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GEOLOGY

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Future of photovoltaic materials with emphasis on resource availability, economic geology, criticality, and market size/growth

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ABSTRACT
The reduction of greenhouse gas emissions depends largely on the availability of clean energy. To harness solar energy, photovoltaic (PV) materials (solar-grade silicon, germanium, gallium, indium, tellurium, selenium, and arsenic) must be available at a reasonable cost. Markets for these critical and specialty materials do not exceed 200,000 tonnes per year; however, they are subject to fast growth rates. Except for solar-grade silicon, PV materials are by-products of base and precious metal extraction. This is motivated in part by environmental and workplace regulations and the need to purify the main commodity to users' specifications. Given favorable market conditions, any PV material can be derived from more than one deposit type. For example, germanium can be recovered as a by-product from bauxite, Mississippi Valley-type, clastic-dominated sediment-hosted zinc-lead, Kipushi-type, Apex-type, and other deposit types. The raw materials required to produce metallurgical-grade silicon (MG-Si), mainly quartzites, are available on all continents. The process is energy intensive, so the availability of abundant, inexpensive, and "clean" power is one of the key parameters in selecting future silicon metal plant sites. MG-Si is the starting material for the production of solar-grade silicon. Although no shortages of PV materials due to a lack of raw materials are expected in the short term, those linked to bottlenecks, geopolitical economic considerations, armed conflicts, natural hazards outside of human control, or commercialization of new technology are possible. The advent of the "circular economy" cannot eliminate the need to increase mine, smelter, and refinery production of PV materials.

RÉSUMÉ
La réduction des émissions de gaz à effet de serre dépend largement de la disponibilité d'une énergie propre. Pour exploiter l'énergie solaire, les matériaux photovoltaïques (PV) (silicium de qualité solaire, germanium, gallium, indium, tellure, sélénium et arsenic) doivent être disponibles à un coût raisonnable. Les marchés de ces matériaux critiques et spécialisés ne dépassent pas 200 000 tonnes par an, mais ils sont soumis à des taux de croissance rapides. À l'exception du silicium de qualité solaire, les matériaux PV sont des sous-produits de l'extraction des métaux de base et précieux. Cette situation est motivée en partie par les réglementations relatives à l'environnement et au lieu de travail et par la nécessité de purifier le produit principal selon les spécifications des utilisateurs. Si les conditions du marché sont favorables, tout matériau PV peut être dérivé de plus d'un type de gisement. Par exemple, le germanium peut être récupéré comme sous-produit de la bauxite, des gisements de zinc-plomb de type Mississippi Valley, des gisements de zinc-plomb dans les sédiments clastiques, de Kipushi-, d'Apex et d'autres types de gisements. Les matières premières nécessaires à la production de silicium de qualité métallurgique (MG-Si , de l'anglais *metallurgical-grade silicon*), principalement des quartzites, sont disponibles sur tous les continents. Le processus étant gourmand en énergie, la disponibilité d'une énergie abondante, peu coûteuse et « propre » est l'un des paramètres clés dans le choix des futurs sites d'usines de silicium métal. Le MG-Si est le matériau de départ pour la production de silicium de qualité solaire. Bien qu'aucune pénurie de matériaux PV due à un manque de matières premières ne soit attendue à court terme, celles liées à des goulets d'étranglement, à des considérations économiques géopolitiques, à des conflits armés, à des risques naturels échappant au contrôle de l'homme ou à la commercialisation de nouvelles technologies sont possibles. L'avènement de « l'économie circulaire » ne peut éliminer la nécessité d'augmenter la production de matériaux photovoltaïques dans les mines, les fonderies et les raffineries.

KEYWORDS
Critical metals, Deposit type, Gallium, Germanium, Indium, Selenium, Silicon, Solar energy, Tellurium, Thin film technology

MOTS-CLÉS
énergie solaire, gallium, germanium, indium, métaux critiques, sélénium, silicium, type de dépôt, tellure, technologie des couches minces

INTRODUCTION

Ongoing efforts to reduce greenhouse gas (GHG) emissions into the atmosphere (i.e., through increased use of electric vehicles, development of renewable energy-generating facilities, and development of energy storage capacity power grids) depend on reliable supply chains of photovoltaic (PV), battery, and magnet raw materials (Arrobas, Hund, McCormick, Ningthoujam, & Drexhage, 2017; European Commission, 2018, 2020;

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Hund, La Porta, Fabregas, Laing, & Drexhage, 2020; IRENA, 2022; Küpper et al., 2018; Simandl, Simandl, & Paradis, 2021). Many studies related to these efforts incorporate high-level trends and numerous assumptions. However, overall, it is very difficult to predict what the future market will be for the above listed categories of materials (Jowitt & McNulty, 2021; McNulty, Jowitt, & Belousov, 2022; Mudd, 2021; Mudd, Jowitt, & Werner, 2017; Simandl et al., 2021; Sprecher, Reemeyer, Alonso, Kuipers, & Graedel, 2017; Werner, Mudd, & Jowitt, 2017).

The terms *battery*, *magnet*, *PV*, and *critical* are used heavily in the media and by the general public, mining promoters, the scientific community, and government organizations. Due to overlap between these terms, it is essential to place PV materials in the proper context. This is covered in detail by Simandl et al. (2021). The main objectives of this paper are to:

(1) provide the reader with an overview of the PV domain;
(2) summarize the resource availability and markets for the main PV materials: silicon (Si), germanium (Ge), gallium (Ga), indium (In), tellurium (Te), cadmium (Cd), selenium (Se), and arsenic (As);
(3) present an overview of the economic geology of PV raw materials; and
(4) highlight the principal development constraints imposed on a resource developer during potential ranking of the projects when dealing with specialty (limited market base) and critical (essential and subject to high supply risk) materials.

This paper provides basic information regarding provenance, uses, criticality, and main market opportunities and constraints in the domain of PV materials relevant to members of the mineral exploration community for project ranking. It also serves as a common foundation for both the traditional (linear economy) and recently repopularized circular economy approaches to mineral resource management, as described by Merli, Preziosi, and Acampora (2018). The article also provides a primer regarding the future availability of PV materials to large manufacturers and government decision-makers who are worried about the availability of future supplies and those establishing impacts of "black swan"–type technical breakthroughs—for example, potential 25% and 33% reductions in the use of copper (Cu) and zinc (Zn) due to commercialization of graphene technology in electricity transmission and corrosion protection (Sprecher et al., 2017). Reduction in demand for these two base metals would have a ripple effect on the availability of their co-products, for example, Cd, Ge, and In (Sprecher et al., 2017).

PV, BATTERY, MAGNET, SPECIALTY, AND CRITICAL MATERIAL CATEGORIES

In this section, we will define PV, battery, and magnet materials and introduce the specialty and critical materials categories required for understanding the ongoing electrification trend.

PV materials

Theoretically, solar radiation could provide more energy than is currently required by Earth's entire population (Solar Energy Industries Association, 2018). The International Energy Agency (2021a) estimated global energy use for 2019 to be 617,337,965 terajoules (TJ). Of this, wind and solar energy represented a small fraction (~2.2%) of global energy requirements (Figure 1). If we consider the net zero emissions scenario presented by the International Energy Agency (2021a), then, in the future, electricity will need to account for a much larger proportion of the total energy demand, and renewable energy sources would have to gradually displace the use of fossil fuels (such as coal, natural gas, and oil) to generate electricity (Figure 2a). In this scenario, wind and solar energy generation (both onshore and offshore energy installations) in combination with hydroelectric and other renewables would need to account for nearly 90% of global electricity generation by 2050 (refer to the third column in Figure 2b). Other models and emission reduction philosophies have been presented. However, they follow the same general trend: The future for the

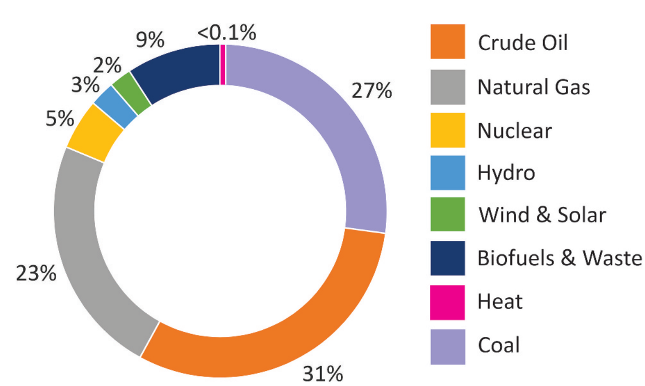

Figure 1. Global energy use by source. The 2019 global energy requirements were largely satisfied by fossil fuels (based on data provided by the International Energy Agency, 2021a)

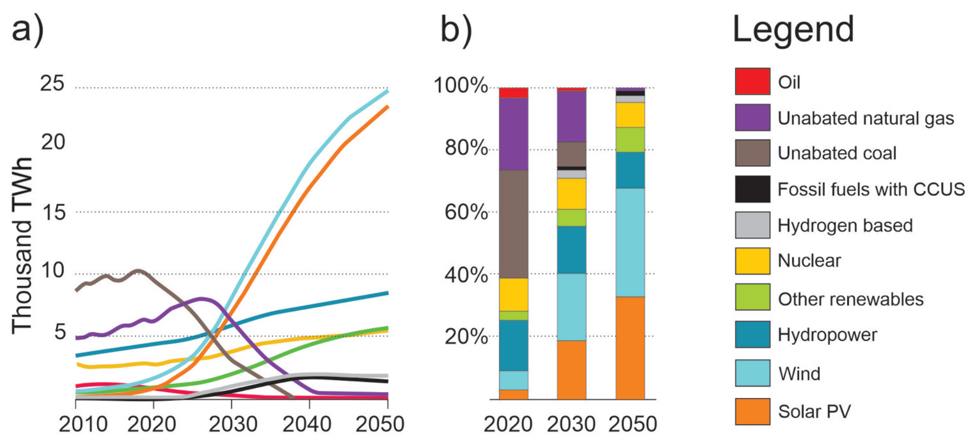

Figure 2. a) Absolute and b) relative global electricity generation estimates by source from 2010 to 2050 assuming the net zero emission scenario (modified from International Energy Agency, 2021b); CCUS: carbon capture, utilization, and storage; PV: photovoltaic

PV industry is bright, and by extrapolation, the demand for raw materials required to manufacture PV cells and solar panels (i.e., PV materials) will increase.

