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SHORT COMMUNICATION

Is alloying a promising path to substitute critical raw materials?

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A long-standing problem in metallurgy has been the alloying of metals and the search for new alloys that can improve performance and replace expensive metals. This decades-long quest for high-performance alloys has led to increasingly complex compositions. The number of possible alloy compositions to explore is literally astronomical. While this enormous range gives hope for the discovery of alternative materials, it also makes trial-and-error research highly speculative. This article will show that while alloying can offer alternatives, the supply risks increases with the number of elements involved and quickly outweigh the supply risks of the element being replaced. Therefore, the possibilities of alloying are not unlimited and a balance must be found between the overall supply risk and the number of elements used. In substitution scenarios, the supply risk increases almost linearly with the number of elements in the alloy. As a rule, effective combinations comprise no more than five elements, all of which are selected from the elements with the lowest supply risk. This significantly limits the range of possible candidates and makes the task of synthesis and characterization more manageable for materials scientists. By considering the multiple dimensions stepping in the supply risk, the list of suitable elements can be further refined and prioritized.
One sentence summary: **Alloying should balance performance and element count to ensure viable materials.**

Keywords: Alloying strategies;CRM (Critical Raw Materials) substitution efficiency;Multi-element system supply risk assessment;Material dependency reduction;Supply chain sustainability;Advanced alloy applications;Companionality

Introduction

The energy transition, i.e. the transition from fossil fuels to renewable energy sources, is expected to be very metal-intensive [1–8]. This is primarily due to the extensive use of metals in renewable energy technologies and infrastructure. For example, metals such as indium, platinum, cobalt and lithium are crucial for solar cells, green hydrogen, wind turbines and batteries for electric vehicles. In addition, rare earths such as neodymium are essential for the powerful magnets in wind turbines and electric motors. The increased use of metals is emphasized by studies such as the International Energy Agency (IEA), which states that demand for critical minerals such as lithium, cobalt and nickel will increase exponentially in line with the rise in global sales of electric vehicles and renewable energy equipment [9].

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This report emphasizes that the transition to a low-carbon future will be mineral-intensive, as these technologies rely heavily on various specialty metals. In this context, alloying emerges as a classic strategy as it offers great potential for combination to create materials with the desired properties, provided they present a lower supply risk – that is, the likelihood of disruption in obtaining its constituent materials. However, the fragmentation between academic research and industrial development can lead to research focusing on devices with a dubious future. For example, there are papers in the literature dealing with new battery technologies based on indium [10] or highly heat-resistant ruthenium-based superalloys [11]. Indium, a material that is crucial for its role as a transparent conductor in indium tin oxide (ITO) used in screens and solar panels, is characterized by its peculiarity of being a by-product: its production does not follow demand [12]. The planning of a new and massive use of indium for new applications would therefore probably jeopardize the display sector. The addition of ruthenium, a metal that is very scarce and essential to the electronics industry, in alloys for applications requiring exceptional heat resistance, harbors significant sustainability and economic risks, that can eventually lead to a supply break. The critical role of ruthenium in hard disc drives, chip resistors and electrochemical capacitors highlights the delicate balance between innovative performance and the prudent use of finite resources. Recent studies have highlighted the complexity and criticality associated with alloying elements in modern materials. Graedel et al. [13] emphasize that many critical materials are employed predominantly as alloying elements, a characteristic that often complicates end-of-life recycling and reduces functional reuse rates. Barnett et al. [14,15] introduce the concept of "compositional flexibility", which addresses this challenge by designing alloys that can achieve consistent performance across a range of compositions. Does alloying remain a promising approach to meet increasing material demand and how can we focus on developing alloys that can effectively mitigate supply risks?

Throughout human history, the development and use of metal alloys has played a decisive role in the progress of civilization. As societies developed, the variety of metals used and the complexity of the alloys produced increased, due to a sophisticated understanding of how to overcome certain technological challenges by combining different metals. The development of alloys began in the Bronze Age, around 3300 BCE, and marked a significant technological leap. Early civilizations discovered that adding tin to copper to make bronze produced a material that was harder and more durable than its components. This alloying process enabled the production of robust tools and weapons that were superior to those made of pure copper and met the need for more reliable and effective agricultural and military equipment. In the Iron Age, iron and steel began to replace bronze for many applications. However, cast iron was difficult to work and often brittle. The invention of steel, an iron-carbon alloy, was a significant improvement, providing much-needed strength, hardness and ductility that cast iron alone could not offer. Developed techniques such as carburizing, where carbon is added during the smelting process, made it possible to produce steel that could be hardened to provide sharp and durable cutting edges while retaining a flexible core. The 19th and 20th centuries witnessed an explosion in the development of alloys, driven by industrialization and the growing technological demands of the time. The invention of stainless steel, which incorporated chromium and nickel into steel, solved the problems of corrosion and made it an ideal material for a variety of applications, including those in harsh or demanding environments, such as medical devices and architectural structures. Lightweight yet strong alloys such as aluminum-magnesium and titanium alloys have also been developed to meet the need for materials that improve the performance of aircraft, spacecraft and military equipment without excessive weight.

