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Critical raw materials in the global high-throughput ceramic industry

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ABSTRACT

The high-throughput ceramic industry is exposed, at the global level, to the risk of shortage and/or sudden price growth of raw materials, particularly Critical Raw Materials (CRMs). The goal of the present study is to overview the dependence on CRMs of a sector transforming a large amount of mineral resources, i.e. the ceramic manufacturing and its supply chain (wall and floor tiles, sanitaryware and tableware, frits and glazes, pigments and inks, and so on). For this purpose, a critical assessment with expert consultation was carried out to quantify demand, uses, recycling and possible substitutes of CRMs. Such data allowed assessing the risk exposure for the ceramic industry at the global level, at the light of expected trends in production and demand for every CRM. The various subsectors into which the high-throughput ceramic industry is divided are exposed differently to supply risk. The production of inks, pigments, dyes and effects for ceramic decoration is mainly exposed to supply risk, and similarly that of frits, glazes and grinding media. End-users of these materials (in particular tile manufacturers) are equally exposed to risk, albeit indirectly. However, the direct use of CRMs in ceramic bodies occurs massively only for feldspar (in different percentages in wall and floor tiles, sanitaryware, and tableware). Other subsectors (silicate refractories and insulators, clay bricks and roof tiles, machinery components, etc.) do not make use of or only make occasional use of certain CRMs. The ceramic industry must implement actions to mitigate the different degrees of supply risk to which the CRM is exposed. The extreme risk (Cobalt and Praseodymium) makes it necessary to search for substitutes and technological solutions to reduce CRM consumption. These actions are also recommended in the case of high risk (Antimony and Lithium). The recommended actions to mitigate moderate risk (Barium, Bismuth, Borates, Feldspar, Tungsten, Vanadium and Yttrium) consist mainly of strengthening the supply chain and improving resource efficiency. No action appears to be necessary for low risk (Cerium, Manganese, Phosphate and Platinum Group), while no risk has been found for Fluorine and Niobium. To ensure the access to CRMs without disruptions, it is appropriate to envisage a medium-long term strategy, involving the various players in the ceramic supply chain.

1. Introduction

The purpose of the present study is to overview the dependence of a high-throughput sector on Critical Raw Materials (hereafter CRMs) taking the ceramic manufacturing and supply chain globally as a case-study. The ceramic industry is a sector transforming mineral raw materials into a wide range of products for various applications: construction, industrial processes, consumer goods and household appliances, healthcare, renewable energies, electronics, transport, and security [1,2]. The perimeter of this study is the part of this industrial sector that has a high-throughput production and its supply chain, i.e., wall and floor tiles, bricks and roof tiles, sanitaryware, tableware and ornamentalware, expanded clay aggregates, clay pipes, and flowerpots. The supply chain includes frits and glazes, pigments and inks, additives, refractories and machinery used in the ceramic production [2,3]. In contrast, the so-called *technical ceramics* are not included, because they

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are the object of high value-added niche applications, making use of a variety of raw materials, individually in small amount [4,5].

The first question, dealing with a mature sector like the ceramic industry and its supply chain, is what does the term “critical raw material” (or “critical mineral”) mean and especially what makes materials critical? [6]. Apart from all raw materials being important, and ceramic production is no exception, some commodities are obviously more of a concern than others [7]. The concept of “criticality” combines a comparatively high risk of supply disruption with a comparatively high economic importance [7,8]. Therefore, the CRM concept does not imply that these materials are considered scarce (or have limited reserves). Furthermore, the criticality can be referred to different levels, from global to regional, up to a single supply chain [9].

The assessment of material “criticality” was first considered by the U. S. National Research Council, which in 2008 proposed a framework based on the impact of a supply restriction and a metal’s supply risk [10]. Afterwards, a variety of methodologies to assess materials criticality have been developed upon that framework, e.g. [6,7,11,12,13]. A review of these studies is beyond the scope of the present paper, and the reader is addressed to existing overviews and discussion about the criticality assessment [14–21].

In the present investigation, we refer to the most recent list of CRMs for the European Union [22], which are classified as ‘critical’ on the following grounds [21,23]:

- having an economic importance that is particularly significant for key sectors of the European economy (e.g., aerospace, defence, health, environmental technologies, consumer electronics, automotive);
- suffering from a high supply risk due to the high concentration of sources in a few countries and the very high dependence on imports;
- being difficult to replace, due to the specific properties of these materials for existing and future applications.

The methodology followed in the determination of criticality is described in the specific literature [7,24].

The industrial ceramics sector is a major consumer of natural raw materials, such as clays, in some specific applications CRMs are used. Thus, the goal of the present study is to quantify, for the first time, the demand of CRMs by the high-throughput ceramic industry, providing details on uses, recycling and possible substitutes. Such data are essential to draw a first assessment of risk exposure for the ceramic industry at the global level, at the light of expected trends in production and demand for every Critical Raw Material.

2. Methodological approach

A detailed study was carried out to identify every specific application where a CRM is used by the high-throughput ceramic industry, consisting of a thorough bibliographic search and expert advice. Extensive published reviews were used to select the bibliographic sources on inks-dyes-pigments [25–27], glazes-frits-engobes [28–30], and ceramic bodies [31–33]. In addition, a panel of twenty-four experts was consulted, individually and confidentially, to prevent conflict of interest. Panellists are technical managers of leading European companies from different branches of the ceramic supply chain (producers of raw materials, wall and floor tiles, inks and pigments, glazes and effects, sanitaryware, tableware, bricks and roof tiles, plants and machinery). This consultation was conducted in the period between the beginning of 2022 and mid-2023. The aim is to collect quantitative information, mainly the concentration of CRM in a certain ingredient of ink/glaze/body and the amount of that ingredient used in each application. It must be considered that the technologies used by the high-throughput ceramic industry are essentially the same all over the world, as are the types of products and components. This globalization ensures the high degree of representativeness of the consultation, not least because technological leadership is held by European industry, which is used to disseminate know-how and innovation to other continents.

The following CRMs were considered (Fig. 1): Antimony, Barium (Barite), Bismuth, Borates, Cobalt, Feldspar, Fluorspar, Lithium, Manganese, Niobium, Platinum Group Metals (PGMs), Phosphorus, Rare Earth Elements (LREEs and HREEs), Strontium, Tungsten, and Vanadium, according to the most recent list of CRMs for the European Union [22]. This list also includes: Aluminium/Bauxite, Arsenic, Beryllium, Coking coal, Gallium, Germanium, Graphite (natural), Hafnium, Helium, Magnesium (metal), Phosphate rock, Scandium, Silicon (metal), Tantalum, and Titanium (metal). These CRMs are used in insignificant quantities (or not at all) by the high-throughput ceramic industry; therefore, they were not considered in the study.

In order to estimate the CRM consumption by the high-throughput ceramic industry, a five-step approach was followed. As the major demand for Critical Raw Materials comes from the ceramic tile production, the two main CRMs’ applications in this subsector are given as examples: digital decoration via inkjet printing (IJP) and full-body (mass-stone) decoration (Fig. 2).

As a first step, the quantity of ceramic tiles manufactured worldwide was taken and the share of tiles subjected to IJP or mass-stone decoration was estimated. The production of ceramic tiles is conventionally expressed in square meters and available data range from 18,399 [34] to 16,377 million square meters [35] for 2021 and 2022, respectively. There are no official data on the breakdown of global production of ceramic tiles for different types of products (e.g., wall or floor tiles; glazed or unglazed tiles; groups according to ISO 13006). Similarly, there is no official information about the global spread of different decoration technologies. Therefore, a reasoned estimate (share percent, converted in square meters) was made based on accessible information regarding production quotas in some countries (Italy, Spain, Turkey, Poland, Brazil) or thanks to data released by technology suppliers regarding the diffusion of IJP or mass-stone decoration (step 1 in Fig. 2). The second step was to obtain a reliable estimate of the average ink weight applied (grams per square meter) for digital decoration and, in parallel, of the average bulk density and tile thickness, to calculate the mass of coloured body (kg). As a third step, the amount of the CRM-bearing ink was evaluated for digital decoration, while in the case of mass-stone decoration, how much pigments are used (both as weight). At the fourth step, the amount of CRM-containing pigment inside the ink was estimated or the same inside the mass-stone colorant (both as weight). The information collected for steps 2, 3 and 4 of Fig. 2 was obtained through interviews with manufacturers of colorants and ceramic tiles. The fifth phase consisted in evaluating the typical concentration of CRM adopted in the industrial production of the ceramic pigment (molar concentration converted into weight percent, then to kg). This result (step 5 of Fig. 2) has been achieved through the scientific literature on pigment synthesis which will be cited on a case-by-case basis in the following sections.

Because the estimates made at each step involve a non-negligible error, the final quantification is affected by considerable uncertainty. A range was reported in the discussion of each CRM, which reflects the breadth of the estimated value window for each stage of the assessment.

A similar approach was followed to estimate the CRMs used in frits, glazes and engobes, obtaining the relevant information through interviews with glaze and frit manufacturers. However, there is a rather wide range of frits and glazes, whose use is not so strictly constrained by technology as in the case of decoration. Therefore, the estimation of the quantities of CRMs consumed is affected by greater uncertainty.

The results obtained for ceramic tiles have been extrapolated globally on the basis of the ratio between European and World production [34,35]. The consumption of CRMs by other subsectors of the ceramic industry was estimated based on the ratio between the production of ceramic tiles and that of sanitaryware, tableware, etc. In most cases, these contributions to the consumption of CRMs were found to fall well within the uncertainty range affecting the main use and therefore partial

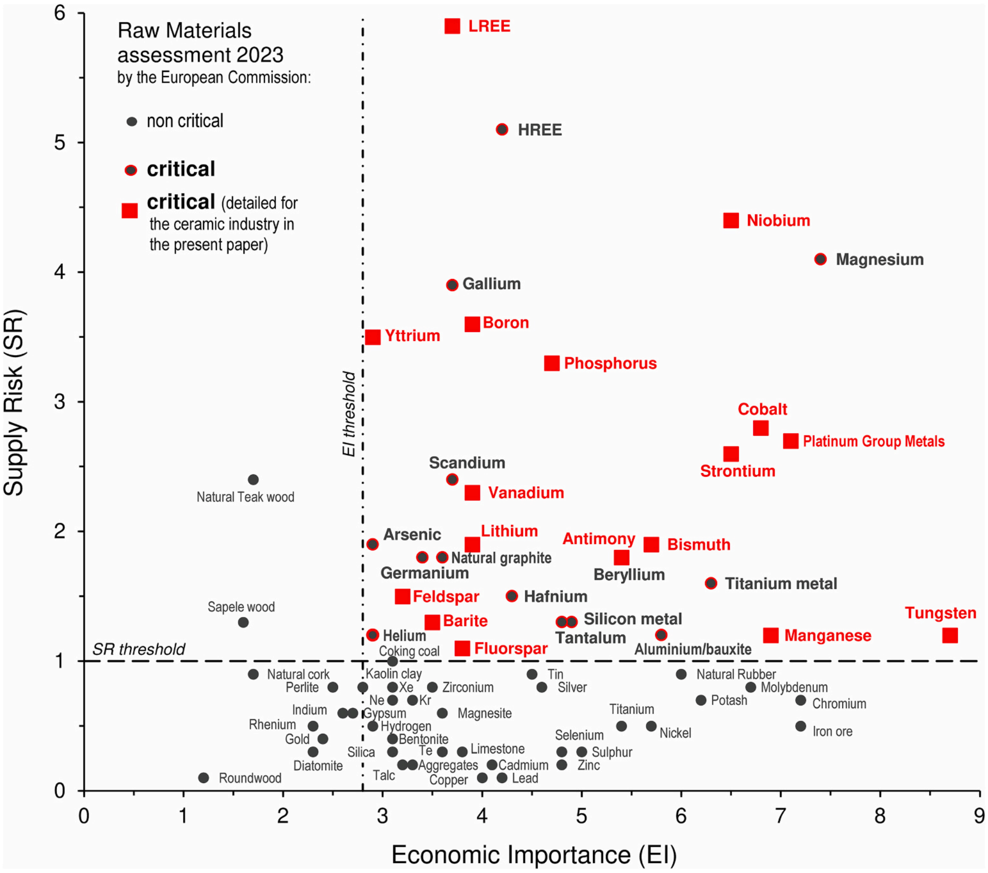

Fig. 1. Assessment 2023 of the raw materials by the European Commission with distinction of non-critical raw materials, CRMs, and those CRMs for the ceramic industry considered in detail in the present paper.

estimates for the various ceramic subsectors are not reported.

