Crystal structure prediction has been widely used to accelerate the discovery of new materials in recent years. Up to this day, it remains a challenge to predict the stable stoichiometries and structures of ternary or more complex systems due to the explosive increase of the size of the chemical and configurational space. Numerous novel materials with a series of unique characteristics are expected to be found in this virgin territory while new algorithms to predict crystal structures in complex systems are urgently called for. Inspired by co-evolution in biology, here we propose a co-evolutionary algorithm, which we name COPEX, and which is based on the well-known evolutionary algorithm USPEX. Within this proposed algorithm, a few USPEX calculations for ternary systems and multiple for energetically-favored pseudobinary or fixed-composition systems are carried out in parallel, and co-evolution is achieved by sharing structural information on the fittest individuals among different USPEX sub-processes during the joint evolution. We have applied the algorithm to W–Cr–B, Mg–Si–O, and Hf–Ta–C, three very different systems, and many ternary compounds have been identified. Our results clearly demonstrate that the COPEX algorithm combines efficiency and reliability even for complex systems.

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where $E_A$, $E_B$, and $E_C$ refer to the ground-state energy of elemental forms of A, B, and C. $E_f$ is a function of the composition, and its calculation requires the knowledge of $E_A$, $E_B$, $E_C$, and $E_{A,B,C_{1-x,y}}$.

Stable compounds shall have negative energy of formation $E_f$; however, this is necessary but not sufficient. The sufficient condition is that the compound be thermodynamically more stable than all of the possible products of decomposition.

As a result, all the thermodynamically stable compounds form a convex hull. As discussed in the introduction section and also demonstrated by Villars and Iwata, there are so many possible stoichiometries that computationally exploring the whole chemical space is impossible. Thus, before discussing our co-evolutionary algorithm, we would like to explain the strategies that we use to navigate the chemical space.

Traditionally, according to the chemical bonding features, molecular, ionic, ionic-covalent, and intermetallic ternary compounds can be divided into four groups, (I) ternary molecular (all non-metals), (II) acids, (III) ternary ionic or ionic-covalent (including a oxysalts), and (IV) intermetallics. Among the 45,000 ternary structures from the Crystallography Open Database (COD), we found (analyzing interatomic distances) that 45% are molecular compounds, 49% are ionic or ionic-covalent, and the remaining 6% are intermetallic compounds. Since our work is focused on crystal structure prediction of inorganic compounds, therefore, the 45% molecular compounds are disregarded in our analysis. In nature, the octet rule governs the formation of ionic or covalent compounds. For instance, by analyzing all the ionic, ionic-covalent compounds and intermetals, one finds that about 46% of them have both the compositions $(AB)_n(AC)_m$, where $AB_n$ and $AC_m$ are stable binary compounds in the corresponding systems) and $A_n(BC_m)$, in which A is a pure element, and $BC_m$ is a stable binary compound in the B–C system. Also, about 35% and 11% are found exclusively in $(AB)_n(AC)_m$ or $A_n(BC_m)$ category, respectively.

It is reasonable that atoms always seek to adopt the most stable electronic configuration. Following this philosophy, one could take advantage of the above principle and explore the chemical space along the pseudobinary joints.

The situation is more complex for predicting ternary intermetals. Since metallic bonding comes from free electrons, the individual properties of the constituent atoms have less influence on the formation of structures than in the case of ionic and covalent compounds. In general, intermetals have a higher propensity to form solid solutions, host significant concentrations of defects, and form unusual stoichiometries. Many ternary stable compounds adopt the same structure prototypes as the binary compounds. This situation holds in many cases, but should not be accepted as a universal axiom.

In conclusion, ternary compounds are usually formed by combining or atom-substituting stable binary compounds. Hence, we can summarize that the promising and efficient way to find the thermodynamically stable ternary compounds is focusing on the compositions along the pseudobinary joints or some fixed-composition obtained by atomic substitution in stable binary compounds. However, one cannot rule out the possibility to find stable ternary compounds which do not follow the above rules. In such a case, fully unconstrained variable-composition ternary structure search is still needed and different exploration strategies are encouraged.

