Thermodynamic Approach to Evaluate the Criticality of Raw Materials and Its Application through a Material Flow Analysis in Europe

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Summary

This paper makes a review of current raw material criticality assessment methodologies and proposes a new approach based on the second law of thermodynamics. This is because conventional methods mostly focus on supply risk and economic importance leaving behind relevant factors, such as the physical quality of substances. The new approach is proposed as an additional dimension for the criticality assessment of raw materials through a variable denoted "thermodynamic rarity," which accounts for the exergy cost required to obtain a mineral commodity from bare rock, using prevailing technology. Accordingly, a given raw material will be thermodynamically rare if it is: (1) currently energy intensive to obtain and (2) scarce in nature. If a given commodity presents a high risk in two of the three dimensions (economic importance, supply risk, and thermodynamic rarity), it is proposed to be critical. As a result, a new critical material list is presented, adding to the 2014 criticality list of the European Commission (EC) Li, Ta, Te, V, and Mo. With this new list and using Sankey diagrams, a material flow analysis has been carried out for Europe (EU-28) for 2014, comparing the results when using tonnage and thermodynamic rarity as units of measure. Through the latter, one can put emphasis on the quality and not only on the quantity of minerals traded and domestically produced in the region, thereby providing a tool for improving resource management.

Introduction

Concern on the availability of raw materials has led to an increment in reports that assess the criticality of minerals. These classifications and lists vary between each country due to different approaches and targets, but also according to domestic availability and demand and to predictable changes in technology and policies. Multiple studies have compared the different approaches between the traditional methodologies used to assess the criticality of nonfuel minerals, focusing on the advantages and drawbacks of each one of them (Erdmann and Graedel 2011; Graedel and Reck 2016; Jin et al. 2016; Skirrow et al. 2013; Zepf et al. 2014; Glöser et al. 2015; Helbig et al. 2016). Still, they mostly provide a comparison between each methodology rather than proposing a different or a unified approach.

Criticality of a resource means that it is scarce and, at the same time, essential for today's society (Van Oers and Guinée

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2016). At world level, many countries have developed criticality assessment reports. The United States has a long tradition related with analyzing the materials that are critical, concerning security interests. The National Defense Stockpile (NDS Program) monitors 160 minerals, of which 92 meet at least one of the vulnerability metrics measured (US DOD 2015). Additionally, reports concerning the critical material strategy of the United States have been developed as well taking into account the internal demand (US DOE 2011). Other countries, such as Japan and Korea, that have been historically dependent on imports of various nonfuel and fossil fuels minerals from overseas have also developed strategies concerning raw materials (Bae 2000; Kawamoto 2008; JOGMEC 2010; Hatayama and Tahara 2015). Regarding territories that are major global mineral exporters, such as Australia, the criticality assessments rely more on their own resource potential to cover the global demand than on assessing external sources (Skirrow et al. 2013).

In the European Union (EU), the initial concern on raw material supply started decades ago (EC 1975), and this issue has been progressively becoming more and more relevant, establishing policies to reduce the use and dependency and elaborating several reports on this matter (EC 2010, 2014). In the 2010 report, 41 nonenergy and nonfood materials where analyzed, 14 identified as critical. In the 2014 report, the initial list was expanded, including new abiotic and biotic materials, and of the 54 materials analyzed, 20 were considered critical (antimony, beryllium, borates, chromium, cobalt, coking coal, fluorspar, gallium, germanium, indium, magnesite, magnesium, natural graphite, niobium, platinum group metals [PGMs], phosphate rock, rare earth elements [REEs; light and heavy], silicon metal, and tungsten). That list included 13 elements previously identified as critical. Tantalum was removed from the list, as the supply risk decreased, and borates, chromium, coking coal, magnesite, phosphate rock, and silicon metal were included, and REEs were divided into heavy and light. The methodology used to assess the criticality of the raw materials analyzed by the European Commission (EC) takes into account several factors. The first one being economic importance, calculated assessing the production of each material associated with mega sectors at EU level and combining it with the mega sector's gross value added to the EU's gross domestic product (GDP). The second factor is the supply risk, divided into two categories: the supply risk linked to unstable governance and the environmental country risk linked to low environmental standards. In both cases, the supply risk is a combination of substitutability, end-of-life (EoL) recycling rates, and high concentration of producing countries with either unstable governance or low environmental standards. In the case of supply risk, it only applies to primary production and could be reduced if more recycling is undertaken or if a raw material could be substituted.

Additionally, the British Geological Survey (BGS) publishes yearly an updated risk list to provide a simple indication on the relative risk of a certain number of commodities that are needed to maintain the economy and lifestyle (BGS 2015).

Meanwhile, other studies have focused not on specific countries, but on the critical raw materials that are necessary to develop emerging or green technologies or in the strategies of securing a stable supply of certain minerals (Angerer et al. 2009; APS Physics 2011; Resnick Institute 2011; Barteková and Kemp 2016). For instance, the Joint Research Center along with the Institute for Energy and Transport analyzed the possible bottlenecks of metals in strategic energy technologies (Moss et al. 2011, 2013). Besides, several articles have analyzed the criticality of selected elements. Harper and colleagues (2015) analyzed zinc, tin, and lead family minerals. Nassar and colleagues (2015) analyzed REEs and Panousi and colleagues (2016) focused on seven specialty metals: scandium, strontium, antimony, barium, mercury, thallium, and bismuth. In all the cases, the factors analyzed were supply risk, environmental applications, and vulnerability to supply.

When observing the critical raw materials selected in each report, it can be seen that not all of them label as critical the same substances and that the criticality concept is usually based on a two-dimension approach. There does not seem to be any global criteria that can help to evaluate the criticality of mineral commodities nor an approach that provides an assessment independent of market and political arbitrariness and that is rooted in the geological and physicochemical characteristics of minerals. Therefore, we propose to include the thermodynamic dimension to fill that void.