The possibility of substitution of a given CRM was evaluated considering technological solutions ready for industrialization or at a good development degree (i.e., demonstrated for a Technology Readiness Level TRL >6). The evaluation is expressed by a scale consisting of five steps: *very difficult* (no technological solution for substitution known to TRL > 6); *difficult* (limited by technological constraints hard to overcome); *feasible* (but only for some ceramic applications); *possible* (limited by some technological obstacles that can be overcome); *available* (already in industrial practice).

The ceramic industry's degree of exposure to the supply risk and price growth of CRMs is represented through five risk profiles: extreme, high, moderate, low, and no risk. These profiles were evaluated on the basis of: i) the share of global consumption of the ceramic industry; ii) the expected future trends in demand and price for each CRM (up to 2030); iii) the possibility of substitution and recycling; iv) the economic and technological relevance of the ceramic application using CRMs. The extreme level absolutely needs actions to mitigate the risk (search for substitutes and technological solutions to reduce CRM consumption). For high-risk exposure, similar actions are recommended. Actions are also strongly suggested to mitigate moderate risk (mainly strengthening the supply chain and improving resource efficiency). No action was recommended to mitigate a low risk. The last profile is risk-free.

3. Results

This chapter examines how critical raw materials are employed by the high-throughput ceramic industry, providing details on commodities, applications, and CRM concentrations in the various materials and components. The way in which a CRM can be replaced in the ceramic production is also critically discussed to provide the information necessary to rank the possibility of substitution. Finally, the demand of the ceramic industry is quantitatively estimated in terms of tonnage, share of global production and related uncertainties and limitations.

3.1. Antimony

Commodity: Sb_2O_3 (sometimes Sb_2O_5) is the industrial source of Antimony.

Use: nowadays the ceramic industry is utilizing Antimony oxide essentially as ingredient of the orange pigment with rutile structure $Ti_{1-2x}Cr_xSb_xO_2$ ($x \sim 0.05$), which has a niche application in body coloration of unglazed porcelain stoneware tiles [26,27]. Further rutile pigments, based on different chromophores (Ni for yellow, V for gray, Mn for brown) have been seldom used in body coloration [27,36,37]. In rutile pigments, Antimony plays as counterion (Sb^{5+}) to balance the charge mismatch due to chromophore incorporation, as between Cr^{3+} and Ti^{4+} [38,39]. In addition, Antimony is occasionally employed as a minor component of the gray pigment $Sn_{1-x}Sb_xO_2$ ($0.3 < x < 0.5$) that is the functional component in electrically conductive glazes for antistatic ceramic floorings [40,41]. This very specific application (e.g., operating theatres, computer rooms) is considered not relevant to the calculation of Sb consumption. Account must be taken that the traditional uses of Antimony have been completely abandoned by the ceramic industry. For instance, the yellow-orange pigment with pyrochlore structure, $Pb_2Sb_2O_7$, usually named *Naples' Yellow*, is listed among the substances of very high concern (i.e., carcinogenic and/or mutagenic and/or persistent, bioaccumulative and toxic) and no longer in industrial use [27,42]. Also, no fining agent is necessary in the production of ceramic glasses (so-called frits) at variance of the silicate glasses for low temperature applications where Antimony is still employed.

Substitutes: Antimony has been sometimes substituted by Niobium, as

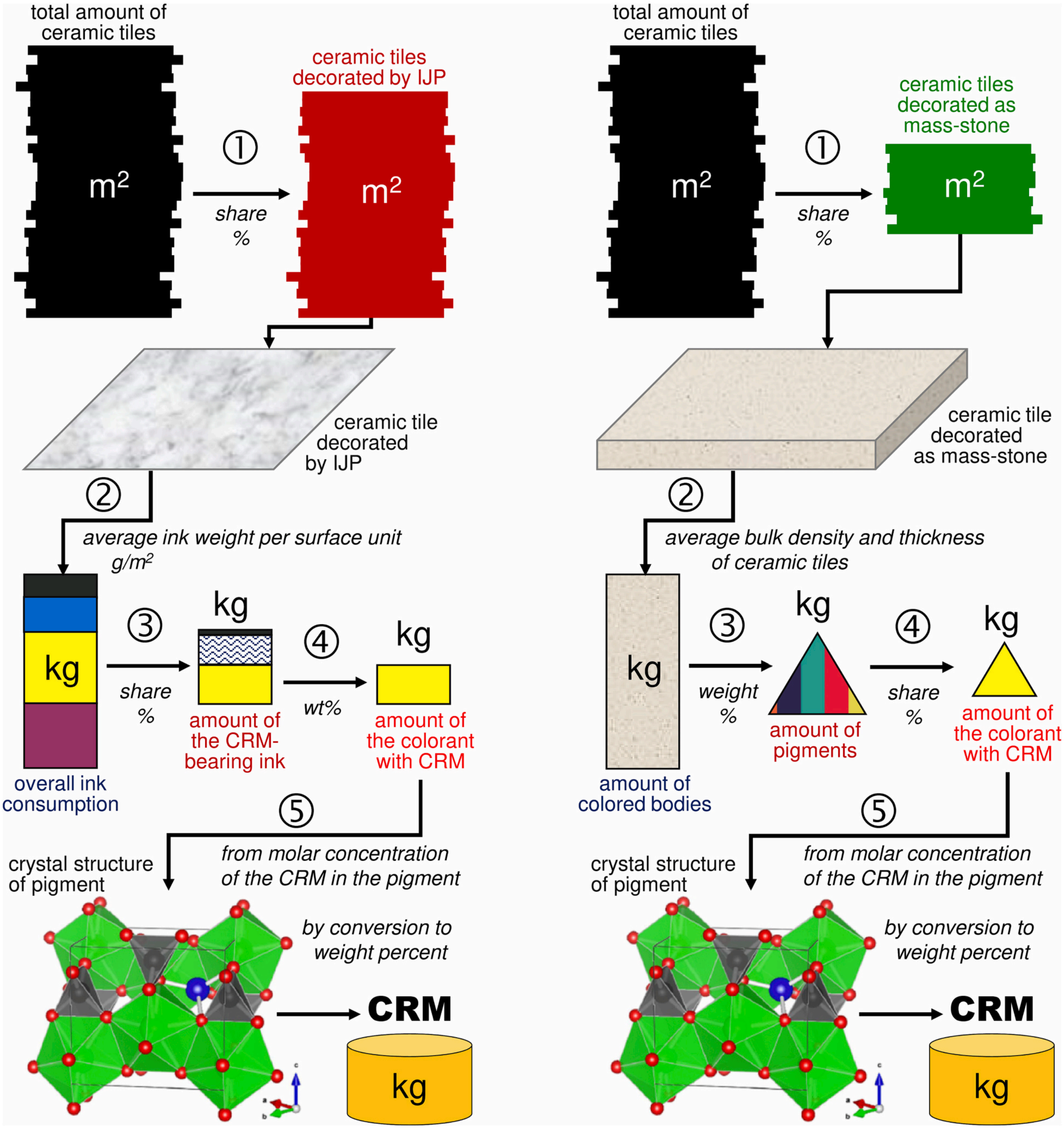

Fig. 2. Methodology followed for estimating the CRM consumption by the ceramic tile industry through inkjet printing decoration (left) and as mass-stone decoration in ceramic bodies (right). See text for explanation of steps 1 to 5.

counterion in industrial rutile pigments, getting similar colors [43,44]. An orange rutile pigment can be obtained by co-doping with Chromium and Tantalum [45]. Another effective counterion is Tungsten but, when used in place of Antimony in Cr-doped rutile pigments, it gives rise to a tobacco brown shade instead of the orange color [27,39]. In any case, the orange pigment $Ti_{1\text{-}2x}Cr_xSb_xO_2$ can be replaced by a proper mixture of pigments for body coloration, e.g., yellow zircon and reddish brown spinel [27]. Nevertheless, the alternative yellow, based on the zircon structure, contains some Praseodymium as chromophore ion (that is among the CRM within the LREE).

Demand by the ceramic industry: approximately 1500 ± 300 tons per year of Sb_2O_5. Such an uncertainty is due to the lack of information on the actual use of the $Ti_{1\text{-}2x}Cr_xSb_xO_2$ pigment at a global level. Thus, the share of the ceramic industry over the global output of Antimony metal (~142,000 tons per year [46]) is estimated at 0.8 ± 0.1%. This value must be compared to recent evaluations, where the glass and ceramics industries would together account for about 5% of the global demand for Antimony [46,47].

3.2. Barium

Commodity: Barium carbonate, $BaCO_3$, is commonly utilized in the ceramic industry as a source of barium.

Use: Barium is a common, but not ubiquitous, component in frits for ceramic tiles and third-fire decorations: from 1% to over 20% BaO by weight, going from high temperature (1200 °C) to low temperature (700 °C) firing schedules [28]. Barium carbonate is widely used in the ceramic industry as an ingredient in glazes acting as a flux, a matting and crystallizing agent (Table 1). Sometimes, $BaCO_3$ is added directly in glaze formulation instead of frit ingredient. Other common applications see $BaCO_3$ as sintering additive in steatite porcelain utilized as electrical insulator [48] and as additive in clay bodies to prevent alkali sulphate efflorescence, especially in brickmaking [49]. Barium occurs as main ingredient of ceramic pigments, uniquely for the primrose priderite $Ba(Ti,Ni)_8O_{16}$ [50] and the yellow perovskite $Ba(Sn,Tb)O_3$ [51]. The former is no longer utilized, while the latter has never entered industrial use (both for color strength worse than the yellow pigments nowadays in use).

