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Review

Carbon nanomaterials as potential substitutes for scarce metals

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ABSTRACT

There is growing evidence of resource problems related to the use of scarce metals in society, including the long-term risk of world-wide depletion of high-grade ores, shorter-term supply deficits and mineral related conflicts. In this study, we explore the idea that scarce metals may be substituted by nanomaterials based on the abundant element carbon, primarily graphene, nanotubes and fullerenes. We depart from a list of 14 geochemically scarce metals: antimony, beryllium, chromium, cobalt, gallium, germanium, gold, indium, niobium, platinum, silver, tantalum, tin and tungsten. We then review scientific papers and patents for carbon nanomaterial technologies that, if successfully implemented, could reduce or eliminate the need for each metal in its main application. For all main applications except for gold in jewelry, such technologies were identified. Most of the identified technologies were described in more than 100 papers. This suggests that there is an ongoing promising development of carbon nanomaterial technologies for applications currently relying on scarce metals. However, we recommend further studies to scrutinize these technologies regarding their environmental performance to avoid problem shifting from metal scarcity to (eco)toxic effects of the carbon nanomaterials themselves or other impacts related to their production and use.

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1. Introduction

1.1. Metal scarcity and dematerialization

In a paper with the suggestive title *Dining at the Periodic Table*, Johnson et al. (2007) discussed the increased societal use of different elements in the periodic table. For example, while a circuit board in the 1980s typically used 11 elements, this increased to 15 in the 1990s and to 60 in the 2000s. They also report how the global mine production of ten metals have increased considerably between 1900 and 2000: aluminum, chromium, nickel, tungsten, copper, zinc, iron, gold, lead, silver and tin. Along the same lines, Ljunggren Söderman et al. (2014) report an increased use of scarce metals in vehicles. They also write that a transition to electric vehicles may further raise the use of scare metals, such as lithium, cobalt, nickel, manganese, silver and copper. This increased demand for a large variety of metals – together with the uneven distribution of metals in Earth's crust – has caused concerns over metal scarcity. The European Commission (2014) has developed a list of critical raw materials, of which most are scarce metals. Criticality is defined there as the combination of high supply risk and high economic importance. The purpose of this list is to ensure a continued supply of these raw materials to the European economy. Other ways to define and assess resource criticality have been developed, which take additional aspects, such as substitutability and environmental impact, into account (Erdmann and Graedel, 2011; Graedel et al., 2012; Nassar et al., 2015). The role of some scarce metals in conflicts has also been highlighted. Similar to drugs, oil and diamonds, profits from selling these minerals are used to fund ongoing conflicts. Important minerals in this context are those containing tin, tungsten, tantalum and gold (3TG) in the Democratic Republic of the Congo (Fitzpatrick et al., 2015).

Taking a longer time perspective, there is growing evidence of long-term depletion of high-grade ores of geochemically scarce metals. By comparing predicted future use to lithospheric stocks, Gordon et al. (2006) concluded that providing today's industrialized country level of services worldwide would require the depletion of all recoverable resources of copper, zinc and platinum as well as near-complete recycling of these metals from that point forward. Skinner (1976) suggested that the depletion of geochemically scarce metal ores would lead to an increased use of iron and other more common metals in different applications, which he termed “a new iron age”. Note that these sources do not speak of depletion in terms of ‘lack of metal atoms’, but the depletion of high-grade ores, which would leave only common rock as source of virgin metals. Although extraction of rare metals from common rock is technically possible, it is very expensive in terms of exergy and money.

There are thus both short- and long-term reasons for reducing the societal use of scarce metals. One strategy for that is to make the use more efficient by *dematerialization*. Dematerialization means a reduction in material and energy use per produced unit of service or utility (Cleveland and Ruth, 1998; Herman et al., 1990; Holmberg and Karlsson, 2000; Reijnders, 1998). A related concept is *dissipation*, which refers to the loss of concentrated material resources due to emissions to the environment, dilution in other materials or landfills (Ayres, 1998, 1999; Zimmermann and Gößling-Reisemann, 2013). According to an assessment by Zimmermann and Gößling-Reisemann (2013), all of the European Union's designated critical materials have dissipation rates higher than 30% and most have dissipation rates higher than 50%. Dematerialization is about reducing dissipation in absolute terms, for instance by reuse, recycling and decreased demand for material products (de Bruyn, 2002; van der Voet et al., 2008).

