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Deposits, composition and technological behavior of fluxes for ceramic tiles

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ABSTRACT

The ceramic tile industry is a big consumer of feldspathic rocks and further raw materials able to act as flux during firing. This demand is currently fed with the recourse to a wide range of sources of igneous, sedimentary, metamorphic and metasomatic origin. The main geological features of flux deposits actually exploited by the ceramic industry are reviewed. The chemical and mineralogical composition is described to have a general picture of raw fluxes as well as average data and compositional perimeter for deposits of different origin. Overall beneficiation routes are drawn to trace the compositional path from deposit to commercial flux. The technological behavior in tile-making is shortly overviewed and new experimental data are provided on flux fusibility (by hot-stage microscopy). A chart is proposed to discriminate fluxes according to different fusibility.

Keywords: ceramic tile; feldspar deposit; flux; fusibility.

INTRODUCTION

Fluxes are fundamental ingredients of bodies and glazes used in the production of ceramic tiles, where they are mostly employed in vitrified and semivitrified bodies, like stoneware and porcelain stoneware (Singer and Singer, 1963; Dondi et al., 2014; Dondi, 2018a). Fluxes have the primary function to melt during firing and provide an adequate amount of liquid phase that is essential for viscous flow sintering (Kyonka and Cook, 1954; Cambier and Leriche, 1996; Zanelli et al., 2011). Alkali feldspars, particularly sodic plagioclase and K-feldspar, are quintessentially considered the ceramic fluxes (Sánchez Muñoz and García Guinea, 1992; Dill, 2010) even though a wide range of minerals can play as flux - including feldspathoids (nepheline, leucite), micas (muscovite, sericite), lithian silicates (lepidolite, spodumene, petalite), magnesian and calcian silicates (talc, chlorite, diopside, wollastonite) and zeolites - besides their fusibility may be far from that of feldspars. Therefore, many kinds of ceramic fluxes are present on the market, which composition and properties depend on geological sources and specific features of the various deposits under exploitation (Dondi, 2018b).

There is a general knowledge on ceramic fluxes, since several reviews were dedicated to deposits of feldspar (Potter, 2006), pegmatite (London, 2005; Dill, 2015a), nepheline syenite (McLemore, 2006), talc (McCarthy et al., 2006) and wollastonite (Robinson et al., 2006). Despite this body of literature, some sources are still neglected (metamorphics, epithermal deposits) or their actual relevance for the ceramic tile industry is underestimated (albitites, acid volcanics). Nevertheless, an exhaustive picture is still lacking, as the link between geology of deposits and composition of raw materials, and technological behavior in ceramic tile-making does not stand out from the literature.

Thus, the goal of the present paper is to overview sources, compositional features and technological properties of feldspathic fluxes and alternative raw materials utilized in the manufacturing of ceramic tiles worldwide.

EXPERIMENTAL APPROACH

The experimental approach follows a rationale consisting of four steps:

i) to collect literature data on raw and beneficiated fluxes used by or proposed to the ceramic tile industry;

ii) to elaborate the raw composition according to the various flux sources;

iii) to gather information on the technological behavior of beneficiated fluxes, integrating literature with new experimental data on the various sources;

iv) to draw a global picture linking geology of deposits with composition and technological behavior of ceramic fluxes.

An overall review of the literature and available industrial data on fluxes used by or proposed to the ceramic tile industry was carried out by gathering geological features of deposits as well as chemical and mineralogical composition of fluxes. For this purpose, over 1,100 literature sources were consulted; only the most relevant are cited here, while the whole body of references is reported in Dondi (2018b).

The chemical composition is the only piece of information always made available in the literature on ceramic fluxes. In order to compare fluxes recovered from the various lithologies, having a different mineralogical composition, a primary distinction was done between alkaline and alkaline-earth fluxes, the latter being those with the sum MgO+CaO>6%wt. This threshold was arbitrarily chosen as the best to discriminate the fluxes based on sodic and potassic minerals (feldspars, feldspathoids, sericite) from those characterized by magnesian and/or calcian minerals (anorthite-rich plagioclase, talc, wollastonite, diopside, chlorite, tremolite, carbonates). Chemical data were elaborated to make easier the comparison of different sources; the following parameters were calculated:

- The equivalent feldspar amount (Fd_{eq}) is the percentage of feldspars corresponding to the Na, K and Ca oxides, expressed as: $Fd_{eq}=(Or_{eq}+Ab_{eq}+An_{eq})$. The equivalent amounts of K-feldspar (Or_{eq}), Na-feldspar (Ab_{eq}) and Ca-feldspar (An_{eq}) are calculated from the weight percent of K_2O, Na_2O and CaO, respectively, in the chemical composition of a given flux:
  $Or_{eq}=\%K_2O\times 5.91$ (i.e., 100/16.92%wt. K_2O in the nominal Orthoclase, $KAlSi_3O_8$);
  $Ab_{eq}=\%Na_2O\times 8.46$ (i.e., 100/11.82%wt. Na_2O in the nominal Albite, $NaAlSi_3O_8$);
  $An_{eq}=\%CaO\times 4.96$ (i.e., 100/20.16%wt. CaO in the nominal Anorthite, $CaAl_2Si_2O_8$);
  this refers to one atom of alkali in the case of K_2O and Na_2O.
- The alkali ratio (AR) is expressed as the fraction of the equivalent amount of K-feldspar with respect to the sum Orthoclase+Albite in equivalent amounts: $AR=Or_{eq}/(Or_{eq}+Ab_{eq})$.
- The alkaline-earth ratio (AER) is expressed as the fraction of CaO with respect to the sum of magnesium and calcium oxides, by weight, AER=CaO/(CaO+MgO).
- The chromophore amount is the sum of total iron oxide and titanium dioxide: $Fe_2O_{3tot}+TiO_2$, where iron is expressed as $Fe_2O_{3\ tot}$ ($FeO+Fe_2O_3$) where divalent oxide was recalculated as trivalent oxide.

As far as the technological properties of fluxes, the thermal behavior under the hot-stage microscope (HSM) was considered (Paganelli, 1996; Venturelli, 2011). Among the characteristic shapes assumed by the specimen during heating, those corresponding to softening and half sphere were chosen as the most representative of the firing behavior of fluxes. Both the softening temperature (T_{soft}) and the hemisphere temperature (T_{melt}) of ceramic fluxes were taken from the literature (Dondi et al., 2001). This data-base was integrated with new analyses of 56 ceramic fluxes from various sources, actually utilized by the ceramic tile industry. The melting behavior was determined with the HSM Misura 3 (Expert System Solutions, Italy) with 10 $°C\times min^{-1}$ of thermal rate, using a cylindric specimen (height 2 mm x diameter 1 mm) obtained by manual pressing of powders (particle size: all passing 100 μm).

RESULTS AND DISCUSSION

Deposits of ceramic fluxes

Feldspathic raw materials and further ceramic fluxes are recovered from a wide range of deposits pertaining to different geodynamic environments (Figure 1). The various sources are arranged in Table 1 (igneous rocks) and Table 2 (sedimentary, metamorphic and metasomatic rocks) where a short geological description is given together with the main lithologies and the type of deposits industrially exploited. Examples of flux deposits are reported for each source.

An important set of deposits are found in granitic suites, where granitoids occur together with the corresponding extrusive and hypabyssal terms (e.g., rhyolites, porphyries) along with acid differentiates (pegmatites and aplites) as valuable flux sources.

Granitoids used in ceramic tile production consist mainly of syenogranite and monzogranite, with leucocratic terms sought-after by the ceramic industry. The global production is estimated to be around 3.6 million tons per year from approximately 50 mines. Major deposits are in Italy: Cacciano, Monte Camoscio and Montorfano (Grisoni and Boriani, 1990); Poland: Stary Łom, Strzeblów I, Pagórki Zachodnie and Pagórki Wschodnie (Lewicka, 2004); Brazil: Jundiaí, Itupeva, Sorocaba and Mogi das

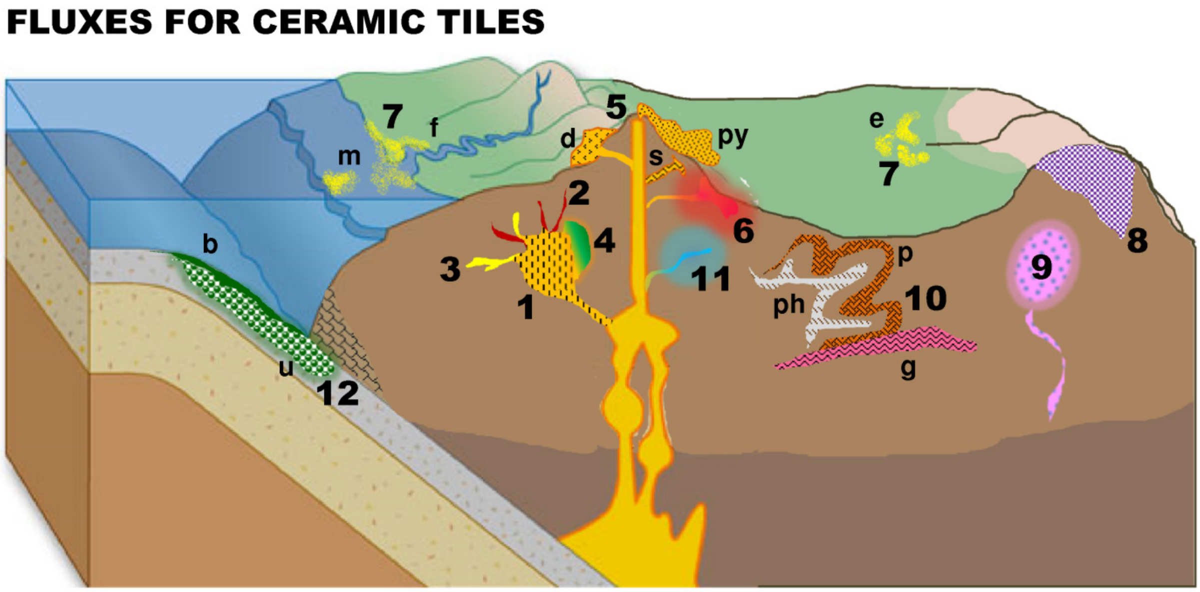

Figure 1. Geological sketch of sources of ceramic fluxes: 1) Granitoids; 2) Pegmatites; 3) Aplites; 4) Skarn deposits; 5) Acid volcanics (d: lava domes and flows, py: pyroclastics) and subvolcanics (s: porphyry); 6) Epithermal alterations (pottery stone, eurite, leucophyllite); 7) Arkosic arenites (e: eolic, f: fluvio-deltaic, m: marine); 8) Nepheline syenites and other silica-undersaturated rocks; 9) Syenites and other intermediate igneous rocks; 10) Metamorphics (g: orthogneiss, p: porphyroid, ph: phyllite); 11) Albitites and products of sodic metasomatism; 12) Basic (b) and ultrabasic (u) igneous rocks.

Cruzes (Motta et al., 1998); United States: Spruce Pine and Monticello (Potter, 2006). Greisenized terms occur in some deposits, like Saint-Austell, Cornwall, UK (Weidner and Martin, 1987); Montebras, France (Dudoignon et al., 1988); Krásno, Czech Republic (Jarchovsky, 2006). A few deposits of alkaligranite (Ahmed et al., 2013), granodiorite (Venturi and Fiori, 1990; Naga et al., 2012) and trondhjemite (Sotillo, 2014) have been exploited or proposed for ceramic tiles.