Substitutes: in glazes, Strontium carbonate is a candidate to substitute Barium carbonate, thanks to chemical affinity of the elements. The feasibility of replacement by other ions (e.g., Pb^{2+}, K^+) is hindered by significant differences in chemical properties and crystal-chemistry (ionic radius and valence). Barium-containing residues, particularly PC and TV screen glass scrap, can replace Ba in frits [52]. Another potential source is the slag from barite treatment, but more research is needed to exploit it as ceramic raw material [53].

Demand by the ceramic industry: the use of $BaCO_3$ in the manufacture of frits and glazes for ceramic tiles, sanitaryware, tableware, and electrical insulators is estimated at around 110,000 ± 15,000 tons per year. This is about 1.5 ± 0.2% of the global consumption of $BaCO_3$ (~7.6 million tons, converted from barite production of ~9 million t, according to [46]). The use as anti-efflorescence additive in brick production is extremely difficult to quantify, but could double the Barium consumption, making the overall ceramic demand close to 3% of the $BaCO_3$ output. This figure falls, however, within the 10% market share of Chemicals [46].

3.3. Bismuth

Commodity: Bismuth oxide, Bi_2O_3, is commonly utilized in the ceramic industry as a source of Bismuth.

Use: The principal uses of Bismuth are in the manufacture of pharmaceuticals, fusible alloys (low melting) and as metallurgical additives [54]. Other uses include nuclear applications, electroceramics, low temperature frits, and pigments. Bismuth is a substitute for Lead in low temperature frits in the $PbO–B_2O_3–SiO_2$ system typically used as enamel for automotive application, glass decoration, and some third-fire applications in ceramic tiles due to the toxicity of Lead [55]. In the ceramic tile industry Bismuth is used as ink to produce a bas-relief pattern on the glaze surface (sink effect). In the past, this effect was achieved typically by applying low melting point compounds such as V_2O_5, but Vanadium pentoxide toxicity and carcinogenicity makes the use of $BiVO_4$ an alternative [27]. Other uses of Bismuth are related to the production of antistatic glazes for ceramic tiles, in which Bismuth plays the role of SnO_2 dopant [56], and antimicrobial glazes [57,58]. Both are niche applications and are not relevant in the calculation of Bismuth consumption.

Substitutes: Bismuth can be replaced by other fluxing oxides in low temperature frits such as Boron and Lead, although none of them are good substitutes. The first due to boron compounds are classified as critical raw materials, while the second because of its toxicity (in fact the industry has replaced Pb_3O_4 by B_2O_3). The use of waste materials, such as Bi-slag, is problematic due to the systematic association with Lead [54,59].

Demand by the ceramic industry: the use of Bi_2O_3 as sink effect in digital decoration can account for 140 ± 20 tons per year. These figures correspond to a share of the ceramic industry as high as 1.2 ± 0.2% of the global market (~10,000 tons per year as Bi metal) that is destined for ~80% to Chemicals [46,60] among which Bi_2O_3 is considered.

3.4. Borates

Commodity: a wide range of raw materials are used as boron source in the ceramic industry: borax ($Na_2B_4O_7·10H_2O$), borax pentahydrate ($Na_2B_4O_7·5H_2O$), anhydrous borax ($Na_2B_4O_7$), colemanite ($CaB_3O_4(OH)_3·H_2O$), ulexite ($NaCaB_5O_6(OH)_6·5H_2O$), and boric acid H_3BO_3 [61,62]. The majority of them are synthetic materials, except colemanite and ulexite, which are minerals.

Use: borates are used in the ceramic industry to produce glazes for building and construction materials (wall and floor tiles, bricks, and roof tiles) as well as for low temperature tableware.

Boron oxide together with silicon oxide and to a lesser extent phosphorus oxide are the main glassy network formers. The incorporation of boron into silica glasses results in a decrease in the melt viscosity and surface tension, reaching a minimum from which these properties increase again. This effect known as borate anomaly is due to the change in boron ion coordination from triangular to tetrahedral [63].

Borax, colemanite, and boric acid are widely used as flux in frits for obtaining glazes employed in wall and floor tiles, some types of bricks and roof tiles, low temperature porcelain, and pipes. Typically, boric oxide content in frits ranges from 0 to 10% [64], depending on the firing temperature and cycle duration; the frits for products fired at higher temperature are the ones with the lowest or nil boron content [54,65,66]. Hydrate borates (borax pentahydrate) are commonly used in this application, although loss of H_2O during the fritting process takes place, as well as colemanite which requires a strict control of the Arsenic

Table 1

CRMs in the high-throughput ceramic industry: common and widespread use (■); limited use or niche application (●); rare or occasional use (○); discontinued use or abandon (#).

Critical Raw Material	wall and floor tiles bodies	clay bricks roof tiles	sanitaryware tableware	frits and glazes	pigments and dyes (glaze or mass-stone)	ceramic inks and effects (IJP)	silicate refractories and insulators	machinery components
Antimony				#	■	○		
Barium		○		■	#		●	
Bismuth				○		●		
Borates				■				
Cerium				○		○		
Cobalt					■	■		○
Feldspar	■	○	■	■				
Fluorspar				#	○			
Lithium	○		●	●				
Manganese	○	○			■	■		
Niobium					#	○		○
Phosphate	●		●	○	○			
Platinum Group					●	○		■
Praseodymium					■	■		
Strontium				■				
Tungsten					■			
Vanadium					■	●		
Yttrium					#			■

content. In the steel industry borax is one of the principal ingredients of the enamels used (called porcelain enamels), being the amount of borax in the frit batch between 20 and 45%, much higher than for ceramic tiles because of the lower temperature of the former. Attempts were made to use boron compounds in whiteware bodies (mainly porcelain stoneware tiles) and bricks to reduce the firing temperature. The solubility of most of the boron compounds prevent its use in products manufactured by wet milling, except for boric acid in small proportions ($<1\%$) [67]. The introduction of higher percentages of boron compounds, apart from increasing the slip viscosity produces close porosity [68]. An interesting effect of soluble boron compounds (ulexite) is the increase of the bending strength before firing as a result of the binding properties imparted to the body [69]. Good results were obtained introducing boric acid, borax, colemanite and ulexite in the manufacturing of bricks regarding the reduction of firing temperature [70]. Currently the high cost of the boron compounds and the side-effects make its use in whiteware bodies negligible.

Substitutes: Boron compounds are hard to substitute by other fluxing primary raw materials as the alternatives are harmful (Lead) or included in the Critical Raw Materials List (Bismuth and Strontium). Borosilicate glass scraps, cathodic ray tubes waste and borate beneficiation by-products could be the best candidates for boron substitution [71,72]. Numerous studies have focused on borate extraction residues, which contain a significant amount of B_2O_3, but their ability to replace boron compounds in glazes is frustrated by the presence of contaminants, such as iron [73]. Glass fiber from the wind blades dismantling could be another source of borosilicate glass if an economical process for eliminating the organic resin and other components of the blades is fine-tuned [74].

Demand by the ceramic industry: around 250,000 tons per year (B_2O_3 content) is the presumable consumption of borates by the ceramic industry. This estimate is derived from the known consumption of B_2O_3 in Europe (~17,000 t in 2022, approximately 70% of porcelain stoneware among tiles) and extrapolated globally assuming a 50:50 ratio between porcelain stoneware and porous tiles. Such an estimation corresponds to $6 \pm 1\%$ of the global output of borates (4.13 million tons per year) but it is outstandingly lower than the share usually attributed to glass and ceramics, i.e., 17% [46]. This could be explained by an overwhelming use in borosilicate glass production [75].

3.5. Cobalt

Commodity: typically, the Co_3O_4 mixed-valence oxide is used.

Use: Cobalt is the quintessential chromophore (as Co^{2+}) to impart blue color to ceramic glazes and bodies (Table 2). It is the main component of the Co_2SiO_4 dye (olivine structure) and of two related pigments with spinel structure: $CoAl_2O_4$ and $(Co,Zn)Al_2O_4$ [76]. In addition, Cobalt is a basic ingredient of black pigments with spinel structure and complex composition: $(Co,Mn,Ni,Fe)(Cr,Fe,Mn)_2O_4$ [77]. These are the colorants present into cyan and black inks extensively utilized in ceramic decoration by inkjet printing [78]. The above-mentioned spinel pigments are also used to make blue and black unglazed ceramic bodies, or bluish green in case of $CoCr_2O_4$ and $(Zn,Co)Cr_2O_4$ pigments [27]. Further applications concern niche products, always with limited demand, that include organo-metallic penetrating inks used to bestow blue shades on unglazed porcelain stoneware [78] and a set of ceramic colorants, going from deep blue to gray-blue shades. These include the pigments based on willemite $(Zn,Co)_2SiO_4$ [76], bunsenite (Ni,Co)O, and spinel: Co_2SnO_4, Co_2TiO_4, $(Co,Al)_2(Al,Ti)O_4$ [27] as well as dyes, like $CoLiPO_4$, $Co_3(PO4)_2$ and $MgCoB_2O_5$ [79]. On the other hand, Cobalt can be present in the steel rollers superalloys (e.g., Inconel) that are sometimes employed in heating and cooling zones with lower temperatures inside fast firing kilns. In any case, Co is only a minor ingredient (up to 15%) of some alloys (e.g., Inconel 617 is one of those eventually used).

Substitutes: In the current state of knowledge, Cobalt has no alternative as a blue colorant in ceramic production. The only non-Cobalt based industrial pigments are the Vanadium-doped zircon $ZrSiO_4$:V [80] and the spinel $NiAl_2O_4$ [81]; candidates are willemite $(Zn,Ni)_2SiO_4$ [82], hibonite $Ca(Al,Ni)_{12}O_{19}$ [83] and cuprorivaite $BaCuSi_4O_{10}$ [84]. Indeed, all these pigments give a turquoise color and not a pure blue. The only known non-Cobalt based substance of deep blue color is the Mn-doped $YInO_3$ perovskite [85] but its use is hampered by high cost, insufficient thermal stability, and because it consists of CRM. Alternatively, pigments that give an intense blue with a lower consumption of Cobalt have been sought – for instance willemite $(Zn,Co)_2SiO_4$ [76] or hardystonite $CaZnSi_2O_7$ [86] – however, their performance in ceramic inks does not seem adequate to current industry standards. On the side of black pigments, a range of Cobalt-free spinels are already available, where the alternative chromophore is Ni^{2+}, although they have a slightly lower color performance than the corresponding spinels with Co^{2+} [27]. Steel rollers containing Cobalt can be replaced by other superalloys (Co-free or with a lower content of this metal).

Demand by the ceramic industry: ceramic colorants account for a consumption of approximately 5700 ± 1000 tons per year of CoO. In terms of global demand of Cobalt (~136,000 tons of Co metal, converted to CoO) the ceramic sector is worth about $3.5 \pm 0.6\%$. This figure is about one fifth of the Cobalt amount globally dedicated to "intentionally dissipative uses" (17% according to [46]).

Table 2
Main pigments, dyes and effects used by the ceramic industry (CRMs highlighted in **bold**).