Co-evolutionary algorithm

The co-evolutionary structure prediction algorithm mimics Darwinian evolution and employs a natural selection of the fittest in combination with variation operators, which has been proven to be very successful. In multicomponent systems, due to their vast compositional space, many structures/compositions have to be sampled (rendering the searches quite expensive), and still it is possible to skip stable compositions. Thus, in order to explore the
configurational space effectively, one could focus on the compositions of the pseudobinary systems or some fixed compositions. Thus sampling task can be divided into several sub-processes, and each of them tackles one part of the compositional space. In biology, co-evolution proved a major force to create biodiversity. Here we take advantage of this idea to propose the COPEX algorithm to manipulate the multiple crystal structure prediction processes. The working procedure of COPEX is shown in Fig. 2 and the main steps are:

1. Gathering the structural information of all the known elemental, binary (including all the stable and low-energy metastable phases), and experimentally known ternary phases in this or similar systems.
2. Taking the above gathered structures as seeds and applying variation operators to generate new compositions and structures.
3. Evaluating the results every ten generations and extracting low-energy structures to form a structure pool.
4. Sharing good structures between different USPEX runs, and manipulating USPEX runs, i.e., launching or terminating pseudobinary or fixed-composition USPEX sub-processes.
5. Constructing the phase diagram of the system, and applying variation operators to generate new compositions and structures.
6. Repeat steps 3–5 until pre-specified halting criteria are achieved.

USPEX has proven to be efficient and reliable for predicting stable structures in fixed-composition and in binary systems. Thus, the USPEX processes in COPEX can accelerate the process to show in Fig. 2 and the main steps are:

1. Gathering the structural information of all the known elemental, binary (including all the stable and low-energy metastable phases), and experimentally known ternary phases in this or similar systems.
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5. Constructing the phase diagram of the system, and manipulating USPEX runs, i.e., launching or terminating pseudobinary or fixed-composition USPEX sub-processes.
6. Repeat steps 3–5 until pre-specified halting criteria are achieved.

USPEX has proven to be efficient and reliable for predicting stable structures in fixed-composition and in binary systems. Thus, the USPEX processes in COPEX can accelerate the process to locate the stable stoichiometry or structure, which in turn will benefit the evolutionary process and generate high-quality structures for the next generation. The phase diagram of the ternary system can be generated using the energies of formation of all structures. Since the phase diagram will change dynamically during the evolutionary process, we set to analyze the phase diagram after every 10 generations and manipulate the compositions and USPEX processes automatically as illustrated in step 4. The success of the evolutionary algorithm for crystal structure prediction relies largely on the various variation operators, i.e., heredity, softmutation, lattice mutation, permutation, and transmutation. Among them, the chemical transmutation operator is designed for variable-composition structure search, which means swapping atoms at randomly selected positions while keeping positions of most atoms unchanged. After every generation of COPEX, we reassign the atomic positions of different elements with closer atomic radii, which turned out to be very helpful to the co-evolutionary process. In the following, we have applied the COPEX algorithm to W–Cr–B, Mg–Si–O, and Hf–Ta–C, three chemically very different systems, and found evidence the high efficiency and reliability of the method.

**Application to the W–Cr–B system**

The W–Cr–B system has attracted extensive attention due to the remarkable mechanical properties and chemical inertness of transition metal borides, such as CrB$_2$, W$_2$CrB$_2$, and W$_4$CrB$_3$. Besides, tungsten chromium borides, such as M$_3$B$_7$ and M$_5$B$_3$ (M refers to metal atoms) commonly exist in the Ni–superalloy single crystal turbine blades as the predominant precipitate phase. For a long time, the transition metal elements were believed to be distributed randomly over the sublattice M in M$_3$B$_7$ and M$_5$B$_3$. However, in our previous work, we have found both from theory and experiment that the transition metal elements are distributed in an ordered fashion in the M$_3$B$_7$ and M$_5$B$_3$ borides, and are stoichiometric, in fact, W$_2$CrB$_2$ and W$_4$CrB$_3$, respectively. Naturally, one may wonder if any other stable ternary compounds exist in the W–Cr–B system. Thus, we chose COPEX to investigate this system.