To address the challenges of the green transition, this paper proposes a comprehensive methodology to assess the supply risks associated with multi-element alloys in order to compare them with the supply risks of the element being replaced. Our approach is to define risk indicators based on the probability of material shortages and to assess these supply risks for different alloy compositions using probability laws. By systematically analyzing these supply risk indicators, we aim to identify the most promising elements for creating effective and sustainable alloy substitutes, but also to understand the impact of the number of elements on the overall supply risk. This methodology simplifies the selection process and reduces the need for extensive experimental synthesis and characterization, facilitating the development of advanced materials to meet future technological requirements.

In this paper, "risk" refers primarily to the challenges associated with securing the raw materials required for alloy production at an industrial scale. Most of the time, this study will focus on the supply risk as defined by the European Union: "Supply Risk is calculated based on factors that measure the risk of a disruption in supply of a specific material (e.g. global supply and EU sourcing countries mixes, import reliance, supplier countries' governance performance measured by the World Governance Indicator, trade restrictions and agreements, availability and criticality of substitutes)" [16]. However, we may sometimes focus on a specific dimension of the supply risk, such as:

- Supply chain concentration risk, often quantified using the Herfindahl-Hirschman Index (HHI), which captures the diversity of supply sources,
- Social and environmental risks, reflecting the ethical and environmental considerations of resource extraction and processing,
- Economic and financial risks, such as price volatility and market accessibility.

Consistently, the "probability" without more specification refer to the "supply break probability", the likelihood of a disruption in the supply of a material. This approach simplifies the interpretation by focusing directly on the risk of a supply issue, rather than its complement (supply probability). We define "acceptable" or "moderate" probabilities of supply disruption using a quantitative framework inspired by established methods for evaluating market concentration in supply risk assessments. Specifically, we draw an analogy with the Herfindahl-Hirschman Index (HHI), a widely accepted measure of market concentration. The HHI adopts a threshold of 0.25 (on a range

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from 0 to 1) as an indicator of a highly concentrated market, associated with increased risks of instability and supply constraints. This threshold is recognized both by the European Parliament for assessing supply security of critical raw materials in the context of decarbonization strategies and by the U.S. Department of Justice for identifying highly concentrated markets. Applying this logic to probabilities, we consider a probability of not being supplied greater than 0.25 as high risk. Conversely, probabilities below this threshold are categorized as "moderate" or "acceptable" for the purpose of our analysis.

Basic considerations of alloying and its probabilities: Model and theory

What does mathematics tell us about the realization of at least one risk for an element of an alloy, and what does this mean for the risk indicators for this alloy? If we consider an alloy XY consisting of elements X and Y, it is reasonable to assume that an extensive parameter (e.g. the carbon footprint, the price, the weight, etc.) of XY results from the sum of its values for X and Y. But how do the risks behave? Can we simply average them? Risk relates to probabilities, and the laws of probability are well known. The probability of being supplied in both X and Y to synthesize XY, if X and Y are independent, is $1 - P(X,Y) = (1 - P(X))(1 - P(Y))$ where $P(*)$ is the supply break probability of $*$. This is fundamentally different from a sum and deserves some comments:

- The combination of probabilities is not linear, unlike extensive quantities,
- The probability remains in a limited range, and the approach to the boundary has a non-linear "price": While prices or quantitative footprints increase steadily without strict limits and only gradually worsen the overall balance, the supply probability $1 - P$ of being supplied decreases exponentially with the number of elements, leading to total unavailability of the product,
- The supply break probability of XY is always greater than the probability of X and the probability of Y, i.e. the average – and maximum – probability: $P(X,Y) \geq max(P(X), P(Y))$; in order to keep it low, both elements must themselves have low probabilities.