In this sense, a first approach to evaluate the material flow analysis (MFA) in Spain and in Europe was previously carried out taking into account fossil fuels and main mineral commodities (Calvo et al. 2015, 2016a). At European level, the weight of the minerals labeled as critical by the EC in 2014, without considering borates and coking coal, was 3.6% when compared with the total domestic extraction of minerals and metals in the EU-28. In 2014, 128 million tonnes (Mt) of minerals and metals were domestically produced, of which 4.6 million corresponded to those minerals labeled as critical. Additionally, of that amount, 61% corresponded to magnesite alone. Therefore, around 1.4% of the total EU domestic production corresponded to the remaining critical minerals. Yet, such a seemingly small amount might become crucial for future economic development.

This is why this article provides a new approach that complements the existing information with a thermodynamic perspective using exergy and thus going beyond tonnage. The main goal is to verify if the so-called critical raw materials are not only critical from an economic importance or supply risk perspective, but also from a thermodynamic one. As described in the following section, a mineral is defined to be thermodynamically critical if it surpasses a certain exergy threshold expressed in gigajoules per tonne (GJ/t). The analysis is then applied to perform an EU-28 MFA for 2014 so as to identify the trade deficits in critical minerals.

Thermodynamic Rarity

The whole extraction rate of mineral resources needs to be quantitatively and qualitatively studied. Common units of measure are mass and monetary prices, and tonnage can be directly obtained from statistical services and mining companies. However such an accounting adds commodities extracted massively with others having an insignificant contribution (i.e., aluminum and gallium). Hence "minor" substances become eclipsed, thus neglecting their importance. Clearly, when using mass as a yardstick, there is the risk of adding apples with oranges, since not all minerals should be equally assessed. One could use market prices as an alternative indicator of quality and thus overcome, in theory, the problem of adding apples with oranges. Yet, the problem with this is that commodity prices are volatile and rarely reflect the physical reality of minerals. For instance, the relationship between market price and the cost of finding, mining, and refining the metal was investigated by Phillips and Edwards (1976). Using copper as a case study, they observed that, assuming that technology was static, a 7.7% decline in grade was equivalent to an 8.3% rise in the price of copper.

Valero (1998) proposed instead a thermodynamic approach. The exergoecology method uses exergy as a yardstick as it does not depend on market and reflects both the quantity and quality of extracted minerals. Exergy measures the degree of thermodynamic distinction a material piece has from its surrounding commonness. Therefore, it allows to physically measure the "rarity" of a piece of matter since the rarer it is, the more it stands out (Valero and Valero 2014).

Thermodynamic rarity is defined as the amount of exergy needed to obtain a given commodity from an ordinary rock with prevailing technologies (Valero and Valero 2015, 2014). In fact, exergy accurately measures, in energy terms, the distinction of a piece of matter with respect to a given reference environment, sometimes also known as the "dead state." When dealing with mineral resources, this dead state is called Thanatia. It represents a resource-exhausted Earth composed of the nearly 300 most common minerals. This ideal model becomes practical when one knows that all minerals and fossil fuel deposits that ever existed constitute less than 0.01% to 0.001% of the Earth crust. Considering these numbers, abiotic resources are deeply scarce in the planet. Thereby, the Thanatia hypothesis implicitly considers that all mineral deposits have been ultimately extracted and all chemical elements oxidized and dispersed throughout the crust. In such a way, Thanatia may be used as a starting point to assess the mineral capital depletion of the planet. Each and every irreversible dispersion of any mineral represents a tiny step toward Thanatia (Valero et al. 2011a, 2011b).

Thermodynamic rarity incorporates two types of costs. First, a physical one, accounting for the exergy resources needed to convert a mineral into a commodity—that is, beneficiation, smelting, and refining processes. In other words, it is the embodied exergy (or exergy cost, kilowatt-hours [kWh]) of the mineral from mine to market. Second, a hidden cost, understood as the free natural bonus provided by nature for having minerals concentrated in mines instead of dispersed throughout the crust (from Thanatia to the mine).

As for this free natural bonus, it is represented by the exergy replacement cost (ERC), defined as the exergy that would be needed to extract a mineral from ordinary rocks (Thanatia state) to the conditions of concentration and composition found in the mine, using prevailing technology. To obtain ERC values for each mineral, the first step is to calculate the minimum concentration exergy required to reconcentrate a complete dispersed mineral in Thanatia back to the initial mine conditions. To do this, one needs to know the average ore grade in the mine (x_m) as well as the concentration in Thanatia's crust (x_c). Since exergy only accounts for reversible processes and the process of separating a substance from a mixture is highly irreversible, an additional factor has to be taken into account, and instead of exergy, we talk about exergy costs. In other words, from a theoretical point of view, the exergy costs of concentrating a mineral would require k times the minimum concentration exergy. This k factor is calculated as the ratio between the real energy required to concentrate and refine a given element from the mine conditions to the precommercial grade and the minimum thermodynamic exergy required to accomplish that same process.

A very relevant factor in ERC is the average concentration in Thanatia's upper continental crust (x_c), in the mine (x_m) and the energy needed to extract and process each element. The concentration or ore grade of a mineral in the mine can be determinant for the energy consumption in the mining, smelting, and refining processes. Indeed, according to thermodynamic laws, when the ore grade decreases in the mine, the energy required to extract the ore increases exponentially. This behavior has been empirically demonstrated for several commodities (Calvo et al. 2016b; Mudd 2010b, 2014). In this sense, recycling allows reducing primary consumption and consequently energy costs. Yet, the exponential increase in material demand makes that even a hypothetical 100% recycling rate (unachievable from a thermodynamic point of view) would not stop primary production. Consequently, under the current scenario, civilization will need to face increasing energy costs associated to mineral production.