Pegmatites and aplites are the classic source of feldspar: about 4.8 million tons are extracted every year from several aplito-pegmatitic fields all over the World (Černý and Ercit, 2005; Dill, 2015a). The nearly 500 active mines represent approximately two thirds of the total flux deposits in operation (Dondi, 2018a). The largest pegmatite districts for the ceramic tile industry are in India: Rajasthan (Joshi et al., 1993) and Andhra Pradesh (Sarkar, 2001); Thailand: Ratchaburi, Ranong and Tak provinces (Suwimonprecha et al., 1993); China: Fujian (Yueqing et al., 1987) and Xinjiang (Zhang and Chen, 2010); north and centre of Portugal (Antunes et al., 2013; Neiva et al., 2012); Argentina: Sierras Pampeanas (Galliski, 2009); Iran: the Sanandaj-Sirjan zone (Masoudi et al., 2002); Brazil: Borborema-Seridó (Beurlen, 1995) and the Eastern Brazilian pegmatite province (Bilal et al., 2001); various areas of South Africa (von Backstrom, 1976). Unusual 'aplite' deposits - which apparent aplitic texture stems from some kind of rock alteration - occur for instance in Italy: granite at Botro ai Marmi, Tuscany (Loschi Ghittoni, 1972) and in the United States: anorthosite at Montpelier, Virginia (Potter, 2006); their production is globally around 0.7 million tons per year.

Acid volcanic and subvolcanic rocks are essentially rhyolites-rhyodacites with minor dacites and comendites, all occurring in a wide range of deposits (lava flows and domes, ignimbrites and other pyroclastics). Hypabyssal terms are typically porphyry veins or stockwork. The total production is around 0.6 million tons per year from about 20 mines worldwide. Acid volcanics are important sources of fluxes in some countries, such as Mexico: Ahuazotepec, Puebla (Solana-Lopez, 2012); Italy: Boca-Lozzolo, Piemonte (Quick et al., 2009), Torniella, Tuscany (Viti et al., 2007) and Murdeghina, Sardinia (Bornioli et al., 1995); Germany: Saarland and Rheinland-Pfalz (Bornhöft and Kleeberg, 2012); Turkey: Kireç, Bileçik (Kara et al., 2009); Russia: Kostomuksha and Roza-Lampi, Karelia (Il'ina et al., 1999).

Syenoids encompass intermediate igneous rocks, both silica-saturated and slightly oversaturated types, like alkalisyenite, syenite, quartz-syenite and monzonite (intrusive) or alkalitrachyte, trachyte and latite (extrusive). The annual output might be around 100 thousand tons on the whole, from few mined deposits. Examples are: Piranshahr in Azerbaijan Qarbi, Iran (Mazhari et al., 2012) and Lavrinha, São Paulo, Brazil (Enrich et al., 2005) for syenite; Siedlec, Lower Silesia, Poland (Ociepa

Table 1. Igneous sources of feldspathic raw materials for the ceramic tile industry.

Source		General description	Lithotypes used as flux	Type of deposit	Example (reference)
Granitoids	GRA	plutonic rocks, rich in feldspars and oversaturated in silica (quartz >20%) with a generally coarse-grained texture	mainly granites (particularly leucogranites) with minor granodiorites, alkaligranites, and some trondhjemites, including peculiar types (greisenised and miarolitic)	syenogranite monzogranite	Montorfano-Mt. Camoscio, Italy (Dino et al., 2012) Tak, Thailand (Nakapadungrat and Putthapiban, 1992)
				leucogranite	Strzeblow, Poland (Ciesielczuk et al., 2008) Tirschenreuth, Germany (Kitagawa and Köster, 1991)
				greisenised granitoid	Montebras, France (Dudoignon et al., 1988) Krásno, Czech Rep. (Jarchovsky, 2006)
Pegmatites	PEG	basement rocks, abundant in feldspars, in most cases acid differentiates of granitoids (or syenoids) characterized by either a very coarse-grained texture (PEG) or a fine-grained texture (APL)	all subtypes: plutonic pegmatites, pseudo-pegmatites, meta-pegmatites and pegmatoids as well as the equivalent terms for aplites	pegmatite aplite	Sierras Pampeanas, Argentina (Galliski, 2009) Black Hills, USA (Norton and Redden, 1990) Borborema-Seridó, Brazil (Da Silva et al., 1995) Oberpfalz, Germany (Dill, 2015b)
Aplites	APL			apparent aplitic texture due to rock alteration	Botro ai Marmi, Tuscany, Italy (Loschi Ghittoni, 1972) Montpelier, Virginia, USA (Owens and Dymek, 2016)
Acid volcanics and subvolcanics	RHY	extrusive acid rocks as lavas, domes, pyroclastics (cinerite, tuff, ignimbrite, pumice and perlite) including subvolcanic and hypabyssal types (veins, stockwork)	mainly rhyolites-rhyodacites, mostly as pyroclastics and porphyry, with minor dacites and comendites	pyroclastics	Ahuazotepec, Mexico (Solana Lopez, 2012) Piloni di Torniella, Tuscany, Italy (Viti et al., 2007)
				porphyry	Türkismühle, Germany (Bornhöft and Kleeberg, 2012) Virauda and Boca, Piemonte, Italy (Quick et al., 2009)
				perlite pumice	Arteni-Aragats, Armenia (Karapetian et al., 2001) Nevşehir, Turkey (Le Pennec et al., 1994)
Intermediate igneous rocks	SYE	silica-saturated or slightly oversaturated (quartz up to 20%) intrusive and extrusive rocks (so-called "syenoids")	syenite, trachyte, and quartz-syenite (quartz 5-20%) with some alkalisyenite and alkalitrachyte	syenite	Lavrinha, São Paulo, Brazil (Enrich et al., 2005) Abu Khruq, Egypt (El-Ramly and Hussein, 1983)
				trachyte	Siedlec, Poland (Ociepa and Slosarczyk, 1988)
Basic igneous rocks	BAS	basic or ultrabasic rocks, both intrusive and extrusive, in a variety of deposits (pluton, stockwork, vein, lava, pyroclastic, etc)	intrusive (diorite, gabbro, anorthosite) and extrusive rocks (andesite, basalt, basanite) including peculiar types (e.g. plagiogranite)	basalt andesite	Rovno, Ukraine (Abramyan et al., 1968)
				gabbro diorite	Taar, Sinai, Egypt (Mörtel et al., 2005)
				plagiogranite	Menta, Valtaro, Italy (Borsi et al., 1998)
				anorthosite	Capivarita, Brazil (Philipp et al., 2010)
Nepheline syenites and phonolites	NSP	silica-undersaturated (quartz free) rocks containing feldspars and feldspathoids (nepheline, leucite, etc).	various lithologies with prevailing nepheline syenite or its extrusive equivalent nepheline phonolite, but also ultrapotassic rocks	nepheline syenite	Blue Mountain, Ontario, Canada (Payne, 1968) Stjernøy Island, Norway (Geis, 1979)
				nepheline phonolite	Lages, Santa Catarina, Brazil (Formoso et al., 1990) České Středohoří, Czech Rep. (Ackerman et al., 2015)
				leucite phonolite synnyrite	Magliano Romano, Latium, Italy (Bertolani, 1993) Synnyr, Eastern Siberia, Russia (Panina et al., 1995)

Table 2. Sedimentary and metamorphic sources of feldspathic raw materials for the ceramic tile industry.

Source		General description	Lithotypes used as flux	Type of deposit	Example (reference)
Feldspathic arenites	ARK	feldspathic sandstones and conglomerates (and the corresponding unlithified sediments).	mostly arkoses and subarkoses, but some lithic arkoses are used as well	eolic	Carrascal del Río, Spain (Bateman and Herrero, 1999)
				fluvio-lacustrine and fan deltas	Logudoro, Sardinia, Italy (Funedda et al., 2000) Hirschau-Schnaitterbach, Germany (Dill et al., 2016)
				marine	Loiano, Bologna, Italy (Cibin et al., 2001)
Metamorphics	MET	metamorphic equivalents of igneous and sedimentary deposits (mostly in the greenschist facies)	mainly phyllite (the peculiar Brazilian filito), orthogneiss and quartzite, even though porphyroid, metagabbro-metadiorite, chloritoschist and mylonite are also used	phyllites	Itapeva, São Paulo, Brazil (Moreto et al., 2008)
				orthogneisses	Tysfjord/Hamaroy, northern Norway (Karlsen, 2000)
				metadiorite	Mikashevichskii, Belarus (Pavlyukevitch et al., 1998)
				porphyroids	Kostomuksha, Karelia, Russia (Puchtel et al., 1998)
				sanidinite	Piano del Pazzo, Italy (Gualtieri and Bertolani, 1991)
				mylonite	Piedade, São Paulo, Brazil (Motta et al., 1999)
Albitites	ALB	metasomatic rocks formed through an albitization process under the action of metamorphic fluids	albitites (almost mono-mineralic bodies where albite replaced plagioclase and K-feldspar)	albitite	Menderes massif, Turkey (Çakır, 2005) Orani-Ottana, Sardinia, Italy (Castorina et al., 2006) Salvezines, Pyrenées, France (Poujol et al., 2010) Albitite Line, Rajasthan, India (Kaur et al., 2012)
Epithermal alterations	EPI	hydrothermal alteration giving rise to a wide range of peculiar rock types, often enriched in sericite	pottery stone (toseki, baidunzi), agalmatolite, eurite, pinite, sericitic roseki, leucophyllite, episyenite and sanidinite	pottery stone	Amakusa, Japan (Nakagawa and Matsuura, 1994)
				eurite	Crocetta, Elba, Tuscany, Italy (Benvenuti et al., 2006)
				sericitic roseki	Mitsuishi, Japan (Ishihara and Imaoka, 1999)
				leucophyllite	Weissenkirchen, Austria (Prohaska, 1991)
				agalmatolite	Minais Gerais, Brazil (Evangelista and Delgado, 2007)
Skarns	SKA	metamorphic zone in the contact halo around igneous intrusions where carbonate rocks are metasomatized	low-iron skarn deposits of wollastonite, diopside, talc, talc-chlorite, talc-magnesite, including tremolite-bearing rocks	talc	Paraná and Bahia, Brazil (Gondim and Jiang, 2004) Yellowstone, Montana, USA (Anderson et al., 1990)
				talc-chlorite	Trimouns, Pyrenées, France (de Parseval et al., 1994) Rabenwald, Steiermark, Austria (Moine et al., 1989)
				wollastonite	Willsboro, USA (Grammatikopoulos and Clark, 2006) Mérida, Spain (Fernández-Caliani and Galán, 1998)
				diopsidite	Slyudyansk, Russia (Vereshchagin et al., 1989) Castro Alves, Bahia, Brazil (Kuzmickas et al., 2013)

and Slosarczyk, 1988) and Ilgin, Konya, Turkey (Kayacı et al., 2010) for trachyte.