Formal derivations to handle probabilities are presented in the supplementary material, in particular in sections IV and V. In particular, the probabilities of systems combining p elements (called p-systems in this paper) are bounded in accordance with the average probability of the individual elements (see Fig. 1). Several conclusions can be drawn from this, in particular the fact that a p-system is low risk only if each element of which it is

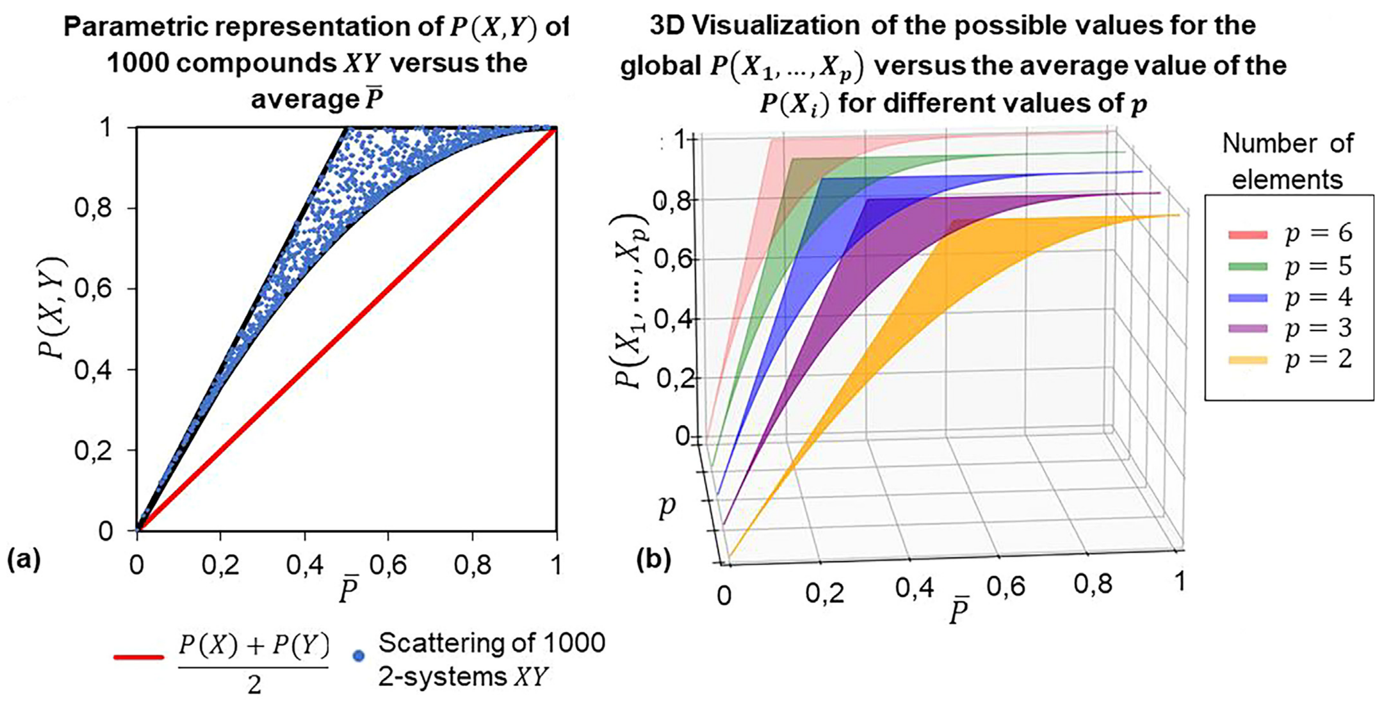

FIG. 1

The global risk rapidly rises with the number of alloying elements (p). On the left, two elements X and Y are alloyed, $p = 2$. The scattering of the global risk of a random couple of independent elements (in blue) is compared to the average risk of each element (in red). The global risk is located in an envelope (whose equation is given in section IV of the supplementary material) that stands clearly above the average value. The area for which the probability remains moderate ($P \leq 0.25$) is a narrow band below the bisector with a slope of 2. On the right, the effect of the number of elements p can be seen: the area corresponding to a moderate global probability is still a narrow band below the bisector with a slope of p. In other words, the global probability can be approximated by the sum of the probabilities for each element. As soon as the average probability exceeds $1/p$, the global probability exceeds acceptable values ($P > 0.25$).

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composed is itself low risk. Then the total probability of a p-system can be approximated by the sum of the probabilities of the individual elements – and not by the average value.

In reality, the supply risks of different elements are not independent. In the numerical method for evaluating supply risks presented in the supplementary materials, we proposed a way to account for the most evident correlations—those induced when multiple by-products of the same host element are utilized.

