The effect of mineralogy, microstructure and firing temperature on the effective thermal conductivity of traditional hot processing ceramics

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Abstract

The present work analyses the effect of mineralogy, microstructure and firing temperature on the effective thermal conductivity of traditional hot processing ceramics. Samples prepared with two quartz-rich kaolinitic clays (BAR1 and BAR2), a fine kaolinitic clay (ARG) and a glaucophane-rich clay (SIF), were fired in the range between 950 and 1350 °C. The effective thermal conductivity is principally affected by the porosity of the body. Mullite further improves the thermal conductivity of BAR1 and BAR2 ceramics, while in ARG samples cristobalite is correlated with the increase in thermal conductivity. In SIF ceramics, the higher densification and the formation of spinel, pyroxene and hematite results in a higher conductivity compared to the other samples. The amorphous phase improves the ceramics' thermal conductivity since it seals voids between particles. In samples in which quartz exceeds 50 wt%, the ceramics' thermal conductivity decreases because of fissures and detachment zones formed after the α-β quartz phase transition. Finally, functional conclusions are drawn on traditional cooking pot and Medieval glass crucibles.

Keywords

Thermal conductivity, Glass crucibles, Cooking Pots, Sifnos, Firing temperature

1. Introduction

The production of ceramics by using natural clays was one of the most important steps for the human civilization. Due to its characteristics and properties, ceramics played a key role in the ancient society and were used for a large variety of applications such as transport and storage vessels, bricks, tiles, cooking pots, decorative objects, technical tools, metal or glass crucibles, pipes, etc. Their technological evolution was influenced by the use of the most suitable raw materials, clay processing and firing technology in order to achieve the desired thermo-mechanical properties, which eventually determined the functionality of a ceramic artefact.

According to Rice (2005), three different use categories can be distinguished in traditional ceramic vessels: storage (e.g. jar), transport (e.g. amphorae), and processing (e.g. crucibles or cooking pots, with heat; mortars, without heat). In the last two cases, the required physical and mechanical properties are more restrictive in terms of functionality.

For example, transport amphorae should have a high tensile strength and toughening in order to provide a steady containment for their content. Otherwise their failure could have caused the loss of the content and endanger of the entire cargo of a merchant ship (Hein and Kilikoglou, 2014; Kilikoglou and Vekinis, 2002; Kilikoglou et al., 1998; Tite, 2008). In the case of hot processing ceramics which were exposed to a heating source, the thermal conductivity is one of the most important physical properties to be considered because it affects the heat transfer in a medium and it is strictly connected to the thermal shock resistance (Kingery et al., 1976; Tite et al., 2001; Velde and Druc, 1999). According to the context of use, the heating source could be set outside the container (i.e. cooking pots, glass crucibles) or inside (i.e. furnaces or early metal crucibles). In the first case, the ceramic should have a high thermal conductivity in order to allow the heat transfer through the container walls and heating of its content; in the second case, the container should have low thermal conductivity in order to reduce heat losses (Allegretta et al., 2014). This is also required in the production of building ceramics in order to reduce energy consumption (Gensel, 2015; Muñoz et al., 2014; Suctu, 2015).

In the last two decades, a lot of studies were published on the effect of raw materials on the thermo-mechanical properties of ceramics (Allegretta et al., 2014; 2015; Dondi et al., 2004; García-Ten et al., 2010a; 2010b; Hein et al., 2008; 2013; Hoard et al., 1995; Jordan et al., 2008; Kilikoglou et al., 1995; 1998; Lassinantti Gualtieri et al., 2010; Müller et al., 2010; in press; Vekinis and Kilikoglou, 1998; Warfe, 2015). Porosity is one of the main parameters which affect the thermal properties of the material. At temperatures below 1200 °C the presence of pores in the ceramic body lowers its thermal conductivity, whilst at higher temperatures the relevant contributions of the radiation and convection in heat transfer can improve the thermal conductivity (Kingery et al., 1976; Kohl, 1964; Litovsky and Shapiro, 1992; Litovsky et al., 1996, Fedina et al., 1997). Several studies demonstrated that the shape and the orientation of pores should be considered because elongated pores perpendicular to the heat flux reduce, more than spherical ones, the heat diffusion in the body (Cernuschi et al., 2004; Hasselman and Johnson, 1987; Hein and Kilikoglou, 2007). However, the consideration of either porosity or bulk density is insufficient for the study of thermal conductivity of a clay-based ceramic, as demonstrated by Dondi et al. (2004) and Lassinantti Gualtieri et al. (2010). In particular, Lassinantti Gualtieri et al. (2010) found a correlation between the effective thermal conductivity and some components of the natural clay used for the preparation of ceramics such as organic material, feldspar and clay content. They also noted that the fine size of the clay contributes to improving thermal conductivity, probably due to a better sintering level. Furthermore, the addition of some additives to the clay mixture can affect the thermal conductivity of the body. Tempering materials such as quartz or granite improve the thermal conductivity of the fired body up to certain content (10-15%), but when they exceed this limit, they produce the opposite result because both the mismatch in thermal expansion and the α-β quartz phase transition create a detachment zone around temper grains (rim porosity) and cracks in the body (Allegretta et al., 2014; Hein et al., 2008). The addition of limestone temper decreases the thermal conductivity of the ceramic in particular when the firing temperature is set above the carbonate decomposition temperature (Allegretta et al., 2014; García-Ten et al., 2010b). The presence of organic materials had a positive effect on the thermal insulation of ceramics (Lassinantti Gualtieri et al., 2010) even if different effects have been observed according to the type of organic material used (straw, seeds, etc) because they produce pores with different shapes (Hein et al., 2013).