Color/effect	Digital decoration by inkjet printing	Mass-stone applications
Blue, Cyan	spinel $\mathbf{Co}Al_2O_4$ olivine $\mathbf{Co}_2SiO_4$	spinel $\mathbf{Co}Al_2O_4$ zircon $\mathbf{V}$:$ZrSiO_4$
Magenta, Red	malayaite $Ca(Sn,Cr)(Si,Cr)O_5$ spinel $(Fe,\mathbf{Mn})(Cr,Fe)_2O_4$	zircon Fe_2O_3@$ZrSiO_4$ penetrating salt (Fe-organometallics)
Yellow, Orange	zircon $(Zr,\mathbf{Pr})SiO_4$ spinel $Zn(Al,Fe,Cr)_2O_4$	spinel $Zn(Al,Fe,Cr)_2O_4$ rutile $(Ti,Cr,\mathbf{Sb})O_2$
Black	spinel $(\mathbf{Co},Ni,\mathbf{Mn})(Cr,Fe,\mathbf{Mn})_2O_4$	eskolaite $(Cr,Fe)_2O_3$ penetrating salt (**Ru**-organometallics)
Green	spinel $\mathbf{Co}Cr_2O_4$ eskolaite Cr_2O_3	spinel $\mathbf{Co}Cr_2O_4$ eskolaite Cr_2O_3
Sink	clinobisvanite $\mathbf{Bi}VO_4$	
Metallic luster	Iron phosphate $Fe_2Fe(\mathbf{P}_2O_7)_2$	
Glossy-Matt	borosilicate glass (**Ba**,**Sr**)	

3.6. Feldspar

Commodity: a wide range of raw materials with variable amount of feldspars, feldspathoids, Na/K ratio, quartz and accessory minerals [87,88]. Source rocks are igneous (granitoids, pegmatite, aplite, nepheline syenite, rhyolite, porphyry, nepheline phonolite, etc.), sedimentary (arkosic sand and gravel) and metamorphic-metasomatic (albitite, orthogneiss, felsite, quartzite, etc.). The most important sources are albitites (sodic feldspar), pegmatites (potassic and mixed feldspar), granitoids and arkosic sands (quartz-feldspathic materials).

Use: feldspar is essentially utilized as fluxing material in ceramic tiles, sanitaryware, tableware, glazes, glassy coatings, and engobes (Table 1). Its technological role is forming a liquid phase at high temperature, allowing the body densification by viscous flow, and creating a vitreous phase embedding crystalline components. Feldspar is introduced in different amount in the various ceramic batches: from a few percent up to 60% and over, depending on the degree of vitrification required [33,89]. The major applications in the high-throughput industry are in porcelain stoneware tiles and slabs (45–60% of the batch), vitreous china sanitaryware (18–32% of the batch) and in glazes (20–70% of the batch).

Substitutes: alternative fluxing minerals, like sericite (i.e., a microcrystalline form of muscovite), can partially or entirely replace the feldspathic fluxes (Table 3). Sericitic rocks currently in use are pottery stone [90], phyllite [91] and eurite [92]. Further non-feldspathic fluxes are less commonly used and in minor amount in ceramic bodies: talc and chlorite [93,94], diopside [95], Lithium minerals [96], carbonates and basic rocks. Also, waste materials can behave as fluxes in ceramic bodies: a range of waste glasses and mining residues entered in the industrial practice, but only small amounts are usually tolerated [73,89].

Demand by the ceramic industry: the ceramic industry is the end user of most feldspathic materials and feldspar substitutes (i.e., 79% according to a recent assessment [46]). The feldspar yearly extracted worldwide ranges from ~29 million tons in 2016 [89] to ~32 million tons in 2022 [46]. According to these figures, the global share destined for the ceramic industry is estimated at about 25 million tons per year (with physiological fluctuations that can reach ±2 million tons from year to year). This value seems to be lower than expected, based on the production of ceramic tiles and sanitaryware. However, such an estimate of porcelain stoneware tile production may be somewhat in excess or, on the other hand, the extraction of feldspar materials (and/or the use of feldspar substitutes) may be underestimated in some countries, especially in Asia.

3.7. *Fluorspar*

Commodity: NaF, KF, AlF_3, and cryolite (Na_3AlF_6) are the fluorine sources used in the ceramic industry.

Use: Fluorspar is used as a flux in the metallurgical sector, clinker production, glass and ceramic industries, and for making synthetic cryolite for the aluminium sector. Transparent fluorite crystals also have important applications in the optical industry. Fluorides have been used for years in small amounts in glass production to increase the fluidity and opalescence of glasses due to the size of F^- ion that is similar to that of oxygen ion, which replacement can interrupt the glass network [63]. The use of F-containing materials in the glass, fibreglass, and ceramic industries has resulted in kiln corrosion problems and environmental contamination, with HF being emitted [97]. Although the installation of very efficient scrubbing systems in glassmaking factories [98] has led to a significant reduction of HF emissions to the atmosphere, the trend in the glass and ceramic industry is to reduce the use of fluorine compounds [99]. In the past, the ceramic tile industry used F-containing compounds in small proportions in the production of some specific glazes (low melting and high thermal expansion corrective frits), but due to environmental issues (HF emissions) this use is practically non-existent. In porcelainware, Fluorine is utilized in the production of opaque glazes as it promotes phase separation and devitrification of alkaline and alkaline earth fluorides, i.e. NaF and CaF_2 [63], although this procedure is not as effective as devitrification of high refractive index crystals such as zircon. Another use of Fluorine compounds, such as AlF_3 and cryolite, is as mineralizer in the synthesis of calcined pigments when a reducing atmosphere is required. Both compounds melt at low temperature, improving the atomic diffusion during the pigment synthesis and reducing the calcination temperature [31].

Substitutes: Fluorine compounds have been substituted in frits by other fluxing materials, and their use was abandoned, unless occasionally in special products, where a peculiar opalescence cannot be obtained otherwise. The use as mineralizers is substantially limited to cases in which the absence of fluorine is detrimental to the synthesis of pigments.

Demand by the ceramic industry: the decline in the use of F-bearing fluxes, up to the virtual abandonment in the production of frits, restricts the use of fluorides to the synthesis of some pigments. The quantities used globally by the ceramic industry are therefore very small and constitute a negligible fraction of the global fluorspar market.

3.8. *Lithium*

Commodity: The main minerals that are object of exploitation as Lithium sources for the ceramics and glass industries occur in pegmatites: spodumene, lepidolite, petalite, ambligonite-montebrasite, and to a lower extent, eucryptite and triphylite-lithiophilite [100,101]. In the EU, important hard-rock mineral deposits occur in Portugal, Czech Republic, Finland, Germany, Spain, and Austria. Significant brine resources exist in Germany with promising possibilities also in Italy, France, and the United Kingdom [102,103].

Use: In ceramics manufacturing constant Li grades are required. The used products range from simple "high Li content feldspar" (usually with a Li content <0.5% Li_2O), to "glass-grade spodumene" (5% Li_2O) and "high-grade spodumene (7.5% Li_2O), the last both used in enamels and

Table 3
Substitution of CRMs used in the high-throughput ceramic industry.

Critical Raw Material	Global demand* (tons)	Possibility of substitution**	Substitution by			Constraints in replacement		
			non-critical RMs	other CRMs	toxic or SVHC	higher cost	worse performance	hazardous toxicity
Antimony, Sb_2O_5	~1500	++		Nb Ta (W)		●	●	
Barium, $BaCO_3$	~110,000	++		Sr			●	
Bismuth, Bi_2O_3	~140	+		B V	Pb			●
Borates, B_2O_3	~250,000	+		Bi	Pb		●	●
Cerium, CeO_2	~15	+++	Fe	P			●	
Cobalt, CoO	~5700	+		V Y In	Ni		●	
Feldspar	$\sim 25 \times 10^6$	+	other fluxes			●	●	
Fluorspar	<10	+++++	other fluxes					
Lithium, Li	~12,500	++	other fluxes				●	
Manganese, MnO	~2000	++++	Fe Cr	V	Ni	●		●
Niobium, Nb_2O_5	<1	+++++		Sb Ta (W)				
Phosphate, P_2O_5	~15,000	++++	Fe	Ce		●		
Platinum Group, metal	<1	++			Ni		●	
Praseodymium, Pr_6O_{11}	~380	+	Zn Fe Cr	V	Ni		●	●
Strontium, $SrCO_3$	~6500	++	Ca	Ba		●	●	
Tungsten, WO_3	~1500	++		(Sb Nb Ta)			●	
Vanadium, V_2O_5	~75	+			Ni		●	●
Yttrium, Y_2O_3	~150	++	Mg	REE		●	●	

*Global consumption by the high-throughput ceramic industry.
**Indicative scale of the possibility of substitution (demonstrated for a Technology Readiness Level TRL > 6): + (*very difficult*, as no solutions are known at TRL > 6), ++ (*difficult*, as limited by constraints hard to overcome), +++ (*feasible*, but only for some applications), ++++ (*possible*, with obstacles that can be overcome), +++++ (*available*, as already in industrial practice).

glazes [104]. Lithium is therefore used in the form of Li-rich feldspar, mineral concentrates, and Lithium carbonate (glaze and glass production). Lithium is the most reactive flux, and its compounds are required for reducing the melting point, the coefficient of thermal expansion and the viscosity of the blends. Special Lithium chemicals such as Lithium borates, fluorides, citrates, Lithium chloride, phosphate, sulfate, and Lithium manganate are also used for special applications in the ceramics industry [105].

The addition of Lithium in the manufacturing of glazes and enamels, along with the above-mentioned positive effects, also increases strength of ceramic bodies, gloss, luminosity, resistance to chemicals and abrasion, and reduce the viscosity of the glaze [105]. In addition to glazes, Lithium is preferentially used in wall and floor tiles (porcelain stoneware) and tableware (earthenware and porcelain).

In the stoneware and earthenware ceramic segments, Lithium is generally used in the form of Lithium minerals with feldspar. Those minerals are spodumene, which allows a greater enrichment in Li (up to 6.5–7% Li) but with a cost disadvantage, amblygonite, lepidolite (up to 3%, usually 1–1.5% together with feldspars) and petalite, whose industrial enrichment is more difficult. Lepidolite is used mixed with feldspars mainly for whiteware blends. In frits, spodumene (2 to 4%) is used mainly to lower the melting temperature, but Li_2CO_3 is usually preferred [106].

In tableware glazes, the addition of 0.5% Li_2O improves the glass's fluidity, uniformity, and higher gloss [107]. In porcelain, the addition of spodumene concentrate at 1 to 1.6% improves densification, mechanical strength and firing temperature. Small amounts of Li_2O, around 0.91%, promote greater densification of the pieces [107].

In sanitaryware, Lithium is preferably not used in the blend's composition, being replaced by potassium and sodium feldspar, to which other fluxes such as calcium carbonate and dolomite are added, among other compounds.