What is the connection between risks and probabilities? While it is undisputed that probabilities have a precise definition and offer the great advantage of allowing a formal and indisputable calculation, in practice they are unfortunately unattainable and can only be perceived through "risk indicators" defined from measurable parameters. Appropriate supply risk indicators (H) should at least be such that they are an increasing function of the probability (P) of risk realization (i.e. the supply break probability), and that the indicator is zero if the probability is zero: $P = f(H)$, where f is an increasing function with $f(0) = 0$. In this case, setting a fixed limit P_0 for the acceptable global probability is equivalent to setting a fixed limit H_0 for the global risk indicator: $P \leq P_0 \Longleftrightarrow H \leq H_0 := f^{-1}(P_0)$. Ideally, the risk indicators would be a linear function of the probability of risk realisation: $H = f^{-1}(P) = \lambda P$. The search for p-systems within this probability limit P_0 then implies that the sum of the risk indicators of the individual elements should remain below the limit of the global risk indicator: $\sum_i H_i \leq H_0$. Even if we do not have access to the probabilities, we know exactly which restrictions must be observed for the risk indicators so that the overall probability of the p-system remains below a certain threshold.

In particular, if we want to look for potential p-systems to replace an element in order to improve its risk characteristics, such as its supply risk, the sum of the risk indicator of the elements that enter into the composition of the p-system should be lower than that of the element to be replaced – and most of the combinations under consideration will only include elements with a risk indicator lower than that of the element to be replaced divided by the number of elements: $H_i \leq H_0/p$. It is of crucial importance that the linear factor λ, which links the probability with the risk indicator, plays no role due to the linearity of the sum and therefore does not need to be evaluated. Even if the linear relationship between the risk indicator and the probability is not far from reality, there is often no simple indication to justify it. Fortunately, as soon as we are interested in the range where the overall probability remains moderate, this linearity is a valid approximation. Indeed, p is probably equal to or greater than 3: it can be assumed that pure elements and alloys of 2 elements are well known, their number is not too large, and that no narrowing method is needed to determine whether a good substituent can be among them. Since the overall probability P_0 is moderate ($P_0 \leq 0.25$) and p is at least 3, the probability threshold for each candidate element P_0/p can be considered low – $P_0/p < 0.1$. We have assumed that the indicator is zero if the probability is zero: for values of P_0 smaller than P_0/p, this function can be approximated by a linear function $f^{-1}(P) \approx P/f'(0)$, which brings us back to the previous case with $\lambda = 1/f'(0)$ and solves the problem. All these considerations are formally derived in the supplementary material in Section V.2.

Results and discussion

At this point, an important conclusion can be drawn regarding the number of components of the alloys in question. Indeed, this behavior of the probabilities has very important consequences in the search for a substitute: while the large quantities increase linearly and without physical limit, the probabilities – and therefore the risks – have a non-linear "price" and can quickly lead to the product simply not being available. The goal of substituting an element such as platinum to mitigate risk involves setting a threshold for the risk indicator value of each element in potential p-substitution schemes to ensure that the global risk value remains below that of platinum. The division by p mentioned above implies that the larger p is, the fewer potential elements remain. At the same time, at least p available candidates are required for a p-system. As the number of possible systems increases with the value of p, the number of better systems than platinum will eventually decrease and reach 0 – and the ratio of potential candidates to replace platinum to the number of possible p-systems will decrease enormously, making it futile to hope to find one by chance, as illustrated in Fig. 2. For illustrative purposes, this analysis is performed based on the supply risk data from the Critical Materials Study [16], assuming that supply risk is indeed related to the supply break probability:

This leads to important conclusions: Although the number of systems increases with the number of elements, the candidate systems cannot combine too many elements. Most candidates combine a relatively small number of elements, typically between 3 and 5 (notably, the cases of Eu and Nb are exceptions due to their exceptionally high supply risks). The more elements are combined, the more important it becomes to focus the search on suitable substitutes, as the proportion of eligible candidates quickly decreases compared to the possible combinations. This is in line with the recycling considerations. Recycling processes are material-specific in order to preserve the properties of the starting materials — if different specific steels are melted together, they lose their enhanced properties and can only be used as low-grade steel— which indicates that very complex alloys are unlikely to have great potential for substitution.