However, all these results are related to clay mixtures fired at temperatures (from 500 to 1000 °C) lower than those used for firing technical ceramics like glass crucibles (Eramo, 2004; 2006a). At higher temperatures (1200-1400°C), new phases form revealing different thermal properties. Also the porosity and the shape of the pores could change according to the viscosity of the melted part. High firing temperatures are reached in a few experimental studies (Michot et al., 2008) but in such cases the results are related to ceramic made with pure standard clay and not with natural clay.

The present work aims to analyse the thermal conductivity of ceramics prepared with different clay mixtures fired in the range between 950 and 1350 °C. Some of these clays were used in the preparation of ancient technical ceramics. In particular, two coarse kaolinitc clays from Switzerland were used in the manufacture of Medieval glass crucibles (Eramo, 2006b), whereas a glaucophane-rich clay from the Greek island of Sifnos is used for the production of cooking pots since the 17th century (Kyriakopoulos, 2015). In addition, a fine kaolinitic clay, already used by us in some previous works on thermo-mechanical properties of ceramics (Allegretta et al., 2014; 2015), was also tested in the present work in order to study the effect of clay particle size and composition on the thermal conductivity of the fired body. The thermal conductivity of these ceramics is discussed on the base of mineralogy, porosity and microstructures in order to consider all the possible variables changing during firing.

2. Materials and Methods

2.1 Raw materials and ceramic preparation

Four different clays were used for the preparation of the samples: two clays (BAR1 and BAR2) were sampled in Switzerland (Court, Ct. Bern), SIF was sampled on the Aegean island of Sifnos (Greece) and ARG is an Ukrainian clay distributed by Imerys Tiles Minerals Italia S.r.l. of Reggio Emilia - Italy. The clays were water sieved and the fraction with particle size greater than 2 mm was removed. After drying the powdered clays, 5 wt.% of water was added and ceramic disks of 30 mm of diameter and 7 mm of height were prepared using uniaxial pressing (25 MPa). This uniform pressure was applied in order to eliminate primary porosity and to avoid effects due to pore shape which could affect the thermal conductivity of the ceramic bodies (García-Ten et al., 2010a). The disks were left drying for 24 h at 100 °C and fired at 950, 1050, 1150, 1250 and 1350 °C using a rate of 150 °C/h and a soaking time of 1 h. As disks made from the SIF clay melted at temperatures above 1150 °C they were not considered in the paper.

2.2 Analytical techniques

Both clays and ceramics were analyzed via X-ray powder diffraction technique. Initial qualitative analyses of the clay fraction of each sample were performed on as-prepared, calcined (550 °C) and glycerol-treated oriented samples (Azaroff and Burger, 1958), using a θ/2θ PANalytical X'Pert pro MPD diffractometer and X'Pert Highscore (PANalytical, version 3.0) with a PDF2 reference database implemented in the software. XRPD data for quantitative phase analyses (QPA) were collected using a θ/θ PANalytical Empyrean diffractometer, equipped with a time multiple strip (RTMS) *PIXcel*^{3D} detector. A 0.125° divergence slit, a 0.25° anti-scattering slit and a soller slit (0.02 rad) were mounted in the incident beam pathway. The diffracted beam pathway included a Ni filter, a soller slit (0.02 rad) and an antiscatter blade (7.5 mm). A virtual step scan of the RTMS detector of 0.026 °2θ was used. The data were invariably collected with high counting statistics (360 s/step) from carefully ground powders, using sideloaded sample holders. The QPA were performed using Rietveld refinements which were carried out means of the fundamental parameters based Rietveld program BGMN Version 1.8.6b (Bergmann et al., 1998). For fired samples, the quantitative phase analysis method using the Rietveld technique was combined with the internal standard method in order to quantify the amorphous phase (Bellotto and Cristiani, 1991; Gualtieri, 1996; 2000; Gualtieri and Artioli, 1995; Gualtieri and Zanni, 1998) formed after the dehydroxilation of clay minerals. Corundum was thus added to the samples (10 wt.%) as internal standard and included in the refinements.