In some circumstances, the alternative use of feldspars is due to:

- Association of Li raw materials to volatile components for which environmental control to the release of gases in the kilns chimneys tends to be increasingly restricted;
- difficulty on the part of the raw material suppliers, in guaranteeing the necessary constant composition of Li in the ceramic blends;
- Li can cause outgassing issues, generating zones of gas release on the surface of the bodies (particularly in segments such as sanitaryware in which manufacture of very large pieces is necessary);
- Lithium minerals like spodumene have a high processing potential (Li metal for batteries) and therefore, companies prefer to wait for the Li metal market evolution (added value).

In Portugal, currently the only EU producing country, mainly lepidolite, spodumene, petalite, amblygonite, potassic-sodic feldspars (1–1.5% Li), and in much lower extent lepidolite concentrates (3% Li) are used to produce ceramic blends.

Substitutes: Substitution for Lithium compounds in ceramics and glazes is possible with sodic (preferably) and potassic fluxes and even alkaline earth metal fluxes. However, all of these have higher melting points and they do not increase the thermal shock resistance to the same degree as Lithium carbonate [108], in addition to imparting much higher expansion coefficients to ceramic compositions; furthermore, acid attack problems can arise with alkaline earth fluxes. Lithium also promotes clearer transparent glazes and lowers both the melting point and the viscosity of glazes. Lead oxide is also a substitute, but in addition to its toxicity, it is less efficient. Zinc oxide and Barium carbonate may in circumstances substitute Lithium [106]. Considerable potential is provided by low-grade by-products of Lithium mining, which have proven to be good substitutes in ceramic bodies [109]. According to SCRREEN [46], Lithium use in glass and ceramics has no substitutes in 44% share.

Demand by the ceramic industry: the Lithium demand for ceramics has a circa 7% p.a. growing trend [110] despite in overall Lithium end-use applications, the ceramics (and glass) share being increasingly smaller, as opposed to the rapid and strongly growing Lithium-ion-batteries share. Therefore, the demand values have a limited time span. As the 2021 data, the worldwide Lithium demand (in Li content) for ceramics and glass ceramics ranged between 12 and 13kt. This value is obtained considering a world production of 107.9 kt Li [111,112] and 14% share for ceramics and glass (Fig. 3) of the Li end-usage distribution, in which glass has a 2 to 3% share [46,113]. The consumption of Lithium in glass ceramics is circa 1% less than the ceramics consumption, being this relation stable, considering the 2015–2019 period [110,114,115].

Currently, Portugal is the only producer of Lithium mineral concentrates (lepidolite, spodumene, and petalite in minor amount) in the EU, with around 530 t (Li_2O content) in 2021, used in the ceramic and glass-ceramic industry. Most of the concentrates consumed in the EU (~1 kt average p.a. Li between 2012 and 2016) are used in ceramics and glass manufacturing. The domestic EU supply of Li concentrates from Portugal, is directly used in this sector, filling a small part (17% in 2016) of the in-use demand [116]. The EU consumption (2016) was approximately 2.8 kt [116], corresponding to circa 11% share of world Lithium consumption in ceramics.

3.9. Manganese

Commodity: manganese oxides, MnO, Mn_2O_3 or MnO_2.

Use: Manganese has just niche applications in the high-throughput ceramic industry, essentially in colorants and as additive in clay bodies (Table 1). Large scale use of Manganese is made mainly in complex spinel formulations, as major ingredient of the jacobsite-like black to coffee pigment $(Mn^{2+},Fe)(Fe,Mn^{3+})_2O_4$ or as minor component of the chromite-like black pigment $(Co,Ni,Mn^{2+},Fe)(Cr,Fe,Mn^{3+})_2O_4$ and the corundum pink pigment $(Al,Mn^{3+})_2O_3$ [27,77,117]. Rutile gray pigments $(Ti,Mn,Sb)O_2$ (sometimes with Nb or W replacing Sb) are now in disuse, while the perovskite $Y(Mn,In)O_3$ [85] which is the most promising alternative to Cobalt such as blue pigment, has not yet entered industrial use due to high cost of Y and In. A classical use of MnO_2 in brick or tile bodies was as additive to promote oxidation of organic matter and Fe^{2+} in order to prevent black core [118]; this practice is still in use (resulting in a characteristic dark brown), but only for marginal productions. MnO_2 can be utilized as bloating agent in lightweight aggregates to improve expansion [119].

Substitutes: Manganese can be replaced in ceramic pigments by other transition metals, e.g., Fe and Ni in black spinel; Cr in pink corundum; V in gray rutile [27]. However, black inks with best performance usually contain Mn [77] and the peculiar jacobsite coffee-black color cannot be reproduced without manganese. An interesting chance is represented by mining waste, which can be utilized as Mn source for ceramic pigments [120,121]. On the other hand, black core and bloating can be prevented in clay bodies through a proper selection of raw materials and firing schedule.

Demand by the ceramic industry: whether as an additive or in niche applications, the use of manganese oxide by the ceramic industry appears to be limited, ranging around 2000 tons per year. This is a negligible fraction of the global consumption, which amounts annually to 13.5 million tons of Mn metal [46,122].

3.10. Niobium

Commodity: Nb_2O_5

Use: only three applications of Niobium are known in high-throughput ceramic production: pigments, photocatalytic coatings, and steel rollers of fast-firing kilns. In pigments, Nb^{5+} can play as counterion in the rutile structure, making it possible to get orange (Cr as chromophore), yellow (Ni), gray (V), and brown (Mn) colors [38,39,43,44]. However, it is Antimony that is currently used by industry and Niobium-containing pigments are virtually not on the market. Nb-doped titania has been proposed as photoactive component in

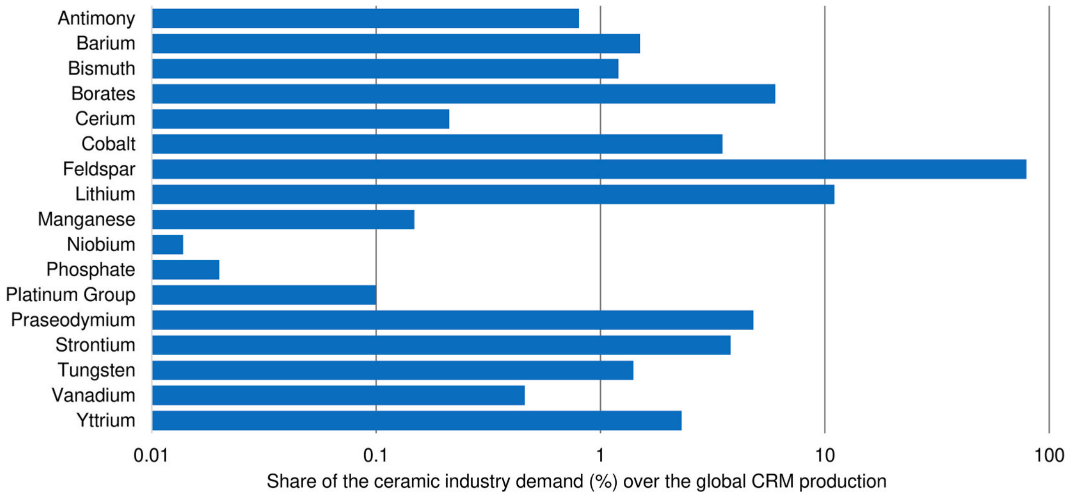

Fig. 3. Consumption of CRMs by the ceramic industry (share of the global CRM production).

coatings with improved photocatalytic activity [123]. At present, self-cleaning and/or antibacterial ceramic products have a limited share of the market, presumably $<1\%$, and are manufactured by licensed technologies, which commonly make use of undoped nanotitania [124]. Niobium containing superalloys are occasionally utilized inside fast-firing kilns, only in heating and cooling zones with lower temperatures. However, Nb occurs as a minor ingredient (up to 5%) only into some alloys (e.g., Inconel 625).

Substitutes: Nb in rutile pigments can be replaced by Sb or W [27] or Ta [45] with more or less the same colorimetric yield. As dopant of anatase for photocatalytic applications, Nb^{5+} can be substituted by other high field strength cations, like Ta^{5+}, W^{5+}, W^{6+} [125]. Niobium in steel rollers can be replaced by Nb-free superalloys with limited loss of performance.

Demand by the ceramic industry: Considering that only the two known applications are rarely put into the industrial practice, the consumption of Niobium due in the ceramic manufacturing can be considered negligible with respect to the global output [126] evaluated at ~72,500 tons per year [46].

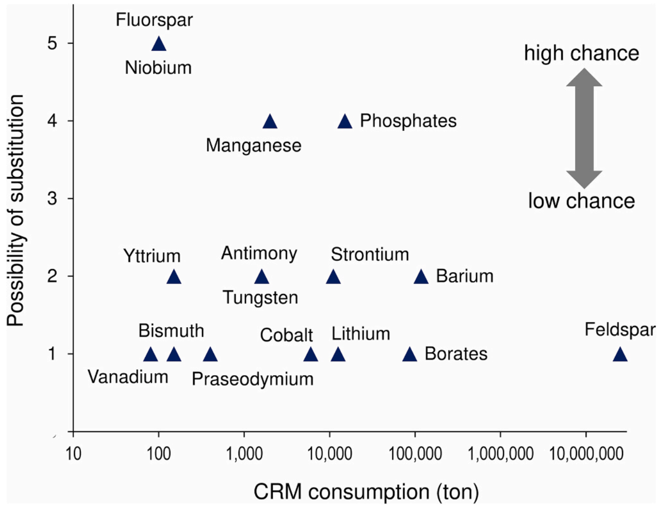

Fig. 4. Consumption of CRMs in the ceramic industry versus their possibility of substitution (1 very difficult, 2 difficult, 3 feasible, 4 possible, 5 available).

3.11. Phosphorus

Commodity: ammonium dihydrogen phosphate $(NH_4)(H_2PO_4)$, sodium tripolyphosphate $Na_5P_3O_{10}$, sodium hexametaphosphate $Na_6P_6O_{18}$, and bone ash (hydroxyapatite from cow bones) are commonly used by the ceramic industry.

Use: the more common application is in ceramic slips, where sodium tripolyphosphate or sodium hexametaphosphate are used as deflocculant [127,128]. A range of phosphate dyes – $LiMPO_4$, $M_2P_2O_7$ and $M_3(PO_4)_2$ with M = Co,Cu,Ni,Fe – is sometimes used to obtain blue, green, brown or yellow colors [27,129,130] typically for medium-low temperature glazes (earthenware and monoporosa tiles). Phosphorus is the major component of bone china (so-called phosphatic porcelain) a kind of tableware, where bone ash constitutes nearly 50% of the batch [131,132]. A classic luster, utilized to impart a metallic gloss to tile surfaces, is based on iron phosphate [133]. Phosphate is sometimes included, as a minor component, in special frits and glazes. Silver sodium zirconium phosphate, $(Na,Ag)Zr_2(PO_4)_3$, is an additive to achieve antibacterial coatings on ceramic tiles and sanitaryware [57,134].