This aligns with the conclusion of research teams focusing on tailoring microstructures to achieve desired material properties without relying on extensive alloying. By architecting imperfections such as grain boundaries and interfaces across different length scales, it is possible to enhance strength, corrosion resistance, and other critical properties through non-alloying strategies. Such approach, sometimes referred to as "plainification" [17], mitigates the disadvantages of alloying, such as supply risks associated with critical or scarce elements and reduced recycling efficiency due to chemical complexity. Intelligent structural design can further maximize performance while minimizing material use. For instance, optimizing the spatial arrangement of active sites in catalysis or enhancing surface-area efficiency allows significant gains in functionality without increasing material consumption [18]. By maintaining simpler chemistries and focusing on microstructure engineering, this strategy promotes sustainability and resource efficiency in advanced material design. As already highlighted [19], approaches such as low-carbon primary production, recycling, scrap-compatible alloy

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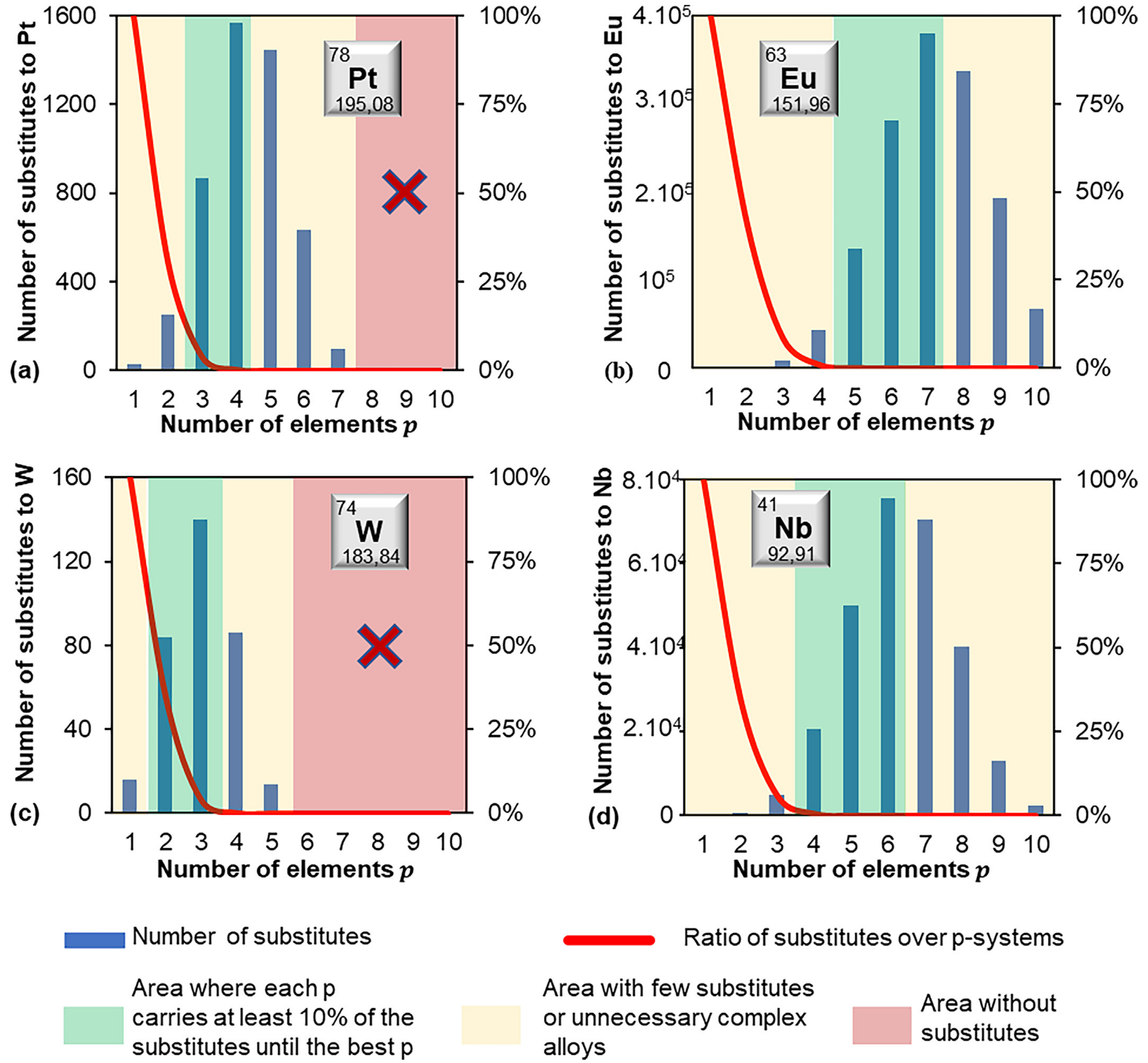

FIG. 2

Research of alloys substituents to improve the supply risk (according to the definition given by the European Union). a. Number of eligible p-systems with a better supply risk than platinum; $p = 3$ corresponds to the most numerous possibilities. **b.** Research of substituents for europium, used to make phosphors, and posing the highest supply risk. **c.** Research of substituents for tungsten, which has a lower supply risk than platinum: fewer alloys, containing fewer elements, are potential candidates to substitute it without worsening the supply risk. **d**. Research of substituents for niobium, an element with high supply risk. Most candidates are alloys with 6 elements.