Before running COPEX, we need to thoroughly gather the structural information of all the stable phases in the corresponding unary and binary systems. If not, COPEX will need to spend unnecessary efforts to explore these systems. The W–B and Cr–B systems were widely investigated in literature (M refers to metal atoms) commonly exist in the Ni–superalloy single crystal turbine blades as the predominant precipitate phase. For a long time, the transition metal elements were believed to be distributed randomly over the sublattice M in M$_3$B$_7$ and M$_5$B$_3$. However, in our previous work, we have found both from theory and experiment that the transition metal elements are distributed in an ordered fashion in the M$_3$B$_7$ and M$_5$B$_3$ borides, and are stoichiometric, in fact, W$_2$CrB$_2$ and W$_4$CrB$_3$, respectively. Naturally, one may wonder if any other stable ternary compounds exist in the W–Cr–B system. Thus, we chose COPEX to investigate this system.

Before running COPEX, we need to thoroughly gather the structural information of all the stable phases in the co-evolutionary process. The following, we have performed two independent COPEX runs of the W–Cr–B system at ambient pressure. Besides W$_2$CrB$_2$ and W$_4$CrB$_3$, we have also predicted three stable ternary compounds, namely, WCrB$_2$, WCrB$_3$, and W$_4$CrB$_3$. The crystal structure parameters of the predicted three ternary compounds are given in Supplementary Table 1. Their elastic constants are given in Supplementary Table 2, and we can see that all of them satisfy Born criteria of mechanical stability. Phonon calculations show no imaginary frequencies in these three compounds, which indicates their dynamical stability. The phase diagram and energies of formation of all the sampled structures are given in Fig. 3.

Here we would like to discuss the structural origins and features of the predicted ternary compounds. The crystal structures of the five ternary phases and some related compounds are drawn in Fig. 4. Among the five ternary W–Cr–B compounds, W$_2$CrB$_2$ and W$_4$CrB$_3$ share the same structural features as other earlier reported phases. Namely, the prototypes of W$_2$CrB$_2$ and W$_4$CrB$_3$ are derivatives of V$_3$B$_2$ and Cr$_3$B$_2$ structure types, respectively, while the prototypes of WCrB$_2$, WCrB$_3$, and W$_4$CrB$_3$ have never been reported before to the best of our knowledge. As shown in Fig. 4, the structure of W$_4$CrB$_3$ consists of two layers where one layer has the same structure as W$_2$CrB$_2$ (see Fig. 4b) while the other is made of...
of W-centered square antiprisms, just like in the structure of W₂B (see Fig. 4a). Therefore, W₄CrB₃ is composed of an alternating array of trigonal prism layer and square antiprism layer. In other words, W₄CrB₃ can be viewed as an intergrowth or a stacking of W₂CrB₂ and W₂B along the [001] direction, indicating that W₂CrB₂ and W₄CrB₃ are very likely intergrown in practice, which agrees with experimental observations. The structure of WCrB₂ has never been reported before, it shares some similarities with CrB and WB. As CrB and WB adopt the same ground-state structure, here we use WB as an example. The ground-state phase of WB crystallizes into the α-WB(amd) structure (also known as α-WB). The zigzag chains formed by B atoms in α-WB are perpendicular to each other along the α-axis as shown in Fig. 4d. One B atom is surrounded by 7 W atoms, which form a capped trigonal prism. What if the zigzag chains are parallel to each other instead of perpendicular? The resulting structure would be the well-known β-WB, which is also constructed by the same capped trigonal prisms.

As shown in Fig. 4e, WCrB₂ is also constructed by the capped trigonal prism, in which one B atom is surrounded by 3 W and 4 Cr atoms. Different from α- and β-WB, B atoms in WCrB₂ form parallel armchair chains. As shown in Fig. 4f, one B atom in WCrB is coordinated by 5 W and 4 Cr atoms, resulting in a slightly distorted capped square antiprism. The polyhedra are arranged in a zigzag way, with a 2₁ screw axis. WCrB has Cmcm space group. Interestingly, the Cr atoms form a sublattice with the lonsdaleite topology. Boron atoms are in a tricapped trigonal prismatic coordination (with 3 W and 6 Cr neighbors). Furthermore, Cr and B atoms form a graphene-like flat layer, penetrated by the hexagonal framework of Cr atoms, and result in an interesting graphene-diamond hybrid structure.

Ternary tungsten chromium borides were thought to be nonexistent for a long time. Our work, however, has uncovered five stable tungsten chromium borides at ambient pressure. In these phases, we see strong hybridization between W–d, Cr-d, and B-p states (Supplementary Fig. 3), indicating strong covalent W–B and Cr–B bonds.

