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Review article

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# Compositional diversity of vitrified silicate ceramics: Delimiting the chemical perimeter of industrial bodies



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#### ABSTRACT

The compositional diversity of vitrified silicate ceramics has been quantified through multivariate statistical analysis and by means of specific chemical parameters of bodies. Distinct compositional spaces can be drawn for porcelains, porcelain stoneware, red stoneware, and silicate glass-ceramics. Porcelain and vitreous china bodies are strongly peraluminous with commonly a potassic character. A sharp boundary at ~79 % alumosity separates them from porcelain stoneware bodies, which are peraluminous with a predominantly sodic character. The comparison of glazed versus unglazed porcelain stoneware revealed essential differences in iron content, but a deeper analysis is needed at the manufacturing district scale. Glass-ceramic bodies are peralkaline and low in silica. Red stoneware is characterized by Fe<sub>2</sub>O<sub>3</sub> content about 3–9 wt% and variable Na/K and alkali-to-alkaliearths ratios. The compositional gap between red stoneware and porcelain stoneware bodies (1.5 % < Fe<sub>2</sub>O<sub>3</sub> < 3 %), still unexploited by industry, is crucial to enable many resource efficiency and waste recycling actions. The formulation of waste-based silicate ceramics usually implies a shift of the chemical composition towards higher Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and lower alkali-to-alkali earth ratio. This can lead to batches that fall outside the compositional space of porcelain stoneware, opening to technological behaviour and technical performance that require further research.

#### 1. Introduction

Vitrified silicate ceramics represent important products in various areas of application, like building materials, household components, and technical ceramics [1,2]. In fact, vitrified silicate ceramics cover most of the global production of tableware, sanitary ware, ceramic tiles, lightweight aggregates [3–7], as well as significant shares in niche applications (e.g., kitchen countertops, electrical insulators, dental prostheses).

These vitrified ceramics are produced with modern variants of materials known since ancient times, such as porcelain [8,9], stoneware [10–12] or crystallizing frits [13,14]. Although knowledge of the properties and formulation of these materials is consolidated, the compositional diversity of the industrial bodies is much less known. Other issues underexplored are the mutual relationships between the different products and whether compositional boundaries between the various materials can be traced.

This lack of knowledge is justified because, for a long time, the ceramic industry produced with conventional formulations and standardized raw materials and the material's composition varied in a rather narrow range even around the world. This situation has changed in recent years under pressure of global drivers:

- shortage of key raw materials: the availability of certain ingredients required in standard formulations (e.g., ball clay, sodic feldspar, potassic feldspar) is well below the potential demand of the ceramic industry [7,15], so much so that in some areas systematic recourse is made to clay or feldspar substitutes [16–20];
- *depletion of mineral deposits*: the ore quality is gradually turning poorer in most mining districts [21,22] and the standard raw materials have been supplying as lower grades (for example, lower alkali content in feldspathic fluxes and alumina content in kaolins);
- resource efficiency: concern about the supply of raw materials and byproducts from local sources is growing [23,24] beyond the constraint of poorer technological properties, because they ensure greater economic and environmental sustainability to mining activities (thanks to lower cost of logistics and full exploitation of deposits);
- *circular economy*: the pressure to increase waste recycling in ceramic production is increasing everywhere and promotes the use of

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residues with different compositional and technological characteristics compared to conventional raw materials [25–28];

- *energy efficiency*: the need to achieve the objectives of reducing CO<sub>2</sub> emissions and energy consumption of ceramic processes [29,30] is pushing towards new batch formulations that allow less intensive firing schedules (lower temperatures and shorter times).

These drivers converge towards a major change in batch design strategies, with greater flexibility in formulations to allow the use of lower grade raw materials and waste materials never used before. The result of these trends is not exactly predictable, apart from an increase in batch complexity, both in terms of the number of ingredients and the alleged expansion of the chemical perimeter [31]. Certainly, any change in the batch design must face knowledge gaps: whether there is a gradual transition or compositional boundaries between the various vitrified silicate ceramics for different applications and, at the same time, whether differences are dictated by technological constraints or by compositional boundaries or both.