design, contaminant-tolerant alloys, and extended alloy longevity provide essential pathways to reduce the environmental footprint of metals while maintaining their high performance. These strategies align with the principles of plain materials, where the demand to reduce the chemical complexity of alloys comes at the expense of an increase in microstructure complexity [20]. By reducing reliance on scarce alloying elements and improving material efficiency, these innovations simultaneously alleviate supply risks and enhance recycling potential. Microstructure engineering and advanced design not only enable superior properties but also reduce the quantities of critical materials required, offering a transformative opportunity to reconcile performance with environmental responsibility.

Using the same reasoning, for any given value of an accepted supply break probability, it is possible to deduce which elements could enter the composition of a p-system and calculate the corresponding number of candidate systems. For each value, it is therefore possible to calculate the maximum possible p-systems

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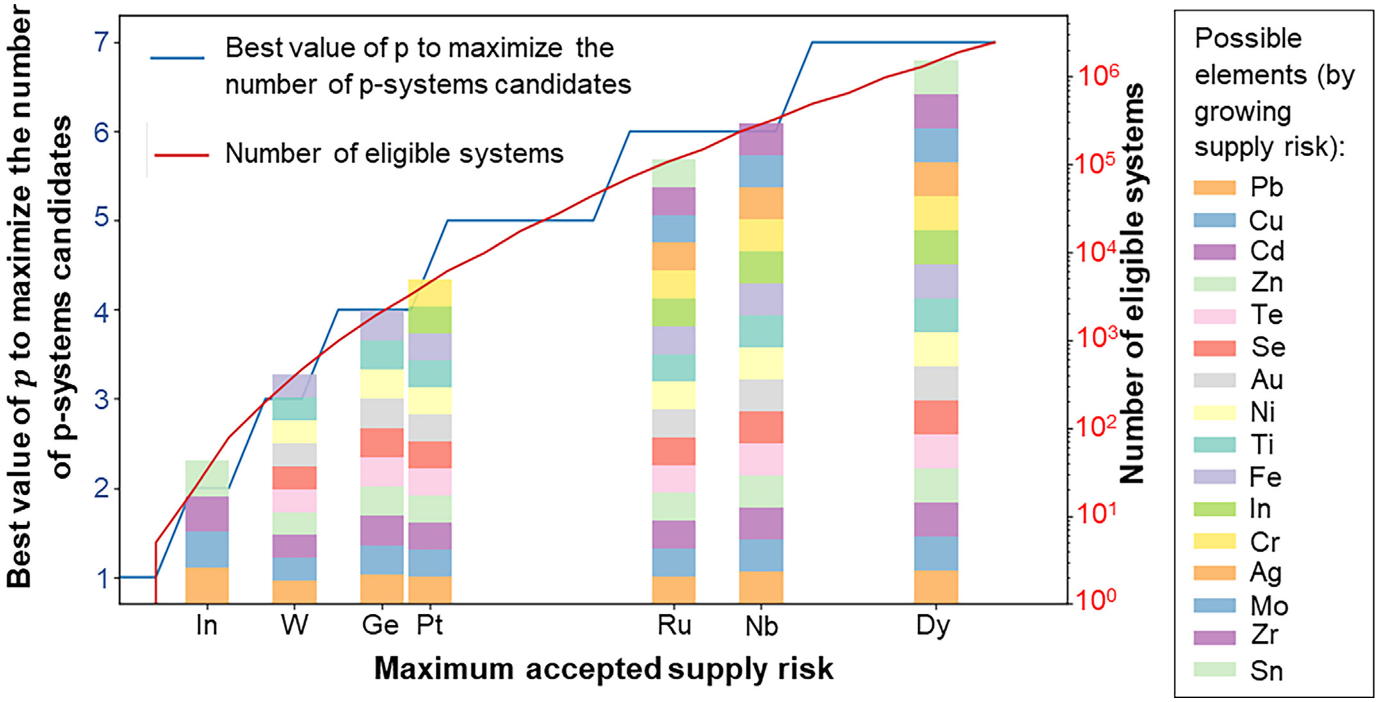

FIG. 3

Number of eligible p-systems for substitution. Representation of the best value of p to look for a p-system substitute (in blue) and the corresponding number of eligible systems (in red) to substitute an element with a given supply risk. Examples of In, W, Ge, Pt, Ru, Nb and Dy are displayed, and the corresponding bars are split with the main eligible elements (i.e. with a supply risk lower than the maximum accepted risk over p, so using one does not generate a constraint on using any other) to enter the composition for the most promising (in number of candidates) p-system. In the case of platinum, the candidate alloys are narrowed down from a virtual infinity to 4900 possibilities.

