line is above the dashed line, the corresponding structure of the ionic compound is unstable relative to the He-inserted compound. Shaded areas present the pressure intervals of stable He insertion.
The reactivity of He with ionic compounds may have significance in geoscience. Earth has a finite supply of helium; and due to the light weight of these atoms, they tend to escape into space. It is therefore of significant interest whether mantle materials could store large quantities of helium. Previously, the miscibility of helium in the mantle has been considered very low due to the hitherto assumed inertness of the element. However, as shown by our work, helium tends to insert into the lattices of elements such as He can become reactive and form new compounds under pressure without the formation of any local chemical bonds.

The reactivity of He with ionic compounds may have significance in geoscience. Earth has a finite supply of helium; and due to the light weight of these atoms, they tend to escape into space. It is therefore of significant interest whether mantle materials could store large quantities of helium. Previously, the miscibility of helium in the mantle has been considered very low due to the hitherto assumed inertness of the element. However, as shown by our work, helium tends to insert into the lattices of elements such as ionic compounds with unequal cation and anion numbers at high pressure—which is a feature shared by most of the minerals in the Earth’s mantle, indicating that they may store considerable amounts of helium. Of course, our calculations apply to the ground state, and the effect of elevated temperatures, inevitable inside the mantle, needs to be addressed. This is beyond the scope of current work and will be investigated later. However, our results, which will be presented in a follow-up study, are in line with recent laboratory experiments that discovered significant uptake of He in SiO$_2$ glass as well as cristobalite, a high-pressure polymorph of quartz, in the pressure range 10–20 GPa.

### Results

**Reactivity of helium with ionic compounds.** In order to test our theory, we chose four ionic compounds MgF$_2$, MgO, Li$_2$O, and LiF, and studied their reactivity with He under high pressure. These four compounds represent ionic compounds of AB$_2$ type, AB type with ±2 charge, A$_2$B type, and AB type with ±1 charge, respectively. CaF$_2$ was also included in our study as it would reveal an important opposing mechanism caused by the occupation of the outer-shell $d$ orbitals under pressure. For comparison, we also further investigated the reaction of Na with He, which can be viewed as the interaction of the ionic compound Na$_2$E with He. We first searched for the most stable structures of these compounds with and without insertion of He atoms under pressures from 0 to 300 GPa. Then, the enthalpy change for the inclusion of He in these compounds is calculated in the same pressure range. The enthalpy differences for the reaction A-B + He $\rightarrow$ A-BHe were calculated as follows:

$$
\Delta H^f = (\Delta H^f_{A-B} + \Delta H^f_{He}) - \Delta H^f_{A-BHe}
$$

Note the difference between $\Delta H^f$ here and the reaction enthalpy. A positive $\Delta H^f$ corresponds to an exothermal reaction, or a thermodynamically stable A-BHe compound. The results of $\Delta H^f$ as function of pressure are shown in Fig. 1. Since the ionic compounds may undergo structural changes under increasing pressure, several $\Delta H^f$-P curves corresponding to different structures are shown. In contrast, the most stable structure of each A-BHe compound remains the same throughout the pressure range.

Let us first compare the results of MgF$_2$-He and MgOHe. The former compound has twice as many anions (F$^-$) as cations (Mg$^2+$); whereas in the latter, their numbers are equal. As shown in Fig. 1a, a 1:1 mixture of MgF$_2$ and He will become stabilized as a ternary compound, MgF$_2$He, between 100 and 150 GPa (at an
interpolated value of 107 GPa). At ambient pressure, MgF$_2$He is 0.25 eV/atom higher in enthalpy than the constituents MgF$_2$ and He. However, at 300 GPa, MgF$_2$He is about 0.05 eV/atom lower in enthalpy (Fig. 1a). We considered adding more He by calculating the stability of MgF$_2$He$_2$ compounds as well (Supplementary Figure 1 and Supplementary Note 1). Although their enthalpy decreases by a small amount from 0 to 50 GPa, it then increases again at higher pressure, and ultimately no stable MgF$_2$He$_2$ could be found. Therefore, MgF$_2$-He compounds can only be stabilized within a limited composition range. In contrast to MgF$_2$-He, MgOHe cannot form any stable compound at any composition ratio. For the 1:1 compound MgOHe, the enthalpy decreases by about 0.1 eV/atom from 0 to 50 GPa, but then increases with further increase of the pressure (Fig. 1b). Reducing the concentration of He to 50% (Supplementary Figure 1b), the enthalpy of MgOHe$_{0.5}$ does not decrease from the value at ambient pressure (+0.36 eV/atom) up to at least 300 GPa (+0.41 eV/atom).