Basic and ultrabasic igneous rocks can be incorporated into ceramic tile bodies, like red-firing stoneware, even though the actual amount used all over the World is hard to be estimated (likely around half million tons per year). A wide range of deposits was proposed, encompassing intrusive and extrusive lithotypes. The former includes gabbro (Moertel et al., 2005; Abdel-Aziz and Aly, 2006), diorite (Anseau and Fierens, 1978; Bobkova et al., 2007), plagiogranite (Bertolani and Loschi Ghittoni, 1982) and anorthosite (Gamlem and Lyng, 1974; Philipp et al., 2010); the latter basalt (Abramyan et al., 1968; Dvorkin et al., 2000; Murzyn and Dyczek, 2009), andesite (Gaprindashvili et al., 1990; Aziz and El-Khaliouby, 2007), basanite and tephrite (Naga and El-Maaty, 1994; Leonelli et al., 2007).

Silica-undersaturated rocks from alkaline complexes are exploited by the ceramic industry, which looks after mainly nepheline syenite and its extrusive equivalent (nepheline phonolite). However, further lithotypes, for instance juvite, urtite, nepheline gneiss, leucite phonolite and synnyrite can also occur in flux deposits. About 20 active mines ensure a global output around 1.5 million tons per year, excluding the amount addressed to the aluminium production. Nepheline syenite for ceramics is principally extracted in Canada, Blue Mountain in Ontario (Payne, 1968), Norway, Lillebukt in the Stjernøy island (Geis, 1979) and Russia, Vishnevogorsk in Southern Urals (Nedosekova et al., 2009). Nepheline phonolite mines are in operation at Lages, Santa Catarina, Brazil (Aumond and Scheibe, 1996); Brenk, Eifel, Germany (Bornhöft and Kleeberg, 2012); Želenický vrch, Czech Republic (Pazdernik, 1997). Ultrapotassic fluxes are known in Italy, where weathered leucite phonolite and tephrite from Latium were in use (Bertolani et al., 1985; Bertolani, 1993). Synnyrite and related kalsilite-bearing rocks from Eastern Siberia, Russia (Kostyuk et al., 1990; Mitchell, 1996) were proposed as ceramic fluxes (Yusupov et al., 1991).

Feldspathic arenites, mainly arkoses, are important fluxes for the ceramic tile industry. They are recovered from sedimentary deposits that can be of aeolian, fluvio-lacustrine, fan deltaic or marine origin (Table 3). The World production is estimated to be about 2.6 million tons per year from at least 35 active deposits. Arkosic sands are largely employed in Italy, especially in the northern Apennines (Bertolani et al., 1984) and the Sassarese-Logudoro basin in Sardinia (De Carlo et al., 1990). Gravel and conglomerate deposits, proximal to a crystalline basement source, are exploited in the Czech Republic, along the Jihlava and Lužnice rivers (Starý et al., 2009). On the other hand, sand deposits in Spain, Carrascal del Río and Río Pirón, Segovia (Sánchez Muñoz and García Guinea, 1992) and Germany, Hirschau-Schnaitterbach in Bavaria (Dill et al., 2016) are exploited to get potassic feldspar as prime product along with quartz-feldspathic fluxes.

Metamorphics are also utilized by the ceramic tile industry with a yearly production around 1.1 million tons, globally, from roughly 20 mines, exploiting various lithologies. The most important flux is a peculiar type of phyllite (so-called *filito*, more or less rich in sericite) mined in Brazil (Biondi and Marczynski, 2004; de Andrade et al., 2008) with the major deposits in São Paulo (Itapeva and Pirapora do Bom Jesus), Paraná (Campo Largo) and Minas Gerais (Igarapé). Sanidinite deposits formed at high temperature by pyrometamorphic processes (Grapes, 2010); a mine was in operation at Piano del Pazzo, Latium, Italy (Gualtieri and Bertolani, 1991). Further sources are: orthogneiss (Karlsen, 2000; Junkes et al., 2012), acid metavolcanics and porphyroid (Il'ina et al., 1999; Palomba et al., 2010), quartzite and mylonite (Motta et al., 1999).

Albitites are unique metasomatic rocks formed by the action of sodium-rich fluids on granitoids and/or acid metamorphics. Such an albitization process can lead to a high degree of replacement of albite after plagioclase and K-feldspar. Albitites represent the major source of fluxes for the ceramic tile industry with over 9 million tons per year from about 70 active sites. The largest deposits are located in the Menderes massif in southwestern Turkey, where several mines are in operation (Çakır, 2005; Uygun and Gümüşçü, 2000). Further active mining districts are in central Sardinia, Italy (Palomba, 2001; Castorina et al., 2006) and eastern Pyrenées, France (Boulvais et al., 2007; Poujol et al., 2010).

Epithermal deposits are generated through low temperature hydrothermal alteration (Allen et al., 1996; Bove et al., 2007) that provides peculiar fluxes (e.g., pottery stone, agalmatolite and eurite) which are featured by significant amounts of low melting minerals, such as sericite. The global output is around one million tons per year by dozens of active mines. Pottery stone is essentially extracted in the Far East, where the Amakusa and Taishu deposits, Japan, can be taken as archetypal (Hirano and Sudo, 1994; Nakagawa and Matsuura, 1994). About further epithermal fluxes, examples of active deposits are: Mitsuishi, Japan (Ishihara and Imaoka, 1999) and Daehyun, Korea (Koh et al., 2000) for sericitic roseki; Weißenkirchen, Austria, for leucophyllite (Prohaska, 1985, 1991); Quadrilátero Ferrifero, Brazil, for agalmatolite (Evangelista and Delgado, 2007); the Elba Island, Italy, for eurite (Maineri et al., 2003; Benvenuti et al., 2006).

Skarn deposits - a general term for the metamorphic halo around igneous intrusions where carbonate rocks

Table 3. Chemical composition of raw deposits of fluxes used by or proposed to the ceramic tile industry. Abbreviations from Tables 1 and 2.

% weight	GRA[1]	GRA[2]	PEG[3]	APL[4]	RHY[5]	RHY[6]	RHY[7]	SYE[8]	SYE[9]	BAS[10]	NSP[11]	NSP[12]
SiO_2	71.1±3.8	73.6±3.0	70.2±4.8	72.9±2.4	72.5±3.7	70.5±2.9	75.3±2.3	62.8±3.3	64.6±3.6	52.5±3.8	55.3±4.4	53.5±4.9
TiO_2	0.3±0.2	0.1±0.1	0.1±0.2	0.1±0.1	0.2±0.3	0.2±0.2	0.1±0.1	0.4±0.2	0.4±0.2	0.3±0.2	0.5±0.5	0.7±0.6
Al_2O_3	14.2±2.0	14.9±2.2	16.2±2.7	15.3±1.9	14.6±1.9	13.8±2.4	14.0±1.5	17.9±1.9	17.4±2.1	29.1±3.1	20.9±2.6	19.3±2.8
Fe_2O_3 total	2.7±1.0	0.7±0.4	0.8±0.8	0.8±0.6	1.1±1.1	1.4±0.7	1.2±0.5	3.9±2.3	2.1±1.2	1.1±1.1	4.2±1.6	5.2±2.8
MgO	0.7±1.0	0.2±0.3	0.2±0.3	0.2±0.2	0.4±0.5	0.7±0.6	0.3±0.2	0.8±0.8	0.6±0.5	0.6±0.4	0.6±0.8	2.5±3.3
CaO	1.5±1.0	0.8±1.1	0.7±0.6	0.8±1.5	1.1±1.1	1.5±0.7	0.3±0.4	2.1±1.3	1.2±0.8	10.9±4.0	2.1±2.1	4.0±3.5
Na_2O	3.6±0.8	4.0±1.2	3.6±2.0	4.5±0.6	2.8±2.0	2.6±1.3	1.2±0.9	5.5±1.5	2.3±2.0	3.6±1.9	8.2±2.1	6.4±3.4
K_2O	4.6±1.1	4.1±1.1	6.6±3.5	4.1±2.1	5.5±3.0	4.8±2.9	5.5±1.6	5.3±1.6	8.2±2.2	0.7±0.5	6.2±2.1	6.3±1.8
L.o.I.	0.8±0.6	1.4±1.2	1.1±1.2	1.2±0.7	1.8±1.8	4.7±2.3	2.1±1.0	1.0±0.7	2.2±2.0	1.4±1.9	1.3±1.3	2.2±1.7

% weight	ARK[13]	MET[14]	MET[15]	MET[16]	ALB[17]	ALB[18]	EPI[19]	EPI[20]	EPI[21]	SKA[22]	SKA[23]	SKA[24]
SiO_2	82.5±7.3	68.9±6.3	73.6±4.1	65.7±8.4	66.6±3.5	66.3±1.9	77.5±3.5	69.4±10.3	50.1±6.1	58.2±8.1	50.8±2.6	52.3±3.6
TiO_2	0.2±0.1	0.3±0.3	0.2±0.2	0.5±0.3	0.4±0.4	0.4±0.1	0.2±0.2	0.3±0.3	0.5±0.1	0.1±0.1	<0.1	0.1±0.0
Al_2O_3	9.5±3.9	15.7±2.4	14.6±2.3	19.8±3.8	18.3±1.5	18.6±1.0	14.1±1.8	21.3±7.9	35.5±3.7	1.6±2.0	1.6±2.9	3.0±2.9
Fe_2O_3 total	0.8±0.8	2.2±1.8	1.1±1.0	2.8±2.6	1.5±1.7	0.6±0.2	0.6±0.5	0.7±0.7	0.4±0.3	0.9±0.6	0.5±0.3	2.8±5.1
MgO	0.4±0.8	0.5±0.6	1.0±1.5	1.0±0.6	0.6±0.8	2.6±0.7	0.3±0.4	0.3±0.3	0.2±0.2	29.5±2.4	1.6±1.7	13.6±6.5
CaO	0.8±1.0	2.0±2.0	0.7±1.2	0.7±1.7	1.0±0.8	1.1±0.5	0.7±1.0	0.1±0.2	0.1±0.1	2.3±4.2	43.8±4.2	24.3±7.4
Na_2O	1.2±1.2	3.1±2.0	2.4±2.1	1.7±3.6	9.8±1.4	8.1±1.1	0.9±1.0	0.4±0.3	0.3±0.2	0.3±0.3	0.2±0.2	0.5±0.6
K_2O	3.2±1.6	6.2±3.2	5.1±3.5	4.3±1.2	0.5±0.6	0.7±0.4	2.9±1.6	4.5±2.4	8.9±2.4	0.4±0.4	0.2±0.3	0.6±1.1
L.o.I.	1.6±1.3	0.9±0.7	1.6±1.4	3.5±1.8	1.0±0.6	1.5±0.5	2.7±1.0	2.9±1.1	3.9±1.6	6.6±5.3	2.5±2.6	3.2±2.9

1: "normal" granitoids (average of 42 samples); 2: leucogranites (n=43); 3: pegmatites (n=119); 4: aplites (n=13); 5: rhyolite-rhyodacite-liparite-comendite (n=35); 6: acid volcanic pyroclastics (n=25); 7: acid subvolcanics and porphyry (n=21); 8: syenites (n=25); 9: trachytes and other intermediate volcanics (n=12); 10: anorthosites (n=10); 11: nepheline syenites (n=72); 12: nepheline phonolites (n=24); 13: arenites, mostly arkoses (n=37); 14: gneisses (n=8); 15: porphyroids and acid metavolcanics (n=5); 16: phyllites, i.e. Brazilian *filito* (n=21); 17: raw albitites (n=23); 18: chlorite-rich albitites (n=7); 19: pottery stone, *toseki* and similar lithologies (n=41); 20: sericitic *roseki* and sericitized rocks (n=19); 21: agalmatolite (n=4); 22: talc-rich skarn (n=29); 23: wollastonite skarn (n=14); 24: diopside skarn (n=8).

are metasomatized (Meinert et al., 2005) - are the source of ceramic fluxes based on talc, chlorite, magnesite, wollastonite, and diopside. They feed the ceramic tile industry with at least one million tons per year from nearly 80 active mines. Well-known talc, talc-magnesite and talc-chlorite deposits are: Trimouns, Luzenac, France (de Parseval et al., 1994); Yellowstone, Montana, USA (Anderson et al., 1990); Paraná, Brazil (Gondim and Jiang, 2004); Rabenswald, Austria (Prohaska, 1985; Moine et al., 1989). The largest wollastonite deposits are in China: Jilin and Liaoning (Yuangui et al., 1983) and in the United States: Willsboro, New York (Grammatikopoulos and Clark, 2006). Diopside is extracted in Brazil, Castro Alves, Bahia (Kuzmickas et al., 2013) and Russia, Slyudyanka near Irkutsk (Vereshchagyn et al., 1989).