Currently, PV cell production relies largely on crystalline Si and to a much lesser extent on thin-film technologies. Third-generation technologies, including organic PVs; copper-zinc-tin sulfide; and perovskite, dye-sensitized, and quantum dot solar cells, are in the early stages of development with limited commercialization. Consequently, materials widely recognized as PV include solar-grade Si (derived from silica raw materials), In, Ga, Ge, and Te (Figure 3). For the sake of completeness, we also include Cd, Se, and As. These PV materials are used alone or in a variety of formulations in thin-film production, such as copper-indium-gallium-selenide (CIGS), cadmium sulfide (CdS), amorphous Si, Ge, gallium arsenide (GaAs), cadmium telluride (CdTe), and indium-gallium-arsenide (InGaAs; Ajayan et al., 2020; Polman, Knight, Garnett, Ehrler, & Sinke, 2016; Simandl et al., 2021; Unold & Schock, 2011). Explorationists, promoters, developers, and the mining community tend to avoid or ignore Cd, As, and to a lesser degree, Se, because of the environmental stigma associated with them.

Overall, crystalline Si, CdTe technology, and CIGS account for 92%, 5%, and 2% of the solar panel market, respectively. All other materials, including those used in the third generation of PV panels (based on organic hybrid, dye-sensitized, and concentrator PV (CPV) technologies) account for 1% of the solar panel market (Chowdhury et al., 2020). Currently, the use of Ge in terrestrial PV applications is limited by its high cost. This is changing because of its increasing use as a semiconductor in multifunction solar cells.

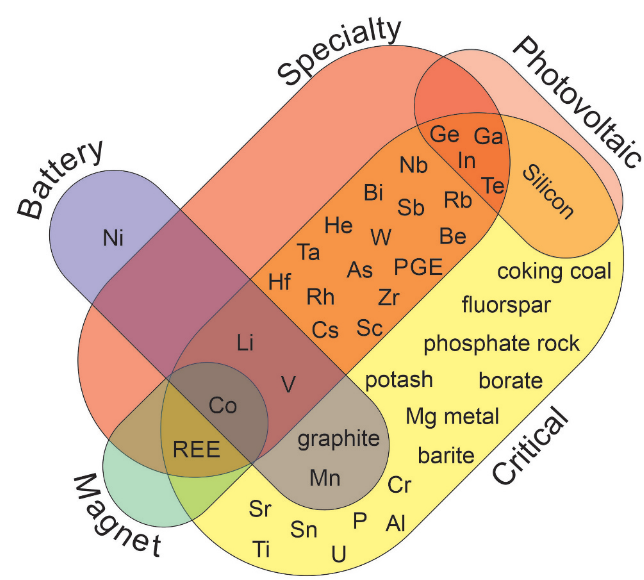

Figure 3. Overlapping material categories. Several of the 41 critical materials shown also belong to photovoltaic (PV), battery, magnet, and specialty categories (*sensu lato*; as used by industrial users, exploration companies, banks, and government organizations). For example, Ge, Ga, In, and Te belong also to PV (thin-film technology) and specialty material categories. Arsenic made a critical materials list; it is a specialty metal and is used in thin-film photovoltaic applications. However, it is seldom referred to as a PV material, at least in part because of associated environmental stigma. Cadmium and Se are not considered critical (therefore not shown); however, they are also used in thin-film PV and battery applications (Simandl et al., 2021)

For the purpose of this paper, we limit our discussion to Si and materials derived largely as a by-product of base and/or precious metal mining—more specifically, In, Ge, Ga, Cd, Te, Se, and As (materials actively involved in the conversion of solar energy to electricity). We leave out aluminum (Al) used for module frames, silica for glass, Cu for cables, Fe and Zn for structural setup, and other materials for a variety of devices and electrical parts needed for transferring energy from the PV modules to the power grid.

Besides technical aspects (e.g., efficiency, durability, ease of manufacturing, and reliability), the availability of raw materials, their relative costs, and social and environmental factors (e.g., end-of-life-waste management; Sica, Malandrino, Supino, Testa, & Lucchetti, 2018; Xu, Li, Tan, Peters, & Yang, 2018) will affect selection of PV systems in the future. The current market-dominance of monocrystalline Si cells and modules is expected to be challenged by multijunction cells by the 2030s (Oberbeck, Alvino, Goraya, & Jubault, 2020). The use of As in PV cell formulations appears to be handicapped since this element is considered to have a particularly negative impact on the environment (Purkayastha, Mishra, & Biswas, 2014).

Battery materials

In the current context, as used by the exploration and mining industry, the term *battery materials* comprises lithium (Li), cobalt (Co), manganese (Mn), vanadium (V), nickel (Ni), and graphite. It commonly overlooks several materials used in lead-acid, Ni-Cd, nickel-metal hydride (NiMH), and other older battery technologies. The term also disregards materials used in batteries that are currently in research development, were recently introduced, or are used mainly outside of North America and Europe (Simandl et al., 2021). Examples of commonly excluded materials are lead (Pb), Cd, sulfuric acid, and certain rare earth elements (REEs: lanthanum, cerium, and yttrium), which may account for 4–18 wt.% of NiMH batteries (Lin et al., 2016) and high-purity iron (Fe) and phosphorus (P) required to produce low-cost Li-Fe-P batteries. Ongoing research and factors that are expected to have an important impact on market growths of specific battery materials are reviewed by Bresser et al. (2018) and Simandl et al. (2021).

Magnet materials

The term *magnet materials*, as used today in trade journals, designates primarily REEs and more specifically neodymium (Nd), praseodymium (Pr), samarium (Sm), dysprosium (Dy), and terbium (Tb) (Simandl et al., 2021). In some technical and industry documents, this term also includes Co. However, exploration and mining journals generally ignore materials used in older magnet technologies such as aluminum-nickel-cobalt (AlNiCo) and yttrium cobalt (YCo_5) magnets. Most importantly, this term ignores materials used in affordable and relatively demagnetization-resistant ferrite or ceramic magnets (e.g., $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$), which currently account for the bulk of global magnet production by weight. Modern neodymium–iron–boron (NdFeB) magnets, also referred to as REE magnets, contain approximately 30 wt.% REEs (mainly Nd and to a lesser extent Dy and lower concentrations of other REEs such as Pr and Tb).

Transportation and renewable electricity generation are the two fastest developing markets for REEs. Currently, REEs account for 8% of the total cost and 50% of the raw material cost for a representative electric vehicle motor (Delfeld, 2018; Hummel et al., 2017). An average electric vehicle presently contains 1–2 kg of Nd-Pr alloy (Roskill, 2018).

In 2018 and 2019, direct-drive NdFeB magnet-based technology was used in 30% of the world's wind turbines. This type of turbine accounts for 8–9% of the global NdFeB magnet production. To satisfy the U.S. Department of Energy's objective of 86 GW of electric power from offshore wind farms by 2050, roughly 15,500 tonnes (t) of Nd would be needed (Roskill, 2019).

Specialty materials

A material with a global production of <200,000 t/year is commonly considered a specialty material (Simandl et al., 2021). The size of the global market (in terms of tonnage) for a typical specialty material does not exceed the annual production of two porphyry copper deposits comparable in size to the Highland Valley mine in British Columbia, Canada. The global annual production of all PV materials other than Si is substantially smaller than 200,000 t/year (Table 1). When the law of supply and demand applies, an aspiring specialty material producer cannot compensate for lower grades by relying on economy of scale (mining and processing larger tonnages of ore) because of the small market base. Individual specialty material operations do not benefit from economies of scale in the same manner as operations producing materials with large market bases, such as those producing Fe or base metals (Cu, Zn, Al, or Ni) from large tonnage deposits. This has major implications on the early ranking of exploration and development projects (Simandl et al., 2021). The exception is when the specialty material is a co- or by-product of another commodity.

Critical materials

Today, the term *critical material*, as used in the exploration and mining industry, describes a material that is subject to significant supply risk and is essential for one

Table 1. Photovoltaic materials compared to Fe and the main base and precious metals in terms of the global annual production, price, reserves, and years of supply of selected materials and main producing countries. Except for Cd and Se, the materials are designated as "critical," and in each case, China is the main producing country. Dashes indicate that information was not available. Unless otherwise indicated, production values represent those produced from mining operations, and prices reported are for North American markets. Lifetimes of reserves (years of supply) were estimated by dividing 2021 global reserve estimates by 2020 production values (market growth-rate was not considered, therefore, "real" lifetimes of reserves would be substantially shorter); compiled from data available in U.S. Geological Survey (2021)

		Material	2020 world production (tonnes)	2020 price (US$/tonne)	Reserves (tonnes)	Lifetime of reserves (years)	Main producing countries
Examples of major commodities and non-critical precious metals		**Au**	3,200	56,906,739	53,000	17	China (12%), Australia (10%), Russia (9%)
		Ag	25,000	643,014	500,000	20	Mexico (22%), Peru (14%), China (13%)
		Cu[1]	20,000,000	6,173	870,000,000	44	Chile (29%), Peru (11%), China (9%)
		Zn	12,000,000	2,403	250,000,000	21	China (35%), Australia (12%), Peru (10%)
		Pb	4,400,000	1,982	88,000,000	20	China (43%), Australia (11%), U.S. (7%)
		Fe (usable ore)[2]	2,400,000,000	119	180,000,000,000	75	Australia (38%), Brazil (17%), China (14%)
		Al (metal)[3]	65,200,000	1,962	-	-	China (57%), India (6%), Russia (6%)
		Ni[4]	2,500,000	14,000	94,000,000	38	Indonesia (30%), Philippines (13%), Russia (10%)
Photovoltaic materials	Critical materials	**As**[5,6]	32,000	420	-	-	China (75%), Morocco (17%), Russia (5%)
		Ga[6,7,8]	300	170,000-570,000	-	-	China (97%), Russia (1%), Korea (1%), Japan (1%)
		Ge[6,8]	130	1,000,000	-	-	China (66%), Russia (4%)
		In[6,8]	900	400,000	-	-	China (56%), Korea (22%), Japan (7%)
		Silicon[8,9]	8,000,000	2,116	-	-	China (68%), Russia (7%), Brazil (4%)
		Te[6,8]	490	55,000	31,000	63	China (61%), Russia (10%), Japan (10%)
		Cd[6,8,10]	23,000	2,300	-	-	China (36%), Korea (13%), Canada (8%), Japan (8%)
		Se[7,8,11]	>2,900	44,092	100,000	-	China (37%), Japan (25%), Germany (10%)

[1] Price for U.S. producer (COMEX price + premium)
[2] Production values are for usable ore, and reserve estimates are for crude ore
[3] Price for ingot
[4] Prices from London Metal Exchange
[5] Production values and price estimates are for arsenic trioxide; prices for imports from China
[6] World production estimates exclude U.S. production
[7] Price range indicates prices for low- and high-purity
[8] Production values represent smelter or refinery production
[9] Production quantities are the silicon content of combined totals for ferrosilicon and Si metal
[10] Average free market price, 99.95% Cd, 10-tonne lots; global ports (c.i.f). Source: Metal Bulletin
[11] U.S., Australia, Iran, Kazakhstan, Mexico, the Philippines, and Uzbekistan not reported

or more of the following: reduction of GHG emissions, the economic well-being of a country, and the national defense of a country (e.g., U.S. Department of Defense, 2013; European Commission, 2017; European Economic and Social Committee, 2022; Hayes & McCullough, 2018; Simandl, Akam, & Paradis, 2015). Evidently, critical material lists evolve with time (Simandl et al., 2015). The ongoing conflict in Ukraine makes many previously published defense-related EU and U.S. critical material lists obsolete. It is expected that the next generation of critical material lists for the EU and the U.S. will be much longer.