Substitutes: Phosphorus-free alternatives are available on the market for deflocculants, dyes, lusters, and antibacterial coatings; thus, its chance of substitution is considered high (Fig. 4). The only application in which phosphate is irreplaceable is bone china, although alternative sources of phosphorus, such as apatite ore [135] or fishbone [136], have been proposed. The possibility of directly recycling phosphate ceramic waste in the manufacturing of bone china was also evaluated [137].

Demand by the ceramic industry: the consumption of phosphate deflocculants by the ceramic industry can range from 10,000 to 20,000 tons per year, approximately. Phosphate-bearing dyes, lusters and frits represent just niche applications, and their contribution to the overall consumption is negligible. The amount of phosphates used by the ceramic industry is just a minimal fraction of the global market of phosphate ores, overpassing 75 million tons per year [46]. The only industrial concern is about the availability of specific sources (e.g., bone ash).

3.12. Platinum Group Metals

Commodity: Platinum Group Metals (PGMs): Iridium (Ir), Osmium (Os), Palladium (Pd), Platinum (Pt), Rhodium (Rh) and Ruthenium (Ru).

Use: PGMs are not used by the high-throughput ceramic industry, except for three niche applications in decoration (silver lustres and penetrating inks) and kiln furniture (high temperature thermocouples). Precious metal decoration is limited to high value-added tableware and ornamentalware, where lustres are typically hand painted over glaze then fixed by third fire [138]. A range of bright or burnish silver lustres, both based substantially on oil soluble sulphur-linked Platinum complexes, is available for different glazes used in porcelain and earthenware [139]. Penetrating inks (also called *soluble salts*) are sometimes used to decorate porcelain stoneware tiles [27]. These inks are based on organometallic complexes, which penetrate into the unglazed raw body, and the chromatic effects developed during firing are exposed by final polishing. Black color is obtained by Ruthenium complexes, while gray shades can be achieved using Palladium [78]. PGM-thermocouples are commonly used for high-temperature measurements in ceramic kilns. Different thermocouples are available: types B, R, and S (up to ~1800 °C) are based on Pt or a Pt-Rh alloy for conductors, where Rhodium varies from 6% to 30%, by weight [140]. There are further PGM-thermocouples suited for inert atmospheres [141,142]: type P (up to ~1400 °C) that makes use of Pd-Pt-Au (55% Pd and 31% Pt) and Au-Pd alloys (35% Pd, by weight), as well as the Iridium-Rhodium alloy type (up to ~2000 °C).

Substitutes: due to their peculiar chemical and physical properties, PGMs are hardly replaceable by other raw materials. However, platinum lustres can be substituted by other decorations based on metallic alloys and special effect pigments [27]. The decorative effect of penetrating inks cannot be reproduced otherwise, but many patterns can still be successfully rendered via inkjet printing. Alternative thermocouples are commercially available for temperatures up to 1300 °C (types K and N, based on Ni-Cr and Ni-Al alloys or Ni-Cr-Si and Ni-Si-Mg alloys, respectively) and also for higher temperatures (types C, D and G, based on W and W-Re alloys).

Demand by the ceramic industry: the recent change in the tableware market made silver lustres much less popular than in the past decades, and the global demand for Platinum is very limited for this application. The consumption of Ruthenium and Palladium through penetrating inks is restricted to a minor share of unglazed porcelain stoneware tiles and is decreasing given the strong increase in the prices of the two metals since 2016. PGM thermocouples are rather durable, and the corresponding need of Platinum and Rhodium is limited. Overall, the consumption of PGMs by the ceramic industry is estimated to be around few kg per year, that is <1% of the global demand for Pt and Ru, and much less for Rh [46,143]. The demand of Palladium and Iridium by the ceramic industry is negligible, while no application is known for Osmium.

3.13. Light Rare Earth Elements (LREEs)

Commodity: CeO_2 and Pr_6O_{11}; occasionally La_2O_3 and Eu_2O_3

Use: the high-throughput ceramic industry makes use of Praseodymium and Cerium. Attempts spent trying to introduce Lanthanum and Europium in ceramic formulations have not been successful and their use is currently negligible. Further LREEs (Neodymium, Promethium, and Samarium) have sometimes been the subject of research for new ceramic colorants, never entered industrial use [27] and will be not considered. **Cerium** is used by glaze-makers for specialties, where is necessary to develop a pearlescent appearance or a luster effect in glazes and glasses for high temperature firing [144]. Such effects, quite popular in the tile production of the last decades, are currently replaced to a large extent by digital decoration. The Pr-doped cerianite pigment, which imparts red-orange color, reached pre-industrialization [145] but its use was abandoned when decoration was converted to inkjet printing [27]. **Praseodymium** is the yellow chromophore by choice, as it is the essential ingredient of the main yellow pigment, zircon $(Zr,Pr)SiO_4$, which is used in both body coloration and inks [78,146]. About one third of yellow inks for digital decoration contain Pr. This pigment is prepared with a Pr concentration around 3% by weight [147]. **Lanthanum** was sometimes used in replacement of Cerium in a niche product (frit with a peculiar pearlescent appearance, where La tends to enhance the iridescence effect). Tiles with phosphorescent glaze were developed based on **Europium**-doped $SrAl_2O_4$ phosphor [148]. In both cases, their commercial diffusion has been negligible.

Substitutes: Difficult to replace the $(Zr,Pr)SiO_4$ pigment, because its yellow color is the purest and the most intense achievable with ceramic technologies. In inkjet printing, whenever less intense colors are acceptable and firing temperatures are lower, spinel-based beige pigments are used $(Zn,Fe)(Al,Cr,Fe)_2O_4$ [149]. A good candidate for its excellent color purity and saturation would be the zircon-encapsulated CdS pigment, which is however unsuitable for inkjet printing and too expensive for body coloration. There are several industrial yellow pigments (baddeleyite ZrO_2:V, cassiterite SnO_2:V, rutile TiO_2:Ni) that could be an alternative, but their tinctorial strength and technological behaviour are clearly worse than yellow zircon [27]. Similar performances were found for srilankite $ZrTiO_4$, but its doping with Sn, V and Y or In makes it expensive and even richer in CRM [150]. Cerium can be replaced by other luster effects [27] or their appearance can be replicated by digital graphics.

Demand by the ceramic industry: the use of Praseodymium for the zirconium yellow pigment is estimated at around 380 ± 70 tons per year of Pr_6O_{11}. These figures correspond to 4.8 ± 0.8% of the global production (about 6900 tons of Pr, equivalent to 8300 tons of Pr_6O_{11}) and match perfectly with recent estimations [46]. It is difficult to assess how much Cerium enters into ceramic frits and effects: a consumption of the order of 10–20 tons per year can be estimated. However, this is a small fraction of world production (about 70,900 tons per year CeO_2) and also of the 12% share globally attributed to glass and ceramics [46] or the 19% share of ceramics plus pigments [151]. The consumption by the high-throughput ceramic industry of Lanthanum and Europium can be considered negligible, while no use of Neodymium, Promethium, and Samarium is known.

3.14. Heavy Rare Earth Elements (HREEs)

Commodity: Y_2O_3; occasionally Er_2O_3, Dy_2O_3 and Tb_4O_7

Use: heavy rare earths are currently not used for industrial ceramic applications; only Yttrium has been utilized in very small quantities as dopant in ceramic pigments and grinding media. Since a decade, Yttria-stabilized zirconia microbeads are largely employed in the high-energy stirring milling of ceramic pigments to obtain ceramic inks for digital decoration [152]. Due to a considerable wear of such grinding media, this turned to be the main HREE consumption by the high-throughput ceramic production. In addition, attempts have been made to introduce various heavy rare earths as doping substances, some of which have been used in industrial production, such as Holmium, Dysprosium and Terbium. **Yttrium** (Y) in combination with zirconium produces very good high-temperature refractories, as it is stabilized at high temperature in its cubic state. Yttrium (Y) is also used as a ceramic pigment in Yttrium aluminates or Yttrium-aluminium perovskites ($YAlO_3$) or chromium-doped $Y(Al,Cr)O_3$. It is a red-coloured industrial ceramic pigment [153,154]. Baddeleyite is doped with V for offering a pigment with a yellow egg coloration, but also con be tuned using Y, among others [155]. Likewise, srilankite doped with V gives a yellow color but for its synthesis needs the use of Y among other counterions [150,156]. In addition, the zirconate $Y_2Zr_2O_7$ can be co-doped with Cr and Pr [157]. **Erbium** (Er) can be used in glasses and porcelain enamels. Erbium Oxide has a pink color, and was sometimes used as a colorant for glass, cubic zirconia and porcelain. **Holmium** (Ho) can be used in marker technology for ceramic products incorporating inorganic luminescent compositions in the form of pigments. Holmium oxide III acts as colorant and for this reason can be applied in cubic zirconia and glass, providing yellow or red color. **Dysprosium** (Dy) is used as long-lasting phosphorescent pigments of the type $SrAl_2O_4{:}Eu^{2+}, R^{3+}$ (R = Dy,Nd).

Terbium (Tb) as Tb^{4+} can replace Pr^{4+} in bright yellow zircon pigment [158]. Cool pigments are employed to get solar-reflective surfaces in ceramic materials, so a pigment red-orange Tb-Fe doped pyrochlore [159]. The other heavy rare earths (**Thulium, Lutetium**, **Gadolinium** and **Ytterbium**) have been the subject of numerous investigations as doping substances, but in no case, they have been taken into industrial production. There is no evidence of heavy rare earths being used industrially, not even in small quantities in products such as frits, glazes, for producing refractory elements, as elements for machinery used for ceramic production, or other additives. Glazed ceramic pieces with luminescent composition containing a crystalline phase of one or more crystalline oxides of Er, Gd, Yb, Tb and Tm, or combinations thereof, in the form of Er_2O_3, Gd_2O_3, Ho_2O_3, Tb_4O_7 and Tm_2O_3 oxides have also been used [160].

Substitutes: The search for substitutes for red pigments is not easy and several alternatives have been proposed, including perovskite doped pigments, but the synthesis is complicated by an uneasy control on accessory phases [27], as in the case of Cr-doped pyrochlore $Y_2Sn_2O_7$ which generates a burgundy to brown color [161,162] or Cr-doped $Y_2Ti_2O_7$ yielding a reddish-brown color [163] and pink $Er_2(Zr,Ti)_2O_7$ doped with Cr [164] but they all suffer from an insufficient tinctorial strength. Further proposals include $CaYAlO_4$ doped with Cr that exhibits pink shades [165]. Other pigments based on the perovskite structure are the stannates $BaSnO_3$ [51,166], which doped with Terbium (Tb) present a pale yellow or light orange shades, but which have not been tested over the full temperature range of use. Yttrium as a dopant in zirconia grinding media can be replaced by Mg, Ce, or Ca, but with worse performance and durability [167,168].

Demand by the ceramic industry: Dysprosium, Erbium and Terbium are used just occasionally, and always in amounts that are negligible if compared to their respective global productions [151]. No significant use of Gadolinium, Holmium, Lutetium, Thulium, and Ytterbium is known in this sector. The only HREE which finds wide application is Yttrium, essentially as dopant of zirconia grinding media used in the manufacturing of ceramic inks, as the production of Y-based pigments was discontinued after the advent of digital decoration. The consumption of Y_2O_3 due to wear of grinding media can be conservatively estimated at about 150 tons per year (uncertainty between 100 and 200 tons per year) which is worth 2.3 ± 1.1% of global production (5100 tons of metal Y, converted into 6500 tons of Y_2O_3). This is a small part of the 65–72% share attributed to ceramics [46,151].