Composition of ceramic fluxes

The diversity of lithologies and genetic conditions of flux deposits reflects into a vast range of chemical and mineralogical composition of raw materials. Such compositional traits are rather well differentiated upon the above-mentioned sources, as it stands out by comparing the major elements of raw deposits, as reported in Table 3, which lists the average of available data (one for each deposit) prior any beneficiation process. In any case, a noteworthy compositional variability is present even within the same source, since data are often characterized by a rather high standard deviation of mean concentrations. The compositional differences between the various sources can be appreciated in the Figures 2 to 5.

Fluxes obtained from granitoids are characterized by high quartz (typically 20-40%) with an equivalent feldspar content (Fd_{eq}) between 60% and 75% (Figure 2C). The main fluxing minerals are both alkalifeldspar (orthoclase, usually perthitic, and microcline) and plagioclase (typically oligoclase) so giving rise to mixed alkali fluxes (AR=0.4-0.6). Some minor components can play as flux: fluorite, topaz, and carbonates that may occur in greisenised rocks (Štemprok, 1987) or in miarolitic bodies in apical portions of batholiths (Thomas et al., 2009). The amount of femic minerals is relatively low, generally around 5% or even below 2% in leucocratic varieties (Table 3). Such a dichotomy reflects in the dual distribution of the chromophore amount (Figure 3C).

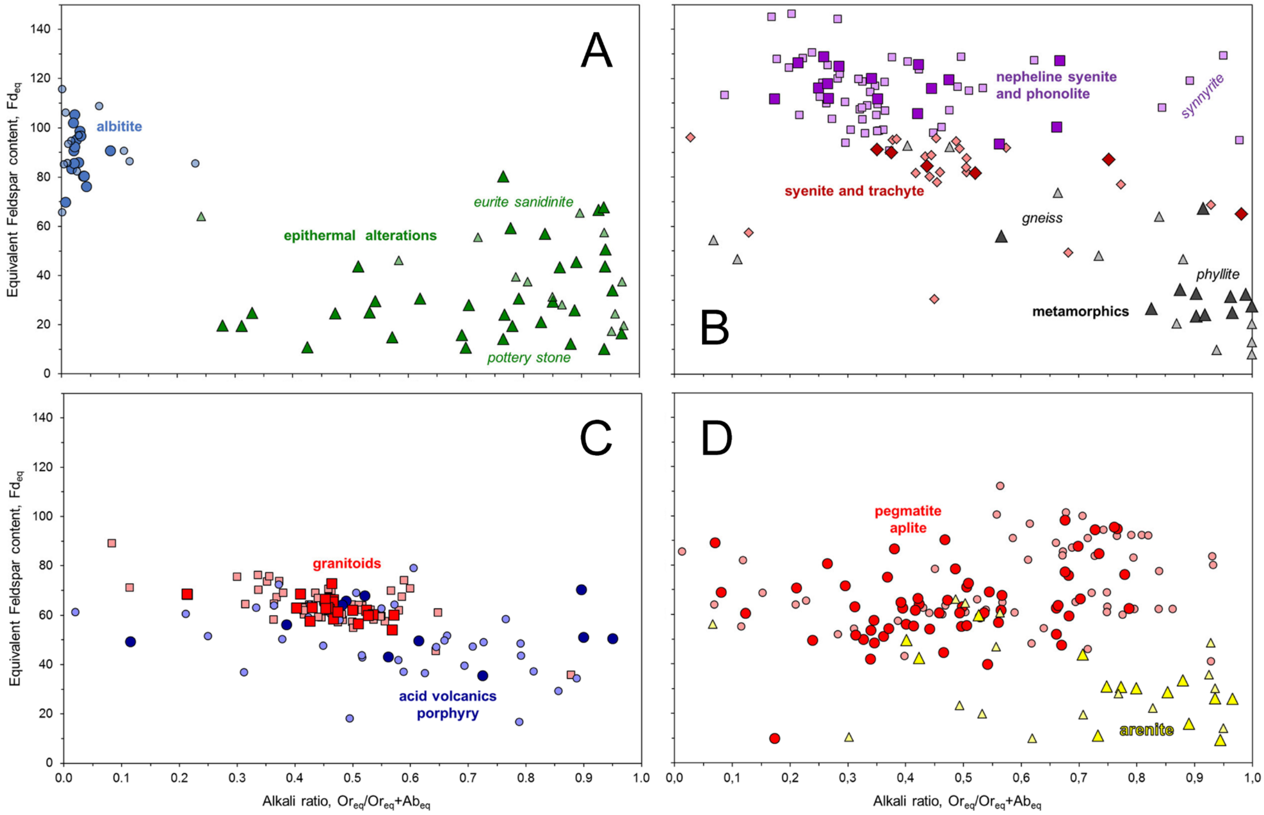

Figure 2. Alkali ratio (AR) vs equivalent feldspar content (Fd_{eq}) for: albitites and epithermal deposits (A); syenoids, silica-undersaturated rocks and metamorphics (B); granitoids and acid volcanics (C); pegmatites, aplites and arenites (D). Larger symbols: deposits used by the ceramic tile industry; smaller ones: deposits proposed for ceramic applications.

Undesirable components encompass fluorine-bearing phases, biotite, muscovite, hornblende, sodic pyroxenes and amphiboles that can occur in alkaline granites, and refractory minerals (sillimanite, andalusite, corundum, cordierite) that may be present in peraluminous granitoids.

Although the extrusive counterpart of granitoids, acid volcanic rocks have a wider range of chemical composition (AR~0.1-1 and Fd_{eq} 30-90%, Figure 2C) and include peculiar K-enriched terms, especially porphyry (Table 3). Anyway, they plot in the rhyolite field of the TAS diagram (Figure 4). The mineralogical composition is complicated by textural issues that depend on cooling conditions and process of put in place. A given mineral (for example a pyroxene) can be present as phenocrystals, microcrystals dispersed in the groundmass, and virtually as component of a vitreous phase. Although not accounted for the chemical composition, these distinct ways of occurrence have important repercussions on both beneficiation yield and technological behavior. Fluxing minerals are alkalifeldspars, typically represented by sanidine or anorthoclase (predominant in rhyolites and alkalirhyolites) and oligoclase-andesine plagioclases (main constituents in rhyodacites and dacites) plus in some cases volcanic glass (Carbonchi et al., 1999) or zeolites, such as clinoptilolite, mordenite and heulandite (de' Gennaro et al., 2003; Palomba et al., 2006). The undesired components usually range from 5% to 15% and include biotite, orthopyroxene, clinopyroxene and refractory minerals present in peraluminous (e.g., cordierite) or altered rocks, like kaolinite, pyrophyllite, etc (Kirov et al., 2011).

Pegmatites and aplites supply fluxes that consist basically of feldspars, quartz and micas, plus a more or less extended suite of rare element minerals (Černý and Ercit, 2005; Dill, 2015a). The equivalent amount of feldspars ranges widely from 40% to nearly 100% (Figure 2D). Both potassic feldspar and plagioclase (most frequently as microcline and albite) can be present in extremely variable proportions (AR fluctuates from about 0 to 0.9). Within this variableness, there are apparently two sets of pegmatites (Figure 2D): one mixed alkali (0.3<AR<0.6) and another distinctly potassic (AR>0.7) which is the most important supplier of commercial potassic feldspar. In addition, a significant contribution to fusibility can be

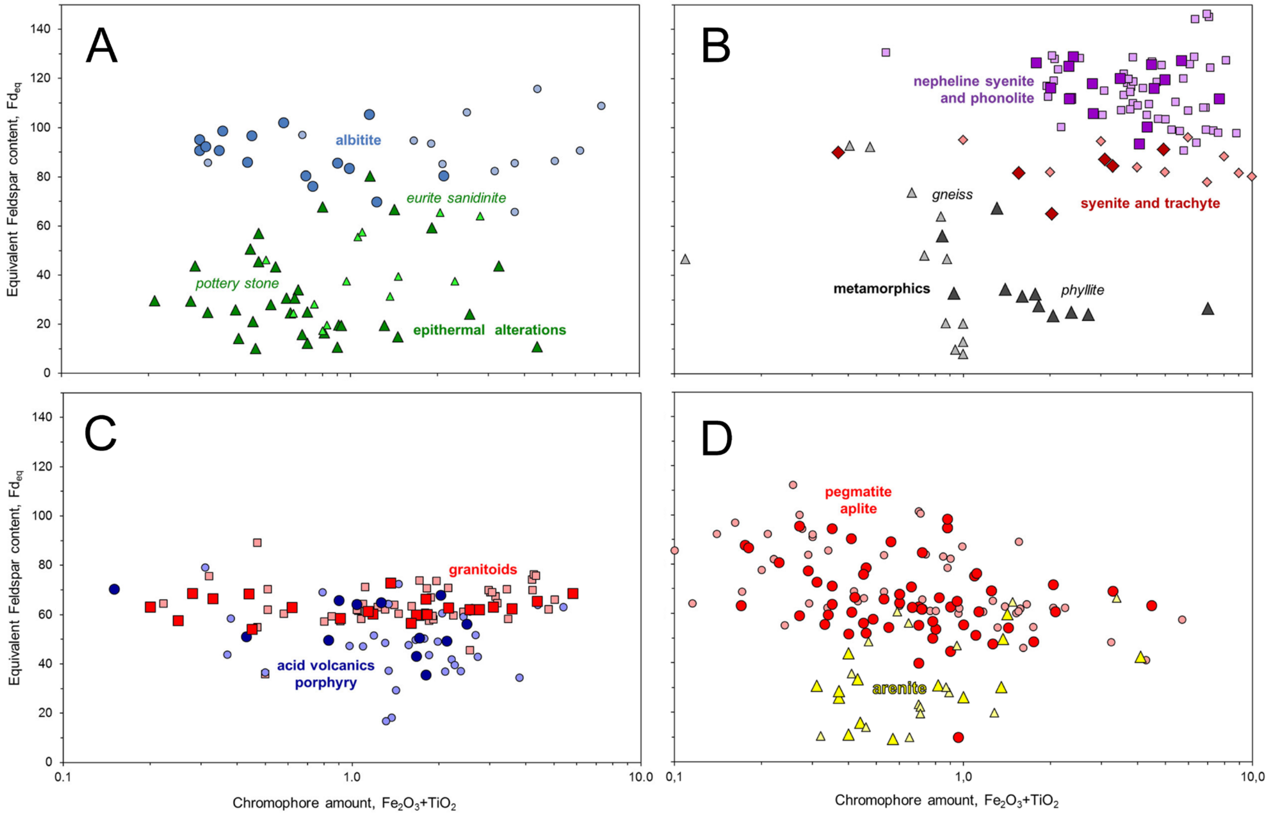

Figure 3. Chromophore amount vs equivalent feldspar content (Fd_{eq}) for: albitites and epithermal deposits (A); syenoids, silica-undersaturated rocks and metamorphics (B); granitoids and acid volcanics (C); pegmatites, aplites and arenites (D). Larger symbols: deposits used by the ceramic tile industry; smaller ones: deposits proposed for ceramic applications.