Many of the materials commonly referred to as PV, battery, and magnet raw materials (Figure 3) are currently considered to be critical (Simandl et al., 2021). An excellent example of a magnet critical material is Nd. It is essential for manufacturing high-performance magnets used in wind turbines, electric car drivetrains, and portable computing and communication equipment (e.g., laptops, tablets, smart phones). It is important to realize that if a given material is designated as critical, the law of supply and demand, which prevails under normal (free market) conditions, does not apply. Financial incentives to producers of critical materials are commonly provided by governments, paragovernmental organizations, or major manufacturing companies. Criticality of a given raw material also encourages vertical integration within industry, the formation of joint ventures, and the signing of long-term contractual agreements to protect existing supply chains or to establish new ones. Furthermore, the constraints limiting the development of many deposits containing specialty materials as discussed in the previous section are eliminated or only partially applicable.

Relationships among material categories

Some materials belong to more than one of the five categories mentioned above (Figure 3). For example, Co belongs to all except the PV material category. Therefore, it can be promoted as a critical, battery, and/or magnet material, depending on available funding opportunities or the availability of government stimuli. For comparison, barite only belongs in the critical material category, so promotional opportunities for barite are far more constrained. Figure 3 also shows that many well-recognized PV materials (Ge, Ga, In, Te) and As are considered critical materials and have a small market base (they also fit into the specialty material category). As discussed earlier, projects targeting materials that plot within the field of specialty materials are severely constrained by the limited market base. Such projects are unlikely to benefit from the economy-of-scale approach that commonly applies to the production of major commodities such as Al, Cu, and Ni; consequently, early project ranking is essential (Simandl et al., 2021).

Until recently, the narrow market base for specialty materials limited the interest of major mining companies in these commodities. However, many specialty materials, including those used in the PV industry, are by-products recovered during base metal or precious metal smelting. For example, Ge, In, and Cd (Figure 4) are recovered at Teck Resources' integrated Zn and Pb smelting and refining complex in Trail, British Columbia, as by-products of Zn from Red Dog ore (Alaska), and Se and Te dioxide are recovered at the Horne smelter in Rouyn-Noranda, Quebec. Other examples of large operations outside of China recovering at least one of the materials used in thin-film PV technologies (i.e., Te, Se, In, and/or As) are Hamburg, Germany, and Pirdop, Bulgaria, smelters, both operated by Aurubis; Toyo smelter of Sumitomo Metals Mining Co. Ltd. and Saanoseki/Oita belonging to JX Nippon Mining & Metals Co. Ltd., both in Japan; Sterlite smelter operated by Vedanta, India; and Ilo smelter operated by Southern Copper Corp., Peru. Several established companies mentioned above and many start-ups are making inroads into recycling electronic products at smelter facilities.

ECONOMIC GEOLOGY OF PV MATERIALS

This section focuses on the economic geology of PV materials and identifies the main deposit types from which a PV material can be extracted either as the main material (i.e., targeted, dominant constituent in terms of value) or a by-product. Theoretical, global, and/or high-level academic or governmental studies provide many more potential sourcing options beyond those presented here. At first glance, many of the potential PV material sources in such studies will appear very appealing or at least plausible. However, they may not be realistic because of serious or even unsurmountable technical or economic challenges.

Our study reports the abundance of individual PV materials in the earth's crust, identifies the common uses and main markets, and briefly discusses ore deposit types currently being exploited and those that could potentially be mined should market conditions improve. It also provides references to relevant studies or regulations addressing real or perceived health and environmental risks related to individual PV materials. Our approach permits the distinction between economically motivated extraction of PV materials, cases wherein the main incentive for by-

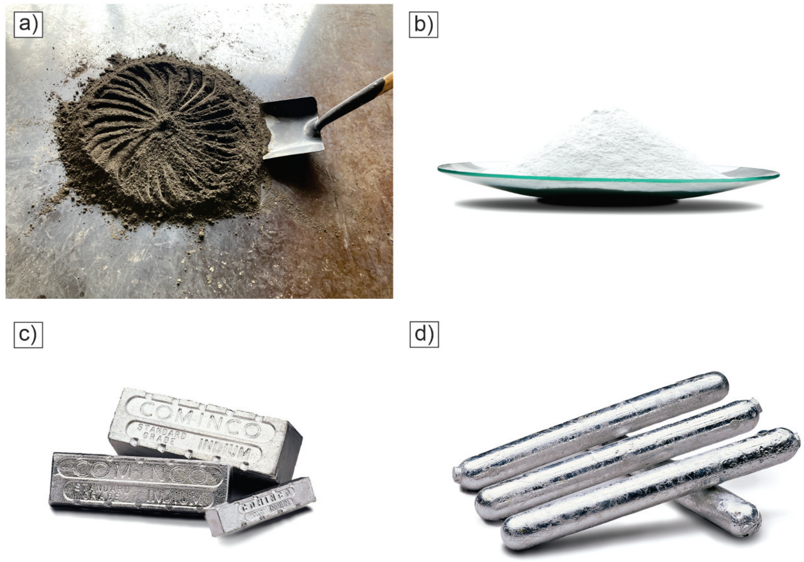

Figure 4. Photovoltaic materials recovered as co-products of base metal smelting: a) Zn-Pb concentrate from Red Dog deposit, Alaska; shovel for scale; b) germanium dioxide free-flowing powder, >99.99% GeO_2; c) indium ingots of standard grade (>99.99% In) weighing 1, 3, and 10 kg; smallest ingot (1 kg) is 150 mm in length; and d) cadmium produced at the Trail smelter, British Columbia, from Zn-Pb concentrates (photographs courtesy of Teck Metals)

product extraction is a technical necessity (e.g., the co-product is an undesirable impurity that must be eliminated from the main product during processing stage) and cases in which a toxic element must be recovered to ensure safe work conditions or eliminate environmental risks.

Silicon

Silicon is a nonmetallic element in Group 14 (carbon family) of the periodic table with atomic number 14. It is the second most abundant element in the earth's crust by weight (31.14%) after oxygen (Rudnick & Gao, 2014). It can be found in a wide variety of minerals and elemental compounds. Silicon dioxide (SiO_2) or silica is one of the most common compounds, forming all quartz polymorphs and varieties, agate, opal, and chert. Quartz is one of the main rock-forming minerals and the main constituent in high-purity sand, sandstone, and quartzite. It is commonly the main constituent of cores of pegmatites and mineralized or barren hydrothermal veins. Silica materials are available on all continents and satisfactory for most common applications, including ferrosilicon and metallurgical-grade silicon (MG-Si). However, in most cases, the silica content of these rocks is too low and the impurities content is too high for direct transformation to solar- or electronic-grade Si.

Solar-grade Si metal

Until 1997, most solar-grade (PV-grade) Si was produced from manufacturing rejects generated from electronic-grade material (Braga, Moreira, Zamperi, Bacchin, & Mei, 2008). Intensive research is underway to produce solar-grade Si economically, safely, and with minimal GHG emissions and environmental impact (Chigondo, 2018). Globally, most of the solar-grade (6N or higher purity) Si is currently obtained by using previously produced MG-Si as a starting material. Metallurgical and chemical methods to achieve this upgrade are reviewed by Chigondo (2018). The raw materials required to produce 1 t of MG-Si comprise 2.7 t of silica material (Figure 5(a,b)) and a similar quantity of reductants (a mixture of low ash coal, charcoal, petroleum coke, and wood chips). The production of MG-Si is energy intensive and requires approximately 11,000–13,000 kWh/t energy input (Legemza, Findorák, Bulľko, & Briančin, 2021). For this reason, the ideal production plant should have access to abundant and low-cost hydroelectric power and be located near acceptable raw material sources and a MG-Si market.

Silica raw materials used to produce MG-Si can be derived from a variety of deposits (Figure 6), including the following:

- barren hydrothermal veins such as Nasafjell quartz veins, Norway (Wanwik, 2015), Quartz Mountain vein, Washington State (Alsobrook & Carr, 1994), and a vein near Hawthone, Nevada (Peterson, 1976)
- cores of pegmatites such as EvjeIveland pegmatite belt, Norway (Müller et al., 2015, 2017; Snook, 2014)

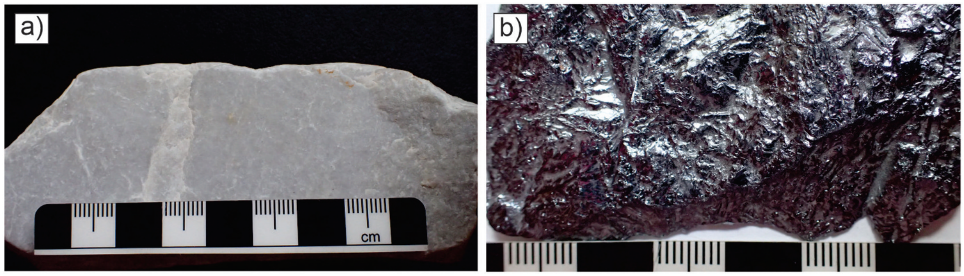

Figure 5. a) Lump of massive and homogeneous quartzite, stratigraphically equivalent to Nonda Formation (locally >95.5% SiO_2), composed of rounded 0.5-mm diameter grains cemented by silica, British Columbia, Canada; b) metallurgical-grade silicon produced by Silicon Metaltech Inc. in Wenatchee, Washington, during the late 1980s from quartzite belonging to the Mount Wilson Formation, southeastern British Columbia (smallest division on scales in both photographs is 1 mm)