As shown in the W–Cr–B phase diagram (Fig. 3), WCrB₂ is located on the WB–CrB pseudobinary joint. The stability of WCrB₂ can be further investigated by taking end-point compounds WB and CrB into consideration. Here we have constructed artificial oC₁₆-WB and oC₁₆-CrB by taking the same structure of WCrB₂, and the energy of formation of WCrB₂ from oC₁₆-WB and oC₁₆-CrB is −0.2 eV/atom. When the atomic positions of Cr and W in WCrB₂ are interchanged, the calculated enthalpy of formation is higher than WCrB₂ by 0.194 eV/atom. Although W and Cr belong to the same group, they occupy distinct positions due to their large difference in atomic radius, which makes W–Cr disorder unfavorable. In summary, five ternary borides have been identified with the help of COPEX.

Application to the Mg–Si–O system

Thanks to several decades of continuing works by geoscientists, reasonable mineralogical models of the Earth’s interior, especially the mantle, are available to some level of approximation. The structural, vibrational, and thermodynamic properties of the two main mantle-forming compounds, Mg₂SiO₄ and MgSiO₃, have been systematically investigated both in experiments and simulations. According to our previous work, extraordinary ternary compounds Mg₃SiO₆ and Mg₃SiO₁₂ have been predicted to be stable at terapascal pressures (relevant to giant planets and exoplanets) in the Mg–Si–O system. And beyond that, one may wonder whether the phase diagram of the Mg–Si–O system is fully understood at the Earth’s mantle pressures. Therefore, we would like to use the COPEX algorithm to further explore the system at pressures relevant to the Earth’s mantle (1–136 GPa). Such study
would further demonstrate the performance of the COPEX algorithm in an ionic-covalent ternary system.

By exploring the whole range of compositions in the Mg–Si–O system at ambient pressure, we constructed the phase diagram of the Mg–Si–O system as shown in Fig. 5a. The vertices and edges of the convex hull refer to stable phases and phase boundaries, respectively. Any compound located on the convex polyhedron is thermodynamically stable. It can be seen that Mg$_2$SiO$_4$ is the only thermodynamically stable ternary compound in the Mg–Si–O system, and the most likely decomposition pathway of Mg$_3$Si$_2$O$_6$ is into MgO and SiO$_2$.

Unexpectedly, our calculation shows no thermodynamically stable ternary compound in the Mg–Si–O system at 28 GPa. In order to further investigate this phenomenon, we then constructed the phase diagram of the pseudobinary MgO–SiO$_2$ system, including the zero-point energy. As shown in Fig. 5b, at zero Kelvin akimotoite (MgSiO$_3$ with ilmenite-type structure) will decompose into periclase (MgO) and stishovite (SiO$_2$) at 27.29 GPa, and then periclase and stishovite will recombine into bridgmanite (perovskite-type MgSiO$_3$) at 28.72 GPa. In other words, both akimotoite and bridgmanite are thermodynamically unstable in the pressure range 27.29–28.72 GPa and therefore a ternary compound instability zone exists, which was also observed in another theoretical work.

By considering the effects of temperature, we have constructed the temperature-pressure phase diagram of Mg$_2$SiO$_4$, as shown in Fig. 5c. The zone of instability of ternary compounds narrows as temperature increases, and eventually disappears at 250 K and 27.62 GPa, and akimotoite will transform into bridgmanite directly without decomposition above 250 K. We can also conclude that the vibrational properties of akimotoite and bridgmanite play an essential role to stabilize them in the Earth’s mantle. Even though the zone of instability of ternary compounds disappears above 250 K, we still need to pay attention to it, since the impurity (Fe, Al, et al.) effect may extend it to higher temperatures. It is possible that this zone crosses the geotherm in some planets, and therefore might have significant influence on the internal structures and dynamics of these planets. Furthermore, ringwoodite decomposes into periclase and akimotoite at 18.63 GPa at zero Kelvin. A triple point between phases ringwoodite-bridgmanite-periclase-akimotoite-periclase is found at 21.5 GPa and 2150 K, which is in reasonable agreement with the literature. In other words, ringwoodite will decompose into periclase and bridgmanite above this point. This phase transition is the main cause of the discontinuity in the mantle at the depth of 670 km. The phase diagram shown in Fig. 5c is essential for determining the temperature distribution in the deep interiors of the Earth.