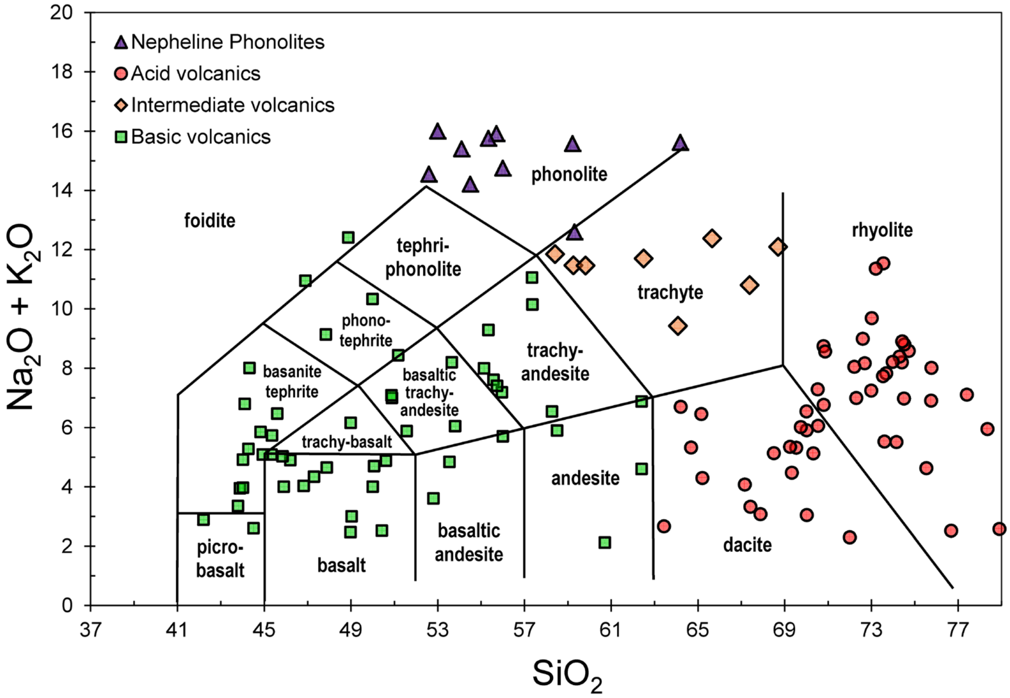

Figure 4. TAS diagram (Irvine and Baragar, 1971) for the classification of volcanic rocks.

provided by lithium minerals (lepidolite or spodumene; less frequently petalite, zinnwaldite, cookeite) that occur in the more evolved parts of pegmatites. Undesired components include muscovite (or biotite-phlogopite in the less evolved stages), tourmaline and garnets, even so the chromophore amount is in many cases below 1% (Figure 3D). Due to variable emplacement conditions and regional zonation, the mineral assemblages can change considerably, even in the same pegmatite field (Norton, 1983; Muller-Lorch et al., 2007). Some "aplites" utilized by the ceramic industry are in reality granitoids (or anorthosites) that suffered a more or less accentuated alteration, mainly by hydrothermal activity (forming sericite, chlorite, pyrophyllite, etc). They are so called because these phenomena induced both textural (fine-grained and homogeneous appearance) and compositional features (leucocratic character for alteration of femic minerals) that made them similar to aplites (*strictu sensu*).

Intermediate igneous rocks contain from ~70% (quartz-syenite) to ~85% (alkalisyenite) of feldspars: predominantly alkalifeldspar (perthites in syenites; sanidine or anorthoclase in trachytes) with some plagioclase (oligoclase). The resulting fluxes have high Fd_{eq} values, from about 70% to 95% (Figure 2B) and a mixed alkali character (AR=0.3-0.8) besides extrusive terms seem to be more potassic (Table 3 and Figure 4). Undesired minerals usually range from 10% to 30% and are commonly represented by biotite and hornblende, while riebeckite and aegirine can be found in alkaline syenites (Enrich et al., 2005; Rattanakawin et al., 2010). In the intermediate extrusive rocks, textural issues should be also considered, having important repercussions on beneficiation yield, as already explained about acid volcanics.

Igneous basic rocks provide essentially alkaline-earth fluxes, constituted by an assemblage of plagioclase and femic minerals, in various ratios, and sometimes also alkalifeldspar, feldspathoids or quartz. Plagioclases (ordinarily andesine-labradorite) are prevailing in diorite and andesite (55-65%) and particularly in anorthosite (80-90%) while they are around 50% in gabbro and basalt. Overall, these sources represent a wide range of basic lithotypes - as shown in the TAS diagram (Figure 4) - that are featured by intermediate values of alkaline-earth ratio (0.3-0.95) and alumina fraction (0.1-0.2) except for anorthosites, which exhibit very high values: AER>0.9 and AF>0.25 (Figure 5A). The chromophore amount is always over 5% and often very high (Figure 5B). Since Ca-rich plagioclases have a high melting point, the fluxing action is mainly exerted by femic minerals, typically represented by hornblende±pyroxene ±biotite in intrusive rocks and orthopyroxene+clinopyroxene ±olivine±hornblende in the volcanic counterparts; also oxides (spinels, ilmenite, etc) usually occur. For this reason, no beneficiation process is carried out, barring feldspar-rich (i.e., anorthosite: Wanvik, 2000) or coarse-

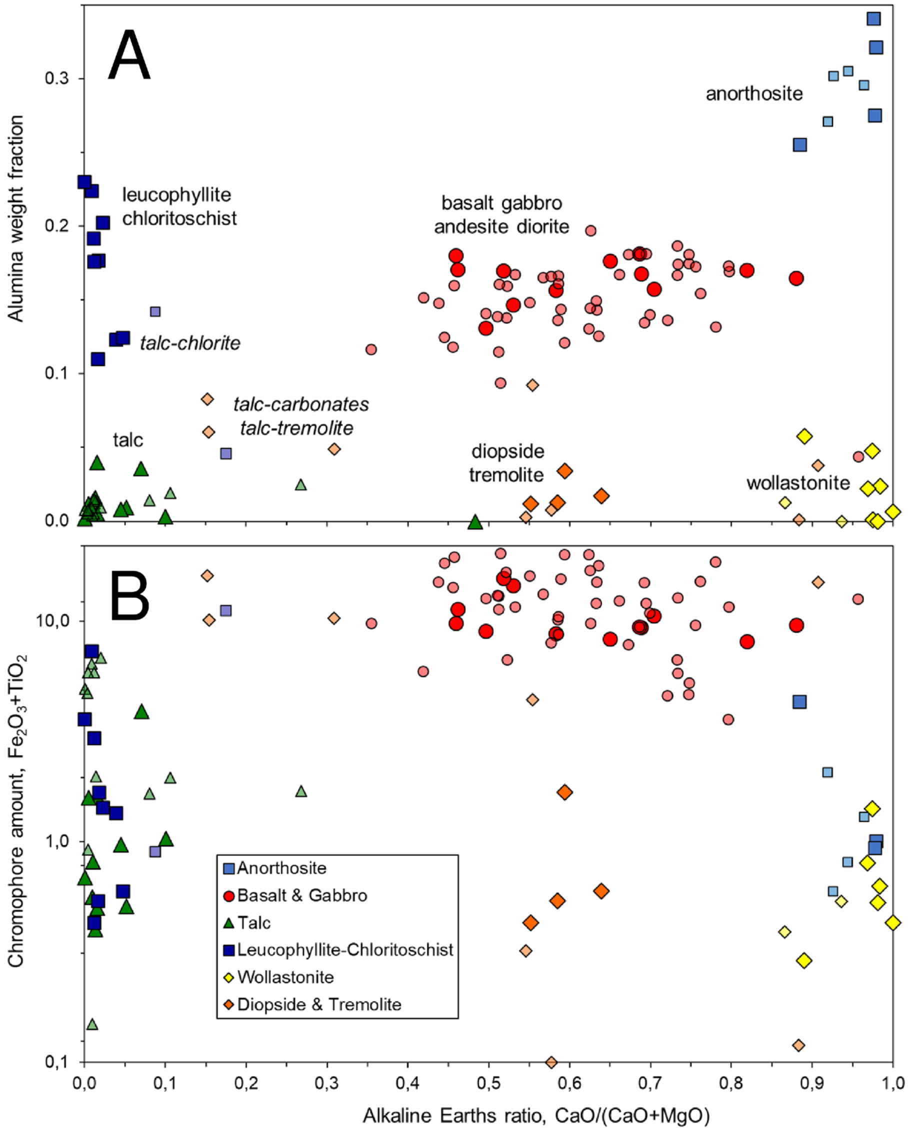

Figure 5. Alkaline-earth ratio vs alumina fraction (A) and chromophore amount (B) for skarn deposit and basic igneous rocks. Larger symbols: deposits used by the ceramic tile industry; smaller ones: deposits proposed for ceramic applications.

grained rocks (e.g., gabbro: Mörtel et al., 2005).

Silica-undersaturated rocks offer a wide range of mineralogical compositions, always dominated by feldspars and feldspathoids: from 60-70% in nepheline phonolite tefrite up to 90-95% in nepheline syenite and phonolite. Feldspathoids are typically represented by nepheline in sodic terms, both intrusive and extrusive, or leucite±kalsilite in potassic and ultrapotassic suites; they can be associated or replaced, while increasing the bulk rock alkalinity, by nosean, haüyne, sodalite, lazurite, cancrinite (Allen and Charsley, 1968; Mitchell, 1996). Feldspars are mainly alkalifeldspar (perthites in nepheline syenite, sanidine or anorthoclase in nepheline phonolite) but plagioclase (typically oligoclase-andesine) turns increasingly important moving towards nepheline monzodiorite and phonolite-tefrite. The resulting fluxes have a characteristic composition (Table 3 and Figure 4) with an equivalent feldspar amount that is always very high (100-150%) and the alkali ratio is mainly between 0.1 and 0.6 (Figure 2B). The Fd_{eq} values overpass 100% because feldspathoids provide more alkalis than the reference value given by feldspars. The main challenge is the high amount of undesired minerals (10% to over 30%) that commonly include biotite±riebeckite±arfvedsonite in intrusive rocks or biotite±aegirine in extrusive ones. As a consequence, the chromophore amount is generally high (Figure 3B).