Now let us investigate the 2:1 binary ionic compounds. Li$_2$O-He contains, in contrast to MgF$_2$, twice as many cations as anions. However, the insertion of He has a very similar effect as in MgF$_2$. While the enthalpy of formation of the Li$_2$OHe compound does not become negative with respect to Li$_2$O and pure He at any pressure in the studied range, it does decrease from +0.25 eV/atom at 0 GPa to almost 0 eV at 300 GPa (Fig. 1c). Its $\Delta H$ is almost on the convex hull at all pressures above 100 GPa (see Supplementary Figure 1c), which agrees with the results of Sun et al. 44. The reaction enthalpies of the stoichiometries Li$_2$OHe$_{0.5}$ and Li$_2$OHe$_2$ also decrease with increasing pressure, but both compounds remain unstable at all pressures studied. In contrast to Li$_2$O-He, LiF-He compounds are not stable, and their reaction enthalpy increases with increasing pressure, i.e., pressure disincentivises the insertion of He in LiF lattices (Fig. 1d).

We also tested the reactivity of He with CaF$_2$, which has an anion:cation ratio of 2:1. The interesting feature of this compound is that it is the prototype of the fluorite structure; remember that the electrode Na$_2$E sublattice of Na$_2$He can be interpreted as the antifluorite structure. For CaF$_2$, a reaction with He does not cause a departure from the fluorite lattice, but results merely in the insertion of He in the octahedral interstitials of CaF$_2$. The formation enthalpy of CaF$_2$He with respect to CaF$_2$ + He shows an intriguing behavior (Fig. 1e): at ambient pressure it is unstable, but its formation enthalpy decreases and becomes negative (stable) at a pressure of about 30 GPa. At pressures higher than 50 GPa, the formation enthalpy increases again, becoming unstable at a pressure of about 110 GPa. The presence of He atoms helps stabilize the ionic compound, but only in the intermediate pressure range of 30–110 GPa. Lastly, we find in agreement with Dong et al. that Na$_2$He becomes stable above 160 GPa and remains thus up to the highest pressure studied (Fig. 1f).

**Structure changes and electronic properties.** Now, let us analyze the trends in the structures of the compounds formed at high pressure. The most notable feature is that the A$_2$BHe compounds were found to have the same stable structure with $Fm\bar{3}m$ symmetry at all pressures; see Fig. 2a for an example. This is the structure of full-Heusler compounds. It is also identical to the Na$_2$He structure when the quasiatoms (E) are considered to be the anions. The second lowest enthalpy structure usually had a symmetry group of $Cmcm$. Its enthalpy was about 0.6 eV/atom higher than the full-Heusler structure throughout the pressure range considered. As in the antifluorite structure, the B ions form an face-centered cubic (FCC) lattice, while the A ions occupy all the tetrahedral sites. This structure ensures that the first neighbor of any ion will be an ion of the opposite charge. The He atoms are inserted into the octahedral sites, thus also forming an FCC lattice. The A$_2$B compounds also share similar structures at low pressure: Li$_2$O and CaF$_2$ adopt the same CaF$_2$-type structure at ambient pressure, and MgF$_2$ takes up the TiO$_2$ structure. 45, 46. However, these structures have large interstices, making for an inefficient packing, and they will not be thermodynamically favored under very high pressure. As pressure increases all three A$_2$B ionic compounds adopt more tightly packed structures where the distance between the closest A-B ions and A-A ions are nearly the same (see Supplementary Table 1, and Supplementary Figure 2).

It is interesting that the A-BHe compounds also adopt the same high symmetry structure throughout the pressure range...

**Fig. 3** Electronic structures of MgF$_2$He and MgOHe. a ELF in the (110) plane of MgF$_2$He-Fm$\bar{3}m$. b ELF in the (100) plane of MgOHe-P$\bar{6}$m/mcm. c The electronic PDOS of MgF$_2$He at 300 GPa; d PDOS of hypothetical compound MgF$_2$[He]. e PDOS of MgF$_2$-Pnma at 300 GPa.
Ionic compounds. The large red and blue + ions in MgF₂ in its most stable structure (Fig. 3a) indicate a high probability of a fully occupied electronic state, as in MgF₂He at the same pressure. We denote this compound as MgF₂[He]. Third, we obtain the PDOS of Mg-\(s^+\) states due to overlap of the atom-centered projection spheres. Most importantly, however, after removing the He atoms from MgF₂He but keeping the structure unchanged (MgF₂[He]; Fig. 3d) the F-2p states are almost unchanged. This implies that the interaction between He and other atoms in MgF₂He is very small, and there is no hybridization and no chemical bond formation.