**Application to the Hf–Ta–C system**

High-performance refractory materials are of crucial significance in some extreme applications, such as gas turbines, heat shields for hypersonic vehicles, and more. For instance, transition metal carbides (TMCs) HfC and TaC are the most refractory materials among binary compounds with the highest melting points of nearly 4000 °C. Hf and Ta are located next to each other in the periodic table and have similar chemical properties, and both HfC and TaC possess the B1 rocksalt crystal structure. Mixing the two binary carbides provides an approach to tune the electronic and mechanical properties. One of the questions immediately rising is whether ternary Hf–Ta–C carbides will be ordered stoichiometric compounds or solid solutions with Hf–Ta disorder. In order to answer this question and explore the configurational space of the Hf–Ta–C system, we performed a COPEX calculation.

Herein, structure searches using the COPEX algorithm with up to 40 atoms in the primitive cell were carried out at ambient pressure. As usual, the stable structures of the pure elements and binary compounds should be provided. We have found four (HfC, Hf$_2$C, Hf$_3$C, and Hf$_4$C) and three (TaC, Ta$_2$C, and Ta$_3$C) stable phases in the Hf–C and Ta–C systems, respectively, at ambient pressure, which is in agreement with the literature. In addition, many low-energy metastable phases like Hf$_2$C$_7$, Hf$_3$C$_5$, Hf$_4$C$_3$, and Ta$_2$C$_4$ were also considered in our calculation. Furthermore, no stable compound has been found in the Hf–Ta system. Taking this information into account, we performed a COPEX search and obtained the phase diagram of the Hf–Ta–C system at ambient pressure, as shown in Fig. 6. Eventually, our study identified 14 stable ternary compounds containing HfTa$_2$C$_3$(P7), HfTa$_2$C$_3$(r3), HfTa$_3$C$_4$(C2/m), HfTa$_3$C$_4$(C2/m), HfTa$_3$C$_4$(R3m), HfTa$_3$C$_4$(R3m), Hf$_3$ Ta$_2$C$_4$(C2/m), Hf$_3$Ta$_2$C$_4$(C2/m), Hf$_3$Ta$_2$C$_4$(R3m), Hf$_3$Ta$_2$C$_4$(R3m), HfTa$_3$C$_5$(Cm), Hf$_2$Ta$_2$C$_3$(C2/m), Hf$_2$Ta$_2$C$_3$(R6). In all of these

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**Fig. 5 Thermodynamics of Mg–Si–O system.** a Mg–Si–O convex hull with energies of formation (in eV atom$^{-1}$, with scale shown by color bar) of the sampled structures at ambient pressure. b Pressure-composition phase diagram of the MgO–SiO$_2$ system. c Pressure-temperature phase diagram of Mg$_3$Si$_2$O$_6$ and its decomposition pathways. The triple point between phases ringwoodite-bridgmanite-periclase-akimotoite-periclase is highlighted by red dot.
Among the 10 ternary phases, Hf₃Ta₅C₈ is different from others. It is formed by intergrowth of one layer of HfTa₃C₄ and one layer of Hf₂Ta₄C₅, as illustrated in Fig. 7m. The four stable ternary compounds, HfTa₃C₄, Hf₂Ta₄C₅, HfTa₅C₆, and Hf₆TaC₆, have already been reported by Smith et al. Structural information for these phases is given in Supplementary Table 3. To verify the dynamical stability of the predicted phases, we performed phonon calculations. There are no imaginary frequencies in the whole Brillouin zone, which indicates that the predicted phases are dynamically stable. We also calculated their elastic constants (Supplementary informations), which all satisfy Born criteria of mechanical stability. It is worth noting that 10 out of the 14 stable ternary compounds are located on the pseudobinary Hf-Ta-C joint, while the other four are not. Therefore, we shall discuss their structural features separately.