The following generalized refinement models were applied for the analyzed samples: background was modelled by a polynomial function with a different number of coefficients depending of the sample, i.e low degree of background polynomial in clay sample and high degree of background polynomial in fired samples; zero point (limits ±0.02°) and sample displacement (±0.03 mm) were always refined. Lattice parameters were refined for all phases with 'reasonable' interval restraints and spherical harmonics models were used to correct preferred orientation, which was observed especially for layer silicates. All the structures used for the Rietveld refinement were taken from the BGMN database with the exception of that of glaucophane (Papike and Clark, 1968); kaolinite and smectites were refined according to a disordered kaolinite and a Na-smectite structure model, respectively.

The particle size distribution of the four clays was studied by water sieving for the fraction between 2000 - 32 μm, and sedimentation applying Stoke's law for particles size less than 32 μm (Tickell, 1965).

In order to study the ceramic microstructures, backscattered electron (BSE) micrographs were acquired on graphite-coated samples using a ZEISS LEO 50XVP scanning electron microscope (SEM), operating at 15 kV. X-ray maps were obtained with a X-MaxN 80 mm^2 SDD detector and Aztec software (Oxford Instruments).

The open porosity was estimated by water immersion (EN 993-1).

Chemical analysis was conducted using a Rigaku Supermini 200 WDXRF equipped with a Pd-anode working at 50 kV and 4 mA. The WDXRF was calibrated using geological standards by SARN (Service d'Analyses des Roches et des Minéraux) and the loss of ignition (LOI) was estimated.

The thermal conductivity (k) of the polished ceramic disks was estimated using a modified Lee's disk apparatus, a device which has proven to be suitable for the reproducible determination of this physical property in insulating materials (Allegretta et al., 2014; Hein et al., 2008; 2013). The two brass disks used as heating and detector disk have a diameter of 30 mm and were connected to two thermocouples linked to a data logger in order to record their temperatures. The heating temperature was set at 120, 220 and 370 °C and the thermal conductivity was estimated at the equilibrium using the Fourier's equation:

$$(T) = \dot{q}_{loss}(T)\frac{x}{A(T_1 - T_2)}$$

where x and A are the thickness and the surface area of the specimen, T_1 and T_2 are respectively the temperatures of the heating and detector disks when the system has reached equilibrium. $\dot{q}_{loss}$ is the heat loss of the detector disk, which has been estimated by recording the temperature curve of the heated disk left for cooling. Since this work aims to analyse the parameters affecting the effective thermal conductivity and does not want to focus its attention on the thermal conductivity of the solid phase only, no correction with pore volume fraction using Maxwell's or Landauer's relations were applied.

3 Results

3.1 Clay characterisation

The mineralogical composition of each clay fraction, as determined by XRPD data and Rietveld refinements, is reported in Table 1, with relative refinement agreement factors. Standard deviation values of weight percents with a 3-σ correction are reported in order to give a more realistic confidence interval for this kind of complex systems. The chemical composition and the particle size distribution of the clay samples are reported in Tables 2 and Table 3, respectively.

The sample ARG, corresponding to the same clay used in three our previous studies (Allegretta et al., 2014; 2015; 2016), is mainly composed of kaolinite (~55 wt%) with minor illite/mica, quartz, smectite and traces of anatase, rutile and alunite. It is a considerably fine clay as 80 % of the sediment shows particle size lower than 2 µm.