Arenite deposits exploited for ceramic fluxes represent the source richest in silica and amongst the poorest in chromophore oxides (Table 3). Their mineralogical composition is strongly dependent on the characteristics of the source basin: climate, erosion rate, dominant physical or chemical weathering, distance of transportation, energy of depositional environment, and principally the lithology of source rocks (Blatt et al., 1979). Quartz is usually the main constituent, since the equivalent feldspar amount is often below 40% (Figure 2D). Arkosic sandstones include feldspars (alkalifeldspar generally prevailing over plagioclase, hence AR typically >0.7, Figure 2D) and lithic fragments (abundant in lithic arenites) along with cement (carbonatic or siliceous) and sometimes a clay matrix. A wide spectrum of minerals can be present in lithic fragments and also as individual grains, particularly if the source basin was proximal and physical weathering predominated over chemical alteration. Minor components are commonly muscovite-sericite, chlorite, amphiboles, serpentine and calcite (which can enhance the fluxing attitude). Iron oxides and hydroxides are the major source of chromophore elements, especially as diagenetic precipitates and coatings on quartz and feldspar grains, or phyllosilicates constituting the mud fraction.

Fluxes obtained from metamorphics have a composition outstandingly varied, because they stem from a wide range of parent rocks. At any rate, ceramic raw materials are recovered from sources affected by a very low, low or intermediate metamorphic degree; thus, the original mineral assemblages are to large extent retained. For instance, data for orthogneiss approach those of granitoids (Figure 2B) or porphyroids resemble acid volcanics (Table 3). A key issue is the stability of fluxing minerals, namely feldspars and sericite, once pressure and temperature increase in burial metamorphism. The threshold can be set at the formation of undesirable components - like muscovite, paragonite, actinolite, kyanite - for some deleterious effect (refractoriness, content in chromophore elements, difficulty in processing, cause of defects in ceramic tile-making). Phyllites constitute a case apart, because the Brazilian deposits exhibit unique features: a fair equivalent feldspar content (Figure 2B) joined with a strong potassic overprint (AR>0.8) and chromophore amounts usually between 1% and 3% (Figure 3B).

Fluxes from epithermal rock alteration originate in a kaleidoscope of environments of formation; this circumstance translates into an extremely wide spectrum of mineralogical parageneses (Allen et al., 1996; Bove et al., 2007). In the resulting lithotypes, the fluxing action is essentially exerted by sericite±ammonium-mica±feldspars, typically present in toseki, roseki, agalmatolite and eurite (Nakagawa and Matsuura, 1994; Koh et al., 2000; Maineri et al., 2003). Secondary alkali-feldspars (microcline, low albite, anorthoclase and sanidine) ±chlorite±sericite feature episyenite and potassic alterations (Nishimoto et al., 2014) while Mg-chlorite±micas±feldspars are found in leucophyllite and magnesium metasomatics (Demény et al., 1997). Such unusual raw materials can be either alkaline fluxes (toseki, roseki, agalmatolite, and eurite) or alkaline-earth ones (leucophyllite). Pottery stone exhibits a potassic character, since AR is mostly >0.7, and an equivalent feldspar content below 40% and sometimes <20% (Figure 2A). The chromophore amount is typically below 1% (Figure 3A). In contrast, eurite approaches the compositional traits of porphyry (Fd_{eq}~70%, AR~0.8, chromophore amount 1-3%). Leucophyllite has distinctive values of alkaline-earth ratio and alumina content (Figure 5A) combined with a chromophore amount around 1% (Figure 5B).

Albitites provide fluxes characterized by a very high amount of sodic plagioclase (mostly albite, An_{0-10}) which is frequently associated to some quartz, leading to AR always below 0.1 and Fd_{eq} values from 70% to 100% (Figure 2A). Biotite, oligoclase, K-feldspar and further minerals present in parent rocks can be found in partially albitized terms. Other components (e.g., chlorite, epidote, kaolinite) may form during weathering or retrograde metamorphic episodes. This phenomenon can lead to intensive chloritization in some geological contexts, as in the Eastern Pyrenées (Boulvais et al., 2007), Sardinia (Castorina et al., 2006) and Calabria. Albitization is a selective process, which brings about a massive enrichment in sodium, along with a strong depletion in potassium and a partial removal of iron, while further elements are not mobilized or only to a minor extent. Although the chromophore amount can vary significantly, the deposits exploited by the ceramic industry exhibit values generally below 1% (Figure 3A).

Skarn deposits exhibit an outstanding variety of minerals and phase assemblages due to the extremely wide spectrum of geological environments and protolith composition (Einaudi and Burt, 1982; Meinert et al., 2005). Overall, alkaline-earth fluxes are obtained with distinct AER values (Figure 5A): predominantly magnesian (talc), essentially calcic (wollastonite) and mixed Ca-Mg (diopside). The chromophore amount is generally low for wollastonite and diopside skarns, while it can span widely for talc of different origin (Figure 5B). Talc deposits contain frequently chlorite and carbonates (magnesite, dolomite, calcite) that can be associated to quartz and feldspars (metasedimentary origin) or serpentine and sulfides (from basic and ultrabasic parent rocks) or tremolite-actinolite in dolomite marbles (Moine at al., 1989; Van Gosen et al., 2004; McCarthy et al., 2006). Wollastonite deposits have often a complex mineral assemblage, encompassing calcite, diopside-hedenbergite, garnet (grossular-andradite), quartz, tremolite and forsterite (Fernández-Caliani and Galán, 1998; Robinson et al., 2006). Diopside skarns can include tremolite, quartz, wollastonite, garnet, epidote, feldspars, tourmaline and carbonates (Vereshchagin et al., 1989; Kuzmickas et al., 2013).

Beneficiation paths of ceramic fluxes

The raw deposits above described can undergo a more or less extended process of beneficiation to get products matching the compositional and technological requirements for commercial fluxes. This processing usually consists of primary and secondary crushing, washing, milling and classification (Abdel-Khalek et al., 1994; Amarante et al., 1997; Potter, 2006; Saklar et al., 2004), but it can entail additional steps, such as attrition, magnetic separation, electrostatic separation, flotation, acid leaching, and micronization (Styriakova et al., 2006; Gougazeh, 2006; Cho et al., 2009; Abouzeid and Negm, 2014). A detailed description of these mineralurgical treatments goes beyond the scope of the present paper and here just a comparison of raw versus beneficiated fluxes is endeavored.

Mineral processing can vary upon the type of deposit and the degree of beneficiation needed to comply the market specifications. It is possible to appreciate, by contrasting the chromophore amount with the equivalent feldspar content, the overall beneficiation path, i.e. the compositional trend from the raw deposit to the commercial flux (Figure 6).

The main target of these mineralurgical treatments is the removal of minerals delivering iron and titanium oxides, and at the same time to preserve the amount of fluxing minerals or even increasing it in the final product. In presence of high amounts of feldspars and feldspathoids, beneficiation essentially draws horizontal paths, implying the separation of iron-bearing minerals with minimal losses in the equivalent feldspar content, as in the case of albitites (Figure 6A) and nepheline syenites (Figure 6B). Mineralurgical treatments of quartz-feldspathic materials tend to define oblique trends, where the reduction of Fe_2O_3 and TiO_2 amounts is achieved together with some enrichment in feldspars: examples are pegmatites (Figure 6C) and granitoids (Figure 6D). Arenites can be treated following two different paths: either a strong enrichment

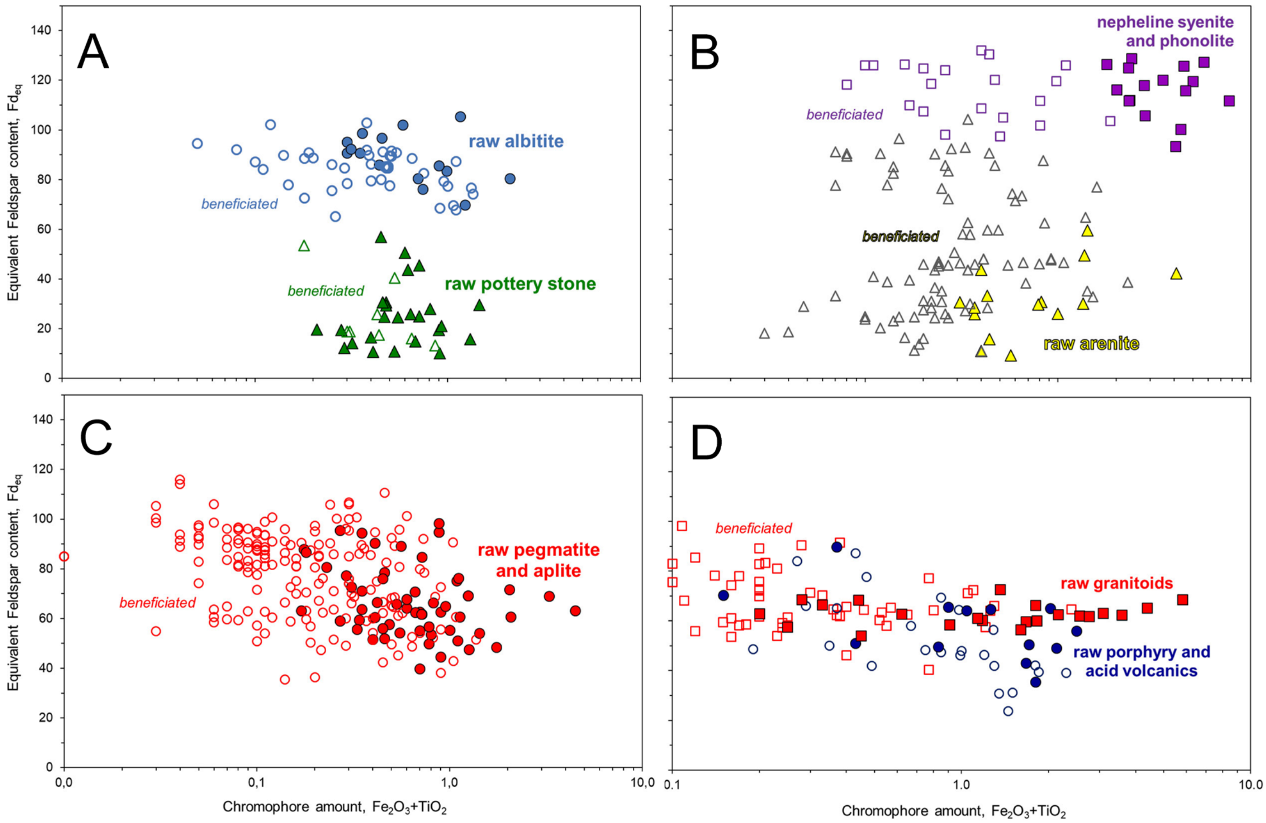

Figure 6. Chromophore amount vs equivalent feldspar content (Fd_{eq}) for raw (filled symbols) and beneficiated fluxes (empy symbols): albitites and epithermal deposits (A); syenoids, silica-undersaturated rocks and metamorphics (B); granitoids and acid volcanics (C); pegmatites, aplites and arenites (D).

in feldspars (involving most of the above-mentioned beneficiation steps) or a conspicuous reduction of chromophores, without any substantial gain in the Fd_{eq} values (Figure 6B). Other sources - like pottery stone (Figure 6A) - are hard to be beneficiated with significant improvements in the chromophore amount and/or the equivalent feldspar content. This is connected with the mineralogical composition (e.g., iron contained in fluxing minerals) and/or the particle size (too fine particles make ineffective many beneficiation techniques).

Technological behavior of ceramic fluxes

Ceramic fluxes must comply with several technological requirements that entail their behavior during the tile-making processing and the properties they are able to bestow on the finished product. Although fluxes may have some effects in every stage of tile manufacturing (e.g., milling, spray-drying, pressing, drying) their role is crucial in the firing process. Fluxes are expected to form a liquid phase at high temperature, so allowing the body densification by viscous flow, and to create a vitreous phase embedding fillers in the finished product (Zanelli et al., 2011).