Note that both costs, physical and ERC costs, are defined as embodied exergies rather than embodied energies. This is because minerals commonly appear with valuable companion metals/substances whose energy consumptions need precise allocations. Regrettably, in the absence of accurate analyses, the embodied energies may be used as "surrogate numbers" of their exergy costs. This is even worse news when they are at the beginning of the value chain of commodities, as it distorts all subsequent calculations. This is why exergy analysis is indeed considered as a rigorous way to allocate costs in life cycle assessment when energy flows come into play (i.e., in a cogeneration plant where heat and electricity are produced simultaneously). When material flows come into play, as is the case in mining and metallurgical processes, allocation is either based on tonnage or on commercial prices when there is more than one by-product extracted. Using tonnage is not always suitable as there can be products appearing with very low concentrations that can even have a higher market value than the major product. With commercial prices, since they are usually very volatile, the result is that allocation strongly fluctuates according to macroeconomic variables. In this respect, Valero and colleagues (2015) demonstrated that if ERC is applied, cost allocation values are similar to those obtained via market prices, hence supporting the idea that the ERC is very close to the value society places on minerals. That said, contrarily to prices, ERC does not fluctuate with external factors linked to market mechanisms, but remains constant.

Thermodynamic rarity varies from mineral to mineral, as is a function of a mineral's absolute scarcity in nature and the state of technology. Presently known thermodynamic rarity values are listed in table 1. A mineral is here denoted as "scarce" when its ERC is high. This happens when the ore grade in Thanatia (x_c) is low, when the difference between the ore grade in the mine (x_m) and in Thanatia is high, and when the energy required to beneficiate the given mineral is important. In the case of the physical costs shown in table 1, global average figures of mining, beneficiation, smelting, and refining values in GJ/t for each commodity are assumed, obtained from different sources from the literature such as from Mudd (2010a), Norgate and Jahanshahi (2010), and Classen and colleagues (2007). In table 1, also information on ore grade in Thanatia's crust (x_c) and in the mines (x_m) can be found. The starting point for obtaining crustal concentrations (x_c) is the composition given by the geochemist Grigor'ev (2007), which is constrained by the conservation of mass statement between the chemical composition of the crust in terms of elements (as proposed by Rudnick and Gao [2004]) and in terms of minerals. As a result, crustal concentrations of the 294 most abundant minerals were obtained (Valero et al. 2011b). The average concentration in world mines (x_m) was mainly obtained from information published by Cox and Singer (1992).

It should be noted that thermodynamic rarity values are not static. They depend on the state of technology, as we assume that the same technology is applied for the current extraction of minerals (to the presmelting grade) than between the dispersed state to the mine. Therefore, while there are no significant technology improvements, thermodynamic rarities will stay within the same range of values. For instance, if there are technological improvements in the mining processing, thermodynamic rarity values will decrease due to the reduction of both hidden cost (ERC) and physical cost (mining and beneficiation). Such a procedure is detailed in Valero and Valero (2015) and Valero and colleagues (2013). Additionally, it also depends on the ore grade, and if the ore grade decreases, the energy needed to replace that mineral will increase exponentially. That said, it is important to state that even if rarity values might change with technological improvements and/or global ore grade decline, figures are more stable than those related with economic importance or supply risk, which fluctuate more strongly with market volatility or political instability. An exercise done with gold showed that incorporating more updated information implied a thermodynamic rarity change of about 5% with respect to early assessments.

Thus, even if they can slightly change, thermodynamic rarity can be used as a reference to provide simple and straightforward information to identify which minerals are more critical from a thermodynamic perspective.

In the case of antimony, for instance, a mineral that has a medium value of thermodynamic rarity, there is a big difference between the concentration in the mines and in the crust, which is reflected by a high value of ERC (474 GJ/t) and lower values of mining, concentration, smelting, and refining energy when compared to other minerals (1.4 and 12.0 GJ/t, respectively). In the case of tellurium, a mineral with a high thermodynamic rarity value, both the average ore grade in the crust and in the mine are very low when compared to other minerals, and the energy needed to extract and concentrate this element is indeed very high (589,366 GJ/t). Combining these two factors, the final value of thermodynamic rarity is thus both dependent not only on the ore grade, but also on the technology and processes used to extract the element.

Accordingly, thermodynamic criticality as defined in this paper is associated to the thermodynamic rarity of minerals, thus considering geological scarcity through ERC values and energy costs required to mine and obtain refined metals with prevailing technologies. This approach provides information on how severe is the loss, or better say, dispersion, of each respective material at the EoL if materials do not become recycled.

New List of Critical Raw Materials

Availability of energy is an indispensable condition in mineral supply, although it is hardly considered in existing criticality assessments. Economic importance and supply risk are more focused on the consumption side, and they were designed to be dimensionless through specific ranking criteria considering different aspects (substitutability, EoL recycling rates, poor governance, environmental standards, etc.). The thermodynamic approach proposed is purely supply side and is expressed in GJ/t. A mineral can be considered very rare and thus "thermodynamically critical," whereas when using only the consumption side other factors come into play, such as declining in consumption due to better substitutes or disuse, phase out of technology, etc. For instance, the use of mercury has declined due to health and environmental issues, but its thermodynamic rarity value is very high. The contrary situation can be observed for phosphate rock or chromium, having low thermodynamic rarity values, but very high economic importance. Therefore, the combination of both aspects, consumption and supply, can provide a more complete list of critical raw materials as it results in a more comprehensive analysis of the risk situation of each commodity.

Taking into account this information, a comparison between the different approaches used in the criticality assessment reports and this thermodynamic approach can be carried out, identifying the risks as low, medium, and high (Table 2).