A characteristic of silicate ceramics is that the definition of the various materials (porcelain, stoneware, glass-ceramics) is extremely wide and usually linked to non-compositional parameters, such as body compactness and colour [17] or processing [13,14]. This stems from the fact that each material can be used for multiple applications responding to different regulations. In addition, the terminology by which these materials are classified is non-standard, generally descending from technical jargon. So, there are several types of stoneware, distinguished by the body colour (red, white, light-coloured) or its relationship with other materials (porcelain stoneware) or physical characteristics (vitrified or semi-vitrified). In the production of ceramic tiles, both porcelain stoneware (Group BI<sub>a</sub>, water absorption WA<0.5 % in accordance with ISO 13006 standard) and red stoneware (Groups  $BI_b$ , 0.5 % < WA<3 %, and  $BII_a$ , 3 % < WA<6 %) are widely used. In the past, other types of vitrified bodies were used, such as light-coloured stoneware, klinker and fine stoneware (Group BIb) which now have marginal market shares [17]. On the other hand, different types of porcelain have long been defined and their terminology refers either to physical characteristics (hard, soft, vitreous china) or to applications (refractory, electrical, dental, etc.). Although porcelain must meet different regulations, depending on the application, the water absorption requirement is generally <0.5 %.

The goal of this study is to establish the compositional diversity of the main vitrified silicate ceramics (porcelain, stoneware, glass-ceramics in their variants). The rationale is therefore to collect a statistically significant number of chemical compositions of industrial ceramic bodies and identify the compositional perimeter of the various materials, with particular regard to the types with the highest consumption on a global scale, such as porcelain stoneware and red stoneware in the production of ceramic tiles. The other objective is to evaluate possible boundaries or transition zones in the composition of different ceramic materials. In addition, the search for poorly explored compositional spaces can offer the possibility of creating new products designed in terms of resource efficiency and circular economy.

#### 2. Methodological approach

The chemical composition of representative samples of vitrified silicate ceramics has been collected from scientific and technical literature. Overall, 561 bodies were considered, pertaining to various materials for different applications (Table 1).

The number of samples indirectly reflects the industrial relevance and the global volume of production, expressed as million tons per year (Mty), which can currently be estimated at around 130–150 Mty for porcelain stoneware, 100–110 Mty for red stoneware, 10–20 Mty of vitreous china, 10–15 Mty of porcelain, and well below 5 Mty for silicate glass-ceramics and specialty products.

In particular, data regard the following bodies:

272 bodies of both glazed porcelain stoneware (S) [32-53] and unglazed/technical porcelain stoneware [12,54-81] with a ratio of glazed/unglazed tiles close to 1.9:1;

67 bodies of red stoneware (R), without any differentiation between groups [54,82–93];

35 bodies of light-coloured stoneware (L) [35,48,60,83–85,88, 94–96];

22 bodies of vitreous china (V) [9,12,97-106];

- 40 bodies of both hard and soft porcelain (P) [97,107–118];
- 32 bodies of silicate glass-ceramics (G) [18,41,42,77,119-127].

In addition, 93 bodies containing waste materials were considered (W + Y), as proposed in the literature for various applications, to verify where the circular economy can shift product compositions. These are 63 waste-bearing porcelain stoneware (W) bodies [12,34,36,39,40,46, 59,63–65,70,74,77,78,80,118,128–130] and 30 waste-bearing porcelain (Y) bodies [102,104,108,111,112,116,117,131–134].

Specialty products were not taken into account because they represent a very small share of the global output of vitrified silicate ceramics and typically exhibit peculiar chemical features. It is the case of niche applications, like phosphatic porcelain (bone china) for translucent tableware [135], leucitic porcelain for dental prostheses [136], zircon-rich porcelain stoneware for super white unglazed tiles [137,

#### Table 1

Vitrified silicate ceramics: materials, examples of applications and standard requirement for water absorption. In **bold** the materials with the largest industrial use currently.

Material			Code	Application	Water absorption
Stoneware	Porcelain	unglazed	S	ceramic tile, BI <sub>a</sub>	≤ <b>0.5 %</b>
	stoneware	super white	-		
		glazed	S		
	Fine stoneware		F	ceramic tile	<3 %
				tableware	<3 %
Light-coloured stoneware Klinker <b>Red stoneware</b>		L	ceramic tile, BI <sub>b</sub>	0.5–3%	
			-	ceramic tile, BI <sub>b</sub>	0.5–3%
			R	ceramic tile, BI <sub>b</sub>	0.5–3%
				ceramic tile, BII <sub>a</sub>	3–6%
	Chemical stoneware		-	sewage pipes, etc.	<3 %
Porcelain	Vitreous china		v	sanitaryware	<0.5 %
	Hard porcelain		Р	tableware	<0.5 %
	Soft porcelain			tableware	<0.5 %
	Bone china		-	tableware	<0.5 %
	Leucite-bearing porcelain		-	dentistry	<0.5 %
	Electro-porcelain		-	insulators	<0.5 %
Glass- ceramics	various types according crystalline phases	to main	G	low CTE materials, high strength materials, micro-electronics packaging, metal joining, etc.	<0.5 %