More detailed discussions of the effects of He insertions on the electronic and atomic structures of ionic compounds can be found in the Supplementary Information (see Supplementary Notes 2 and 3 as well as Supplementary Figures 2 and 3).

The driving force of He insertion. Now we will focus on the mechanism of why stable He + ionic compounds form under pressure. The key issue is why He forms stable compounds with 1:2 (or 2:1) ionic compounds but not with 1:1 compounds. The reason for this can be more easily explained using an example in one spatial dimension. In Fig. 4, we present a very simple, one-dimensional (1D) representation of ionic crystals. The figure shows that in a 1D ionic compound with cationic/anionic ratio of 1:1 (AB type), the cations and anions in an atomic unit of A-B-A (here, we set A as +1 positive-charged and B as −2 negative-charged ions) that repeat indefinitely. At the interface of two A-B-A units we will have two A ions repelling each other. Thus, when NG atoms are inserted in between two A ions, the distance between these two A ions increases, which lowers the Madelung energy, making the structure more stable. 1D ionic chain model based purely on Coulomb interactions can be solved analytically (see the Supplementary Note 4 and Supplementary Figure 4) and confirms that the insertion of He in A₂B-type compounds will lower the Madelung energy, whereas the insertion in AB-type compounds will raise the Madelung energy.

As revealed by the density functional theory calculations and the subsequent analysis of the electronic and structural properties of real He-inclusion materials, it is suggestive that the essence of the mechanism of their stabilization is a modification of electrostatic interactions, i.e., the change of the Madelung energy. This theory is revealed clearly by the simple 1D picture just introduced. However, when discussing the stability of real three-dimensional (3D) materials under pressure, many other factors need to be considered, which will somewhat obscure the above simple argument. Obviously, the effect of the insertion of helium is much smaller in 3D materials because the interstitial sites are naturally larger. Interestingly, both He-inserted AB₂ and AB types of ionic compounds show high symmetry lines in their structures (Fig. 2c, f) with the same pattern as we show in Fig. 4.

In order to study the effect of the insertion of He atoms in ionic compounds, we discuss separately the two enthalpy contributions of PV work and internal energy, i.e., \( \Delta E = E + PV \). We then monitor the changes \( \Delta E \) and \( \Delta(PV) \) upon the insertion reaction, i.e. between the constituents and the product compound. We calculate and plot the two terms as functions of pressure in Fig. 5 for all compounds considered (see more compounds in Supplementary Note 5 and Supplementary Figure 6). It is obvious that \( \Delta(PV) \) is zero at ambient conditions (\( P = 0 \)). For reactions involving AB₂ or A₂B compounds, \( \Delta(PV) \) quickly drops to significantly negative values as a function of pressure. It becomes about −0.2 eV/formula unit for Li₂O and

![Fig. 4 One-dimensional schematics of He insertion in AB and A₂B types of ionic compounds. The large red and blue filled circles represent the ions with +2 and −2 charges; the small red filled circles represent the ions with +1 charge; the white circles represent the neutral helium atoms.](image-url)
Fig. 5 Relative changes in PV work, internal energy $E$, and Madelung energy $E_M$ for He insertion. a–e The corresponding data of helium inclusion into a MgF$_2$, b MgO, c LiF, d Li$_2$O, e CaF$_2$, and f Na. Relative changes in PV work, internal energy $E$, and numerically determined Madelung energies $E_M$ changes per formula unit are shown with red star, blue hexagonal, and square purple solid lines, respectively.

Fig. 6 The changes of the volume as a function of pressure for He insertion. a MgF$_2$, b MgO, c LiF, d Li$_2$O, e CaF$_2$, and f Na. The dashed lines refer to a sum of the volume of the ionic compounds and elemental helium, whereas the solid line is for the ternary compound. Shaded areas present the pressure intervals of stable He insertion.
MgF₂ compounds and −0.5 eV/formula unit for Na₂E beyond 50 GPa. CaF₂ is an exception, with Δ(PV) slightly lower than zero at 50 GPa and positive at higher pressure. In contrast to AB₂-type compounds, the value of Δ(PV) for AB compounds is mostly positive, except for a slightly negative value at low pressure (50 GPa).