From the phase diagram (Fig. 6) we can see that the Hf-Ta-C pseudobinary phase boundary line is the richer area that contains more low-energy structures in the global Hf-Ta-C energy landscape. The 10 stable ternary phases along this line all adopt the B1 rocksalt structure in which the metal atoms occupy a face-centered cubic lattice and carbon atoms fill the octahedral interstices (see Fig. 7a). Different ratios of Hf to Ta and ordering schemes result in a number of distinct phases. One can easily analyze the arrangement of metal atoms on the (001) plane of the B1 structure. Given this perspective, as shown in Fig. 7b, HfTa₅C₆ is obtained by substituting one tantalum atom of TaC with one hafnium atom at intervals of 8 tantalum atoms in each horizontal atom array. HfTa₃C₅, HfTa₄C₆, and HfTa₅C₈ can be constructed following the same principle. In contrast, HfTa₃C₄ and HfTa₅C₈ follow another rule, in which the whole tantalum atom array is replaced by hafnium atoms. The former is arranged alternately by one row of hafnium atoms and three rows of tantalum atoms, while the latter is arranged alternating one row of hafnium atoms and one row of tantalum atoms. Interestingly, Hf₆TaC₆, Hf₅TaC₇, and Hf₄TaC₈ can be constructed by swapping the hafnium and tantalum atoms of HfTa₅C₆, HfTa₄C₇, and HfTa₃C₈, respectively. Among the 10 ternary phases, HfTa₅C₈ is different from others. It is formed by intergrowth of one layer of HfTa₅C₄ and one layer of HfTa₃C₆, as highlighted in Fig. 7i.

The four stable ternary compounds, Hf₆TaC₆, Hf₅TaC₇, Hf₄TaC₈, and Hf₃TaC₉, which do not belong to the pseudobinary Hf-Ta-C system, are vacancy-ordered derivatives of the rocksalt structure, as illustrated in Fig. 7m-r. Hf₃TaC₉ inherits the structure prototype of the stable binary carbide Ta₆C₃. By substituting the tantalum atoms at 4i-sites (Wyckoff position) in Ta₆C₃ with hafnium atoms one gets the structure of Hf₃TaC₉. In addition, an alternating arrangement of vacancies of one in every three layers of carbon atoms can be observed. Furthermore, by substituting half of hafnium atoms alternately with tantalum atoms, one can further get the HfTa₅C₆ structure. Similarly, Hf₅Ta₄C₇ can be obtained by replacing hafnium atoms at 3b-sites with tantalum atoms of the Hf₃TaC₈ phase. Interestingly, HfTa₅C₆ forms a sandwich quasi-2D structure that distinguishes itself from the other predicted structures. Besides, by removing all the carbon atoms in the vacancy layers of HfTa₅C₆ and slightly shifting the remaining atoms, one can get the structure of HfTa₄C₅. In total, all the ternary stable phases in the Hf-Ta-C system have one basic prototype, and structures with ordered distribution of metal atoms and vacancies have lower energies than disordered structures. In addition, the simplest stoichiometries of all the stable ternary compounds predicted here can be simplified into either Hf₉Ta₅C₋ₓ₋ₓ₋ₓ or Hf₉Ta₅C₋ₓ₋ₓ₋ₓ₋₋ₓ (x = integer). Based on our findings, the highest concentration of vacancies in Hf₉Ta₅C₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ is 1/3.

Performance of the co-evolutionary algorithm and its verification

In order to verify the effectiveness of our co-evolutionary algorithm, we have compared its performance with the conventional USPEX algorithm. In such comparative runs, the number of sampled structures should be kept at the same level. Considering the complexity of the ternary system, a long computational search is needed in every single run. For instance, about 20 thousand structures were searched in the W-Cr-B and Hf-Ta-C systems. The benchmark results are given in Table 1. In the W-Cr-B system, by sampling around 20k structures the two COPEX runs successfully predict all the five stable ternary compounds, while in contrast, no stable ternary compounds are found by conventional USPEX. We have continued one USPEX run until over 30k structures were sampled, and then one stable ternary compound, WCrB₂, was found. However, in the Mg–Si–O and Hf-Ta-C systems, the results (see Table 1) also show that COPEX algorithm works much better than conventional USPEX algorithm.

In addition, in order to evaluate the net effort of co-evolution, we have performed several comparison runs with/without co-evolution. The equivalent number of independent USPEX processes ran in parallel is the same as in COPEX, while the co-evolution module remains inactive, we may call such runs as M-USPEXs. In the W–Cr–B system, the results show two of the five stable ternary compounds, WC₅B and WC₃B, were found in the M-USPEXs run. We can see that M-USPEXs already surmount the performance of the conventional USPEX, and importantly, the net benefit for co-evolution can be evidenced by the prediction of the remaining three compounds, WC₃B, WC₅B, and WC₆B. Similar comparative calculations are performed in the Mg–Si–O and Hf–Ta–C systems, the results (Table 1) demonstrate the net benefit of the co-evolutionary algorithm.