This fluxing ability is often summarized under the term fusibility. It must be clear that fusibility is a behavior and not a property attributable to ceramic raw materials and batches. In principle, only single phase crystalline materials do exhibit a melting temperature. In contrast, vitreous phases gradually soften while the temperature is increased, as a consequence of the viscosity decrease. Mineral mixtures do not fuse together, strictly speaking, but undergo a partial melting, ideally according to eutectic proportions, even if kinetic factors often dominate in industrial firing schedules. Thus, the “degree of fusibility” is an attempt to classify the complex behavior stemming from crystalline and vitreous phases reacting together as the temperature is raised.

The degree of fusibility can be evaluated through in-situ experiments by observing the morphological changes occurring to specimens during heating (Paganelli, 1996; Dondi et al., 2001). A typical evolution entails subsequent steps that can be detected by hot-stage microscopy for increasing temperature: from sintering to “melting” (a conventional definition corresponding to the hemisphere shape) with the intermediate stages of softening and sphere (Figure 7A). In some cases, an additional stage occurs between the softening and sphere temperatures (Figure 7B): it consists in a more or less accentuated bloating, likely connected with some gas release originated by chemical reactions taking place during firing. The tendency to bloat has relevant implications in the firing of ceramic tiles and must be kept under strict control.

Among the various shapes pointed out in Figure 7, the most useful to define the overall behavior of a flux are the softening temperature (T_{soft}) and the melting temperature (T_{melt}). These parameters are significant for different reasons: the former is somehow related, in complex systems, with the incipient melt formation (hence the solidus temperature). Nonetheless, the latter records the occurrence of a large amount of liquid phase (thus approaching the liquidus temperature). It is possible to appreciate different behaviors by contrasting the softening

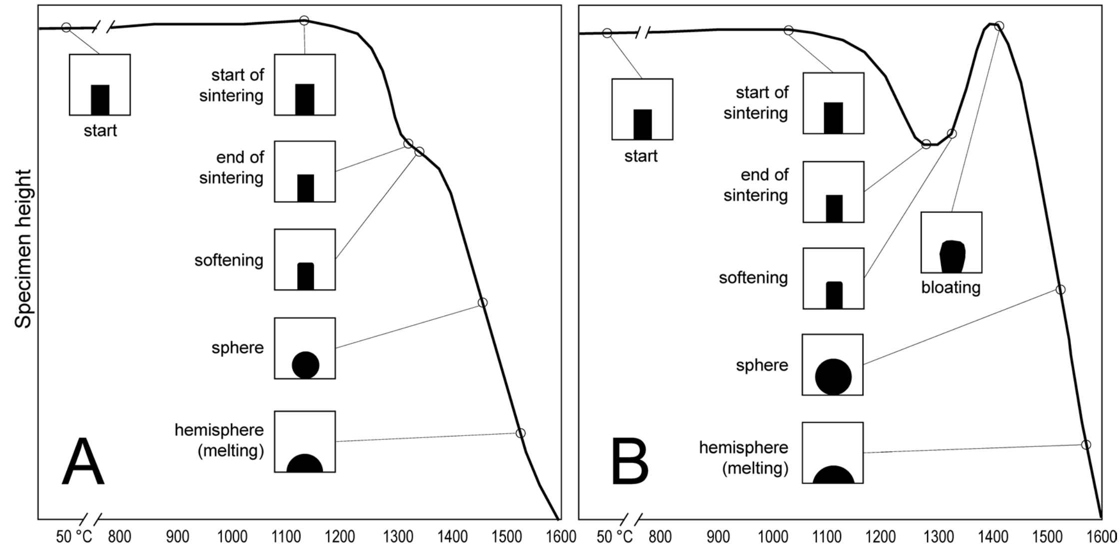

Figure 7. Example of firing behavior of ceramic fluxes observed under hot-stage microscope: A) typical feldspathic material and B) feldspathic flux showing a bloating stage.

temperature with the melting temperature. Monophasic materials exhibit T_{soft} close to T_{melt}, but the other cases show a certain distance from the 1:1 line (Figure 8A). This happens in polyphasic materials, especially when solid solutions are present (plagioclases are a very common example).

The characteristic temperatures depend on the amount of fluxing minerals. Taking into account the firing behavior of ceramic fluxes (Table 4 and Dondi et al., 2001) a rough trend stands out: the larger the equivalent feldspar content is, the lower both T_{melt} and T_{soft} are (Figure 8B). However, a second trend can be observed, shifted to lower T_{soft}, that can be attributed to larger amounts of iron oxide, which seem to lower T_{soft} more than T_{melt}. Refractory minerals, such as quartz, tend to increase both the characteristic temperatures (Figure 8A).

Ceramic fluxes from the various geological sources are characterized by a different degree of fusibility, as shown in Figure 9A. Although some raw materials from igneous basic rocks and skarn deposits plot close to the 1:1 line (being almost monophasic: talc, wollastonite, anorthosite) the remaining points draw an overall, oblique trend. Many fluxes obtained from granitoids, arenites, acid volcanics and metamorphics (including some pegmatites and aplites) exhibit a limited fusibility, with $T_{soft}>1350$ °C and $T_{melt}>1550$ °C. Oppositely, nepheline syenites and igneous intermediates have an excellent fusibility, with $1200<T_{soft}<1300$ °C versus $1300<T_{melt}<1500$ °C. Also, sodic feldspars (from albitites and pegmatites) have an enhanced fusibility, since $1250<T_{soft}<1350$ °C and $1350<T_{melt}<1500$ °C. Further fluxes - mostly mixed Na-K and K pegmatites, aplites and granitoids, including sericite-based phyllites as well - plot in the range $1300<T_{soft}<1400$ °C and $1480<T_{melt}<1550$ °C.

Overall, the above described degree of fusibility can be classified, considering also the known behavior of different fluxes in ceramic manufacturing, according to the chart of Figure 9B, which discriminates five classes with increasing fusibility and a zone of high risk of bloating. Along with fusibility, another important issue for ceramic fluxes is the occurrence and extent of bloating. This phenomenon appears to be triggered by the amount of iron oxide: a direct relationship is conspicuous, as shown in Figure 10A, even though the correlation coefficient is rather low ($R^2=0.3$) likely because further variables play a significant role in the degree of expansion. This is somewhat linked with the retention of gas bubbles, which is expected to be positively related with the melt viscosity that in turn is affected by the silica/alumina ratio. As a matter of fact, the degree of bloating scales directly with SiO_2/Al_2O_3 (Figure 10B). A repercussion of these observations is that a given amount of iron will affect more a quartz-feldspathic flux, since it has a higher silica/alumina ratio, than a high-grade feldspathic one. This circumstance may concur to justify the apparently exaggerate attention that end-users pay to the amount of iron oxide in ceramic fluxes, which is frequently well beyond the claimed darkening of the body color. This because the occurrence of a significant amount of iron oxide can affect the high temperature stability and related firing deformations too.

CONCLUSIONS

Fluxes are gaining a growing importance for the ceramic tile industry with the progressive shift from clay-based bodies (e.g., red stoneware or porous tiles) towards vitrified and semi-vitrified bodies (among which porcelain

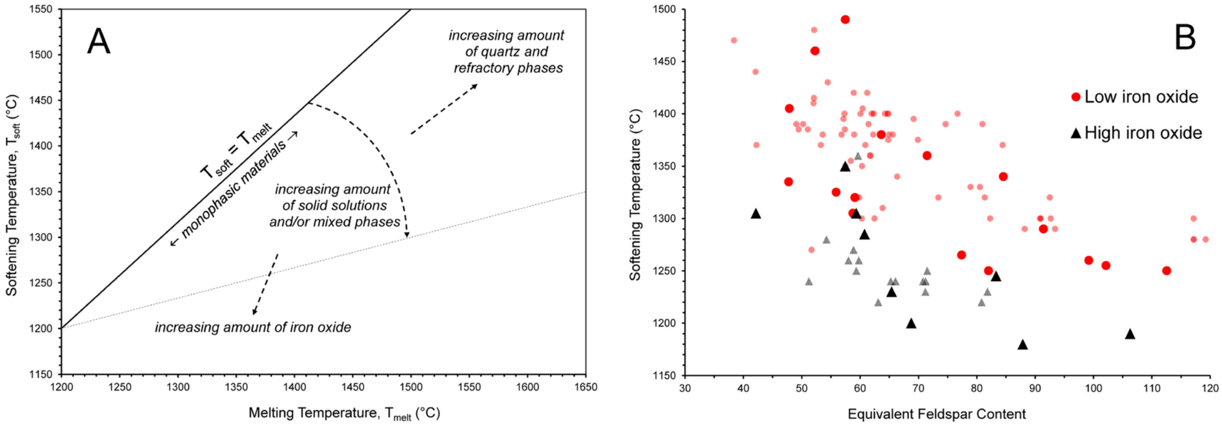

Figure 8. Fusibility chart showing the expected effect of flux components on the softening and melting temperatures (A). Effect of the equivalent feldspar content and the amount of iron oxide (low <1.8%, high >1.8%) on the softening temperature (B); large symbols: this work; small ones: data from Dondi et al., 2001.

Table 4. Firing behavior and composition of ceramic fluxes (experimental data, this work).