1.2. Transmaterialization and carbon nanomaterials

Another strategy for reducing the societal use of scarce metals is *transmaterialization*. It can refer to change of the materials used in society in general (Labys, 2002; Labys and Waddell, 1989), but is here used in the stricter meaning of substituting materials that are scarce and hazardous (Holmberg and Karlsson, 1995, 2000). A number of previous studies have discussed and investigated the potential for substituting scarce materials. Reijnders (2016) discussed the substitution of chromium, manganese, molybdenum, niobium, nickel, vanadium and tungsten in steel by more common materials, such as aluminum, magnesium, nitrogen and silicon. Graedel et al. (2015) investigated the substitution of approximately 60 different metals by substitutes available in the near term. Several studies have investigated the availability and potential substitution of scarce materials in solar cells, such as cadmium, telluride, selenium, gallium, indium and ruthenium (e.g. Andersson et al., 1998; Espinosa et al., 2012; Tao et al., 2011). Many experimental studies investigating the technical performance of potential substitutes to scarce materials also exist.

The present analysis is about the potential substitution of scarce metals by the abundant material carbon. It is the tenth most common element in Earth's crust (Wedepohl, 1995). The annual societal carbon turnover includes almost 10 000 million metric tonnes in the form of coal, petroleum and natural gas (U.S. Energy Information Administration, 2012) and about 2000 million metric tonnes of biogenic carbon harvested in forests and on agricultural land (Berndes, 2014). These numbers exceed the production volume of iron, the most common industrial metal (1200 million metric tonnes of pig iron were produced in 2015 (Fenton, 2016)), and are vastly greater than the turnover of any scarce metal (see e.g. Table 1).

Recent years' research and development have expanded the applications of carbon far beyond those of the traditional allotropes graphite and diamond, mainly by the discoveries of carbon nanomaterials (CNMs). The most commonly mentioned ones are fullerenes, carbon nanotubes and graphene, but there are also others that are being researched, such as graphyne, graphdiyne, graphone, graphane (Peng et al., 2014) and carbon quantum dots (Shen and Liu, 2016). Some CNMs have properties similar to those of metals, such as high strength, high electric and thermal conductivity, and high chemical and structural stability also at high temperatures (Geim and Novoselov, 2007). They can also be dispersed in other materials, such as polymers, whereby the polymer obtains some of the CNMs' properties (Kim et al., 2010).

Table 1
Scarce metals selected and their main applications (data for different years in the 2000s). EU: European Union. US: United States. Source for abundance in Earth's crust: Wedepohl (1995). Source for annual global production: Mineral commodity summaries from the United States Geological Survey (USGS). Source for current main applications: see Sections 3.1–3.11.

Scarce metal	Abundance in Earth's crust (ppm)	Annual global production (metric tonnes/year for 2015)	EU criticality and/or US conflict material	Current main application (approximate share)
Antimony (Sb)	0.3	200 000	EU	Flame retardants (60%)
Beryllium (Be)	2	300	EU	Conductive materials (40%)
Chromium (Cr)	100	30 000	EU	Corrosion protection (90%)
Cobalt (Co)	20	100 000	EU	Strong materials (40%)
Gallium (Ga)	20	400	EU	Semiconductor (80%)
Germanium (Ge)	1	200 000	EU	Optical fibers (30%)
Gold (Au)	0.003	3000	US	Jewellery (70%)
Indium (In)	0.05	800	EU	Transparent electrodes (60%)
Niobium (Nb)	20	60 000	EU	Alloys (90%)
Platinum (Pt)	0.0004	200	EU	Catalytic converters (50%)
Silver (Ag)	0.07	30 000	–	Electronics (20%)
Tantalum (Ta)	1	1000	US	Capacitors (20%)
Tin (Sn)	2	300 000	US	Solders (50%)
Tungsten (W)	1	90 000	EU, US	Strong materials (50%)

1.3. Aim of the study

The fact that carbon is an abundant material and that CNMs have properties similar to metals gives a first indication of the CNMs' potential for substituting scarce metals. In this study, we search for a further indication, which would be the existence of early-stage CNM technologies with potential use in applications currently involving scarce metals. Consequently, the aim of this study is to identify early-stage CNM technologies with potential use in these applications. Rather than reviewing a few specific applications in detail, a broader selection of scarce metal applications is considered in the review. A discussion about further steps towards a transmaterialization from scarce metals to CNMs is provided in the end of the article. For simplicity, both metals and metalloids are referred to as metals in this study.