138], extruded stoneware for ceramic tiles (klinker) and sewage pipes [96,139], Ba-doped porcelain for electrical insulators [140]. Most silicate glass-ceramics have alumina-poor compositions with SiO<sub>2</sub> below 60 %, so far from the other vitrified silicate ceramics (e.g. [119,141]).

The compositional comparison was made based on chemical parameters related to ceramic properties, with particular regard to sintering behaviour. In vitrified silicate ceramics, densification occurs by reactive viscous sintering [76], which is governed primarily by the physical properties of the vitreous phase [142,143]. Determining factors are the viscosity of the melt formed at high temperature and the viscosity of the bulk body, which depend on the chemical composition of the melt and on the solid load [144,145]. These factors are influenced by parameters such as:

Alumosity: i.e., the Al<sub>2</sub>O<sub>3eq</sub>/(Al<sub>2</sub>O<sub>3eq</sub> + Na<sub>2</sub>O<sub>eq</sub>) weight ratio, where Al<sub>2</sub>O<sub>3eq</sub> represents the sum of Al<sub>2</sub>O<sub>3</sub> plus Fe<sub>2</sub>O<sub>3</sub> (expressed as molar equivalent of Al<sub>2</sub>O<sub>3</sub>) while Na<sub>2</sub>O<sub>eq</sub> represents the sum of Na<sub>2</sub>O plus K<sub>2</sub>O, MgO and CaO (expressed as molar equivalent of Na<sub>2</sub>O); in glass-ceramics, Na<sub>2</sub>O<sub>eq</sub> can include also BaO, SrO, PbO, ZnO and Li<sub>2</sub>O [77]. The silicate melt viscosity is inversely proportional to alumosity with a steep relationship in the peralkaline field and a mild trend in the peraluminous one, i.e., alumosity below and over 62.4%wt., respectively [146].

*Total silica*: the weight percentage of  $SiO_2$  in the body, which is directly proportional to the melt viscosity [147,148].

*Flux ratio*: Or/(Or + Ab + An), expressed as equivalent amounts of potassic, sodic and calcic feldspars, which were calculated as follows: Or = %K<sub>2</sub>O/16.92, Ab = %Na<sub>2</sub>O/11.82, An = %CaO/20.16. Changes in the Na/K ratio can affect the melt viscosity and the formation/persistence of crystalline phases [149].

Silica excess: the weight percentage of SiO<sub>2</sub> not bound to feldspars, which was calculated as total silica minus the contribution of potassic feldspar (Or  $\times$  0.6476), sodic feldspar (Ab  $\times$  0.6874) and calcic feldspar (An  $\times$  0.4320). This parameter can affect both the melt viscosity (as SiO<sub>2</sub> dissolved in the liquid phase) and the bulk viscosity (as quartz is the main component of solid load).

Alkali to alkali-earths quotient, calculated as  $(Na_2O + K_2O)/(MgO + CaO)$  weight ratio, can influence the melt viscosity [146,150].

Total iron oxide and iron to aluminium quotient, calculated as  $Fe_2O_3$ <sub>total</sub> and  $Fe_2O_3/Al_2O_3$  weight ratio, respectively, can affect the firing behaviour of silicate ceramics via melt viscosity and redox reactions [148,151].

A multivariate statistical analysis was performed in order to discriminate the vitrified silicate ceramics on the basis of chemical composition and the above described parameters. A principal component analysis was carried out (variance-covariance matrix) by the PAST software [152].

#### 3. Results and discussion

The multivariate statistical analysis shows a clear distinction between the various vitrified silicate ceramics according to their chemical composition (Table S1, supplementary material). In fact, plotting the main components PC1 and PC2 (which together explain 91.8 % of the compositional variance) the points related to porcelain stoneware, red stoneware, glass-ceramics and porcelains are distributed in distinct fields (Fig. 1). The overlaps of these fields are very limited and refer to few samples with borderline chemical characteristics. There are large overlaps only for porcelain and vitreous china, while in the case of lightcoloured stoneware, there is a partial superposition with the fields of porcelain stoneware and vitreous china.