When there was no categorization available, such as in the case of the EC reports, the risk has been considered high. In the case of BGS (2015), as they generate a risk list of all the commodities ranked from 1 to 10, only minerals with a risk

Table 1 Values of exergy replacement cost (ERC), thermodynamic rarity, and energy needed for the mining, concentration, smelting, and refining stages for selected commodities, expressed as GJ per tonne of element

Mineral	x_c [g/g]	x_m [g/g]	*ERC [GJ/t]*	*Mining and conc. [GJ/t]*	*Smelting and refining [GJ/t]*	*Thermodynamic rarity [GJ/t]*
Aluminium (Gibbsite)	1.38E-03	7.03E-01	627	30.5	23.9	681.7
Antimony (Stibnite)	2.75E-07	5.27E-02	474	1.4	12.0	487.4
Arsenic (Arsenopyrite)	4.71E-06	2.17E-02	400	9.0	19.0	427.0
Barite[a]	7.09E-04	9.50E-01	38	0.9	—	38.9
Beryllium (Beryl)	3.22E-05	7.80E-02	253	7.2	450.0	710.2
Bismuth (Bismuthinite)	5.10E-08	2.46E-03	489	3.6	52.8	545.4
Cadmium (Greenockite)	1.16E-07	1.28E-04	5,898	263.9	278.5	6,440.4
Chromium (Chromite)	1.98E-04	6.37E-01	4.5	0.1	36.3	40.9
Cobalt (Linnaeite)	5.15E-09	1.90E-03	10,872	9.2	129.0	11,010.2
Copper (Chalcopyrite)[a]	6.64E-05	1.67E-02	292	35.3	21.4	348.7
Fluorite	1.12E-05	2.50E-01	183	1.5	—	184.5
Gallium (in Bauxite)[a]	1.76E-05	5.00E-05	144,828	610,000.0	—	754,828.0
Germanium (in Zinc)[a]	1.41E-06	3.00E-03	23,750	498.0	—	24,248.0
Gold[1]	1.28E-09	2.24E-06	553,250	110,057.0	—	663,307.6
Graphite[1]	2.41E-04	1.50E-01	20.39	1.1	—	21.5
Gypsum	1.26E-04	8.00E-01	15	0.2	—	15.2
Indium (in Zinc)[a]	5.61E-08	4.50E-04	360,598	3,319.7	—	363,917.7
Iron ore (Hematite)	9.66E-04	7.30E-01	18	0.7	13.4	32.1
Lead (Galena)	6.67E-06	2.37E-02	37	0.9	3.3	41.2
Lime	8.00E-03	6.00E-01	2.6	0.4	5.8	8.8
Lithium (Spodumene)	3.83E-04	8.04E-01	546	12.5	420.0	978.5
Magnesite[a]	2.50E-02	4.20E-01	26	9.5	—	35.5
Manganese (Pyrolusite)	4.90E-05	5.00E-01	16	0.2	57.4	73.6
Mercury (Cinnabar)	5.73E-08	4.41E-03	28,298	157.0	252.0	28,707.0
Molybdenum (Molybdenite)	1.83E-06	5.01E-04	908	136.0	12.0	1,056.0
Nickel (sulphides) Pentlandite	5.75E-05	3.36E-02	761	15.5	100.0	876.5
Nickel (laterites) Garnierite	4.10E-06	4.42E-02	168	1.7	412.0	581.7
Niobium (ferrocolumbite)	8.10E-06	2.00E-02	4,422	132.0	—	4,554.0
Palladium	3.95E-10	8.02E-07	8,983,377	583,333.3	—	9,566,710.3
Phosphate rock (Apatite)	4.03E-04	5.97E-03	0.4	0.3	4.6	5.3
Platinum	3.95E-10	8.02E-07	4,491,69	291,666.7	—	4,783,356.7
Potassium (Sylvite)	2.05E-06	3.99E-01	665	1.7	—	666.7
REE (Bastnaesite)	2.54E-07	6.00E-02	348	10.2	3.7	361.9

(*Continued*)

Table 1 Continued

Mineral	x_c *[g/g]*	x_m *[g/g]*	*ERC [GJ/t]*	*Mining and conc. [GJ/t]*	*Smelting and refining [GJ/t]*	*Thermodynamic rarity [GJ/t]*
Rhenium	1.98E-10	2.33E-04	102,931	156.0	—	103,087.0
Silver (Argentite)	1.24E-08	4.27E-06	7,371	1,281.4	284.8	8,937.6
Sodium (Halite)	5.89E-04	2.00E-01	44.07	3.3	39.6	86.9
Tantalum (Tantalite)	1.58E-07	7.44E-03	482,828	3,082.8	8.1	485,918.9
Tellurium (Tetradymite)	5.00E-09	1.00E-06	2,235,699	589,366.1	39.2	2,825,104.3
Tin (Cassiterite)	2.61E-06	6.09E-03	426	15.2	11.4	452.6
Titanium (Ilmenite)	4.71E-03	2.42E-02	4.5	7.2	128.1	139.8
Titanium (Rutile)	2.73E-04	2.10E-03	8.8	13.8	243.8	266.4
Tungsten (Scheelite)	2.67E-06	8.94E-03	7,430	213.0	381.0	8,024.0
Uranium (Uraninite)	1.51E-06	3.18E-03	901	188.8	—	1,089.8
Vanadium	9.70E-05	2.00E-02	1,055	136.0	381.0	1,572.0
Yttrium-Monazite	1.30E-04	3.00E-04	159	1,198.3	—	1,357.3
Zinc (Sphalerite)[a]	9.96E-05	6.05E-02	155	1.5	40.4	196.9
Zirconium (Zircon)	3.88E-04	4.02E-03	654.43	738.5	633.0	2,025.5

Note: Values of x_c and x_m are referred to the mineral where the given element is mainly obtained (shown in parenthesis in the first column).
[a]Updated from Valero and Valero (2014).
GJ = gigajoules; g/g = grams per gram; GJ/t = gigajoules per tonne; conc. = concentration.

index of 6 or higher have been included. Additionally, we have considered the following limits to create three risk categories of high, medium, or low values of thermodynamic rarity, all measured in GJ/t. High risk corresponds to values greater than 1,000 ± 5%[1] GJ/t (such as cobalt, gallium, or gold), medium is between 100 and 1,000 GJ/t (such as aluminum, bismuth, or nickel), and low are less than 100 GJ/t, such as barium, iron, or graphite. This categorization has been created so the data are uniformly distributed (with an average of 18 elements per category), trying at the same time to use round numbers.