2. Methods and materials

2.1. Selection of scarce metals and applications

From a geochemical standpoint, all metals except for silicon, aluminum, iron, calcium, magnesium, sodium, potassium and titanium are scarce in the sense that they are mined from high-grade ores that risk depletion (Ljunggren Söderman et al., 2014; Skinner, 1976, 1987). Disregarding these abundant elements, as well as metals without stable isotopes, leaves us with about 60 naturally occurring geochemically scarce metals. In order to make a review feasible, this analysis employs a more narrow selection. The European Union's list of critical metals (European Commission, 2014) and the United States' list of conflict materials (Fitzpatrick et al., 2015) are employed as points of departure considering the high policy interest in these metals' scarcity. From these lists, magnesium, its corresponding mineral magnesite and silicon were omitted since they are not geochemically scarce. Non-metallic materials (borates, coking coal, fluorspar and natural graphite) were also omitted. To reach a more manageable sample size, all elements in the rare-earth element group were left out, as well as the platinum group metals with the exception of platinum itself. We then added the precious metal silver, for which scarcity issues have been highlighted in other sources (Graedel et al., 2015; Pihl et al., 2012). This gives a list of 14 metals (Table 1). For each of the metals, its main application in terms of share of annual consumption was identified (see Section 3 for references). Only these main applications of the metals were considered and constitute the basis of the review.

2.2. Review procedure

CNM technologies were sought in Scopus, Google and the Patent Full-Text and Image Database (PatFT) of the United States Patent and Trademark Office up to, and including, the year 2016. Since the metals are used in different applications, different search terms relevant for the specific case were used iteratively. Typically, the name of different CNMs and the metal's name were used. In addition, terms related to the main applications (e.g. flame retardants in the case of antimony) were also employed in an iterative way. An example of a search string is: (graphene* OR "carbon nanotube*" OR fullerene*) AND "flame retardant*". Sometimes, the name of the scarce metal currently used in the application was used to ensure relevant hits. Only hits being patents, scientific journal papers, conference papers, book chapters and electronic articles with explicit authors were considered. Only texts in English were included. All hits that are not patents are here referred to as papers. Only original studies were considered – not reviews. Most hits on Google were webpages and we then tried to identify if there was a paper or patent source behind in a backward snowballing manner (Wohlin, 2014).

2.3. Review framework

We employed a two-dimensional framework for reviewing CNM technologies. The first dimension of the framework is how developed the technology is. We consider the technology to be more developed if it is described in many patents and papers. We also consider the technology more developed if it occurs in a patent than in a paper, since patents often describe technologies that are of interest for commercialization (Jaffe and Trajtenberg, 2002). While the number of papers and patents could merely indicate larger interest in a technology instead of state of development, such an interest would likely lead to faster development. The second dimension is at which level a future substitution could occur. The first substitution level is when the metal element itself is directly substituted by a CNM. The second substitution level is when the material that the metal is part of is substituted by a CNM or CNM-containing material. Furthermore, full substitution often occurs via early use in hybrid technologies or in specific niche applications

(Kemp, 1998; Raven, 2007; Sandén and Azar, 2005). An example of a hybrid technology at the material level is the iron-wood water wheels of the 18th century, used before the full substitution of iron for wood. An example of a niche market is how aluminum was first used in ornaments and jewelry due to its high cost and extraordinary appearance. We therefore also note the occurrence of suggested hybrid technologies and niche markets in the review.

3. Results and discussion

For all selected metals, with the exception of gold, CNM technologies with potential use in the scarce metals' main applications were identified (Table 2). Following the review framework, the technologies have, however, reached different stages of development. The technologies are listed accordingly in Table 2, descending from stronger indication of development to weaker. The most developed technology is graphene and CNT for use in transparent electrodes, potentially replacing indium. The uses of CNMs as semiconductors, conductive materials, flame retardants, strong materials, corrosion protection and in capacitors also show relatively strong development. In fact, CNM technologies for these seven scarce metal applications were described in so many papers that they could not all be read in detail, thus the '>100' notation in Table 2. The uses of CNMs in solders, optical fibers and catalytic converters are seen as less developed since fewer patents and papers describing such technologies were found. Most of these CNM technologies existed with both graphene and CNTs, but for catalytic converters, only graphene technologies were identified, and for solders, only CNT technologies were identified. For flame retardants, strong materials and corrosion protection, fullerene technologies were also identified, but to a much lesser extent than graphene and CNTs. Most of the substitutions of scarce metals with CNMs would occur at a material level and only two would occur at an elemental level: the substitution of silver in conductive materials and the substitution of platinum in catalytic converters. This is because these two metals exist in pure, non-alloy form in their respective applications.