Sample	Classification			Firing behavior				Chemical composition (weight percent)									Main fluxing
code	Type	Fd_{eq}	AR	T_{soft}	T_{melt}	V_{rel}	BI	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	L.o.I.	minerals
Grn. 2SG	GRA	68.8	0.432	1200	1395	57.9	1.30	70.6	0.4	12.0	4.1	0.1	1.9	4.0	4.4	1.7	AFd, Plg
Grn. 50	GRA	57.5	0.498	1490	1650	19.9	0.89	79.1	0.1	11.0	0.6	0.2	0.8	3.2	4.5	0.5	AFd, Plg
Grn. F2	GRA	57.5	0.511	1350	1555	57.6	1.19	76.9	0.1	12.5	1.2	0.2	0.2	3.3	4.9	0.8	AFd, Plg
Peg. C.A.1	PEG	71.5	0.703	1360	1565	*n.bl.*	*n.bl.*	74.1	<0.1	14.6	0.1	0.2	0.2	2.5	8.4	0.4	AFd, Plg
Peg. LFV	PEG	84.6	0.760	1340	1500	0.0	0.60	70.0	<0.1	16.0	0.1	0.1	0.1	2.4	10.8	0.3	AFd, Plg
Peg. C.A.2	PEG	58.8	0.082	1305	1495	*n.bl.*	*n.bl.*	77.7	<0.1	14.3	0.1	0.2	1.7	5.5	0.7	0.4	AFd, Plg
Peg. S	PEG	52.3	0.647	1460	1599	52.2	1.16	75.3	<0.1	14.2	0.8	0.2	0.2	2.2	5.6	1.5	AFd, Plg
Peg. SM	PEG	65.4	0.120	1230	1360	64.2	0.91	65.9	0.3	18.3	1.6	2.3	1.1	6.3	1.2	2.4	AFd, Plg
Apl. BaM	APL	59.1	0.779	1320	1495	17.9	1.02	71.0	0.3	16.1	0.6	0.8	1.2	1.4	7.0	1.5	AFd, Plg, Ser
Apl. SIL	APL	63.6	0.250	1380	1500	15.9	0.89	75.4	<0.1	14.9	0.2	0.1	0.4	5.5	2.6	0.7	AFd, Plg
Apl. SIL2	APL	42.1	0.294	1305	1470	70.3	1.16	70.7	0.5	16.6	2.4	1.1	1.1	3.1	1.8	2.4	AFd, Plg
Rhy. S1	RHY	47.9	0.911	1405	1595	60.2	1.25	75.9	0.1	13.3	0.9	0.1	0.1	0.5	7.3	1.7	San, Plg
Alk.Sye	SYE	99.2	0.381	1260	1475	6.7	0.80	64.8	<0.1	19.4	0.6	0.1	0.3	7.2	6.3	1.3	AFd, Plg
Sye. 1QS	SYE	87.9	0.335	1180	1305	53.3	1.23	63.5	1.0	15.3	6.0	0.1	1.1	6.5	4.7	1.0	AFd, Plg
Sye. 3QS	SYE	83.3	0.359	1245	1365	31.4	1.05	64.2	0.5	15.8	5.9	0.1	1.9	5.6	4.5	0.6	AFd, Plg
Sye. 4NS	SYE	96.1	0.393	1100	1345	40.3	1.18	59.0	0.3	18.0	6.4	0.1	1.0	6.6	6.0	1.7	AFd, Plg
Sye. Cbs	SYE	82.0	0.266	1250	1450	*n.bl.*	*n.bl.*	69.2	0.1	16.9	0.7	0.1	1.3	6.6	3.4	0.9	AFd, Plg
NSP A40N	NSP	123.9	0.376	1270	1385	0.0	0.61	57.7	0.1	23.6	0.1	0.1	1.5	8.7	7.4	0.9	AFd, Nep
NSP E	NSP	102.2	0.356	1255	1450	4.1	0.76	64.4	<0.1	19.6	0.5	0.1	0.3	7.7	6.1	1.3	AFd, Nep
NSP EQ	NSP	112.6	0.342	1250	1440	11.7	0.84	61.7	<0.1	20.9	0.5	0.1	0.2	8.7	6.5	1.4	AFd, Nep
Snd. Col8	ARK	47.8	0.542	1335	1555	20.0	0.96	79.5	0.1	9.0	0.8	0.3	2.5	1.9	3.2	2.6	AFd, Plg, Clc
Snd. LT	ARK	11.4	0.710	1545	1650	1.1	0.99	90.8	0.1	3.8	0.3	0.2	0.1	0.4	1.3	0.5	AFd
Myl. PdS	MET	55.9	0.566	1325	1525	*n.bl.*	*n.bl.*	71.8	0.1	16.7	0.7	0.3	0.4	2.8	5.2	2.1	AFd, Plg
Myl. PdA	MET	29.0	0.937	1385	1595	*n.bl.*	*n.bl.*	68.3	0.2	19.3	1.0	0.2	0.6	0.2	4.2	5.8	AFd, Plg
Qtz. 5RD	MET	10.5	0.967	1510	1650	*n.bl.*	*n.bl.*	94.3	0.1	3.0	0.2	0.2	0.1	0.0	1.7	0.4	AFd
Alb. SN3	ALB	77.4	0.026	1265	1355	4.0	0.78	66.3	0.5	17.9	0.5	3.0	1.7	8.0	0.3	1.8	Alb, Chl
Alb. T.std	ALB	91.4	0.019	1290	1405	0.0	0.71	69.4	0.3	18.5	0.1	0.2	0.7	10.3	0.3	0.4	Alb
Alb. Tauá	ALB	106.3	0.007	1190	1275	*n.bl.*	*n.bl.*	63.8	0.1	17.9	2.4	1.0	3.2	10.7	0.1	0.3	Alb
Alb. TF	ALB	60.8	0.153	1285	1420	75.3	1.09	69.1	0.4	17.1	1.4	0.7	1.1	5.6	1.4	1.7	Alb
San. SIV	EPI	59.3	0.767	1305	1525	124.8	1.44	68.3	0.6	15.7	2.0	0.1	1.0	1.5	7.0	3.3	San
Diop. C.A.	SKA	-	-	1265	1272	*n.bl.*	*n.bl.*	51.4	0.1	3.4	1.6	16.7	24.4	0.2	0.1	1.6	Dio, Plg
Talc OS	SKA	-	-	1350	1447	*n.bl.*	*n.bl.*	46.0	0.2	11.0	2.0	30.0	0.5	0.1	0.3	9.5	Tlc, Chl
Wol. 46	SKA	-	-	1355	1420	*n.bl.*	*n.bl.*	50.5	<0.1	0.5	0.2	1.0	46.0	0.1	0.1	1.5	Wol
Wol. G325	SKA	-	-	1340	1430	*n.bl.*	*n.bl.*	51.5	<0.1	0.2	0.3	0.6	45.8	0.1	0.1	1.3	Wol

n.bl. = not bloating. □ = not applicable. Minerals: AFd = alkalifeldspar, Alb = albite, Chl = chlorite, Clc = calcite, Dio = diopside, Nep = nepheline, Plg = plagioclase, Tlc = talc, Wol = wollastonite.

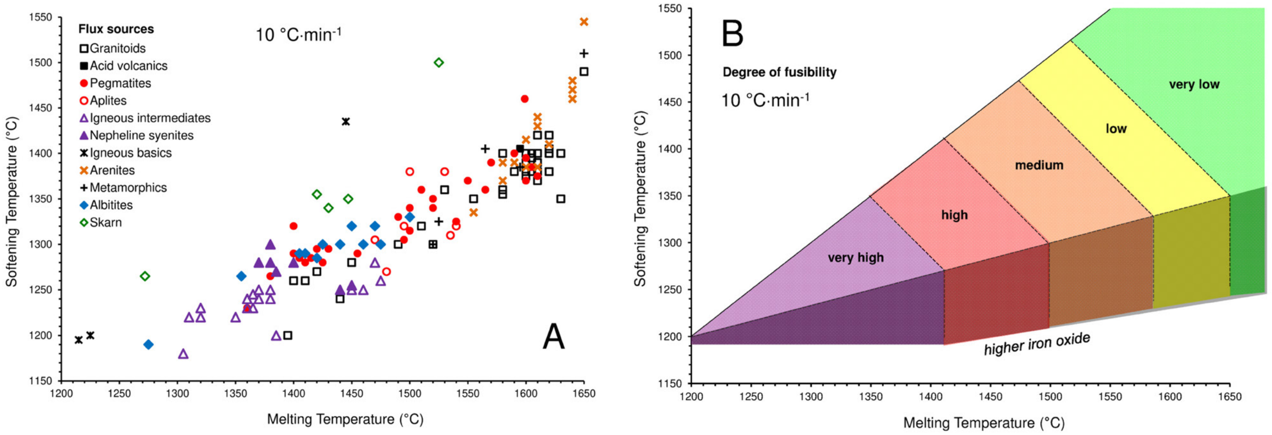

Figure 9. Degree of fusibility of ceramic fluxes from various geological sources (A) and chart depicting the fields of fusibility from very low to very high (B) and a zone of high risk of bloating (higher iron oxide).

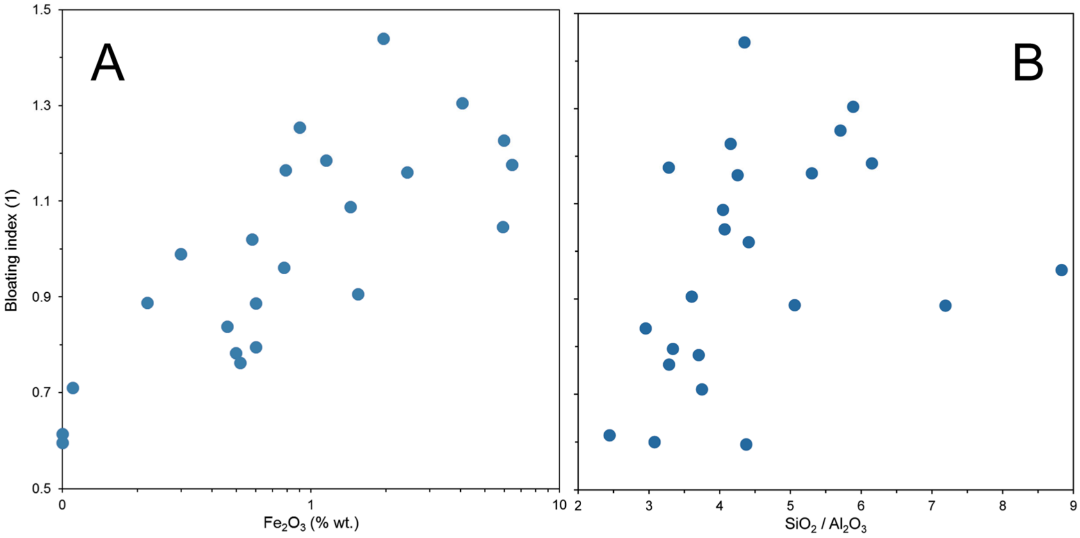

Figure 10. Bloating index in function of the amount of iron oxide (A) and the silica/alumina ratio (B) in samples exhibiting some tendency to bloat.

stoneware is the leading product) that consist to a large extent of feldspathic materials. The global production of ceramic tiles, current deployed around 13 billion square meters per year, implies a demand of approximately 250 million tons per year of raw materials (including clays, fluxes and fillers).

The present overview has for the first time put in evidence the outstanding variety of flux deposits actually exploited by the ceramic industry. These sources are no longer restricted to the classic pegmatitic and aplitic fields, but extend over the entire suite of acid igneous rocks, encompassing intrusive (granites to granodiorites), extrusive (rhyolite to dacite lavas and pyroclastics) and hypabyssal terms (porphyry veins) as well as metamorphic counterparts (metapegmatites, orthogneisses, porphyroids) and hydrothermally altered types, mostly derived from volcanic parent rocks (e.g., pottery stone). However, the most important flux suppliers nowadays are sodic metasomatics (albitites) and sedimentary deposits (arkosic sands) because these sources match some crucial market requirements: high fusibility (albitites) or low cost (sands) combined with large reserves and relatively low content in iron oxide. Nevertheless, further sources constitute strategic resources for future supply, like sericite-based fluxes (e.g., phyllites) or silica-saturated and unsaturated rocks from alkaline complexes (primarily syenite and nepheline syenite). The full exploitation of these deposits, having large amounts of femic minerals, represents a technological challenge still open, as it is the massive use of alkaline-earth fluxes recovered from skarns, basic igneous rocks and corresponding metamorphics.

From this standpoint, such a knowledge of current geological sources and possible alternatives is fundamental to draw any industrial strategy for the medium- to long-term supply of fluxing raw materials, particularly in the case of large-scale users as ceramic tile manufacturers. A possible impact of this much wider concept of “feldspar mineral resource” with respect to the conventional definition entails the following recommendations:

- all the lithologies actually utilized by the ceramic industry should be taken into consideration in survey and mapping of industrial minerals to get a more accurate estimation of resources;
- robustness of the supply chain of ceramic fluxes should be evaluated accounting for different sources and technological value to infer the actual economic and environmental sustainability;
- more studies should be addressed to the characterization and assessment of mineral resources suitable as ceramic fluxes, trying to link geological, compositional and technological aspects;
- potential criticalities in the exploitation of ceramic fluxes should be approached by considering the convolution of geological and technological issues, as those presented here.

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