Table 2 represents a summary of the different reports analyzed and incorporates information on the thermodynamic rarity of each commodity as well.

As this article focuses on the mineral scarcity and trade in the EU-28, the list of critical raw materials selected by the EC (2014) is used as a reference for this comparative analysis. The goal is to not only compare this two-axis methodology with the thermodynamic rarity approach, but also to combine them to create a three-axis approach. Note that a similar exercise could be done with any of the methodologies presented in table 2.

Consequently, we propose to label a certain commodity as "critical" if it is considered so in two of the three axes. The EC sets the criticality border for supply risk at 1 and at 5 for economic importance. The criticality border for rarity values is set at 1,000 ± 5% GJ/t (i.e., high rarity).

Starting with the values provided for the supply risk for different mineral commodities, we can see in figure 1 thermodynamic rarities of commodities as a function of the supply risk (due to data variations, the vertical axis is in logarithmic scale). The commodities represented in gray are those considered critical by the EC in the 2014 report.

When comparing these two variables, it is obvious that there are some commodities which have high values of thermodynamic rarity, meaning that they are more scarce and difficult to extract, such as gold, tantalum, or tellurium. Even so, they are not considered critical from a supply risk point of view by the EC. Tantalum was indeed included in the EC report of 2010, but was excluded in 2014 as it was stated that the supply risk had decreased. Even if the extraction data coming from conflict regions are not always accurate, Congo production in 2000 was 9% of the total share and 17% in 2014. In the case of Rwanda, it was the leading tantalum producer in 2015, with a share of 50% of the total world production, and has displaced Australia and Congo as the main producers.

Additionally, there are other minerals that have high thermodynamic rarity values, but are not included in the critical raw material list of the EC; such is the case of silver, vanadium, molybdenum, or lithium. On the contrary, other commodities with lower values of thermodynamic rarity are indeed considered critical, such as magnesite, graphite, or chromium. For instance, in the case of graphite, it has a high economic

Table 2 Comparison of critical material lists from different studies

Element	*EC (2014)*	*Bae (2000)*	*Angerer and colleagues (2009)*	*JOGMEC (2010)*	*EC (2010)*	*Achzet and colleagues (2011)*	*APS Physics (2011)*	*Resnick Institute (2011)*	*US DOE (2011) (medium term)*	*Moss and colleagues (2011, 2013)*	*UKERC (2014)*	*BGS (2015)*	*Thermodynamic rarity (Valero and Valero 2014)*
Aluminium		○										○	◐
Antimony	●	◐	●	○	●							●	◐
Arsenic												●	◐
Barium												●	○
Beryllium	●				●							◐	◐
Bismuth												●	◐
Borates	●												—
Cadmium						●		●		○		◐	●
Chromium	●	◐		●		●						○	○
Cobalt	●	◐	●	●	●	●	●	●	○		●	●	●
Coking coal	●												—
Copper		○	●			○						○	◐
Fluorspar	●				●							◐	◐
Gallium	●	●	●	●	●	●	●	●	○	●	●	●	●
Germanium	●		●		●	●	●	●		◐	●	●	●
Gold												○	●
Graphite	●				●					◐		◐	○
Hafnium										◐			—
Indium	●	●	●	●	●	◐	●	●	○	●	●	●	●
Iron												○	○
Lead		○										○	○

(*Continued*)

Table 2 Continued

Element	*EC (2014)*	*Bae (2000)*	*Angerer and colleagues (2009)*	*JOGMEC (2010)*	*EC (2010)*	*Achzet and colleagues (2011)*	*APS Physics (2011)*	*Resnick Institute (2011)*	*US DOE (2011) (medium term)*	*Moss and colleagues (2011, 2013)*	*UKERC (2014)*	*BGS (2015)*	*Thermodynamic rarity (Valero and Valero 2014)*
Lithium		●		○		◐	●	●	◐		●	●	●
Magnesite/ Magnesium	●	●			●							●	○
Manganese		◐		●					○			○	○
Mercury												◐	●
Molybdenum		◐		●		◐				○		●	●
Nickel		●		●					○	○		○	◐
Niobium	●	◐	●	◐	●			●		◐		◐	●
PGM	●	●	●	◐	●	●	●	●		◐	●	●	●
Phosphate rock	●					○							○
REE	●	●	●	◐	●	●	●	●	●	●	●	●	◐
Selenium		◐	●				●	●		◐	●	◐	—
Silicon (metal)	●	●											○
Silver			●			○	●	●		○	●	◐	●
Strontium				◐								●	—
Tantalum			●	◐	●							◐	●
Tellurium						●	●	●	◐	●	●		●
Thallium		◐											—
Thorium												○	—
Tin			●							◐		○	◐
Titanium		●	●	○								○	◐
Tungsten	●	●		●	●	◐						●	●

(*Continued*)

Table 2 Continued

Element	EC (2014)	*Bae* (2000)	*Angerer and colleagues* (2009)	JOGMEC (2010)	EC (2010)	*Achzet and colleagues* (2011)	*APS Physics* (2011)	*Resnick Institute* (2011)	*US DOE* (2011) *(medium term)*	*Moss and colleagues* (2011, 2013)	UKERC (2014)	*BGS* (2015)	*Thermodynamic rarity (Valero and Valero 2014)*
Uranium						●						○	●
Vanadium		◒		●		◒				◒		●	●
Zinc		○										○	◒
Zirconium		●										○	●

Note: ● = high risk, ◒ = medium risk, ○ = low risk. When there is no categorization available, the risk has been considered high. In the case of the BGS (2015) risk list, values from 4.8 to 6.5 have been considered low risk, 6.6 to 7.5 medium risk, and higher than 7.6 high risk. As for thermodynamic rarity values, it represents high, medium, or low values (in GJ/t). PGM = platinum group metals; REE = rare earth elements; GJ/t = gigajoules per tonne.

importance, as it is used in many different sectors (34% for electrodes, 20% refractories, etc.), and in the supply-risk side, it usually has a very low substitutability index.