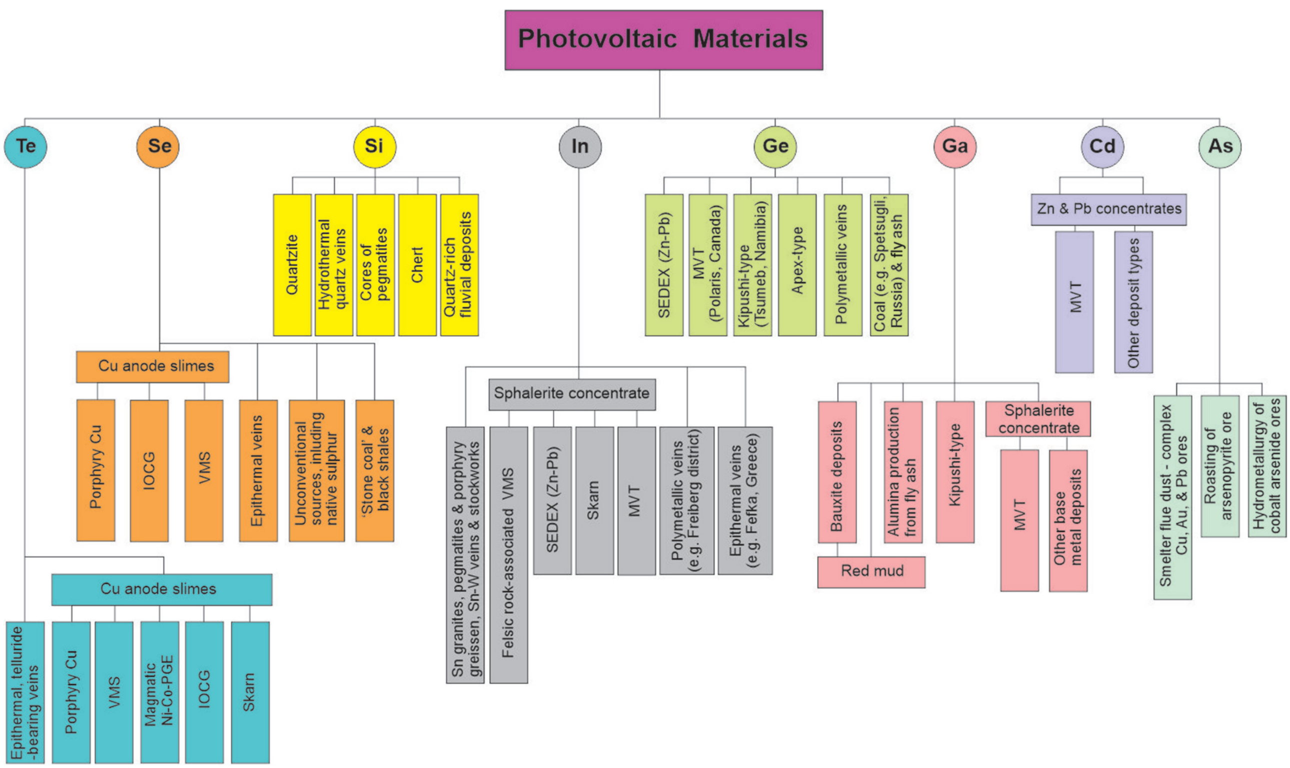

Figure 6. Deposit types providing ore for production of photovoltaic materials. Solar-grade Si is derived from MG-Si that is produced mainly from quartzites. Silica from hydrothermal veins and pegmatites may have fewer chemical impurities but it is not as readily available and, in many cases, it does not meet physical specifications. Blending of raw materials is an option. Indium is recovered mainly as a by-product of Zn from sphalerite concentrates and to a lesser extent from Sn ores. It can be also extracted from complex ores if market permits. Germanium is mainly a by-product of zinc from clastic-dominated sediment-hosted Zn-Pb (SEDEX) and Mississippi Valley-type (MVT) deposits. It is also recovered from three coal deposits (or from the related fly ash) in Russia and China. Gallium is recovered mainly as a by-product of Al from bauxite and to lesser extent as a co-product of Zn. Sphalerite concentrates from low-temperature deposits such as MVT deposits have high Ga content. Some Ga is recovered from coal-related fly ash as by-product of alumina (Al_2O3). Tellurium is recovered mainly from Cu anode slimes created during Cu extraction from Cu concentrates. The concentrates themselves can be created from a variety of deposit types. Extraction of Te from the epithermal precious metal-bearing (e.g., the Emperor Gold Mine, Fiji) and telluride-bearing deposits (e.g., Dashuigou vein system, China) is strongly market dependent. Similarly to Te, selenium is extracted mainly from Cu-anode slimes. Arsenic is largely produced from flue dust during Cu, Au, and Pb smelting, roasting Au-bearing arsenopyrite ores, and the Bou Azzer Co -Ni -Fe -As (±Au, ±Ag) district, Morocco; orpiment and realgar (AsS) are also considered As ore minerals. Large quantities of As trioxide are being recovered globally and safely disposed of or stored/ stockpiled for future use. Abbreviations: IOCG: iron oxide copper-gold; PGE: platinum group element; VMS: volcanogenic massive sulfide

- quartzites such as Tana Mine, Norway (Wanvik, 2015) and the Horse Creek Silica deposit and other deposits within the Mount Wilson and Nonda Formations in British Columbia (Simandl, Jacobsen, & Fischl, 1992)
- coarse components of quartz-rich fluvial deposits such as unconsolidated silica gravel from Pee Dee River area, North Carolina (Alsobrook & Carr, 1994)
- in special cases, cherts such as Moora deposit within the Noondine Chert, Western Australia (Abeysinghe, 2003)

Solar-grade Si is derived largely from MG-Si, which is produced mainly from quartzites. Quartz from hydrothermal veins and pegmatites may have fewer chemical impurities than quartzite lumps but is not as readily available, and in many cases, it does not meet the physical specifications discussed below. The blending of raw materials is an option.

Silica raw materials (generally >99.7% SiO_2, preferably >99.8% SiO_2) used to produce MG-Si (typically >98.5% Si) and chemical-grade Si (99.0–99.99% Si) are relatively readily available, but specifications required by individual Si makers vary. In general, the Al, Fe, Ca, Ti, B, As, and P contents of the raw material are closely monitored. According to Alsobrook and Carr (1994), the source rock should contain more than 98.5% SiO_2 (typically 99.3 to 99.8% SiO_2), <0.1% Fe_2O_3, <0.15% Al_2O_3, <0.2% CaO, <0.2% MgO, and <0.2% loss on ignition (LOI). Some raw materials for chemical-grade Si require higher reactivity and low Al_2O_3 content (e.g., <0.05% Fe_2O_3, <0.10% Al_2O_3, <0.005% CaO, and <0.002% TiO_2; Alsobrook & Carr, 1994).

The chemical composition is not the only parameter that determines the suitability of raw silica material for MG-Si. Physical properties are also important. There is no universally accepted list of silica raw material properties to test, but basic information is provided by Schei, Tuset, and Tveit (1998). The mechanical strength and resistance of silica lumps to thermal shock and softening properties are two of the most important parameters that need to be evaluated (Aasly, 2008; Alsobrook & Carr, 1994). The ideal size of raw material particles (lump size) depends mainly on the design of the plant and the physical properties of the material itself. According to Aasly (2008), raw material particles commonly range from 10 to 150 mm in size. Alsobrook and Carr (1994) indicate that in the USA, silica lumps exceeding 2.54 cm in size are preferred. Because the highest-purity silica materials for MG-Si production have commonly non-ideal physical properties, significant research goes into the selection of raw materials and electrothermal process optimization (e.g., Zobnin, Torgovets, Pikalova, Yussupova, & Atakishiyev, 2018). However, most of this research remains proprietary.

The transformation of silica to MG-Si or chemical-grade Si involves the following carbothermic reduction reaction (Maldonado, 2020; Xakalashe, Tangstad, Jones, & den Hoen, 2011):

$$SiO_2(s) + 2C(s) \rightarrow Si(l) + 2CO(g)$$

MG-Si and chemical-grade Si are classified into a variety of commercial products according to the main contained impurities (commonly Fe, Al, and Ca). For example, designation 553 (typical MG-Si) refers to Si products with ≤0.5% Fe, ≤0.5% Al, and ≤0.3% Ca, and designation 2202 refers to products with ≤0.2% Fe, ≤0.2% Al, and ≤0.02% Ca. The level of impurities is reflected in the price (e.g., Table 2). The main uses of MG-Si and chemical-grade Si are to produce Al and other specialty alloys (ferrosilicon is used largely in the production of ferroalloys) and to manufacture silicone (with applications in sealants, adhesives, lubricants, medicine, cooking utensils, and thermal and electrical insulation), respectively. A small proportion of MG-Si is further chemically or metallurgically purified (e.g., Ceccaroli & Lohne, 2003; Degoulange, Perichaud, & Trassy, 2008; Safarian, Tranell, & Tangstad, 2012; Yadav, Chattopadhyay, & Singh, 2017) to yield polysilicon at ≥99.9999% Si (N6) purity or better for use in the production of solar cells. The Siemens process (including its improved variations) accounts for 90% of polysilicon production. The second most common (alternative) production method relies on a fluidized bed reactor and involves silane pyrolysis (Yadav et al., 2017).