In Fig. 1, the patents are plotted along a timeline, indicating a cumulative build-up of knowledge. The first patent in the sample was issued in 2004 for conductive materials, while patents for strong materials and corrosive protection were first issued in 2014 and 2015, respectively. In 2016, the dominance of patents related to transparent electrodes is evident.

The results of the review are presented in more detail for each scarce metal application in Sections 3.1–3.11. A list of all identified patents can be found in the Appendix A.

3.1. Antimony in flame retardants

The current main application of antimony is in the form of antinomy trioxide (Sb_2O_3) and other antinomy oxides in halogenated flame retardants, and this application covers approximately 60% of the global antimony use (Butterman and Carlin, 2004). In synergy with halogenated flame retardants, the antimony compounds interrupt the creation of free radicals during the combustion (Laoutid et al., 2009). The exothermic reaction is thereby slowed down, which leads to cooling, reduced supply of flammable gas and ultimately to the seizing of the fire. Research towards finding alternatives to such flame retardants is ongoing and CNMs is one alternative being pursued (Betts, 2008; Laoutid et al., 2009). CNMs dispersed in a polymer material can reduce fire by forming a barrier on the surface of the polymer (Arao, 2015). This barrier prevents heat and oxygen from reaching the combustion zone, and prevents evaporated polymer gas from leaving the polymer and fuel the combustion.

There is much experimentation and many competing technology designs in this area. The CNMs graphene and CNT can be used separately (e.g. Kashiwagi et al., 2005), in conjunction with conventional halogenated flame retardants (e.g. Dittrich et al., 2014), together with many other materials (e.g. Gao et al., 2016; Guan et al., 2016), in oxidized form as graphene oxide (e.g. Edenharter et al., 2016) and in functionalized forms (e.g. Cai et al., 2016). A smaller number of studies considering fullerenes as flame retardants also exist (e.g. Fang et al., 2008). If CNMs are applied as a surface coating instead of being dispersed in the polymer, the flame retardant effect is immediate and stronger (Arao, 2015). Early attempts to use CNMs as an alternative to halogenated, antinomy-containing flame retardants are thus ongoing and CNMs have even been suggested to "pave the way for future materials combining physiochemical and thermo-mechanical performances with enhanced flame retardant behavior" (Laoutid et al., 2009). Note, however, that other nanomaterials based on abundant materials, such as nanoclay, are also investigated as alternatives to antimony and brominated flame retardants (e.g. Martins et al., 2017).

3.2. Beryllium and silver in electronics

The main application of beryllium is in electronics (European Commission, n.d.). More specifically, most beryllium is used in the alloy beryllium copper (BeCu). Adding beryllium to copper increases the strength and thermal stability, which is required in some electronic products. The share of beryllium in BeCu is often

Table 2
Results of the review. Carbon nanomaterial technologies were identified for all metals and applications except for gold in jewelry. G stands for graphene, CNT for carbon nanotubes and F for fullerenes.

Scarce metal	Main application	Number of patents	Number of papers	Substitution level	Carbon nanomaterial substitute
Indium (In)	Transparent electrodes	18	>100	Material	G, CNT
Gallium (Ga)	Semiconductors	8	>100	Material	G, CNT
Beryllium (Be) and silver (Ag)	Conductive materials	6	>100	Material (Be) and elemental (Ag)	G, CNT
Antimony (Sb)	Flame retardants	5	>100	Material	G, CNT, F
Cobalt (Co), niobium (Nb) and tungsten (W)	Strong materials	5	>100	Material	G, CNT, F
Chromium (Cr)	Corrosion protection	3	>100	Material	G, CNT, F
Tantalum (Ta)	Capacitors	3	>100	Material	G, CNT
Tin (Sn)	Solders	2	22	Material	CNT
Germanium (Ge)	Optical fibers	0	2	Material	G, CNT
Platinum (Pt)	Catalytic converters	0	2	Element	G
Gold (Au)	Jewellery	0	0	–	–