The different behaviors of Δ(PV) are caused by the different volume changes for A₂B and AB compounds during the reaction with He. This volume change ΔV is summarized in Fig. 6. It shows that the insertion of He into the lattice of both A₂B and AB types of compounds reduces the overall volume at low pressure, i.e., ΔV < 0; it is advantageous (purely from a PV work perspective) to store helium inside the compounds instead of as separate constituents. However, the volume reduction is much more significant for A₂B type of compounds. At ambient pressure, ΔV/formula unit is −0.6 and −0.75 Å³ for MgF₂ and Li₂O reacting with He, respectively. In contrast, ΔV is only about −0.1 Å³ for MgO and −0.03 Å³ LiF reacting with He. This distinct difference between A₂B and AB types of compounds originates ultimately from the different balance of Coulomb interactions (Madelung energies) of the two types of compounds. As illustrated in the 1D model above, there is strong A-A repulsion in A₂B compounds. As a result, A₂B compounds assume larger volumes per atom at low pressure to minimize these repulsions, thereby leaving more room for the insertion of He in their lattices. However, the He-insertion compounds all seem less compressible than the constituents: for both A₂B and AB compounds, ΔV increases with increasing pressure and eventually, for MgO, Li₂O, LiF, and CaF₂, becomes positive at sufficiently high pressure. That means that the He-inserted lattice has a larger volume than the separate constituent ionic compound and He.

In contrast to the Δ(PV) term, the insertion of He in the lattice of both AB- and A₂B-type compounds causes large increases of the internal energies at ambient and low pressures, ΔE > 0 (Fig. 6). This is due to the disturbance of the electronic structure of the ionic compounds caused by insertion of the NG element. At lower pressure, the gain in Δ(PV) is not large enough to overcome the large increase of internal energy upon insertion of He. Therefore, at lower pressure, He cannot react with ionic compounds regardless of the cation:anion ratio.

Under increasing pressure, the internal energy balance ΔE for He insertion decreases significantly. Although this is generally true for both AB and A₂B ionic compounds, the decrease of ΔE is more remarkable for the latter (Fig. 5). For example, ΔE changes from 1.05 eV/formula unit at 0 GPa to −0.02 eV/formula unit at 300 GPa for MgF₂; whereas it only changes from 1.08 eV/formula unit at 0 GPa to 0.75 eV/formula unit at 300 GPa for MgO. A similar trend can also be found in the Li-based compounds, except that ΔE actually increases in the pressure range from 0 to 50 GPa for LiF. Because Δ(PV) either changes only slightly or increases with increasing pressure, it is indeed the dramatic decrease of the internal energy change ΔE that eventually leads to the stabilization of A₂BHe compounds at sufficiently high pressure.

What causes this decrease of ΔE upon He insertion? One major factor is the change of the Madelung energy as explained in detail for the 1D model. That change of the Madelung energy ΔEₘ can be calculated by assigning effective charges to each atom in the crystals of both the pure ionic compound and the He-inclusion compound. The Bader charges are used as the effective charges for the ions. The results for ΔEₘ, for all compounds and pressures, are also shown in Fig. 5. It is obvious that in general ΔEₘ behaves very similar to ΔE under increasing pressure. The correlation between ΔEₘ and ΔE indicates that the drastic decrease of the latter under pressure is indeed caused by the change of the Madelung energy. The only major exception occurs in the low-pressure region of Na₂He. This is not surprising because Na is not an electride at lower pressure (<200 GPa). Interestingly, Na can form a stable compound with He at 150 GPa, before Na itself becomes quasi-ionic. This can be explained by the theory based on the electrostatic interaction because there is a strong interplay between the electride state and the He insertion. As He is inserted into the Na lattice, it will increase the size of the interstitial sites. Therefore, the quantum orbital energy at the interstitial sites will be lowered, which will help the formation of an electride. In turn, the local charges in any electronegative phase will stabilize the insertion of He in the lattice.