The approximate price of polysilicon over the last 10 years was less than US$30/kg (Figure 7a), compared

Table 2. Examples of common commercial Chinese silicon grades and corresponding prices (SMM, 2022)

Grade[1]	553	521	421[3]	3303	2202
Price (US$)[2]	2,895	3,105	3,255	3,180	4,650

[1]Grade designation (e.g., 553 indicates Fe ≤ 0.5%, Al ≤ 0.5%, and Ca ≤ 0.3%)
[2]Prices as of January 25, 2022; converted assuming 1 RMB = US$0.15, East China; grain size 10-100 mm, packing in jumbo bags
[3]421 is considered by some as chemical grade

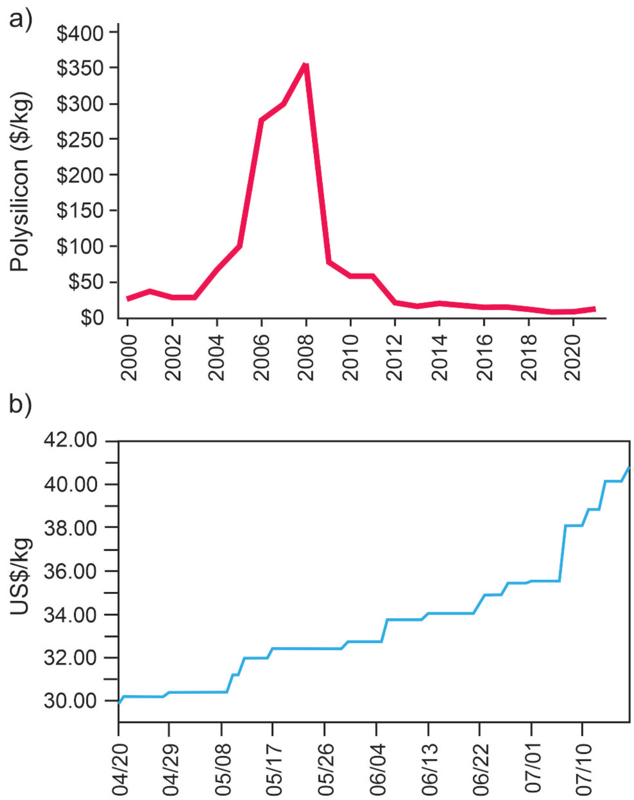

Figure 7. a) Variation in polysilicon spot prices from 2000 to 2021, showing classical spike from 2005 to 2009 (source: BloombergNEF, 2021); b) spot prices of solar grade (1st class) polysilicon in China from April 20 to July 19, 2022 from SunSirs Commodity Data Group (2022)

to less than US$0.05/kg for the raw silica from which it is derived. Processing is energy intensive, and without government interventions, solar-grade Si prices would likely be US$70/kg (Chigondo, 2018; Louwen, van Sark, Schropp, & Faaij, 2016). There is much ongoing research into finding methods to produce solar-grade Si that are lower cost, are less energy intensive, and emit less GHG (e.g., Darghouth, Aouida, & Bessais, 2021; Marchal, Krug, McDonnell, Sun, & Laine, 2015; Moudgal et al., 2022; Nagahata et al., 2021). However, recently, polysilicon prices have increased substantially, and they continue to rise steadily (Figure 7b). This is having an impact on the planning and cost analysis for future projects. Opinions are divided as to what will happen to polysilicon prices over the next year. If they remain strong or further increase for an extended period of time, the door will reopen for alternative PV technologies, and some of the funds previously allocated for future solar energy projects may be reallocated to wind energy projects. The type and quantity of GHG emissions during solar-grade Si metal production are strongly controlled by the source of the electricity used (e.g., coal, hydroelectric, solar, or wind; (Saevarsdottir, Kvande, & Magnusson, 2021). This may be a significant factor in the selection of future Si metal plants if the criticality aspect overrides basic economic considerations and reduction of GHG emissions is considered. However, polysilicon production appears to be following an opposite (100% economically controlled) trend. In 2012, Hemlock was the largest polysilicon producer, whereas in 2020, the top 10 polysilicon producers were (Pickerel, 2021):

(1) Tongwei (China)
(2) Wacker (Germany/USA)
(3) Daqo New Energy (China)
(4) GCL-Poly (China)
(5) Xinte Energy (China)
(6) Xingjiang East Hope New Energy (China)
(7) OCI (South Korea/Malaysia)
(8) Asia Silicon (China)
(9) Hemlock (USA)
(10) Inner Mongolia Dongli Photovoltaic Electronics (China)

Since 2020, GCL has become the second-largest producer, and Wacker dropped to fourth place. Based on recent projections by analyst Johanes Bernreuter, by 2023, China will control 90% of the global production of solar-grade polysilicon (Hall, 2022). According to the same analyst, GCL-Poly, Daqo, and Xinte Energy use very low-cost electricity generated by coal-fired plants (Pickerel, 2021). If this is correct, then the polysilicon produced in the above operations would be accompanied by very high GHG emissions relative to polysilicon from operations relying on hydroelectric power. Furthermore, Si production in Xinjiang East Hope is suspected to be at least partially based on forced labor (U.S. Department of Homeland Security, 2021; Hall, 2022).

Occupational health hazards in the production of solar-grade Si depend on the method used (e.g., Ramírez-Márquez, Villicaña-García, Cansino-Loeza, Segovia-Hernández, & Ponce-Ortega, 2020). Si metal appears to have lower environmental impact than other PV materials used in thin-film technologies; nevertheless, Nguyen, Field, and Sierra-Alvarez (2020) point out that some compounds or intermediate products related to production of solar-grade Si are irritants.

Indium

Indium is a soft, post-transition metal with atomic number 49 and atomic weight of 114.8; it is a member of group 13 on the periodic table (Figure 4c). Its properties are similar to those of its vertical neighbors, Ga and thallium. Indium tin oxide (ITO) accounts for most (probably 70% or more) global In consumption. ITO thin-film coatings are primarily used in flat panel displays (touch screens and flatscreen televisions). Solar panels containing CIGS, alloys, solders, compounds, electrical components, and semiconductors account for the rest of the In market (Schuyler Anderson, 2022a). This element has been reported in ocean seawater, air, soils near smelters, and rainwater (Fowler & Maples-Reynolds, 2015); however, more research is needed on its environmental behavior and increasing concentrations in natural environments (White & Shine, 2016). The potential impacts of In on the environment are considered by Jabłońska-Czapla and Grygoyć (2021), Nguyen et al. (2020), and Nkuissi, Konan, Hartiti, and Ndjaka (2020). Although In is generally considered relatively nontoxic, acute exposure through inhalation and the carcinogenic potential of In compounds are of concern (White & Shine, 2016).

Most In is recovered as a by-product from zinc (sphalerite) concentrates and to a lesser extent from Sn concentrates. It can also be extracted from more-complex ores if market permits. The In content of the continental crust is estimated at 0.066 ppm (Hu & Gao, 2008). The geology of In-bearing resources is addressed by several researchers (e.g., Frenzel, Hirsch, & Gutzmer, 2016a; Paradis, 2015; Schwarz-Schampera & Gunn, 2014; Schwarz-Schampera & Herzig, 2002; Werner et al., 2017). Overall, In is enriched, was extracted from, or is currently produced from a variety of deposit types (Figure 6):

- porphyry Sn deposits (e.g., Llallagua tin porphyry, Bolivia; Hyrsl & Petrov, 2006)
- greisens and related veins and stockworks/breccias such as East Kemptville and Duck Pond, Canada (Wilson, 2019)
- felsic rocks associated with volcanogenic massive sulfide (VMS) deposits such as Kidd Creek, Canada (Pinto et al., 2014), and Neves-Corvo, Portugal (Frenzel et al., 2019; Pinto et al., 2014)
- clastic-dominated sediment-hosted Zn-Pb deposits such as Rammelsberg, Germany, where purified sphalerite concentrate contained 65–75 ppm In (Kraume, Dahlgrün, Ramdohr, & Wilke, 1955)

Structure-controlled Pb-Zn-Ag, Cu-Zn-Pb-Ag-Sn, and Sn-W polymetallic veins such as Ag-rich polymetallic veins of the Freiberg district, Germany (Seifert & Sandmann, 2006), and subepithermal veins and breccias such as Pefka and St. Philippos, Greece (Voudouris et al., 2022), are also important or potential sources of In. Furthermore, In is enriched in some deposits, for example, the Dulong Zn-Sn-In deposit in southwest China (Xu et al., 2021) and skarns within the porphyry-related Morococha district, central Peru (Benites et al., 2021). Overall, Mississippi Valley–type (MVT) deposits have lower In content than clastic-dominated sediment-hosted Zn-Pb deposits, VMS deposits, polymetallic veins, and high temperature replacement deposits (Frenzel et al., 2016a). There are exceptions to this rule such as the MVT Polaris Mine, Canada, where In content of concentrate averaged 100 ppm (Pinto et al., 2014).

Recent advances in In metallurgy are discussed by Pradhan, Panda, and Sukla (2018). World refinery In production is estimated at 900 t/year (Table 1), and production outside China is probably just over 400 t/year. Most market studies agree that significant inroads have been made into In recycling in recent years. According to Pradhan et al. (2018), the tonnage of In obtained via recycling of liquid crystal display monitors exceeds the tonnage mined; however, this statement is not confirmed by Ciacci, Werner, Vassura, & Passarini (2018) and Schuyler Anderson (2022a). Furthermore, because of the recent emphasis on the circular economy, efforts are being made to determine whether In extraction from tailings, such as the Freiberg district tailings, Germany, is economically feasible (e.g., Martin, Janneck, Kermer, Patzig, & Reichel, 2015).

Germanium

Germanium is a metalloid with atomic number 32 and atomic weight of 72.63. It belongs to chemical group 14 in the periodic table. Relative to most other PV materials (e.g., As and Cd), Ge is considered safe. For in-depth reviews of Ge toxicity and potential impacts on the environment, see Jabłońska-Czapla and Grygoyć (2021) and Nkuissi et al. (2020). The Ge content of the continental crust is estimated at 1.3 ppm (Hu & Gao, 2008), and Ge belongs to the PV, critical, and specialty material categories (Figure 3).

The geology of Ge was reviewed by Frenzel, Ketris, and Gutzmer (2014), Frenzel, Ketris, Seifert, and Gutzmer (2016b), Melcher, Buchholz, and Gunn (2014), and Shanks et al. (2017). The main Ge-bearing deposit types are shown in Figure 6. Despite relatively low Ge content, clastic-dominated sediment-hosted Zn-Pb deposits are currently the main sources of Ge because of the large volume of Zn (sphalerite) concentrate being processed (Figure 6). For example, Red Dog in Alaska contains 104–249 ppm Ge in sphalerite (Kelley et al., 2004), and the Alaska Department of Environmental Conservation reports an average of 79 ppm Ge in the Zn concentrate from this deposit (Marsh, Hitzman, &

Leach, 2016). Carbonate-hosted MVT Zn-Pb deposits from Montana, Kentucky, Illinois, and Tennessee deposits average 255 ppm Ge (Bernstein, 1985). Kipushi-type deposits (e.g., Kipushi, DRC, and Tsuneb, Namibia) are or were historically important sources of Ge (Höll, Kling, & Schroll, 2007; Melcher, Buchholz, & Gunn, 2014; Paradis, 2015). These deposits, which are relatively uncommon, may have an average Ge content reaching several hundred ppm in the Cu sulfide-rich portions of the ore bodies. Slags produced by smelting ore from these deposits may also be significant sources of Ge (Höll et al., 2007). Bulk samples (not concentrate) from the Kipushi deposit in DRC averaged 68 ppm Ge (Kampunzu, Cailteux, Kamona, Intiomale, & Melcher, 2009). As with all PV materials (except for Si), there is currently no production from deposits whose main product is Ge. The former Apex Cu mine in Washington State was briefly reactivated (after the Cu ore was exhausted) in the 1980s to mine the oxidized Fe-rich, Ge-bearing material that was left behind. Germanium was concentrated chiefly in goethite (≤0.5% Ge), hematite (≤0.7% Ge), and limonite (≤0.5% Ge), whereas jarosite and limonite were the main Ga hosts, containing up to 0.7% and 2% Ga, respectively (Bernstein, 1986).