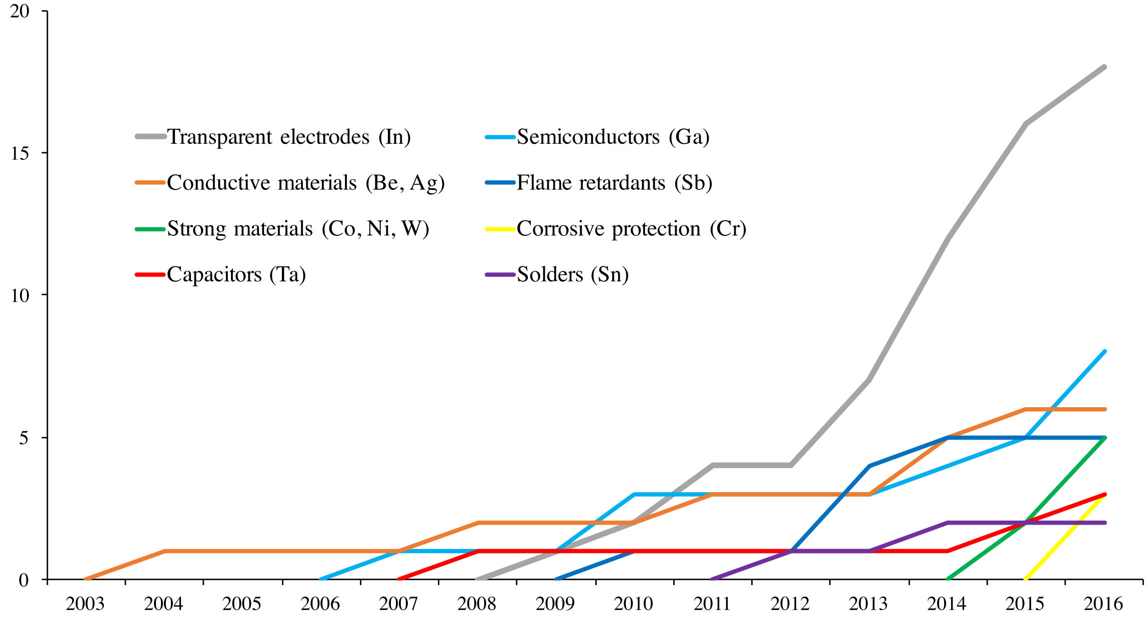

Fig. 1. Graph showing the cumulative number of patents for the carbon nanomaterial applications over time. The scarce metals in parenthesis are those currently used for the application.

0.5–3%. This use of beryllium is thus strongly linked to the use of copper and this hybrid material can be seen as a way to extend the use of copper as electric conductor. Silver is also mainly used in electronics due to its exceptionally high conductivity (Thomson Reuters, 2015). Beryllium and silver are discussed jointly here since they are used in the same type of application.

The high strength and conductivity of graphene and CNTs are relevant properties in this context. Papers have reported that graphene could replace copper as conductive material in computer chips (Politou et al., 2016; Soldano et al., 2013), possibly without major alterations of the fabrication process (O'Shea, 2009), and in battery electrodes (Rana et al., 2014). CNTs have also been reported as an alternative to copper in both computer chips and electrical wires (Lekawa-Raus et al., 2014; Soldano et al., 2013) and it has been shown that fibers of stacked CNTs outperform copper wires in terms of specific conductivity (Zhao et al., 2011) and current-carrying capacity (Wang et al., 2014). A number of hybrid technologies, where copper and graphene are used together to improve corrosion resistance and conductivity of copper, have also been demonstrated (e.g. Mehta et al., 2015). Beryllium as an element is not mentioned specifically in these sources, but would be indirectly substituted at a material level (i.e. BeCu) if graphene or CNTs were to replace copper.

Regarding silver, there also exist papers with explicit suggestions of replacing silver with graphene and CNTs as conductive material (Aitola et al., 2015; Benwadih et al., 2014). Hybrid materials where graphene is used together with silver in printable electronics have also been developed, leading to a decreased amount of silver being used (e.g. Meschi Amoli et al., 2015). In addition, copper-graphene hybrid technologies have been developed with the motivation of replacing the costlier silver (Luechinger et al., 2008).