The clay samples BAR1 and BAR2 are both composed principally by quartz (up to ~75 wt%), kaolinite (19 and 21 wt%, respectively) and very small quantities of micas and calcite (less than 4 wt%). In sample BAR2 also traces of hematite were found. Both BAR1 and BAR 2 are characterised by a consistent sandy component (respectively 65 and 55 %) and the rest is equally distributed between the silt and clay fraction. The clay sample from Sifnos consists of glaucophane (up to 46 wt%) and minor components of quartz, micas, epidote, and kaolinite, whereas plagioclase, dolomite, garnet, rutile and hematite are present in very low amounts. More than 40 % of the SIF clay is in the range of sand, while silt and clay fraction are respectively attested at 27 and 32 %. SIF clay is characterized by higher contents of K_2O, Na_2O, MgO, CaO, as well as a relevant concentration of Fe_2O_3 (11.45 %) with respect to ARG, BAR1 and BAR2 clays (Table 3).

3.2 Ceramic characterisation

3.2.1. Phase analysis from XRPD

The results of the Rietveld quantitative phase analyses of the fired samples are reported in Table 4. Values of Rwp range from 3.71 % to 9.14 % (Table 4), testifying for the refinement goodness.

In the ceramics made from the ARG clay sample, the principal crystalline phase is quartz and the amount of this phase remains almost constant up to the temperature of 1150 °C. At of 950 °C the amorphous, clearly visible by a broad hump in the background in the range of 15-30° and a spinel-type phase, forms from decomposition of clay minerals. Moreover, a spinel-type phase, indicated by the three broad reflections at about d = 2.39, 1.98 and 1.40 Å, and traces of a weakly crystallized mullite (protomullite or primary mullite) are detected at this temperature, as reaction products of metakaolinite. In agreement with assessments reported in Allegretta et al., (2016) the spinel type phase was interpreted as a γ-Al_2O_3 spinel phase with very limited Si-for-Al substitution. In samples fired at 950 °C and 1050 °C, the amount of protomullite does not exceed 10 wt%, whereas the content of this phase, as well as its crystallinity, increases significantly at higher firing temperatures (Table 4). The concentration of γ-Al_2O_3 spinel does not change from 950°C to 1050 °C, but decreases significantly at 1150 °C, until disappearing completely at 1250 °C, with the simultaneous formation and increase of the well crystalline mullite and the formation of cristobalite. The concentration of γ-Al_2O_3 spinel does not change from 950°C to 1050 °C, but decreases significantly at 1150 °C, until disappearing completely at 1250 °C, with the simultaneous formation and increase of the well crystalline mullite and the formation of cristobalite.

The amorphous content slightly decreases from 950 °C to 1150 °C and then increases limitedly up to 1350 °C. Through this interval the nature of the amorphous phase changes, as from 1250 °C onward a vitreous phase starts to form as will be better described in the discussion paragraph. Such extended vitrification is inversely correlated with quartz content (Fig. 3C).

In samples BAR1 and BAR2 quartz is the only crystalline phase present up to the firing temperature of 1050 °C

in addition to amorphous mainly formed from kaolinite decomposition. No distinct reflection of mullite or broad humps of spinel-type phase were detected in the powder patterns. At 1150 °C the amorphous content drops drastically in both BAR1 and BAR2 ceramics, in coincidence with the crystallization of mullite and cristobalite. The amount of mullite in these samples remains almost constant from 1150 to 1350 °C, whereas cristobalite increases progressively in this temperature range (from 2.8 to 13.4 wt% in BAR1 and from 3.5 to 17.8 wt% in BAR2). The ceramics prepared from the Sifnos clay show a rather complex mineralogical composition with spinel, pyroxene, hematite and plagioclase, representing the main newly formed phases. The amounts of these phases do not show significant variations in the temperature range from 950 to 1150 °C, with the exception of hematite and spinel which show a limited increase with the firing temperature, exceeding the estimated standard deviation values. The content of the amorphous range from 53 to 57 wt%, with limited differences from sample to sample within the range of the experimental error. Mg-Al and Fe-Al spinels and pyroxenes are the main products of glaucophane and garnet decomposition. The increase of hematite amounts in fired samples compared to the original clay could be related to the oxidation of poor crystalline Fe oxy-hydroxides not detected in XRPD of raw clay. The decomposition of original epidote could have contributed to formation of plagioclase, pyroxenes and hematite.

The small increase of quartz observed in all the samples fired at 950 °C compared to the original clay, may be explained as the result of a passive increase due to calcination of clay minerals and calcite, but also by a difficult of the Rietveld approach to quantify low crystalline phases,(e.g. metakaolinite), which do not present intense diffraction lines. This justify the use of standard deviation values of weight percents with a 3-σ correction (Table 4), which we consider more realistic for the present data.