Germanium is currently recovered from the fly ash derived from three coal and lignite deposits (Dai et al., 2021): the Spetsugli, a high-Ge coal deposit in Russia (Arbuzov et al., 2021a; Arbuzov, Spears, Ilenok, Chekryzhov, & Ivanov, 2021b; Seredin, Danilcheva, & Piestrynsky, 2001; Seredin & Finkelman, 2008); the Lincang deposit in southwest China (Dai et al., 2021; Hu et al., 2009); and Wulantuga deposit in Inner Mongolia, China (Dai et al., 2021; Dai & Finkelman, 2018). Similar deposits are known or are likely to exist in other parts of the world.

Gallium

Gallium is a metal with atomic number 31 and atomic weight of 69.732. It is part of group 13 (Boron group) of the periodic table; it sits below Al, above In, to the right of Zn, and to the left of Ge. Its physical properties are similar to those of Al and In. Gallium is considered nontoxic in its elemental form and despite its low melting point (29.76 °C), it is safe to handle. Nevertheless, some Ga compounds are mildly toxic, and others are corrosive (e.g., gallium chloride). For an in-depth review of its toxicity and potential impacts on the environment, see Jabłońska-Czapla and Grygoyć (2021), Nguyen et al. (2020), and Nkuissi et al. (2020).

Gallium belongs to the PV, critical, and specialty material categories (Figure 3). Its concentration in the continental crust is estimated at 18.6 ppm (Hu & Gao, 2008). Most of the Ga global yearly production (~90%) is obtained from bauxite ores as a co-product of Al manufacturing (Figure 6), as indicated by Butcher, Brown, and Gunn (2014). The geology of Ga was reviewed by Foley, Jaskula, Kimball, and Schulte (2017), and the compilation of Ga resources in bauxite deposits was provided by Schulte and Foley (2014). Some MVT Zn-Pb deposits (*sensu lato*; including the Irish-type), such as Lisheen, Ireland, contain 300–1,600 ppm Ga (Marsh et al., 2016). The Kipushi-type deposits (e.g., Tsumeb in Namibia; Söhnge & Houghton, 1964) and Kipushi Mine in the Zaire-Zambia copper belt, DRC, produced significant tonnages of Ga (Ivanhoe Mines, 2022). Similar to the MVT deposits, the Kipushi-type deposits are hosted by carbonate platform rocks and are associated with karst, solution collapse breccias, and related features (Foley et al., 2017; Hitzman, Kirkham, Broughton, Thorson, & Selley, 2005). They differ from MVT deposits mainly by their complex polymetallic signatures (Cu-Zn-Pb -Ag-As-Sb-Ge-Ga). Sphalerite is the main Ga-bearing mineral in MVT deposits, whereas gallite occurring as inclusions in renierite, germanite, and Cd-rich sphalerite is the main Ga carrier in Kipushi-type deposits (De Vos, Viaene, Moreau, Wautier, & Bartholomé, 1974). Depending on market conditions, gallium could also be conceivably recovered from the processing of sphalerite ores derived from traditional clastic-dominated sediment-hosted Zn-Pb deposits. For example, the Ga content of sphalerite concentrate from Red Dog, Alaska, is 26 ppm Ga (Marsh et al., 2016). To our knowledge, Ga is not currently recovered from this deposit. It is being recycled from scrap generated during the manufacturing of microelectronic components containing gallium arsenide (GaAs), gallium phosphide (GaP), and gallium nitride (GaN). It is expected that in the future, it will be increasingly recovered from CIGS-based thin-film PV products. Other potential sources of Ga (Figure 6) are coal fly ash, red mud (Al industry waste), and flue dust from furnaces producing elemental P (Lu et al., 2017).

Interestingly, despite its criticality, for economic reasons (at least in part because of the limited market), Ga production is relatively low (Table 1). Most plants that produce Al from bauxite are not recovering Ga (Butcher, Brown, & Gunn, 2014); they treat Ga as an unwanted impurity. High-level theoretical assessments of potential sources also suggest that fly ash produced by coal combustion may become a future source of Ga (Frenzel et al., 2016b). From a practical standpoint, the recovery of Ga as a by-product of base metals appears to be a much better option in western industrialized countries since the combustion of coal is on the decline. No coal deposits are currently mined for their Ga content (Lu et al., 2017), and under current market conditions, the recovery of Ga from fly ash is also uneconomical. Nevertheless, there is continued exploration to find commercially viable methods to recover critical elements, including Ga from fly ash (e.g., Lu et al., 2017; Xue et al., 2019). Less than 5% of fly ash produced in China is processed for the recovery of critical metals (Wang et al., 2018) and probably mostly for Ge recovery.

Cadmium

Cadmium is a silver-white metal (Figure 4d) with atomic number 48. It is chemically similar to Zn and mercury (two adjacent metals within group 12 of the periodic table). It has an oxidation state of + 2 in most of its compounds. Because Cd is a nonbiodegradable toxic substance affecting almost all life forms (including humans), contamination of the environment during mining, extraction, recycling, or disposal of Cd-containing waste is a major environmental concern (Chellaiah, 2018; Suhani, Sahab, Srivastava, & Singh, 2021). Occupational safety and health aspects related to Cd are covered by the U.S. Occupational Safety and Health Administration (2022b). As a relatively low-cost material (Table 1), Cd is used mainly for manufacturing Ni-Cd batteries. Other end uses include CdTe for thin-film solar cells (PVs), radiation-detecting imaging equipment, metal alloys, anticorrosive coatings, stabilizing of polyvinyl chloride (PVC), and pigments (Callaghan, 2022).

The Cd content of the continental crust is estimated to be 0.06 ppm (Hu & Gao, 2008). Primary Cd is recovered mainly from sphalerite concentrates as a by-product of Zn production. It is also recovered to a lesser extent as a co-product of Pb production (Figure 6). In general, the Cd content of sphalerite concentrates from high-temperature ore deposits (e.g., porphyry Cu and skarn deposits) is lower than that of sphalerite concentrates from low-temperature deposits such as MVT deposits (Schwartz, 2000; Wen et al., 2016). Consequently, from a geologist's perspective, concentrates from MVT or clastic-dominated sediment-hosted Zn-Pb deposits are a good source of Cd (Figure 6). However, Cd is not universally recovered as a by-product of Zn because of existing market constraints, and in some countries, relaxed or unenforced regulations concerning the disposal of Cd-containing slags or tailings do not encourage recovery of this metal. A significant proportion of Cd is recycled from spent batteries.

Tellurium

Tellurium is a silver-white metalloid with the atomic number 52. It belongs to group 16 of the periodic table. It has similar chemical properties to Se and S, two adjacent elements within the same group. The Te content of the continental crust is estimated at 0.027 ppm (Hu & Gao, 2008). Relative to Se and As, Te is considered to be mildly toxic. For in-depth reviews of toxicity and potential impacts on the environment, see Jabłońska-Czapla and Grygoyć (2021) and Nkuissi et al. (2020).

Predominant uses of Te are in the production of CdTe for thin-film solar cells (40%), bismuth telluride (BiTe) for thermoelectric devices used in cooling and energy generation (30%), as an alloying additive (15%), and as a vulcanizing agent and accelerator in the processing of rubber (5%). Other applications include catalysts for synthetic fiber production (10%; Schuyler Anderson, 2022c). Conceivably, Te can be recovered as a by-product during electrorefining of polymetallic sulfide concentrates derived from many porphyry, VMS, magmatic Ni-Cu-PGE (platinum-group element), iron oxide-copper-gold, epithermal, and skarn deposits (Goldfarb et al., 2017).

Globally, most Te (>90%) is recovered from Cu anode slimes (Figure 6). Typical Cu and silver (Ag) anode slimes contain 1–4% Te; contents up to 9% Te were reported from some refineries in central Asia and Russia (Goldfarb et al., 2017; Moats, Davenport, Demetrio, Robinson, & Kareas, 2007). As a rule of thumb, Te recovery is not economically justifiable if the sulfide ore contains <0.002% Te, and for most operations, the recovery of Te hardly exceeds 0.065 kg/t Cu (Yin, 1995, 1996; Yin & Shi, 2020). The above rule of thumb should be applied with caution because Te prices have fluctuated significantly since 1996. The reasons for the low recovery rates of valuable metals such as gold (Au), Ag, and Te from Cu slimes are discussed by Green (2013).

In the past, Te was processed from Au-Te ores at the Vatukoula (formerly Emperor Gold Mine) epithermal deposit in Fiji, but it is not currently being recovered (Börner et al., 2021). Since the 1990s, few deposits were reported in literature as being mined primarily for Te. Two of these are vein systems in southwestern China, commonly referred to as Dashuigou and Majiagou (Goldfarb et al., 2017; Mao et al., 2002; Yin & Shi, 2020), where Te is present largely in tellurides, mainly tetradymite (Yin & Shi, 2020). The Dashuigou deposit was mined as a source of sulfur (S) for 10 years before Te was discovered in corresponding tailings. The deposit was recognized as a source of Te and later, Au, Bi, Ag, and Se were confirmed as possible co-products (Jingwen, Yuchuan, & Jiaxiu, 1995). After more than 35 years, the search for environmentally and economically acceptable methods to extract Te from Dashuigou is ongoing (Shao, Diao, Ji, & Li, 2020), and the same applies to other telluride-bearing veins (e.g., Yang et al., 2019).

The Kankberg deposit in Sweden, interpreted as a VMS deposit (Goldfarb et al., 2017), was originally mined for Cu and Zn. Currently, it is mined for Au, Ag, and Te. From 2012 to 2020, 3.4 million t of ore averaging 3.6 g/t Au, 9 g/t Ag, and 162 g/t Te were extracted (Voight & Bradley, 2020). Depending on the criticality of Te and the prices of Te, Au, and Ag in the future, this deposit may be considered a Te-Au mine. However, under current market conditions, the value of contained Te in the ore is approximately 5% of that of contained Au.