3.3. *Chromium in stainless steel*

Stainless steel is the leading application of chromium (Papp, 2014), accounting for approximately 90% of the global consumption (Johnson et al., 2006). The alloying of chromium and steel is primarily done in order to provide corrosion protection. Graphene has been investigated as a potential corrosion barrier for metals that may avoid the need for alloying the steel with chromium. The reasons for this is its impermeability, which prevents oxygen and water from reaching the metal surface, and its thermal and chemical stability, which ensures the stability of the graphene protective layer (Chen et al., 2011). It is also electrically conductive, which enables its use in applications where the metals' conductivity is essential (Böhm, 2014). The good adhesion of graphene onto other materials enables the application of such surface coatings (Koenig et al., 2011). Graphene and graphene oxide layer coatings have been shown in papers to prevent corrosion of copper, nickel, copper nickel alloys and iron (e.g. Kang et al., 2012; Prasai et al., 2012). In addition to using graphene only, graphene and CNT nanocomposite coatings, where the graphene is added to a polymer material, has been successfully used as corrosion protection, for example for steel (e.g. Böhm, 2014). Based on these results, graphene composite coatings have been suggested as a potential future substitute for chromium alloys in the steel industry. A few studies on fullerene corrosion protection also exist, for example for iron (Sittner et al., 2002).

3.4. *Cobalt, niobium and tungsten in alloys and hard metals*

Cobalt, niobium and tungsten are all used to produce strong, hard and tough materials and are therefore discussed together. The leading use of cobalt globally is in hard materials (cemented carbides) and alloys (e.g. with nickel and iron) (European Commission, n.d.). The leading use of niobium is as alloy is steel (Papp, 2015). The leading use of tungsten is in cemented carbides and as alloy in steel (Leal-Ayala et al., 2015). These metals are thus seldom used in pure form and only in cemented carbides is one of the metals (tungsten) the main constituent. One way to substitute these metals at a material level is to replace the steel and cemented carbides that contain these metals by other materials with high strength and toughness. Monocrystalline graphene is famous for being the strongest material known (Lee et al., 2008). Polycrystalline graphene has lower toughness and defects can reduce the strength even further (Shekhawat and Ritchie, 2016). CNTs also have high strength (Liew et al., 2015), and so has graphene oxide, although the latter's strength decreases with the number of graphene oxide layers (Young et al., 2012). It has furthermore been shown that the addition of graphene, CNTs and fullerenes to numerous materials, including polymers (e.g. rubber, epoxy and polypropylene) and concrete, increases their strength (e.g. Liu and Kumar, 2014; Potts et al., 2011). Several references mention that CNMs, Graphene – either alone or in polymers – has been explicitly mentioned as a potential substitute for steel in the aircraft industry, where strong and light materials are needed (e.g. Dhiman and Dhamija, 2014). Similarly, CNTs have been proposed to be able to “replace traditional aerospace metallic materials [often light-weight aluminium alloys] to reduce the weight in space structures” (Jackson et al., 2016). Aerospace could thus potentially be a niche market for strong and hard CNMs. More generally, Ranjbartoreh et al. (2011) write that “these superior mechanical properties [to steel] should render [graphene paper – a modified form of graphene] an excellent material for engineering applications.”

3.5. Gallium in semiconductors

Gallium is mainly used in the form of gallium arsenide (GaAs) in semiconductors, which are in turn used in light emitting diodes, integrated circuits, transistors and solar cells. This application accounts for about 80% of global gallium use (Jaskula, 2015). Many papers discuss the use of graphene as semiconductor – in particular in the context of replacing silicon as a semiconductor material (e.g. van Noorden, 2006) – and graphene-based integrated circuits, transistors and semiconductor devices have been presented in papers (e.g. Avouris et al., 2007; Lin et al., 2011). Graphene itself is a zero-gap semiconductor, but different ways to induce asymmetry in the graphene structure, thereby creating a band gap, have been proposed (e.g. van den Brink, 2010). Hybrid technologies where graphene and silicon are used together have also been developed (e.g. Kim et al., 2011). CNTs have also been discussed as potential alternatives to silicon as semiconductor material and CNT-based integrated circuits, transistors and semiconductor devices have also been presented (e.g. Avouris et al., 2007; Chen et al., 2014). Considering the similarities between silicon and GaAs applications, much of this reasoning can be extended to GaAs as well. There is also an explicit suggestion that CNTs could replace not only silicon, but also GaAs, in electronics (Riede et al., 2011).

3.6. Germanium in optics

About 30% of all germanium is used in the form of germania (GeO_2) in optical fibers (European Commission, n.d.). The light-transmitting core of optical fibers often contains silica doped with germania. The reason for this use is that germania has a high refractive index and low optical dispersion. There exist one paper describing a successful attempt to use polymers doped with CNTs as core material in optic fibers (Uchida et al., 2009) and one paper that used graphene as core material in optical fibers (Das and Sahoo, 2016). The later study concludes that “optical fibers made of graphene core are more advantageous than existing silica material”. No patents where CNMs are used in optical fibers were found. However, graphene, CNT and (to a much lesser extent) fullerenes have been proposed for use in components that alter light-based signals from optical fibers and transform them to electronic signals. Such components are bottlenecks for data transfer and include polarizers, modulators, switches and sensors (e.g. Bao and Loh, 2012). The use of CNMs in these devices can help speeding up broadband data rates and may result in CNM spill-over into optical fibers.