The picture shown by PCA is largely replicated when plotting points in the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3eq</sub>-Na<sub>2</sub>O<sub>eq</sub> phase diagram, which also takes into account Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, MgO and CaO through the total silica-alumosity diagram (Fig. 2A). In fact, there is a clear complementarity in the composition of porcelains, porcelain stoneware and silicate glassceramics. Porcelains are characterized by a wide range of total silica



**Fig. 1.** Principal Component Analysis of vitrified silicate ceramics: porcelain stoneware (S), porcelain (P), vitreous china (V), glass-ceramics (G), red stoneware (R) and light-coloured stoneware (L). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and an accentuated peraluminous character, on average greater for porcelain than vitreous china. Porcelain stoneware is also peraluminous - although with lower alumosity, between 66 % and 79 % - except for a few cases that fall between the meta-aluminous line and the vertical cotectic line (alumosity 62-66 %). Therefore, a boundary between porcelain stoneware and porcelains emerges clearly, around 79 % alumosity, which is likely related to the different manufacturing processes (Table 2). This boundary is presumably dictated by the fundamental microstructural role played by mullite in porcelain to ensure high mechanical performance [8,153]. This role requires the development of secondary mullite, with a high aspect ratio, which is only found in strongly peraluminous systems after prolonged firing schedules [76, 154]. On the other hand, glass-ceramics fall mostly in the peralkaline field, in many cases with silica contents well below 60 % (therefore outside the diagram of Fig. 2A). This is consistent with the glass-ceramic process, which requires melting of the batch before controlled crystallization [13,155]. Therefore, the compositions of the G bodies plot at relatively low liquidus temperatures, precisely to limit the energy consumption of the melting process.

The points of red stoneware are distributed in an alumosity-silica space rather wide (Fig. 2B), such as to overlap to a large extent with the fields of porcelains, porcelain stoneware and silicate glass-ceramics. It should be borne in mind that the samples considered are representative of different categories of ceramic tiles, both vitrified and semi-vitrified [17,54,86].

Light-coloured stoneware bodies have chemical compositions that straddle, in terms of alumosity and total silica, the S and V + P fields (Fig. 2B). As a matter of fact, these mixtures were obtained with formulations whose clay/flux ratio is intermediate between those of porcelain stoneware and porcelains [17,85].

A discriminant not contemplated by alumosity - which considers together sodium, potassium and calcium - is the flux ratio, which substantially quantifies the incidence of potassium on the total Na + K + Ca (Fig. 3). Contrasting flux ratio and silica excess, a quite clear distinction can be appreciated between porcelain stoneware and glass-ceramics on one side versus porcelains and red stoneware on the other side (Fig. 3A). In particular, porcelain stoneware and glass-ceramics have a more or less pronounced sodic character, with S generally more siliceous than G. Porcelains always have a rather high silica excess. Although classically formulated with potash feldspar, these industrial bodies have a fairly wide range of flux ratio, from distinctly potassic to mixed K-Na, up to rather sodic for some vitreous china bodies. Red stoneware batches are characterized by a wide range of excess silica and flux ratio: from potassic and siliceous bodies to mixed Na-K with excess silica ones, similar to porcelain stoneware. Light-coloured stoneware is known in two variants: sodic and potassic [54,85].



**Fig. 2.** Alumosity-silica diagram for vitrified silicate ceramics: A) porcelain stoneware (S), porcelain (P), vitreous china (V) and glass-ceramics (G); B) red stoneware (R) and light-coloured stoneware (L). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

 Table 2

 Typical industrial firing conditions of vitrified silicate ceramics.