Selenium

Selenium is a nonmetal with atomic number 34. It belongs to group 16 (chalcogens) of the periodic table. Its properties are intermediate to those of S and Te located directly above and below it, respectively. Selenium shares some similarities with As.

Environmental issues related to Se are reviewed by Gebreeyessus and Zewge (2019), who report that low doses (<40 μg/day) of dietary Se are essential for human health, but higher doses (>400 μg/day) have adverse physiological effects. Severe Se deficiency can cause health problems in humans (e.g., Keshan disease), as discussed by Li et al. (2013). Environmental contamination and human poisoning with high concentrations of Se (selenosis) have been documented in many parts of the world (e.g., Fordyce 2007), including the classic Yutangba village case in China. Historically, stone coal (combustible, low-heat value, high-rank black shale) enriched in Se was mined near this village. Because of Se contamination, all local livestock died, and 19 of 23 villagers showed symptoms of Se poisoning (Mao, Su, & Yan, 1990; Mao, Zheng, & Su, 1997; Zhu et al., 2012).

As discussed earlier, Se is an essential component of CIGS used in the manufacturing of thin-film solar cells. However, its main uses are in electrolytic production of Mn, as a minor constituent in a variety of Cu, Pb, and steel alloys (40% combined), and in glass manufacturing (25%). Other uses include the manufacturing of blasting caps, as a selective oxidation catalyst, in plating solutions, and in rubber compounding chemicals (Schuyler Anderson, 2022b). Amorphous Si and CdTe are possible substitutes for CIGS in thin-film PV technology.

The Se content of the continental crust is estimated at 0.09 ppm (Rudnick & Gao, 2014). Some porphyry Cu, iron oxide-copper-gold, VMS, epithermal, and native S deposits (Figure 6) and a wide variety of unconventional occurrences (e.g., phosphorites, shales, polymetallic nodules, and marine seafloor sediments) are rich in Se. Coal is reported to contain 0.5–12 ppm Se, but under current market conditions, Se extraction from coal is not economical (Funari et al., 2021). Similar to Te, most Se (approximately 90% of its total annual production) is recovered as a by-product during Cu refining (Figure 6) from Cu anode slimes (Kavlak & Graedel, 2013; Lu, Chang, Yang, & Xie, 2015). Such slimes commonly contain 5–25% Se and 2–10% Te. They are also commonly enriched in Au, Ag, and PGEs, whose recovery is the focus of Cu slime treatment; thus, the recovery rates for Se and Te are low, 50% and 70–80%, respectively (Ludvigsson & Larsson, 2003; Lu et al., 2015; Wang, 2011).

Should the Se market improve significantly, it is conceivable that efforts would be made to recover Se from Cu anode slimes more efficiently (Lu et al., 2015). Furthermore, Se could potentially be recovered from the La'erma and Qiongmo Au-Se chert- and slate-hosted deposits in China (Wen & Qiu, 1999), where the Se content commonly ranges from 18.0 to 57.5 ppm, with a maximum of 7,700 ppm (Liu, Zheng, Liu, & Su, 2000). Potentially, it could also be recovered from other black shale-hosted deposits such as Zunyi (Ni-Mo-Se) and Yutangba (Se) deposits in China (Wen & Carignan, 2011) and from the Kisgruva-type (Se-Te enriched) VMS deposit in Norway (Bullock et al., 2018).

Arsenic

Arsenic is a metalloid, with atomic number 33 and an atomic weight of 74.9216. It belongs to group 15 of the periodic table and exists in a variety of inorganic and organic forms (Sattar et al., 2016). It is a hazardous metalloid, with associated toxicity and carcinogenicity concerns (Costa, 2019; Mandal & Suzuki, 2002; Sodhi, Kumar, Agrawal, & Singh, 2019). Occupational safety and health aspects related to As are covered by the U.S. Occupational Safety and Health Administration (2022a). High-purity As metal is used as GaAs in PV cells, cellular handsets, and LED (light-emitting diode) bulbs. It is used in automotive lighting and projectile hardening, among other applications. Arsenic is essential in military, space, and telecommunications domains (George, 2021a). In some countries, As is still used in wood preservatives; this may account for a significant proportion of the global tonnage (~32,000 t; Table 1). Silicon and CdTe are the main potential substitutes for GaAs in solar-cell applications.

The As content of the continental crust is estimated at 5.7 ppm (Hu & Gao, 2008). Information in the public domain is limited regarding As production. This is in part because most commercial-grade As is produced in countries that historically provided limited access to technical and environmentally relevant information (i.e., China, Morocco, and Russia; Table 1). Globally, As is mostly recovered in the form of smelter flue dust (Figure 6), as many operations try to avoid the stigma associated with well-known historic As contamination issues.

Arsenic is a major constituent in arsenides, sulfides, oxides, arsenates, and arsenites. It commonly occurs in metalliferous deposits in close association with Cu, Fe, V, Co, scandium (Sc), Ni, Mn, chromium (Cr), Zn, titanium (Ti), Au, Cd, Pb, Ag, antimony (Sb), P, tungsten (W), and molybdenum (Mo). Arsenopyrite (FeAsS), found in high-temperature hydrothermal precious metal (mainly Au)-bearing and polymetallic veins, is perceived to be the main As-bearing mineral. However, As-rich pyrite [$Fe(S,As)_2$] is probably widespread (Smedley & Kinniburgh, 2002). Arsenic has been recovered from Cu-Au ores (e.g., enargite, Cu_3AsS_4) and other nonferrous or precious metal-bearing ore minerals found in porphyry Cu deposits, VMS deposits (Long, Peng, & Bradshaw, 2012; Nazari, Radzinski, & Ghahreman, 2017), and "five-element vein type" deposits where it is a major constituent (Scharrer, Kreissl, & Markl, 2019).

Current As production comes largely from flue dust produced during Cu, Au, and Pb smelting, roasting Au-bearing arsenopyrite ores, and the Bou Azzer Co-Ni-Fe-As (±Au, ±Ag) district (Morocco). Realgar (AsS) and orpiment (As_2S_3), typically found in low-temperature geological settings, were used to produce As in China (Wu et al., 2017), Peru, and the Philippines. Arsenic is found in some hot spring settings and in the volcanic sublimates (Pekov et al., 2018). Arsenic-containing residues and smelter dusts from nonferrous metal plants represent a large As resource, but they are not commonly processed to recover marketable As trioxide and are disposed of or stockpiled for future refining (George, 2021b). For example, 237,000 t of As trioxide was stored underground in the Yellowknife Giant Mine in northern Canada, which produced gold from 1948 to 2004 (Government of the Northwest Territories, 2022). Large quantities of As trioxide are being recovered globally and safely disposed of or stockpiled for future use.

Details of As metallurgy and As immobilization are not within the scope of this paper. An excellent review is provided by Nazari et al. (2017). We are not aware of any ongoing exploration program targeting As as a primary commodity.

DISCUSSION

There is a fundamental difference between assessing the availability of solar-grade Si (the primary product and workhorse of the PV industry) and other active materials used in thin-film PV cells. The latter materials are recovered mainly as by-products of precious and base metals. Furthermore, In, Ge, Ga, Cd, Te, Se, and As have market bases ranging from 130 to 32,000 t/year (Table 1), well below the upper limit defining the specialty material category (i.e., 200,000 t). Consequently, the classical concept of economy of scale does not apply to the development of projects targeting these materials (Simandl et al., 2021). Furthermore, except for Se and Cd, thin-film PV materials belong to the critical material category, and Cd also belongs to the battery material category (Figure 3).

Geological availability, exploration implications, and aspects of economic recovery

A wide variety of deposit types are enriched in PV materials (Figure 6). However, except for Si, only under special market circumstances are the PV material-bearing deposit-types considered to be primary (principal) exploration targets. In most cases, PV materials are co-products of base or precious metal recovery. However, under current market conditions, the recovery of these co-products is not economical for many operations. For example, during Cu production, slimes from copper anodes are an important potential source of critical materials (e.g., Se, Te, As, Sb, and Bi). Among these, Se, Te, and As are of particular interest because they are considered to be PV materials. Recent estimates indicate that such slimes could theoretically provide 7,900 t/year Se, 2,300 t/year Te, and 24,000 t/year As (Moats, Alagha, & Awuah-Offei, 2021). Therefore, Cu slimes alone contain more than twice the current global annual Se production, more than four times the current global annual Te production, and an equivalent of three quarters of the global annual As production (Table 1).

Similar to Cu anode slimes, which are a potential source of Se, Te, and As, Zn concentrates represent an important potential source of Ge, Cd, In (Figure 6), and to a much lesser extent Ga, which is obtained mainly (90% of global production) from bauxite ores as a co-product of Al manufacturing.

Theoretically, although unlikely, the annual supply of a given PV material (e.g., Ge, Ga In, Cd, Te, Se, or As) recovered as a by-product of its associated primary commodity (e.g., Al, Cu, Zn, Pb, Ni, and Au) could be augmented by increasing the production of the corresponding base or precious metal (assuming that the appropriate circuits within smelters have adequate capacities). More realistically, however, supplies of a given PV material can be increased by adding appropriate recovery circuits to existing smelters that currently do not recover those materials (Simandl et al., 2021) or by "sweetening" the regular smelter feed by blending in a small tonnage of ore concentrate from a deposit rich in the highly sought-after by-product. Frenzel, Mikolajczak, Reuter, and Gutzmer (2017) considered the supply potentials of Ga, Ge, and In as by-products from base metal ores and concluded that their supply potential significantly exceeds current primary production; their findings are consistent with our conclusions.

Photovoltaic materials as exploration targets

It is possible that in the future and under appropriate market conditions, the targeting of deposit types with high or above average contents of PV materials could become common practice. In exceptional circumstances, such deposits may possibly become primary exploration targets (e.g., Apex Mine and Kipushi-type deposits for Ge; Vatukoula Au-Te epithermal deposit in Fiji for Te). Current methods used in the exploration for base and precious metals can be applied in the search for PV materials, with some degree of customization. The "direct indicator mineral exploration" concept, based on the application of traditional geochemical concepts in combination with modern mineral liberation analysis —originally developed and tested in the field for Nb- and REE-bearing deposits—is applicable to a wide variety of specialty material-bearing deposits, including those containing elevated concentrations of Ge, Ga, In, and Te (Simandl et al., 2017).