from combinatorial operators and to determine the value of *p* that maximizes the number of possible p-systems (Fig. 3). This work shows that for most elements there is no real reason to consider alloys of more than 5 elements if one focuses solely on reducing risk (knowing that the highest value of supply risk achieved for a single element is 0.56 for Dy). In fact, this optimal number might shift when considering other aspects of sustainability and device performance. Of course, the elements with the lowest supply risk (Pb, Cu, Cd, Zn, etc.) will always come first as potential compounds for an alloy.

From a supply risk point of view, the potential of alloys to replace critical elements is real, but much more limited than the possible combinations suggest, as the risks of the individual components quickly add up and reach the supply risk of the element to be replaced. In concrete terms, the most numerous candidates combine 3–5 elements, depending on the accepted supply risk. It is probably futile to look for systems with more than 5 elements, particularly when considering that design must ease recycling. In any case, the elements with the lowest supply risk are naturally the first to be considered as possible components of the alloys under consideration, as shown in Fig. 4. The total number of eligible alloys can range from hundreds to thousands and can certainly be narrowed down even further by considering other parameters: prices, production volumes and reserves, ESG (Environmental, Social, and Governance) criteria, other risks, etc. [21]. This preliminary work is crucial for materials scientists and helps them to focus the challenging task of characterization on serious candidates.

While the supply risk is a critical factor in the development of sustainable alloys, it is equally important to ensure that the selected materials meet the required performance criteria. As Bréchet and Ashby [22] emphasize, material selection should adopt a multi-criteria decision-making approach that balances performance attributes, such as mechanical strength, corrosion resistance, and thermal stability, with supply considerations. This framework allows for a systematic evaluation of trade-offs, ensuring that alloys not only mitigate supply risks but also deliver the functionality needed for their intended applications. By employing performance indices and material property charts as outlined in their work, it is possible to identify candidates that optimize both performance and sustainability.

Conclusions

This limitation of alloying possibilities, which can go so far as to exclude certain chemical elements from the outset, does not dash the hope of finding alloys that combine performance and risk control. The experimenter is left with numerous and varied possibilities, both in chemical formulation and design, to imagine high-performance substitutes that meet the great challenges of our time. As in the past, the combination of elements remains a powerful lever to achieve the desired properties, relying primarily on abundant materials. However, to make the search for these

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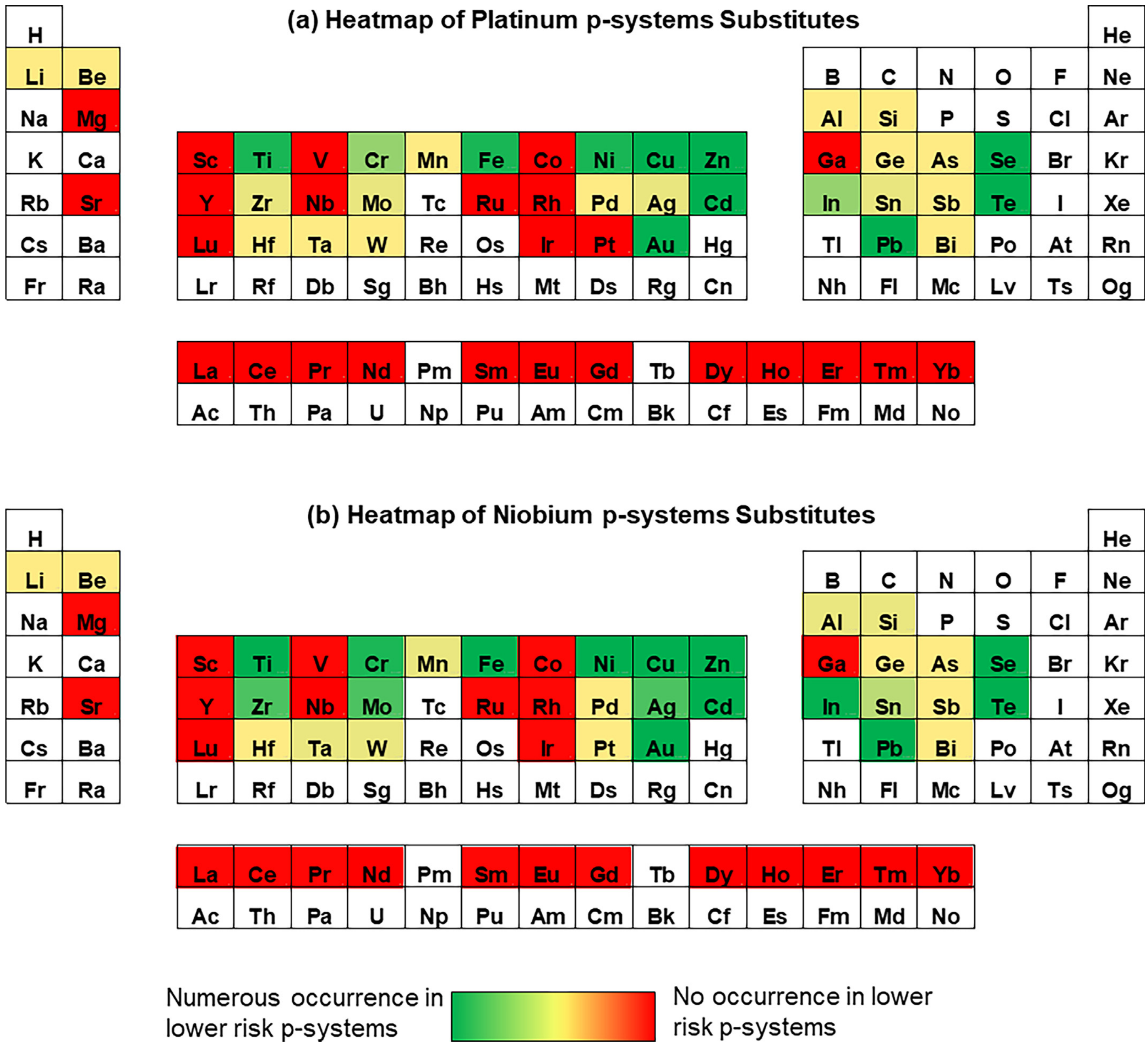