One may wonder how the co-evolutionary algorithm enhances the structure sampling in the evolutionary searches. Here we have constructed a low-dimensional representation of the complex high-dimensional atomic environments of the W–Cr–B system as an example. Principal component analysis (PCA) of the local structure environment based on the smooth overlap of atomic positions (SOAP) descriptor was performed. In such a way, the structures, especially the local atomic environments, sampled by different algorithms can be described and compared in a low-dimensional manner, amenable to visualization. By analyzing all the structures sampled by COPEX and USPEX, we have built the PCA maps shown in Fig. 8. One can see that both COPEX and USPEX algorithms can generate structures diversely, which is the fundamental requirement for the success of a structure prediction algorithm. Furthermore, the stable ternary compounds are all located in the hot sampled region of the PCA map from the COPEX run, indicating the co-evolutionary algorithm spends more effort in the area(s) of the energy landscape where stable structures exist.
We have also compared the chemical composition sampling intensity maps obtained by COPEX and USPEX for the Hf–Ta–C system. The results show that COPEX has an enhanced sampling region as highlighted in Fig. 9, in which nine out of the ten predicted stable ternary compounds are located. USPEX shows similar but much lighter sampling intensity than COPEX. In other words, USPEX lays the foundation which ensures the sampling diversity and COPEX further enhances the sampling of the promising regions of the chemical space.

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**DISCUSSION**

Predicting the crystal structure of ternary and more complex compounds is very challenging, as the chemical and configurational space expands dramatically with increasing number of atomic types and the total number of atoms. Here, we propose an algorithm to address this challenge, developing the algorithm called COPEX, coupled with the powerful evolutionary algorithm USPEX and based on the idea of co-evolution. Within COPEX, multiple USPEX processes are carried out in parallel, where two of them target the whole configurational space while the rest are designed to focus only on the most promising area of the compositional space. Co-evolution is achieved by sharing structural information on the fittest individuals among the different USPEX processes during the evolution. Through sharing high-quality structures, COPEX can maximize the characteristic of the self-improving evolutionary algorithm and improve the success rate of structure prediction.

In order to demonstrate the performance of the COPEX algorithm, we have chosen three quite different systems, the intermetallic systems W–Cr–B and Hf–Ta–C, and the ionic-covalent system Mg–Si–O, to explore. The atomic radii of Cr and W are significantly different, while the atomic radii of Hf and Ta are almost the same. This explains the different behavior of these two systems. In the W–Cr–B system, besides W2CrB2 and W4CrB3, we have also found three stable ternary compounds, WCrB, WCrB2, and WCr2B, belonging to new structure types. In the Hf–Ta–C system, we have identified 14 stable ternary compounds, all of which are based on the B1 rocksalt structure type including four compounds with vacancy ordering. For the Mg–Si–O system, besides Mg2SiO4 and MgSiO3, no other ternary compound has been found at pressures up to 40 GPa. Importantly, we have found...
at low temperature a region of decomposition (27.29–28.72 GPa at zero Kelvin) where no stable ternary compounds exist.

In conclusion, we have applied COPEX to three representative systems W–Cr–B, Mg–Si–O, and Hf–Ta–C, and then evaluated its performance based on benchmark tests, and analyzed its sampling efficiency using a low-dimensional representation of the complex high-dimensional atomic environments and chemical composition space. The results demonstrate the reliability and efficiency of this methodology and illustrate that COPEX is a powerful tool for predicting new complex materials.

**METHODS**

**DFT calculations**

Density functional theory (DFT) calculations within the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) code, implemented in the VASP code, are used for structure relaxations and total energy calculations. The all-electron projector-augmented wave method is used, with a plane-wave kinetic energy cutoff of 600 eV and k-point mesh with the reciprocal-space resolution of 2π×0.02 Å−1. Phonon calculations were performed using Phonopy code using the force constants calculated by VASP.

**COPEX calculations**

The COPEX calculations were performed by following the procedure shown in Fig. 2 and the sub-processes were carried out using the evolutionary algorithm USPEX. In the two USPEX runs that cover the whole ternary chemical space, 100 structures are produced in each generation, while in other USPEX runs, 60–80 structures are produced. In each USPEX run, structures of the first generation were produced randomly. For variable-composition searches, the fractions of structures produced by random structure generator, heredity, softmutation, lattice mutation, and transmutation were 35, 35, 10, 10, and 10% in the second generation. For fixed-composition searches, the fraction of structures produced by random structure generator, heredity, softmutation, lattice mutation, and permutation were 35, 35, 10, 10, and 10% in the second generation. In subsequent generations, the weights of variation operators were adjusted dynamically. Stability of a compound is determined using the thermodynamic convex hull construction.