3.15. Strontium

Commodity: $SrCO_3$ is the industrial source of SrO for the ceramic industry

Use: nowadays the ceramic industry is utilizing Strontium oxide essentially as ingredient of frits and glazes [169] in substitution of Barium oxide and Zinc oxide. Strontium oxide is used in matt frits substituting partially of Barium oxide to slightly modify some properties of the obtained glazes. In this way Strontium oxide increases the thermal expansion and chemical resistance of matt glazes based on Barium oxide. Other properties, such as color and gloss, do not significantly change as the devitrification of Strontium silicates and aluminosilicates during the tile firing takes place.

The second use of SrO is related to the partial substitution of ZnO in transparent and opaque frits due to the high cost of this component [170]. ZnO plays the role of powerful fluxing in both frits and its substitution by SrO up to 20% does not change the glaze characteristics (color, gloss, opacity, thermal expansion, etc.) except for the sealing temperature which slightly decreases. In addition, the use of SrO instead of ZnO also has the advantage of not degrading the inkjet pigments [171]. The introduction of SrO in the system SiO_2–Al_2O_3–CaO–MgO–Na_2O–K_2O has been studied recently [172], confirming the reduction of the characteristic temperatures and viscosity during the glaze melting and giving rise to a higher smoothness surface.

Substitutes: Strontium oxide can be replaced by other alkaline earth oxides such as Calcium and Barium oxides to obtain matt frits in which silicates and aluminosilicates can devitrify during the tile firing, although some changes in the matt appearance and chemical resistance can arise. Other alternatives are the valorization of panel glass from PC-TV screens, in which the presence of BaO (8.0%) and SrO (8.5%) can promote the crystallization of Celsian [173,174] or the valorisation of LCD glass, which contains 4.2% SrO [73].

Demand by the ceramic industry: an accurate assessment of the amount of Strontium used by the European Union ceramic industry led to approximately 1400 tons per year of $SrCO_3$, still, many uncertainties arise trying to extrapolate this figure to the ceramic production worldwide. This is because Sr-bearing glazes and glasses are not made by all manufacturers, but are special products addressed to some types of tiles (and slabs in particular). A conservative estimation – based on the assumption that Sr-containing frits and glazes are used for about one third of the global tile production – leads to approximately 6500 ± 1500 tons per year of $SrCO_3$. This figure represents about 3.8 ± 0.9% of the global market (~144,000 tons, as Sr content, corresponding to ~170,000 tons per year of $SrCO_3$) and falls within the share (5–10%) attributed to glass production [46].

3.16. Tungsten

Commodity: Tungsten oxide, WO_3

Use: Tungsten oxide is utilized by the ceramic industry essentially for colorants and effects [27]. The main application is in body coloration of unglazed porcelain stoneware tiles, through the tobacco-coloured pigment with rutile structure $Ti_{1-2x}Cr_xW_xO_2$ ($x \sim 0.05$), where Tungsten plays as a counterion [38,39]. Additional rutile pigments are known, based on different chromophores (Ni for yellow, V for gray, Mn for brown; all with W as counterion) but have rarely been used in industrial production [26]. Niche applications see Tungsten oxide as ingredient of Ti–Cr–W organometallics for penetrating inks [78] and as luster effects based on scheelite $CaWO_4$ [175]. However, in the last years, the massive use of the inkjet technology has led to the replacement of W to form $CaWO_3$ by a solid solution ZrO_2-CeO_2 which devitrifies from frits [176].

Substitutes: no other ceramic pigment has a tobacco color like W-Cr-bearing rutile. However, a similar shade can be obtained for body coloration by mix design of reddish brown pigments (based on spinel and hematite structures). The luster metallic effect can be obtained with a range of compounds, including iron phosphates, cerianite CeO_2, tenorite CuO, powellite $CaMoO_4$ and NiCoCrAlY alloy [144,177,178].

Demand by the ceramic industry: Tungsten consumption by the high-throughput ceramic industry is thought to be around 1500 tons per year (ranging from 1300 to 1800 tons per year, due to considerable uncertainty in the actual use of W-bearing pigment). This estimate is worth 1.4 ± 0.3% of the global output (~87,000 tons of W metal, corresponding to ~109,000 tons of WO_3) and a significant fraction of the 7–8% share attributed to the use of Tungsten for catalysts and pigments [46,179].

3.17. Vanadium

Commodity: Vanadium pentoxide, V_2O_5, and ammonium metavanadate, NH_4VO_3, are commonly used

Use: in the ceramic sector, Vanadium basically enters the formulation of pigments and effects (Table 1). The advent of digital decoration, however, has led to the disuse of mordant pigments, such as yellows based on Vanadium oxide nanoclusters included in the baddeleyite or cassiterite structures [26], while it has made sink effects applied via inkjet (with V_2O_5 largely replaced by $BiVO_3$) in common use [27]. The most popular V-bearing pigment is the turquoise blue $ZrSiO_4$:V^{4+}, where the chromophore is tetrahedrally coordinated in an interstitial site of the zircon crystal lattice [80,180]. Its use is now restricted to body coloration, and seldom in turquoise blue inks. Niche applications of Vanadium include penetrating inks (buff) and gray rutile pigments [27,36,78].

Substitutes: Vanadium cannot be easily replaced when used as sink effect, as the main alternatives are Lead compounds (long banned from the ceramic industry). Most Vanadium-based pigments have substitutes already widely used: e.g., Zircon-Pr for yellow or hematite-eskolaite for gray [27]. Only the turquoise color does not have an equivalent currently used on an industrial scale; possible alternatives entail pigments with Ni^{2+} in tetrahedral coordination (like hibonite, willemite or spinel) which, however, suffer from the limitations related to the toxicity of nickel oxides [81,82,181,182] and never entered in industrial production. Vanadium-rich waste has been proposed for corundum pigments, but the contextual presence of undesirable elements makes industrial scale-up very difficult [183].

Demand by the ceramic industry: Vanadium consumption in ceramic pigments and effects can be prudently estimated at 70–80 tons per year of V_2O_5 equivalent. This figure reflects the limited use of V-bearing pigments and sink effects in today's digital decoration and represent a negligible fraction of the global production of Vanadium [184].

4. Discussion

The discussion focuses on specific aspects not covered in the previous section, namely recycling, reliability of estimates and risk exposure. This is the first study, as far as is known, to assess the critical issues of the ceramic supply chain.

4.1. Recycling

The ceramic process includes a high temperature consolidation step that implies a profound transformation of raw materials. As a matter of fact, the original minerals are mostly transformed into new formed crystalline or amorphous phases [185,186]. As a consequence, a direct recycling of any residue of the ceramic industry as primary raw material is not possible, and the only cases regard components of machinery, like steel rollers and PGMs present in thermocouples.

What is possible, and widely practiced, is a recycling as secondary raw materials, in particular fired bodies of ceramic tiles, sanitary-ware, bricks and roof tiles [73]. Strictly speaking, it is not a direct recycling like fluxes, since ceramic bodies have chemical and phase composition as well as physical and technological properties modified by the firing process compared to the original feldspathic minerals. Therefore, the replacement of feldspars with ceramic scraps is only possible for limited quantities, usually below 5% by weight in industrial practice.

Most of the CRMs used by the high-throughput ceramic industry are for the decorative coatings (i.e., frits, glazes, pigments, dyes, effects, digital and penetrating inks, Table 1). Ingredients of glazes and frits (Ba, Borates, Ce, Feldspar, Li, Sr) as those of dyes and penetrating inks (Co, P, Pd, Pt, Ru, V) become an integral part of the glass network and are not extractable after mild leaching [186]. The glaze layer on ceramic products is very thin, being common to have just 0.1–0.2 kg per square meter, which can reach up to 0.6 kg/m^2 just for the application of glass shards. The ceramic inks are typically printed on average at 10 g/m^2 as an extremely thin and discontinuous layer between the substrate and a protective glassy cover. The pigment or effect present in the ink is intimately dispersed in the ceramic matrix as ultrafine particles (diameter 300–400 nm). The CRM concentration in the finished product can be estimated to 0.3–0.4 g/m^2 for idiochromatic pigments (spinels containing Co and/or Mn; sink effect based on Bi and V) or below 0.1 g/m^2 for allochromatic pigments (as Pr-bearing yellow zircon) as well as matt or bright effects (containing Ba, Ce, Sr). In the case of mass-stone applications, the pigment is coarser grained (5–20 μm) and is finely dispersed in the ceramic matrix as well, typically in a small amount (1% on average). Any CRM (Co, Mn, Pr, Sb, V, W) is therefore present in low to very low concentration in the ceramic product to be recycled. In all the above-mentioned applications, the CRMs are intimately dispersed in the ceramic matrix (glaze or body) and their use appears to be dissipative, with no chance of recycling under economically sustainable conditions.

4.2. Risk of supply

The various subsectors of the ceramic industry are exposed to different degrees of risk in the CRM supply. It is the production of inks, pigments, dyes and effects for ceramic decoration to be mainly at risk. Analogous situation is that of frits, glazes and grinding media. The end-users of these materials (particularly the tile manufacturers) are therefore exposed to the risk equally, albeit indirectly. However, the direct use of CRM in ceramic bodies occurs massively only for feldspar (in different percentages in wall and floor tiles, sanitaryware, and tableware) while silicate refractories and insulators, clay bricks and roof tiles, and machinery components do not make use of or occasionally use only a few CRMs (essentially Ba, Mn, P).

Different profiles can be drawn by considering the share of CRMs used in the high-throughput ceramic industry on the global production, possibility of substitution and/or recycling, expected market and price trends (Fig. 5):

Extreme risk: Cobalt and Praseodymium – their use by the ceramic industry is common and widespread with an important share of the global production (Table 4). In the next future, a strong increase in demand and price is expected to occur, but any substitution has a low probability of success with current knowledge and technologies. Both Pr and Co are replaceable by alternative pigments, but this solution brings about intolerable changes in the coloring performance. Thus, actions to mitigate the risk are absolutely necessary, particularly the search for adequate substitutes in ceramic inks and the development of technological solutions to substantially reduce the CRM consumption in the ceramic decoration.

High risk: Antimony and Lithium – unlike Lithium, the ceramic use of Antimony appears to be limited to niche applications, which implies a small share of the global production. However, a strong increase in both demand and price must be faced (Table 4). Especially in the last decade, the strong growth trend in Lithium demand for rechargeable batteries has been unbalancing the distribution of the traditional Lithium applications worldwide, with a continuous and hasty loss of share for all other applications. This strong global change will be reflected in the supply of industrial grade Lithium, which demand growth is expected to outpace supply. Consequently, there may be a future risk of under supply of technical grade Lithium compounds, irreplaceable for some segments of the ceramic and glass industry that use Li-based materials in their products. Concerning possible alternatives, Antimony can be substituted in the titania orange pigment by other CRMs (Nb and Ta) but with a considerable cost increase. Lithium replacement in glazes is hindered because alternative solutions suffer from remarkable performance loss, but in other ceramic segments substitution is already practiced. Actions to mitigate the shortage risk are recommended, particularly the search for affordable technological solutions to limit the consumption of Lithium (e.g., substitution by K and Na feldspar combined with other smelters and compounds) and Antimony (e.g., mix design of different pigments).