Type of vitrified ceramics	Firing temperature, <i>T</i> (°C)	Duration of firing cycle (cold-to- cold), <i>t</i> (h)	Intensity of firing schedule, $T \times \sqrt{t}$
Porcelain stoneware	1190–1230	0.7–1.2	$1150\pm100$
Waste-bearing porcelain stoneware	900–1220	0.5–1.0	$1000\pm150$
Light-coloured stoneware	1140–1200	0.5–1.0	$1040\pm110$
Red stoneware	1050-1180	0.5-1.0	$920\pm160$
Vitreous china	1220-1270	8–14	$4000\pm400$
Porcelain	1250-1350	18–24	$5800\pm500$

A very important parameter for vitrified silicate ceramics is the iron content, which allows one to clearly distinguish whiteware from red stoneware (Fig. 3B). As for red stoneware, which has  $Fe_2O_3$  in the 3–9% range, there seem to be two subpopulations: one with similar contents of Na and K, while the other is distinctly potassic. At variance, both porcelain stoneware and glass-ceramics exhibit low iron concentrations, exceptionally up to 2 %  $Fe_2O_3$ , while light-coloured stoneware has on average higher percentages of iron oxide. Overall, porcelain and vitreous china have a low Fe content that distinguishes them from the L bodies with a more potassic character.

The incidence of alkali-earths discriminates the more potassic bodies (Fig. 3C): red stoneware has more CaO and MgO on average (hence a lower alkali-to-alkali-earths ratio), while porcelains have higher ratios. Light-coloured stoneware plots into an intermediate position. In the most sodic batches, alkali-earths are more abundant in glass-ceramics than in porcelain stoneware (and in L and V bodies with a sodic character).

Porcelain stoneware bodies used to manufacture ceramic tiles are allegedly different whether for glazed or unglazed (so-called "technical") products. It should be noted, however, that a direct comparison is not without pitfalls, since the distinction between the two types has, over time, become increasingly questionable. In addition, in recent years a dichotomy has emerged between ceramic tiles and slabs according to different sizes and production technologies [156,157]. This has repercussions on the formulation of porcelain stoneware bodies at least as important as the presence or absence of glaze. However, the chemical composition of unglazed porcelain stoneware seems to be largely superimposed on that of the glazed version, for example by contrasting flux ratio and silica excess (Fig. 4A).

Among the various functions, the glaze layer is designed to hide the colour of the support, so that the bodies in glazed porcelain stoneware

can in principle tolerate greater quantities of chromophores (especially iron). Although there is a large overlap of data, it can be appreciated how on average the glazed porcelain stoneware actually has a higher  $Fe_2O_3/Al_2O_3$  ratio than the unglazed type (Fig. 4B).

The ceramic industry is under increasing pressure to make production more environmentally and socio-economically sustainable [29,30]. In recent years, general drivers, such as circular economy and resource efficiency, have had some impact on the batch design of vitrified silicate ceramics [24,158]. Therefore, it is important to understand the effect on body formulation, especially waste recycling, and shortening the supply chain by using local raw materials [27,52,81,159]. For this purpose, the alkali-to-alkali-earths ratio is contrasted with the Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (Fig. 5) mainly to unveil any changes in the content of MgO, CaO and Fe<sub>2</sub>O<sub>3</sub>, which in standard bodies are in small concentrations (below 1 %).

In Fig. 5A, both red stoneware and glass-ceramics plot in compositional spaces that are distinct (due to high Fe<sub>2</sub>O<sub>3</sub> and alkali-earths, respectively) from the other vitrified silicate ceramics. The latter define fields with large overlaps, where however porcelains have on average lower Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and higher alkali-to-alkali-earths ratio than porcelain stoneware and light-coloured stoneware. Referring to field S, trends induced by the introduction of waste materials or by the recent use of lower grade raw materials in porcelain stoneware bodies can be revealed (Fig. 5B). Plotting representative points of porcelain stoneware with waste (W), it can be observed that, although many formulations fall within the field of standard S, there is a certain tendency towards lower alkali-to-alkali-earths ratios. In fact, the use of some types of waste leads to an increase in MgO and/or CaO [27]. This moves some bodies within the field of glass-ceramics, with possible repercussions in technological terms, such as lower densification efficiency and dimensional stability at high temperatures [77].

Replicating this analysis for V and P batches, new formulations with waste (Y) plot in many cases outside the field of porcelain composition, going in the direction of both higher MgO and CaO levels, and higher  $Fe_2O_3/Al_2O_3$  ratio (Fig. 5C).

Recently, the effect of the partial disruption of the supply chain on the formulation of porcelain stoneware has been observed. This circumstance overlaps with the actions taken to increase resource efficiency. In both cases, the trend is towards greater use of raw materials with lower cost and carbon footprint, often locally sourced. As a matter of fact, the bodies S, formulated after 2021, exhibit on average higher Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratios, which in many cases place the new batches in a compositional space not occupied before by any vitrified silicate ceramics, being intermediate between porcelain stoneware and red stoneware (Fig. 5B). Specific studies are lacking to understand whether there is a gradual transition between S and R or a boundary dictated by changes in sintering mechanisms [76,85].