These results can be combined with those presented in figure 2, showing thermodynamic rarity values as a function of the economic importance. Again, the values in gray represent those commodities selected as critical by the EC in the 2014 report and similar results can be inferred. Substances, such as gold, lithium, molybdenum, silver, tantalum, tellurium, and vanadium, that are critical when considering thermodynamic rarity values are not considered critical when assessing only economic importance.

Therefore, taking into account that the given commodity belongs to at least two of the three categories (economic importance, supply risk, and rarity), we propose to include in the criticality list of the EC created in 2014 the following commodities: lithium, molybdenum, tantalum, tellurium, and vanadium, as they are not critical from a supply risk point of view, but are indeed critical from a thermodynamic rarity and economic perspective point of view. Note that gold and silver are not included in the list, as they are only critical from a thermodynamic rarity point of view. That said, should the economic importance or the supply risk of such commodities increase, then gold or silver would also enter into the criticality list as proposed in this procedure.

Material Flow Analysis

After carrying out the identification of the critical raw materials with the different approaches specified in the previous sections and the description of their main physical and socioeconomic features, the next objective has been compiling accurate data on availability and material flows for the selected critical raw materials for Europe (EU-28). The main aim is to compare the material flows results using a mass-based and a thermodynamic-based approach. For this endeavor, multiple databases, both national and international, have been consulted, such as the mineral statistics from the BGS and the United States Geological Survey, as well as other reports made by the EC and national statistics services from European countries. For the imports and exports, EUROSTAT databases have been used to compile information on material trade between EU-28 and the rest of the world, not considering then the internal flows between EU-28 countries.

Using Sankey diagrams, an MFA of the critical material flows in EU-28 has been accomplished for 2014 for the mineral commodities selected as critical with a three-dimension approach, combining supply risk, economic importance, and thermodynamic rarity. In this type of diagrams, the inputs of the system are represented by imports and production, and the outputs are the exports, recycling, and materials consumed within the EU-28. Import and export data were obtained from EUROSTAT databases, not considering the internal trade between the different countries of the EU-28. Accordingly, Europe has been considered as a black box where materials are produced

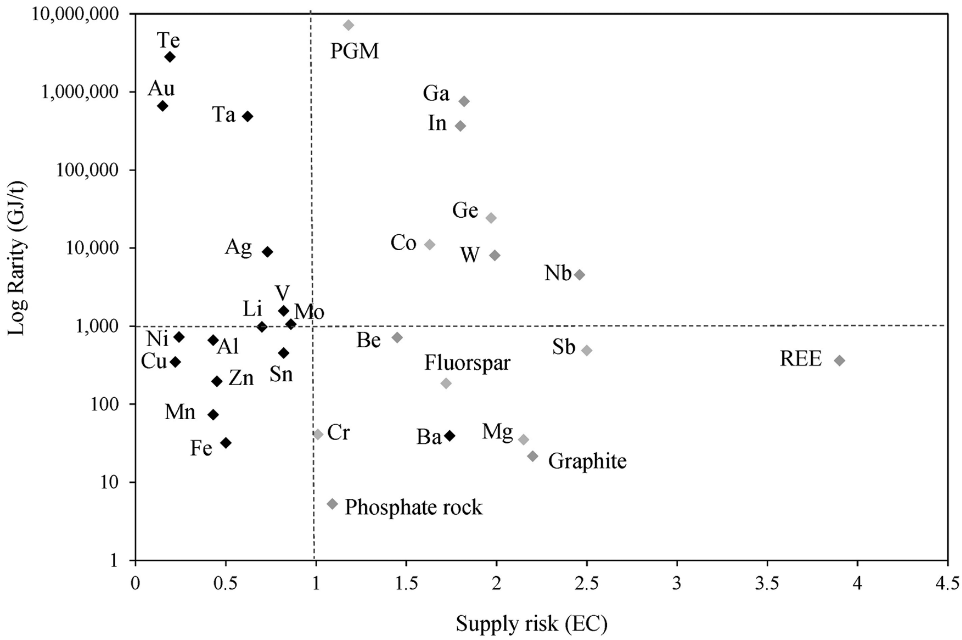

Figure 1 Thermodynamic rarity as a function of the supply risk (data according to the EC 2014b). Elements in gray are those labeled as critical by the European Commission (EC). GJ/t = gigajoules per tonne; PGM = platinum group metals; REE = rare earth elements.