FIG. 4

Heatmap periodic table showing the occurrence of the use of elements in the potential substitutes. a. Heatmap for Platinum substitution (~1000 p-systems with a lower supply risk). **b.** Heatmap for Niobium substitution (~10,000 p-systems with a lower supply risk). Naturally, the occurrence of elements is strongly correlated with the value of their supply risk, and does not depend much of the element to substitute. Therefore, most candidates for substitution will be made of Pb, Cu, Cd, Zn, Te, Se, Fe, Ti, Ni, Au etc. If other risks than the supply risk defined by the European Union are considered, the results would likely be very different.

elements efficient and systematic, it is important to integrate the constraints that we want to respect a priori.

In this study, we defined a method for screening low-risk alloys as a surrogate for CRMs (Critical Raw Materials). While intuition suggests a combinatorial explosion of possibilities as the number of elements in the alloy composition increases, the constraints of risk limitation – underpinning the very notion of "critical" materials – and the laws of probability composition show that the actual possibilities are much more limited, comprising "only" thousands of possible alloys, most of which combine 3–5 different elements. These numbers vary, of course, depending on the CRM to be replaced. The more elements are combined, the more important it is to focus the search on the eligible substitutes from the outset, as the proportion of eligible candidates quickly decreases compared to the possible combinations. The number of candidates remains considerable considering the time required to perform the synthesis and characterization necessary to assess the substitution potential of an alloy. It therefore makes sense to further narrow down the list of alloys that can be considered as substitutes by combin-

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ing different risk indicators in terms of environmental footprint, prices, ethics, etc. *Since recycling must already be considered in the design phase, the candidates that contain a lower number of elements (less than 5) – and are the most common – should always be favored. This marks a pivotal transition in the history of metallurgy: from the era of alloying, which unlocked unprecedented material performance, to the era of design and microstructuring basic elements, where these performances are preserved through intelligent engineering, enabling a more sustainable and responsible use of materials.*

Author contributions

F.R. conceived, designed, wrote original article and led the overall project; **A.N.**, **J.Z.**, **U.C.** conceptualization, design, administration, editing of the article and analysis. All authors analyzed their data, and all authors contributed to the discussion, commented, reviewed, and approved the paper.

Data and materials availability

All data needed to evaluate the conclusions in the paper are present in the paper or the supplementary materials and are available on reasonable request.

CRediT authorship contribution statement

François Rousseau: Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Alexandre Nominé:** Writing – review & editing, Project administration, Funding acquisition, Formal analysis, Conceptualization. **Janez Zavašnik:** Writing – review & editing, Validation, Resources, Project administration, Conceptualization. **Uroš Cvelbar:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Conceptualization.

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Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary material to this article can be found online at https://doi.org/10.1016/j.mattod.2025.01.015.

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