The correlation of ΔEₘ and ΔE is not perfect even for compounds consisting of very hard ions. There are several reasons for this. First, it is hard to truly determine the effective charge of anion in the compounds. The nominal charges are integer numbers and they are usually much larger than the actual charges and the Bader charges. As a matter of fact, these charges may also change with pressure (see the Supplementary Figure 5). However, reasonable variations of the charge values, e.g., by using different calculation methods do not alter the conclusions drawn here. Second, a simple spherical charge distribution model may not work very well for ionic compounds, especially under pressure (notice the non-spherical ELF isosurfaces in Fig. 3a, b). Third, there might be large contributions to the internal energy beyond the Madelung energy. The insertion of He in the ionic compounds increases their lattice constants while at the
same time also blocking the respective interstitial area for other electrons’ wavefunctions. The overall effect may raise or lower the kinetic energy of the electrons of the filled anion shells and further influence the internal energy. Lastly, for ionic compounds consisting of heavier ions, such as CaF₂, the change of the internal energy may have a turning point and again increase with pressure, opposite to the trend of the Madelung energy. This counteracting factor will be discussed in detail below.

Opposing factors to He insertion. In this section, we will examine the question why He-inserted ABₓ or AₓB ion compounds are sometimes not stable even though the reaction potential from the Madelung energy is already significant. For instance, as shown in the previous section, the reaction enthalpy of He + Li₂O decreases with increasing pressure but never becomes negative. Although the Madelung energy and the internal energy both decrease with increasing pressure while He is inserted into the Li₂O lattice, they never form stable compounds. Furthermore, CaF₂ forms a stable compound with He but only in a limited pressure range from 30 to 110 GPa. In this case, higher pressure destabilizes the He-inserted ionic compound. Such behavior is also shown in an earlier work of Sun et al. for a number of alkali halogenides. For example, we find K₂S to form a stable compound with He in the pressure range from 1.5 to 6.1 GPa (1.3 to 5.8 GPa in the work of Sun et al.⁴⁵).

We will first investigate the unusual behavior of He insertion into the CaF₂ lattice. Foremost, its volume change ΔV increases dramatically with increasing pressure (Fig. 6e). Therefore, although its Madelung energy evolution would stabilize the He insertion, the overall formation enthalpy starts to increase at pressures above 50 GPa and the He insertion is not favored at any pressure. This distinct behavior compared to other ionic compounds is due to the fact that the energy of the Ca-3d orbital is lowered under high pressure, and it becomes partially occupied. This alters dramatically the simple picture of He insertion into this ionic compound. As shown in Fig. 7a, the occupation of the Ca-3d orbital increases from about 0.1 at ambient pressure to 0.3 or 0.4 at 100 GPa. Correspondingly, the charge transfer from Ca to F decreases. As a matter of fact, the Bader charge of Ca in both the CaF₂ and CaF₂:He compounds decreases from about 1.65 e at 0 GPa to about 1.45 e at 300 GPa. In comparison, the Bader charge of Mg (in MgO and MgOHe) changes much less, from about 1.76 e at 0 GPa to 1.73 e at 300 GPa. A significant charge transfer from F to Ca-3d orbitals leads to greatly reduced repulsive interactions among F⁻ anions, which lowers the volume of CaF₂ under pressure. The overall effect is ΔV > 0 for the helium insertion reaction, which is thus disfavored under pressure. Furthermore, the occupation of the 3d orbitals can lower the kinetic energy under high pressure, because the 3d orbital can largely penetrate into the core region due to the lack of core states with the same angular momentum. This gain in kinetic energy is more significant for CaF₂ than CaF₂:He since the previous compound is more closely packed. This explains why the internal energy difference ΔE increases slightly while the pressure is higher than 150 GPa, opposed to the decreasing trend of ΔEₘ. The different behavior of CaF₂ illustrates that the insertion of He into ionic compounds might be complicated by other factors if the composite species are heavily polarized.

Similar effects arising from the occupation of an orbital with higher angular momentum can also be seen in the Li₂O compound. The Li atom has an electron configuration of 1s²2s². However, under high pressure, some of the electrons will be transferred into the 2p orbital. As shown in Fig. 7b, the occupancy of the 2p orbital increases from about 0.2 or 0.3 at 0 GPa to 0.9 or 1.3 at 300 GPa. Due to the lack of any lower shell p orbital, the 2p orbital has no radial node and can largely penetrate into the core region. This essentially reduces the size of the Li ions, which eventually leads to the positive ΔV in Fig. 6c.