The cost of criticality

Despite having a modest market base, PV materials are the subject of concentrated efforts by the United States, European Union, Japan, Russia, China, and many other industrialized countries to establish or maintain their own ("safe") supply chains (Simandl et al., 2021). Under these circumstances, the law of supply and demand *sensu stricto* does not apply. Duplication of exploration and development efforts is taking place, and unless commonsense prevails, subeconomic projects will be developed. The European Union, the United States, and Japan should at least partially rely on supply of raw materials from world-class deposits or smelters located in Canada and Australia or in other allied countries, rather than forcing development of subeconomic deposits at home.

Circular economy

A potential developer must keep in mind that market conditions for PV materials may be affected by changes in environmental regulations and/or society's degree of adherence to the principle of a circular economy. This is particularly the case for materials such as Cd, Se, and As, which are monitored very closely by environmental agencies in most developed countries. In those countries, extracting Cd, Se, and As as co- or by-products of base or precious metals may be less expensive than their long-term storage/immobilization in tailings or their continuous extraction from tailing effluents. Nevertheless, the fact remains that in 2016, many Cu smelters considered Sb, As, bismuth (Bi), Cd, chlorine (Cl), fluorine (F), Pb, mercury (Hg), uranium (U), and Zn in complex Cu ores as deleterious penalty impurities (International Mining Newsletter, 2016). To the authors' knowledge, the situation has not changed significantly since 2016. There is nothing wrong with the circular economy concept as summarized by Merli et al. (2018), but currently, some PV materials (e.g., As, Se, and Cd) can be perceived either as valuable materials or deleterious impurities (based on their concentration, market conditions, smelter design, and other factors). Obviously, the reconciliation of the high-level circular economy approach and a pragmatic "from the ground up" approach based on technical parameters and mineral economics is required.

Price fluctuations and spikes typifying specialty and critical materials

A sharp increase in price (a price spike) of any material, including those covered by this paper, may lead to an exploration rush, expansion of existing production, addition of new circuits to recover temporarily overpriced by-product, temporary increases in production by existing suppliers, and even the development of new projects. Potential developers and investors should be aware of price spikes that are especially common in the case of specialty materials (Simandl et al., 2021). Excellent examples are the prices of polysilicon (primary product; Figure 7a) and Te (by-product of Cu; Figure 8). In both cases, a sharp rise in price was contemporaneous with a material shortage, and the price came down as soon as demand was satisfied. Of particular interest is Te because it is largely a co-product of Cu processing. The sharp rise in the Te price from 2005 to 2011 preceded the recent sharp increase in global Te refinery production, which was accompanied by a price decline (Figure 8). More importantly, it appears that, contrary to what most of us would expect, the intensity ratio of Te recovery (defined as tonnes of Te recovered/tonnes of Cu produced) decreased significantly from 4×10^{-5} in the 1960s to 1×10^{-5} in 2010 (Bustamante, Gaustad, & Alonso, 2018). The improvements in metallurgical recoveries at existing plants, the discovery of new deposit type(s), technological breakthroughs, material substitutions by end-users, and increasing levels of

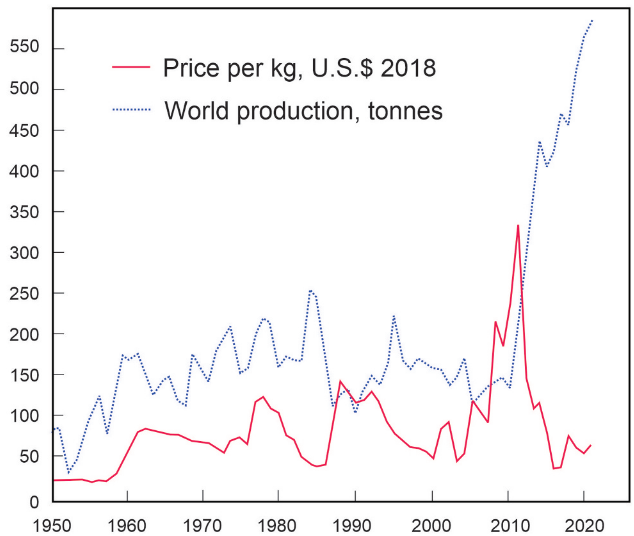

Figure 8. Tellurium refinery production and price from 1950 to 2021 (modified from Smith, Holwell, & Keith, 2019)

recycling may all have an important impact on future markets and affect commodity prices. Furthermore, starting materials used in thin-film PVs require a minimum of 6N purity (99.9999%) (Jamarkattel et al., 2020; Munshi et al., 2019). Most of the polysilicon used in PV applications currently range from 8N to 11N (U.S. Department of Energy, 2022). The costs of purifying the element from 2N or 3N to 6N or better are substantial and in many cases require access to proprietary technology. The purification step is commonly under-emphasized or skipped over during promotional activities aimed at potential investors, in high-level governmental or scientific studies, and by the global media.

Which PV materials will dominate in the future?

Silicon is a widespread, naturally occurring material in the earth's crust. Therefore, by extension, monocrystalline solar-grade Si is considered benign to the environment relative to competing thin-film technologies incorporating Cd, Te, As, Se, In, Ge, and Ga. This is a huge advantage from a promotional point of view. However, the issues related to recycling and disposal of PV cells, panels, and modules are not as clear-cut as presented to the general public by commercial installers of PV panels. For this reason, chemical composition and the end-of-life issues specific to PV cells, panels, and modules (including those based on monocrystalline Si) are subject to intense scrutiny (e.g., Ballif, Haug, Boccard, Verlinden, & Hahn, 2022; Deng, Chang, Ouyang, & Chong, 2019; Dias et al., 2021; Heath et al., 2020). At this stage, it is difficult to determine what long-term influence these environmental impact studies and life-cycle analyses of PV modules will have on the selection of PV materials in the future and which type of modules will be favored in the long term.

In the short- or medium-term, shortages of PV raw materials due to a lack of resources in the ground are highly unlikely because resources are globally available and geographically unconstrained. The smelting and refining stages of supply chains are geopolitically constrained (Table 1). It is more likely that shortages will be caused by supply disruptions linked to civil unrest, military conflicts, pandemics, and supply chain bottlenecks (e.g., the lack of capacity to produce sufficient tonnage of polysilicon of 6N purity or better). Should the public pressure create sufficient resistance so that manufacturers boycott sources of polysilicon relying on slave labor or those having unacceptably high GHG emissions/t of product, polysilicon shortages may develop.

SUMMARY

The world is going through an exploration and development boom fueled by anticipated market growth projections and government and manufacturer concerns for the availability of "critical" raw materials. Most PV materials are considered to be critical. Major critical raw material industry users, departments of defense, and governments consider the big picture and tacitly accept that many of the proposed and ongoing exploration and development projects will fail, especially those that are promotional. Individual investors and boards of directors of companies aiming to enter the supply chain and achieve long-term profits need to consider several important factors to minimize their risk. Knowledge of the market base for PV materials and an ability to distinguish between current and projected market conditions are required before committing funds to new exploration or development projects or to the addition of new extraction circuits to existing base metal, precious metal, or Al smelters. Technological breakthroughs, possible material substitutions, the popularity of the circular economy concept, regulations mandating specific material recovery for environmental reasons, and the criticality aspect of the PV domain make it difficult to project future market growth rates of individual PV materials. Overly optimistic projections of market growth rates or competing criticality-related governmental initiatives internationally (within geopolitically aligned blocks) may result in the addition of new mines, increased smelter recovery capacity, or the ramping up of existing production, ultimately flooding the market. Underestimating the growth rate would result in missed development opportunities and potentially future shortages of PV materials. This can further result in losses in the manufacturing sector, the inability of governments to meet GHG emission reduction targets, and increased concerns for national security.

Here are key aspects that are specific to PV materials:

- Silicon-based solar cells dominate the PV industry. Raw silica materials with the chemical and physical properties required to produce MG-Si are available on all continents. Most of the solar-grade Si currently on the market is being produced from MG-Si as a starting material.
- Silicon production is energy intensive; therefore, sites with abundant, clean, and inexpensive hydroelectric power are preferred locations for future Si plants. Consequently, global Si production is geographically constrained by the historic availability of abundant and inexpensive (not necessarily clean) energy and by relaxed environmental guidelines in China and Russia. These countries remain the largest global suppliers of silicon-ferrosilicon products. Should a less energy intensive and low-cost Si production method be commercialized, the production of Si would not be geographically constrained, and Si would probably dominate the PV industry for many decades to come.
- All PV materials used in thin-film technologies, except for Se and Cd (Table 1), are considered to be critical. Production of these materials (including Se and Cd) is dominated by China. Supply interruptions to European and North American countries due to geopolitical and economic pressures, drought-related hydroelectricity rationing, armed conflicts, or other force majeure events are possible.

Because the expected life of solar panels is estimated to be 25–30 years, which corresponds approximately to the age of the first generation of widely available (commercial) panels, not many panels have been recycled to date. Heavy metal contamination of the environment is of global concern, not only during mining, processing, and manufacturing phases, but also during the recycling and disposal of panels.

CONCLUSIONS

Based on current predictions by the International Energy Agency (2021b), the International Renewable Energy Agency (2022), and others, the future of the PV industry is bright, and there will be increasing demand for PV materials. It remains to be determined whether crystalline Si will remain the predominant technology in the long-term, whether multijunction cells and panels will be fully commercialized, and which materials will be favored for thin-film PVs. If the current quest for maximum conversion efficiency continues, it is probable that polycrystalline Si having 8N to 11N purity will remain the norm in the foreseeable future. The use of 6N or 7N purity Si is now considered a minimum for PV applications. In any case, electrification-related markets open new opportunities for exploration, mining, smelting, and refining companies, who are more than happy to step up their activity to meet increasing long-term demand for solar-grade Si and other PV materials (co-products of base and precious metals exploration). Most, if not all, PV materials are on EU and U.S. critical material lists, and deposits containing these materials are popular exploration targets. In mineral exploration, ranking of projects according to their development potential is recommended to reduce risk; however, it becomes extremely important when dealing with specialty materials (materials with a restricted market base) having high unit value. The high unit value makes these materials worldwide travelers.

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AUTHOR CONTRIBUTIONS

George J. Simandl and Suzanne Paradis proposed this article based on their experience and supplemented it by relevant literature search and original data analysis. Subsequent modifications, complementary research, and critical revisions were conducted by Laura Simandl.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

There are no ethical issues associated with this manuscript.

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