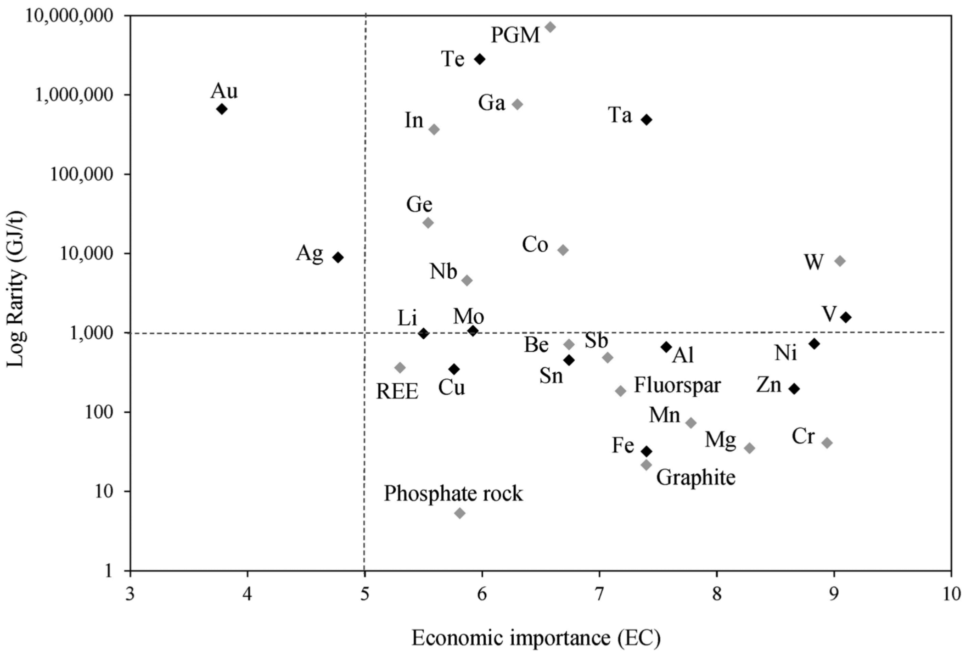

Figure 2 Thermodynamic rarity as a function of the economic importance (data according to the EC 2014b). Elements in gray are those labeled as critical by the European Commission (EC). GJ/t = gigajoules per tonne; PGM = platinum group metals; REE = rare earth elements.

(i.e., extracted), imported, exported, or consumed. Tonnage for all incoming and outgoing flows were converted into rarity (expressed in million tonnes of oil equivalent [Mtoe]), considering thus world average mineral ore grades and exergy costs for prevailing technologies of mining, concentrating, smelting, and refining (table 1). Hence, those commodities with larger exergy costs have a greater weight in the figure (i.e., they are thermodynamically more relevant).

As there is no individual recycling rates available for each of the member states of the EU, average recycling rates for metallic minerals have been used (UNEP 2011). The recycling rate selected for this study is recycled content, as it is an absolute indicator that measures the quantity of recycled materials from

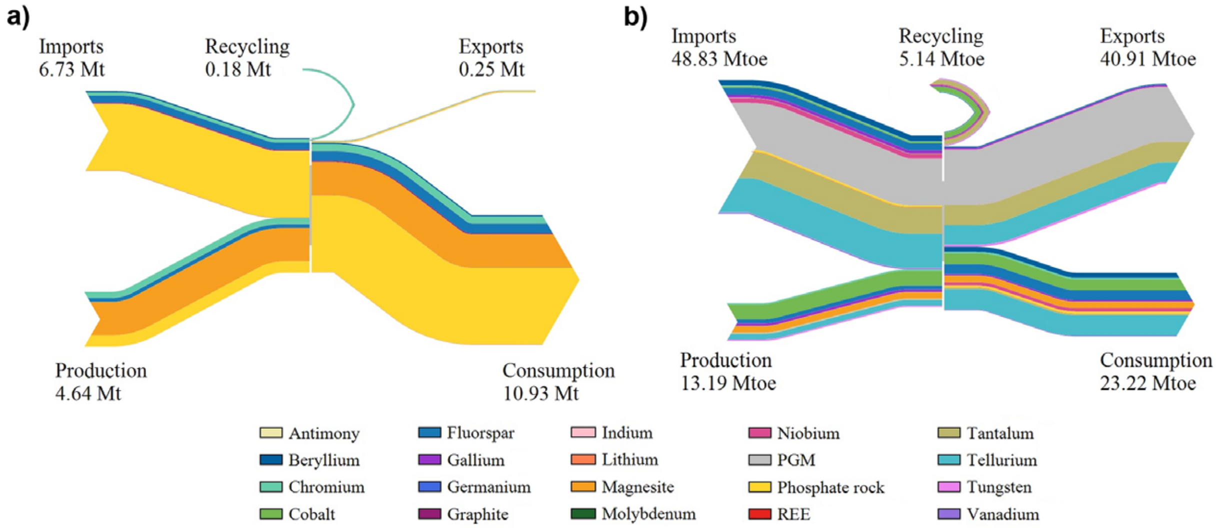

Figure 3 Sankey diagram of the flows of the materials selected as critical for the EU-28 for 2014 in (a) million tonnes (Mt) and in (b) million tonnes of oil equivalent (Mtoe) (right). Data for imports and exports have been collected from EUROSTAT and BGS statistical services. EU = European Union; PGM = platinum group metals; REE = rare earth elements.

EoL products used as scrap in production and in fabrication, over the total amount of metal that enters into the industrial life cycle of an element (i.e., from primary and secondary sources). Therefore, it is a measure of how much primary mining has been avoided by using secondary metal. Material flows in exergy have been transformed from GJ/t into Mtoe using a conversion factor (1 Mtoe = 42,000,000 GJ).

For comparative purposes, the diagram has been represented using the information in tonnes (figure 3a) and then in Mtoe (figure 3b) using the thermodynamic rarity values of each commodity shown in table 1. Even if all the information of the substances selected as critical in this study has been included in the figure, due to their lower values when compared to other substances, both in mass and thermodynamic rarity terms, not all of them can be seen at this scale. Such is the case of gallium, germanium, and indium, with smaller production and trade values. Additionally, in the case of tantalum, the trade data (imports and exports) that have been used are from BGS statistics (BGS 2016), where they do not differentiate between extra- and intra-European trade.

When analyzing the material trade in the EU-28 in mass terms, the minerals that are mostly imported are chromium, nickel, and phosphate rock, which, in the latter case, makes sense as this product is the basis for the agricultural sector and the domestic phosphate rock production is almost negligible when compared to the internal demand. Regarding domestic production, magnesite accounts for 61% of the total share, which is again a product needed for the agricultural and industrial sector. Still, other minerals that are internally produced are chromium and phosphate rock, with a share of 11% and 21%, respectively. As the main materials produced are industrial minerals that are usually neither recycled nor exported, clearly they are used within the EU-28, accounting for the total share of the consumption. In mass terms, recycling and exports contribute only to 3.9% of the total outputs of the system.