**Fig. 3.** Flux ratio of vitrified silicate ceramics as a function of silica excess (A), content of iron oxide (B) and alkali/alkali-earths ratio (C). Symbols and abbreviations as in Fig. 1 and Table 1.

The technological feasibility of vitrified silicate ceramics with higher levels of iron and alkali-earths, as argued in the literature, suggests that an enlargement of the compositional field is feasible for porcelain and porcelain stoneware. However, the diffusion of waste-based bodies in industrial production is still limited (porcelain stoneware) or negligible (porcelain). An obstacle to their diffusion is a knowledge gap on the



**Fig. 4.** Comparison of glazed and unglazed (technical) porcelain stoneware: A) flux ratio versus silica excess; B) alkali-to-alkali-earths ratio to iron oxide-to-alumina ratio.

effect played by sintering promoters (Mg, Ca, Fe and other elements) that may be present in the residues in concentrations above the usual range for whiteware [20,52,78,159,160]. Therefore, in-depth studies on the role of sintering promoters are needed as well as modelling of firing behaviour of new vitrified silicate ceramics.

#### 4. Conclusions

The compositional diversity of vitrified silicate ceramics has been quantified, both through multivariate statistical analysis and by means of specific chemical parameters. The compositional fields of the main products are separated, case by case, with boundaries or partial overlappings.

Porcelain, porcelain stoneware and silicate glass-ceramics typically have different ranges of alumosity and/or total silica. These values define distinct compositional spaces that fall into the peralkaline field (glass-ceramics) or the peraluminous field (porcelain stoneware, and in a more pronounced way porcelain and vitreous china).

Sharp boundaries can be traced between porcelain stoneware and porcelain (occurring at alumosity  $\sim$ 79 %) and between porcelain stoneware and glass-ceramics (close to the meta-aluminous line). Such



limits are likely due to constraints on the chemical composition descending from process conditions and product performance.

Porcelain stoneware and red stoneware have, as expectable, different ranges of  $Fe_2O_3$  and  $Fe_2O_3/Al_2O_3$  ratio. Conventional batches clearly show the existence of a gap between the two materials, approximately in the 1.5–3%  $Fe_2O_3$  range, drawing a compositional space since long been unexploited by industry. It can be assumed that this gap reflects not merely the natural difference in the chemical composition between red clays and ball clays, since a technological justification may exist, although not yet disclosed.

Red stoneware actually consists of a complex set of compositions, with variable Na/K and alkali-to-alkali-earths ratios. It would deserve a specific study to disclose its sintering behaviour, going deeper than the limited data available in the literature.

The comparison of glazed versus unglazed porcelain stoneware revealed, as expected, essentially differences in iron content. However, an in-depth analysis is needed to prevent systematic bias (e.g., different raw materials from country to country) by focusing the comparison at the manufacturing district scale.

Light-coloured stoneware is now in disuse, both as sodic and potassic variants. However, it has an interest as its chemical composition is substantially intermediate between porcelain stoneware and vitreous china, and because it could tolerate higher percentages of  $Fe_2O_3$ .

The formulation of waste-based silicate ceramics usually implies a shift of the chemical composition of porcelain and porcelain stoneware bodies towards higher  $Fe_2O_3/Al_2O_3$  ratio and lower alkali-to-alkali earths ratio. This can lead, in many cases, to batches that fall outside the compositional space typical of industrial ceramics, opening questions about technological behaviour and technical performance that require specific studies to be answered.

#### CRediT authorship contribution statement

**Sonia Conte:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Chiara Molinari:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Sonia Javed:** Writing – review & editing. **Michele Dondi:** Writing – review & editing, Writing – original draft, Project administration, Methodology, Data curation, Conceptualization. **Chiara Zanelli:** Writing – review & editing, Supervision, Conceptualization.

## Declaration of competing interest

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

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ceramint.2024.09.024.

**Fig. 5.** Alkali-to-alkali-earths ratio as a function of iron oxide-to-alumina ratio for (A) vitrified silicate ceramics; (B) porcelain stoneware compared to wastebased bodies and formulations more recent than 2021; (C) porcelains compared to corresponding waste-bearing bodies. Symbols and abbreviations as in Fig. 1 and Table 1.

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