3.7. Gold in jewelry

Gold is mainly used in jewelry, accounting for about 50% of global gold use (George, 2015). The popularity of gold in jewelry is likely due to its persistence against corrosion and other chemical reactions, but also due to its shine, scarcity and cultural history. Other metals are used as jewelry as well, including silver, platinum and tungsten. The persistence of these metals is probably a crucial property here – few would want their jewelry to become damaged, dissolved or discolored. CNMs satisfy this property. However, we have found no example of CNMs being used as jewelry, not even on Google. We did find jewelry made from carbon fibers, but they consist of micro-sized (i.e. not nano-sized) fibers of carbon.

3.8. Indium in displays

Indium is mainly used as indium tin oxide (ITO) in transparent electrodes in flat displays – this application accounts for about 60% of global indium use (European Commission, n.d.). The replacement of ITO by graphene is proposed in several papers (e.g. Blake et al., 2008; Segal, 2009). Notably, Bae et al. (2012) write that they “expect that transparent graphene electrodes [used in flat displays] can replace indium tin oxide in the near future.” There also exist examples of graphene-ITO hybrid materials in papers (e.g. Liu et al., 2016). Similar claims of replacing ITO exist for CNTs (e.g. Chhowalla, 2007; Zhou and Azumi, 2016). The reason for why graphene and CNTs could replace ITO is that they, similarly to ITO, are transparent and electrically conductive. In addition, graphene and CNTs are stronger and chemically more stable, which gives them a benefit compared to ITO (Blake et al., 2008; Zhou and Azumi, 2016).

3.9. Platinum in catalytic converters

The main application of platinum is in catalytic converters that reduce air pollution from vehicles with internal combustion engines (Loferski, 2015). Several studies discuss the use of graphene and CNT as catalysts. For example, there are reports of graphene being able to replace platinum as catalyst in fuel cells if doped with non-metal atoms such as nitrogen or boron, or used together with relatively abundant metals such as iron and manganese (e.g Huang et al., 2012; Liu et al., 2014). Apparently, graphene enhances the catalytic activity of such metals. Fuel cells could become an important future application of platinum. Similar reports of catalytic properties, either by being doped or by enhancing the properties of more abundant metals, exist for CNTs (e.g. Yan et al., 2015). It thus seems that CNMs, either doped by non-metal elements or by working together with non-noble metals, can have similar properties as platinum in catalytic converters. Two theoretical studies have used quantum mechanical modeling to calculate that graphene could function as a catalyst for exhaust gases specifically. One regarded the reduction of nitrogen oxides by nitrogen-doped graphene (Zhang et al., 2014), and the other regarded carbon monoxide oxidation by graphene oxide (Esrafili et al., 2016).

3.10. Tantalum in capacitors

The largest application of tantalum is in capacitors, which accounts for about 20% of global consumption (Soto-Viruet et al., 2013). A layer of tantalum and a conductive material or electrolyte form the two electrodes of the capacitor, with a thin layer of tantalum oxide (Ta_2O_5) in between as the dielectric material. Several attempts to develop CNM-based capacitors exist. One example is the development of graphene-boron nitrate-graphene capacitors with potential application in nanoelectronics (Özçelik and Ciraci, 2015). Another is the graphene oxide-CNT hybrid dielectric material described by Biswas et al. (2015).

The reviews by Ke and Wang (2016) and Pan et al. (2010) describe how graphene and CNTs can be used as electrode materials in so-called supercapacitors (also called ultracapacitors). Supercapacitors have extra high capacitance, but have a slightly different envisioned application than ordinary capacitors – as replacement for conventional rechargeable batteries based on lithium. However, the use of graphene in this nearby area could thus constitute a potential niche market and may spill over to the development of tantalum-free ordinary capacitors.