3.2.2 Microstructure and porosity

The microstructures observed under the scanning electron microscope account for relevant differences among samples from the four series of ceramic tests. Pore shape and distribution are heavily influenced by particle size distribution of the clay.

The BSE images of ARG clay test pieces fired at 950 °C, 1150 °C and 1350 °C clearly show an evolution of size, shape and distribution of pores, as consequence of clayey matrix dehydroxilation and cracking of coarse quartz grains as well. Highest densification was reached at 1150 °C, whilst diffused small rounded pores in the range between 2 and 10 µm were observed at 1350 °C (Fig. 1).

BAR1 and BAR2 series show similar microstructures. Coarse quartz grains are the prevalent portion of the ceramic body and no densification occurred up to 1150 °C (Fig. 1), wheres at higher firing temperature the decrease of the porosity (Table 5) indicates the occurrence of densification. Between 1150 °C and 1350 °C the limestone fragments from the original clay of BAR2 produced

isolated Ca-rich domains which evolved in partial melting of the ceramic body, giving closed pores. SEM observations reveal some tridymite crystallised from the melt around quartz grains (Fig. 2), but the amount of tridymite nuclei is too low to be detected from XRPD.
In the samples of SIF series the original presence of sheet silicates and platy particles give elongated open porosity at 950 °C, which decreased progressively at higher firing temperatures becoming more rounded and spherical. Incipient melting of feldspars, micas and amphiboles is already present at 950 °C and some bloating up to 1150 °C. Coarse quartz cracking is observed, but negligible rim porosity (Fig. 1).

3.4 Thermal Conductivity

As a general trend our data (Table 5) show that the increase of the firing temperature involves an improvement of the effective thermal conductivity (k_{eff}.). However, some exceptions and peculiarities come out from the different ceramic bodies. In the samples of the ARG series, a continuous increment of k_{eff} is observed up to 1150 °C passing from 0.63-0.67 to 1.17-1.22 W/m·K. At higher firing temperatures, the effective thermal conductivity remains constant. A slight increase in thermal conductivity, when the test temperature passes from 120 °C to 370 °C, is also observed in all the ARG ceramics.
The BAR1 and BAR2 series of ceramics show an increase in k_{eff} with firing temperature, with the exception of samples fired at 1150 °C, which exhibit a reduction of the thermal conductivity to 0.64 and 0.73 W/m·K, respectively, thus reaching values comparable with those recorded for ceramics fired at 950 °C. In samples fired at 1250 and 1350 °C, the thermal conductivity increases again achieving values ranging from 0.99 to 1.20 W/m·K for BAR1, and from 1.09 to 1.37 W/m·K for BAR2. In samples from both the BAR1 and BAR2 series, the thermal conductivity reduces with the test temperature, with the unique exception represented by samples fired at 1150 °C, which show an increase of k_{eff} passing from 120 to 370 °C.
Finally, ceramic prepared with the SIF clay are the most conductive ones. When fired at 950 °C, they reach 1.03-1.07 W/m·K, a value of thermal conductivity observed only at higher temperatures in the case of ceramic prepared with the other clay mixtures. At the firing temperature of 1050 °C, the thermal conductivity reaches its maximum and remains constant at 1150 °C. Also in this case, the increase of the test temperature results in a reduction of the thermal conductivity which becomes relevant for SIF_1150 which passes from 1.56 to 1.45 W/m·K.

4 Discussion

4.1 Analysis of the factors which affect the effective thermal conductivity of ceramics

The change of firing temperature produces several changes in the ceramic disks in terms of porosity, mineralogy and microstructures and the variation of these factors influences the effective thermal conductivity of ceramic bodies. A general view of these changes as a function of the firing temperature is shown in Figure 3. The nature of the clay and the firing temperatures influence considerably the open porosity, as well as the shape and distribution of pores. The overall impact of the porosity on the effective thermal conductivity is higher than that produced by amorphous and crystalline phases. As a matter of fact, thermal conductivity and porosity have opposite trends (Figure 3), indicating that the increase in firing temperature reduces the open porosity and improves the thermal conductivity of the ceramics.

Plotting the thermal conductivity versus the porosity (Fig. 4), a correlation coefficient of 0.67 is found, even if different clay mixtures are considered. These results are in accordance with previous literature (Dondi et al., 2004; García-Ten et al., 2010a; Lassinantti Gualtieri et al., 2010) showing a direct correlation between thermal conductivity and bulk density. Secondary porosity formed during firing is negligible for ARG samples and becomes progressively more important in BAR and SIF. Whilst ARG and SIF clays show incipient densification between 1050 and 1150 °C, and 950 and 1050 °C respectively, BAR clays show densification only at T > 1150 °C. At this temperature, local melting in Ca-rich micro-domains gives closed porosity (Fig. 1) and decreases of apparent porosity (Table 5).