On the other hand, if we represent this same information using thermodynamic rarity, expressed in Mtoe, the situation changes drastically. In the case of imports, the minerals that stand out notably are PGM, tellurium, tantalum, beryllium, and niobium, with shares of 35.1%, 25.6%, 19.6%, 4.3%, and 3.2%, respectively. In this case, we can see that, even if the imports of those same substances from a mass term perspective seemed less relevant (2% of the total share imports), these same numbers expressed in thermodynamic rarity terms (88% of the total share of imports) can help us to better understand the respective criticality of those substances, as we are taking into consideration other factors such as their scarcity in the crust and in the mines. In the case of domestic production, cobalt, magnesite, fluorspar, and tellurium accounted for more than 86% of the total domestic EU-28 production in Mtoe. For instance, if we only look at magnesite, we saw that in mass terms that the domestic production accounted for 61% of the total, but in rarity terms, this number is reduced to only 18%, as magnesium is one of the most common elements found in nature and the energy needed to extract it is not so high when compared to other substances, such as tellurium, whose content in the crust is 5 million times lower than magnesium.

Additionally, it is noteworthy the relevance of exports in the outputs of the system when compared to the diagram in mass terms. Exports, that only represented 2.2% of the total outputs in mass terms, when expressed in thermodynamic rarity account for more than 59%. The main substances exported from the EU-28 in this case are PGM, tantalum, and tellurium, minerals whose thermodynamic rarity values are very elevated as seen in table 1. Even if there are virtually no mines that extract those minerals within the EU-28, there are many processing facilities that integrate smelting and refinery processes whose main final product are precious metals. For instance, the smelt refinery in Antwerp (Belgium) currently produces seven precious metals, being platinum and palladium among them, along with other precious and base metals, such as silver, gold, tellurium, indium, or REEs (Hagelüken and Meskers 2010). Once they are recovered, these products are supplied back into market and exported, even generating a small trade deficit when compared to imports, as is the case of PGM. It is also notable that one of the main importers of palladium in the last few years has been the United States, both in unwrought and powered forms.

In summary, while analyzing only in mass terms the EU mineral trade, several shortcomings can be detected, whereas including thermodynamic rarity allows to put more emphasis on the commodities that are more critical, at least from a thermodynamic point of view. Note that such an exercise would be impossible to be carried out when assessing mineral trade in terms of supply risk or economic importance, as both indicators are dimensionless. Hence, thermodynamic rarity has this further advantage over the other two criticality dimensions. As can be seen in figure 3, indeed, most of the commodities that stand out match those labeled as critical by the EC. Additionally, when observing only the mineral trade in mass terms, Europe could be classified as a producing country, as the internal production almost equals the imports. Only when expressing this trade in thermodynamic rarity terms, it can be seen that Europe has an important deficit in internal production of critical raw materials which need to be imported from other regions.

Conclusions

This paper has incorporated a new dimension in the criticality assessment of raw materials, namely, the thermodynamic rarity approach. As was seen, in combination with the supply risk and economic importance factors usually considered in conventional assessments, it provides additional insights related to the physical aspects of the commodity. Particularly, rarity incorporates two types of costs: first, the embodied exergy (or exergy cost, kWh) of the mineral from mine to market. Second, a hidden cost, understood as the free natural bonus provided by nature for having minerals concentrated in mines instead of dispersed throughout the crust. The latter is represented by the ERC, defined as the exergy cost that would be needed to extract a mineral from ordinary rocks to the conditions of concentration and composition found in the mine, using prevailing technology. From this viewpoint, it stands out that some minerals that have high rarity values are usually not categorized as critical when using only an economic importance and supply-risk approach. Still, the energy and ore grade of those substances are properties that could become even more critical in the future. Therefore, it is proposed that when a given commodity is considered to have a high risk in two of the categories "economic importance," "supply risk," and "thermodynamic rarity," it is labeled as critical.

With this approach, the list of raw materials proposed by the EC in 2014 has been complemented incorporating the rarity dimension. Lithium, molybdenum, tantalum, tellurium, and vanadium, which are not considered critical by the EC, are in this new proposed list as their thermodynamic rarity is very high. Phosphate rock, magnesite, graphite, and chromium in turn are not thermodynamically rare, but are relevant from an economic importance and supply-risk perspective and thus are kept critical. On the contrary, some minerals that have high rarity values (i.e., >1,000 GJ/t), such as gold or silver, are not included in the list, since as of yet their economic importance and supply risk is not considered high.

With this new list, an MFA for the EU-28 was carried out to show the physical importance of the raw materials traded; the analysis was additionally performed in rarity terms. This way, one avoids the problem of mixing "apples with oranges" and thereby eclipsing commodities that can be relevant to the economy. For instance, the domestic production of magnesite accounts for 61% of the total internal production when expressed in mass terms, but this number is reduced to only 18% when using thermodynamic rarity. Regarding imports, in mass terms it seems that most of the material imported is phosphate rock, with a share of approximately 83%. Yet when analyzing the imports in rarity terms, phosphate rock only accounts for 1.4% and PMG, while tellurium, tantalum, beryllium, and niobium account for 88%. Thus, using only mass as a yardstick in assessment reports can generate incomplete results, leaving behind other factors such as the physical quality of mineral resources. This way, minerals that were not considered in the critical raw material list, but are indeed critical from a physical point of view, can be taken into account. This information is especially useful in terms of resource management, since it allows targeting additional substances that are especially critical not only from an economic or supply-risk point of view, but also from a strictly thermodynamic point of view. Particularly, as it strongly relates to energy consumption, it points to those minerals where more recycling efforts should be placed, since it is a way to significantly lower those costs.

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Note

1. Considering possible deviations associated with data quality.

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