**Table 1. Benchmark tests using crystal structure prediction algorithms COPEX and USPEX applied to different systems at ambient pressure.**

| System | Algorithm | Npop | Ngen | Pran | Nsam | Ncom |
|--------|-----------|------|------|------|------|------|
| W–Cr–B| COPEX1    | 100  | 171  | 35 ± 6 | 19879 | 5    |
|        | COPEX2    | 100  | 173  | 35 ± 5 | 20133 | 5    |
|        | USPEX1    | 100  | 178  | 35 ± 7 | 20186 | 0    |
|        | USPEX2    | 100  | 180/275 | 35 ± 3 | 20150/30053 | 0/1 |
|        | M-USPEXs  | 100  | 179  | 35 ± 6 | 20168 | 2    |
| Mg–Si–O| COPEX    | 100  | 32   | 35 ± 4 | 3471  | 1    |
|        | USPEX1    | 100  | 34   | 35 ± 4 | 3452  | 0    |
|        | USPEX2    | 100  | 34   | 35 ± 2 | 3491  | 0    |
|        | M-USPEXs  | 100  | 34   | 35 ± 4 | 3571  | 0    |
| Hf–Ta–C| COPEX    | 120  | 163  | 35 ± 5 | 21400 | 10   |
|        | USPEX1    | 120  | 167  | 35 ± 5 | 21769 | 2    |
|        | USPEX2    | 120  | 171  | 35 ± 6 | 21635 | 1    |
|        | M-USPEXs  | 120  | 167  | 35 ± 5 | 21711 | 5    |

Npop, Ngen, Pran(%), Nsam, and Ncom refer to the population size per generation, generation size in every single search, percentage of structures generated randomly, total number of sampled structures, and the number of predicted ternary compounds in each system. All calculations were performed at ambient pressure. Structures with up to 40 atoms in the primitive cell are considered.

**Fig. 8 PCA maps of the W–Cr–B system.** Structures are taken from the COPEX (upper panel) and USPEX (lower panel), respectively. The map is colored according to the sampling intensity, divided into 29×26 bins, and the color bar refers to the number of sampled structures in each bin. The five stable ternary compounds are highlighted by red dots. The PC1 and PC2 refer to the first and second principal components, respectively.
In step 5, information on all the sampled structures is gathered and the composition-enthalphy phase diagram is constructed. Importantly, edge lines of the convex hull on the phase diagram are the potential searching paths. Searching priority of these pseudo-binary systems is ranked by the numbers of low-energy structures along the path inspired by the Bell–Evans–Polanyi principle闻) and paper[61, 62], which demonstrated that low-energy minima are clustered in compact regions of the configurational space. In addition, whenever a ternary compound appears on the current phase diagram, its composition will be added to the list of fixed-composition sub-processes. One can set how many USPEX sub-processes are to be run in parallel, but all the promising pseudo-binary and fixed-composition systems are recommended to be searched eventually. COPEX will launch new USPEX sub-processes based on the above criteria.

In our work, the top 10% structures based on the rank of fitness according to their enthalpy will be deemed as low-energy structures. For instance, COPEX can easily filter out that MgO–SiO$_2$, MgSiO$_3$, and Mg$_2$SiO$_4$ are the promising systems that shall be explored. The two ternary variable-composition USPEX sub-processes are kept alive during the whole COPEX search. The pseudo-binary or fixed-composition sub-processes are evaluated every 10 generations, and run on subsystems that only produce structures that are far above the updated convex hull, will be terminated. Naturally, COPEX can reactivate such sub-processes as the search continues. One can also launch or terminate sub-processes manually.

### DATA AVAILABILITY

The data supporting the findings of this study are available within the paper and Supplementary Information. Structures of all stable and some low-energy metastable structures are available via Github at: https://github.com/Dustglaxy/Co-evolutionary-crystal-structure-prediction-algorithm-for-complex-systems.

### CODE AVAILABILITY

The program of this study will be available in the upcoming version of USPEX.

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