3.11. Tin in solders

Tin is mainly used in solders (50% of global use) together with other metals such as lead, silver and copper (International Tin Research Institute, 2013). Tin's low melting temperature, electric conductivity and thermal conductivity make it suitable for this purpose. In papers, there are numerous examples of CNT-based solder technologies, often referred to as conductive adhesives (Li et al., 2010). For example, Mir and Kumar (2012) and Li and Lumpp (2006) report the development of CNT-epoxy composite conductive adhesive and Yung et al. (2009) describe an interconnect based on aligned CNTs. These technologies are described as potential replacements for conventional tin- and lead-based solders, and the high conductivity of CNTs provides the foundation for the technologies. There are also many examples of hybrid materials between CNMs and conventional solder materials, such as the incorporation of CNTs in Sn–Ag–Cu solders (e.g. Sun and Zhang, 2015) and Sn–Ag–Cu solders reinforced with graphene (e.g. Huang et al., 2016).

3.12. Limitations and further studies

We would like to highlight that this is not a predictive study. Although many CNM technologies have been identified, we cannot tell from our study whether these will actually substitute the scarce metals or not in the future. However, the existence of these CNM technologies means that those who would like to see an escape from the current use of scarce metals to more abundant elements have something to work with. In this study, we took the main applications of a range of scarce metals as starting point. Another approach that may reveal other substitution opportunities would be to depart from one or several specific CNMs and review which scarce metals these could potentially replace. Yet another approach would be to scrutinize a specific substitution of one scarce metal by one CNM in more detail. We also acknowledge that substitutions can happen not only at element and material levels, but also at higher technology levels. An historical example of a technology-level substitution is the replacement of cameras using photographic film with digital cameras. In the 1990s, the photographic industry was the largest user of silver in the United States (Purcell and Peters, 1997). One can argue that semiconducting materials that enabled digital technology indirectly caused a decreased use of silver, since silver-containing films were no longer needed when digital cameras pushed analog cameras out of market. However, such technology-level substitutions are difficult to identify far in advance and was therefore not searched for in this review.

In order to facilitate a transmaterialization from scarce metals to CNMs, the identified early-stage CNM technologies should also be scrutinized based on their environmental performance. Ellenbecker and Tsai (2011) cautioned that new nanomaterials may be framed as less hazardous substitutes to existing materials, but may also cause severe environmental and human health impacts. Such impacts of graphene and CNTs have been reviewed in previous studies (Arvidsson et al., 2013; Helland et al., 2008; Hu and Zhou, 2013; Zhao et al., 2014). These reviews show a considerable lack of information, indicating the need for further studies on environmental and health impacts of CNMs.

There could also be tradeoffs with other environmental and resource issues occurring throughout the CNM technologies' life cycles. For example, it could be that the increased use of CNMs will also increase the use of some scarce metals that are used in conjunction or during CNM production. One noteworthy example identified was the use of tin, silver, copper and nickel together with graphene and CNT in solders. An additional tradeoff could be between the use of scarce metals and energy use. Such issues need to be investigated on a case-by-case basis using life cycle assessment (LCA) and other environmental assessment methods. Two such studies already exist. In an LCA study comparing carbon nanofiber-reinforced polymer nanocomposites with steel as body panels in cars (potentially containing cobalt, niobium and/or tungsten), it was found that given low carbon nanofiber concentrations, the nanocomposite could reduce the life cycle energy use of the body panels due to reduced fuel consumption in the use phase (Khanna and Bakshi, 2009). A recent LCA study comparing the indium-containing ITO and graphene in transparent electrodes found that graphene could be preferable both with regards to the use of scarce metals and energy use (Arvidsson et al., 2016). Thus, in these two cases, there was no tradeoff between using more abundant resources and reducing energy use.

4. Conclusions

As long as there is an extensive use of scarce chemical elements – a “dining at the periodic table” (Johnson et al., 2007) – there will always be problems related to critical and scarce materials. Considering the abundance of the element carbon, a transmaterialization from scarcer materials to carbon could be beneficial from a resource use perspective. In this article, we search for potential substitution of 14 scarce metals in their main applications. While no suggestion to replace gold in jewelry with CNMs was identified, we found early-stage CNM technologies for potential use in the main applications of antimony, beryllium, chromium, cobalt, gallium, germanium, indium, niobium, platinum, silver, tantalum, tin and tungsten. In particular, CNM technologies for transparent electrodes, semiconductors, conductive materials, flame retardants, strong materials, corrosion protection and capacitors have reached far in terms of number of scientific papers and patents. For most technologies, there were explicit descriptions of the CNMs as potential substitutes to the scarce metals. To avoid substitution leading to problem shifting, CNM technologies should be further scrutinized regarding environmental performance over their full life cycle.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jclepro.2017.04.048.

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