Furthermore, our proposed He insertion mechanism and the opposing factors are readily applied to many other AₓB or AB₂ compounds as well as Ne insertions in ionic compounds. Several examples are discussed in the Supplementary Information (see Supplementary Notes 5 and 6, as well as Supplementary Figures 6, 7, and 8).

In summary, we propose that chemically inert elements such as He have a prevalent propensity to react with ionic compounds that have unequal numbers of cations and anions. The He atoms do not form any chemical bonds with the ions in the compounds. However, the insertion of He atoms will lower the otherwise strong repulsive Coulomb interactions between the majority ions with the same charge, and therefore lower the Madelung energy. We also show that the recently discovered reactivity of He with Na originates from the same energetic driving force.

Methods

Structure search. In order to test our hypothesis that the insertion of He atoms can lower the Madelung energy of certain types of ionic compounds, we selected a number of compounds with different cation/anion ratios: Li₂O (2:1); LiF (1:1); MgF₂ (1:2); MgO (1:1); and CaF₂ (1:2), as the test compounds reacting with He. Extensive crystal structure searches were conducted by use of the particle swarm optimization algorithm implemented in CALYPSO (Crystal structure Analysis by Particle Swarm Optimization)⁴⁴-⁵⁶. A series of efficiency-improving techniques available in the code were employed, including symmetry constraints, bond characterization matrix, and coordination characterization function, etc. The effectiveness and the efficiency of this crystal search method have been proven by numerous early calculations. With the aid of this powerful method, we obtained the predicted stable structures of the He-inserted ionic compounds and the products of reactions between them and helium. We selected a pressure interval from 0 to 300 GPa and 100 GPa pressure steps for the structure predictions.

Formation enthalpy and electronic structure calculation. The formation enthalpy and electronic properties of products were calculated by DFT as implemented in the VASP⁵⁷ package, in which the generalized gradient approximation within the framework of Perdew-Burke-Ernzerhof⁵⁸ describes the exchange-correlation functional and the projector augmented wave method⁵⁹-⁶¹ was used to describe electron-ion interactions. For Li (Na, Mg, Ca), the 1s (2s) states were included in the valence. The plane wave cutoff energy is set as 900 eV. The k-point meshes with interval smaller than 2π × 0.05/Å was used for the ab initio calculation and the enthalpies are converged within 1 meV/atom.

Madelung energy calculation. The Madelung energy was calculated using a Fourier method that is implemented in the Vesta⁶² program. There are two important parameters, including the radius of ion spheres and the Fourier coefficient cutoff frequency. The charge-density distribution, ρ(r), of an ion is defined inside a sphere as ρ(r) = ρ₀ [1 − 6(r/C₀)² + 10(r/C₀)⁴ − 5(r/C₀)⁶] for r < C₀ else ρ(r) = 0, where s is the radius of the sphere. The sphere has to be smaller than half of the interatomic distances. It is determined by testing the convergence of the Madelung energy, a standard procedure as recommended by the VESTA program. The Fourier coefficient cutoff frequency for the long-range Coulomb potential is set as 2π for all the calculations. This is also a value recommended by the program.

Bader charge calculation. The calculation of the electron population was performed using the Bader Charge Analysis code developed by the Henkelman group in the University of Texas at Austin⁶³. While calculating Bader charges, we found that the charges on the He atoms, although very small, are not exactly zero. We would like to point out that this does not mean there is a net charge transfer during the insertion of He into ionic compounds. The He-1s orbital is fully occupied and the 2s orbital is much higher in energy. Therefore, there is no quantum orbital available for any electron transfer. However, while one calculates charges using the Bader analysis, the charge enclosures around He atoms are determined by the zero flux sheets of the total charge density. Even if He atoms form covalent bonds with the surrounding atoms, the total charge density is the overlap of He electrons and the electrons of neighboring ions. Therefore, the enclosed charge around He might be slightly different from 2. The Bader charge of He in Na₂He is even higher because the charge in the interstitial sites (quasimolecules) overlaps more with the He atoms.
Data availability. The data supporting this publication are available from the authors on request.

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Author contributions
M.S.M. proposed the mechanism and designed the study. Z.L., J.B., and M.S.M. conducted most of the calculations. M.S.M., D.Y., and H.L. coordinated and guided the research. All authors were involved in data analysis and result discussions. S.V. contributed to the Madelung energy analysis. M.S.M, Z.L., J.B., A.H., E.Z., and H.L. wrote and revised the manuscript together.

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