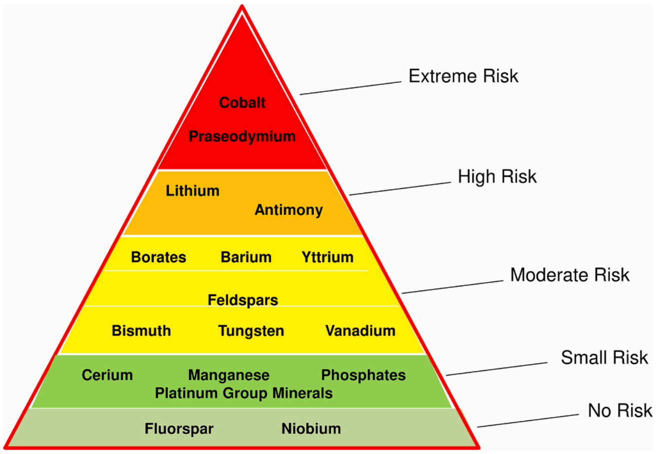

Fig. 5. Profiles of supply risk (shortage and/or price growth of CRMs) at which the high-throughput ceramic industry is exposed.

Table 4
Share of CRMs used in the high-throughput ceramic industry on the global production, past and expected market trends [46] and price variation [111].

Critical Raw Material	Global demand* (tons)	Share of the ceramic industry over the global CRM production	Global CRM demand		Price variation	
			2016–2022	2023–2030	2016–2022	2023–2030
Antimony, Sb_2O_5	~1500	0.8%	-25%	+40%	+90%	strong increase
Barium, $BaCO_3$	~110,000	1.5%	stable	+30%	-9%	increase
Bismuth, Bi_2O_3	~140	1.2%	+10%	slight increase	-14%	slight increase
Borates, B_2O_3	~250,000	6%	-20%	+20%	+20%	increase
Cerium, CeO_2	~15	<0.1%	stable	stable	stable	decrease
Cobalt, CoO	~5700	3.5%	stable	strong increase	+140%	strong increase
Feldspar	~25 × 10^6	79%	stable	slight increase	+60%	slight increase
Fluorspar	<10	<0.1%	+40%	increase	stable	slight increase
Lithium, Li	~12,500	11%	+150%	strong increase	+320%	strong increase
Manganese, MnO	~2000	<0.1%	+25%	increase	+45%	increase
Niobium, Nb_2O_5	<1	<0.1%	+20%	+20%	stable	slight increase
Phosphate, P_2O_5	~15,000	<0.1%	-10%	slight increase	+15%	slight increase
Platinum Group, metal	<1	<0.5%	stable	slight increase	Ru** +1300%	increase
Praseodymium, Pr_6O_{11}	~380	4.8%	+100%	strong increase	+60%	strong increase
Strontium, $SrCO_3$	~6500	3.8%	+70%	increase	+80%	increase
Tungsten, WO_3	~1500	1.4%	stable	+40%	+80%	increase
Vanadium, V_2O_5	~75	<0.1%	+30%	increase	+170%	increase
Yttrium, Y_2O_3	~150	2.3%	stable	increase	+220%	slight increase

* Global consumption by the high-throughput ceramic industry.
** Ruthenium.

Moderate risk (I): Borates, Barium and Yttrium – common and widespread use by the ceramic industry with a small but significant share of the global production. For all three CRMs, the outlook seems to predict some increase in both price and demand. The main concern is the difficulty to substitute Ba in high temperature frits and glazes (and B in lower temperature ones). At the moment, this replacement is possible only by a toxic and banned substance (Pb instead of B) or through other CRMs (Sr instead of Ba; Bi instead of B) or accepting a worse performance (surface roughness feel and acid attack) if Ca is used instead of Ba. Actions to mitigate the risk are therefore strongly suggested, but as substitution seems unlikely in the current state of knowledge, efforts should be directed also towards a strengthening of the supply chain.

Moderate risk (II): Feldspar – the ceramic industry is the major end-user, but strong differences in price and demand exist upon the types of feldspathic materials (sodic, potassic, mixed Na-K, quartz-feldspathic, etc.). The risk mitigation should basically act to prevent criticalities in the supply chain of key raw materials, especially the high grade sodic and potassic feldspars.

Moderate risk (III): Bismuth, Tungsten and Vanadium find a very specific use in ceramic production and gain a very small share of the global output. Nonetheless, some increase in demand and price for these CRMs is expected, making it advisable to find solutions to mitigate the supply risk. The replacement of Bi, V and W is theoretically feasible with alternative pigments and effects (but with a significant increase in cost, loss of performance, or use of toxic substances, such as PbO). These cases are problematic because it is objectively difficult to replace the CRM in its niche application, while the economic conditions for an in-depth search for alternative solutions commonly do not exist. Therefore, actions to mitigate risk should focus on improving resource efficiency, optimizing CRM consumption to be able to withstand possible price increases.

Low risk: Cerium, Manganese, Phosphate, and Platinum Group Metals – ceramic applications represent <0.1% of their global market, and stable or limited increase in price and demand are forecast. Furthermore, they are easy to replace when in common and widespread use (Mn and P). When of special use, there are already substitutions as ingredient of pigments and inks. Thus, no action seems necessary to mitigate the risk.

No risk: Fluorine and Niobium – use in strong decline and easily substitutable in the ceramic industry. No worries about expected price and demand increase.

4.3. Data reliability

This paper seeks to provide, for the first time, a complete and homogeneous picture of the dependence of the high-throughput ceramic industry on CRMs. Since there are no global statistics on ceramic production, the data obtained are the result of complex estimates (based on various parameters adopted in industrial practice) and elaborations (optimal values and national or continental statistics extrapolated to a global scale). Nevertheless, the results obtained in many cases correspond to recent estimates, which also indicate a share for ceramics, of the use of CRMs.

However, the figure of the ceramic demand is affected by a certain degree of uncertainty, which has been estimated on a case-by-case basis, and which may represent a significant percentage of the average value. This uncertainty interval gives a measure of how much the actual consumption of CRMs in the ceramic industry can actually deviate from the indicated value. Importantly, by taking the higher or lower values of the uncertainty range, no CRM would change its attribution to a given risk profile of the ceramic supply.

The approach followed in this study was possible thanks to the high degree of homogenisation of ceramic production from a technological point of view. Ceramic tiles (i.e., the subsector that has the greatest impact on the supply of CRMs) are produced all over the world with the same technologies and similar raw materials, especially in the case of decoration and coatings. The global and systematic diffusion of tile decoration by inkjet printing, which is also being transferred to the tableware sector, makes the estimates regarding pigments, dyes and inks rather robust. In fact, it is the strong constraints of inkjet technology [89,187,188] together with the short list of suitable colorants (Table 2) that make it possible to estimate the needs of the ceramic industry with less uncertainty.

The constraints for mass-stone decoration, mainly focused on quantity and cost of the pigments used [26], allow estimates that can be made with a much greater uncertainty. This is a consequence of the little-known fraction of unglazed porcelain stoneware tiles, decorated by mass-stone techniques.

The uncertainties in the evaluation of CRMs used in coatings depend on the fact that the content of B, Ba and Sr varies not only depending on the ceramic product [28,30], but also on the individual choices of glaze manufacturers and end users.

5. Conclusions

The high-throughput ceramic industry is exposed, at the global level, to the risk of shortage and/or sudden price growth of raw materials, even though with clear differences depending on the CRM and the end-user. It should be considered that the production of building materials is fundamentally driven by demographic trends and expectations of improving the standard of living, so no decline in demand for ceramic materials is expected in the decades to come.

In order to estimate the risk exposure for every CRM used in the ceramic production, relevant information has been collected for each industrial subsector by expert consultation and relevant literature. By this way, different risk profiles were drawn by considering the share of CRMs used by the ceramic industry over the global production, possibility of substitution and/or recycling, expected demand and price trends.

The main actions to mitigate supply risk consist of:

A) development of technological solutions capable of reducing CRM consumption (e.g. decoration techniques that require less pigment to obtain the desired color);
B) search for suitable CRMs substitutes (e.g., new Co-free blue pigments or redesign of ceramic batches to replace high-grade feldspars);
C) improving resource efficiency (e.g., by recycling of CRMs or exploiting domestic sources);
D) strengthening the supply chain (i.e., by sustainable logistics and secure access to CRMs sources).

However, technological solutions that allow to replace or use less CRMs in ceramic production are available, as far as the authors knowledge, at low levels of readiness. In addition, any possibility of improving the supply of CRMs through recycling appears very low, because the use in ceramic manufacturing is largely dissipative. This situation requires a considerable R&D effort for industrial scale-up. All this implies the involvement of different skills and know-how as well as considerable costs, which are probably not entirely covered by economic benefits or configure a long time for return on investment, especially in the case of niche applications. For future work, it is therefore appropriate to envisage a medium-long term strategy for the ceramic sector, which makes it possible to go beyond the capabilities of a single industrial group and which involves the entire ceramic supply chain, even better with an international perspective.

Among the various subsectors of the ceramic industry, decoration (inks, pigments, dyes, effects and grinding media) and coatings (frits, glazes) are the most exposed to risk for the supply of CRMs, which is indirectly extended to end-users (especially tile manufacturers). Other subsectors, namely silicate refractories and insulators, clay bricks and roof tiles, and machinery components, do not use, except occasionally, CRMs.

For the ceramic industry, five supply risk profiles have been identified, each of which requires specific mitigating actions (which constitute targets for research in the near future):

- *extreme* (Cobalt and Praseodymium) for which risk mitigation actions (A and B of the above list) are urgently needed;
- *high* (Antimony and Lithium) for which actions A and B are mainly recommended to mitigate the risk;
- *moderate* (Barium, Bismuth, Borates, Feldspar, Tungsten, Vanadium and Yttrium) for which actions C and D are suggested;
- *low* (Cerium, Manganese, Phosphate and Platinum Group) for which no specific actions appear to be compelling;
- *no* risk (Fluorine and Niobium).

CRediT authorship contribution statement

Javier García-Ten: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation, Conceptualization. **Michele Dondi:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Data curation, Conceptualization. **José Vítor M.B. Vieira Lisboa:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Data curation, Conceptualization. **Mónica Vicent Cabedo:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation, Conceptualization. **Luis Pérez-Villarejo:** Writing – review & editing, Writing – original draft, Validation, Investigation, Data curation. **Elisa Rambaldi:** Writing – review & editing, Writing – original draft, Validation, Investigation. **Chiara Zanelli:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

Michele Dondi reports financial support was provided by European Union-Next Generation EU. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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