In addition to the porosity, mineralogical changes play an important role in the achievement of specific thermal properties. The correlation between thermal conductivity and mineral phases developed during firing are shown in Figure 5. Figure 5A indicates that the thermal conductivity increases with increasing percentage of the amorphous phase in the samples. Although very weak, the observed trend could be explained considering that the amorphous phase, strictly related to the firing temperature, closes the pores creating a continuum among crystalline phases. Furthermore, according to Smith and al. (2003) the thermal resistance at the grain boundary between two solid phases of different nature is higher than the resistance produced in continuous single-phase materials (i.e. the amorphous phase). These factors seem thus to contrast an opposite effect related to the lower thermal conductivity of the amorphous compared to that of the minerals from which it forms (Kingery et al., 1976)

For similar firing temperatures, the formation of the amorphous is not uniform in all the samples, as it depends by the amount of clayey matrix and its composition: in ceramics formed by BAR1 and BAR2 clays, which showed not more than 23 wt% of clay minerals, the amorphous phase does not exceed the 25 wt% (Table 4, Fig. 3A and B), whereas in samples from ARG and SIF clays (Table 4,

Fig. 3C and D), containing 83 wt% and 88 wt% of aluminosilicate, respectively, a greater amount of the amorphous is formed (from 40 to 57%). Moreover, higher vitrification is observed in SIF clay owing to its more complex chemical composition and the lower eutectic compared to those of ARG clay. The evolution of amorphous contents in kaolinite-based samples (i.e. ARG, BAR1 and BAR2) between 950 °C and 1350 °C can be explained with three main reaction steps: 1) complete dehydroxylation of phyllosilicates (950 – 1050 °C); 2) part of the amorphous derived from the dehydroxylation of phyllosilicates is transformed in new crystalline phases (e.g. protomullite, cristobalite, spinels) (1050 – 1150 °C); 3) quartz grains start to melt as consequence of fluxes present in the matrix (1150 -1350 °C). While in the step 3 ARG body tends to stabilize amorphous, BAR1 and BAR2 crystallizes cristobalite (Fig. 3). Actually, mullite and cristobalite are the main newly formed crystalline phases in kaolinite-based fired bodies (ARG, BAR1 and BAR2 ceramics). Both mineral phases have a high thermal conductivity which is 4.7 W/m·K for mullite (Brea et al., 2005) and 6.2 W/m·K for cristobalite (Kunugi et al., 1972) while traditional ceramics are in the range of 0.3-1 W/m·K (Allegretta et al., 2014; Dondi et al., 2004; García-Ten et al., 2010a; 2010b; Hein et al., 2008; Lassinantti Gualtieri et al., 2010). It suggests that the formation of mullite and cristobalite further contributes to the improvement of the effective thermal conductivity in the above kaolinite-based fired bodies (Michot et al., 2008; Bournet el al., 2015) over the increase due to densification. However, they play different roles according to the ceramic system in which they form and, hence, to the starting clay mixture. In ARG samples obtained from a very fine clay type containing about 55 wt% of kaolinite, the formation of a weakly crystalline mullite (about 6 wt%) is associated with the formation of γ-Al_2O_3 and amorphous silica at 950 °C. From 1150 °C onward, a well crystalline mullite is formed in the samples, i.e. secondary mullite, and the amount of this phase increases significantly with the firing temperature (Table 4), together with the strong reduction of porosity (from 0.32 to 0.08), the disappearance of γ-Al_2O_3, the decrease of the amorphous phase and the crystallisation of few cristobalite (lower than 3 wt%). In ARG samples the main cause for the increase in the effective thermal conductivity is the densification of the body (porosity goes from 0.32 to 0.01), but a further contribution to the k_{eff} improvement is given by the formation of mullite, as demonstrated by the correlation plot in Figure 5B. In the case of BAR samples, no correlation is observed between the thermal conductivity and mullite, which show almost constant contents from 1150 °C to 1350°C (Fig. 3A and B), but in these samples the cristobalite content increases progressively passing from about 3 wt% to about 18 wt% (Fig. 3A and B) in the same firing range. By plotting the amounts of cristobalite with the values of the thermal conductivity (Fig. 5C), a fair correlation is observed in BAR1 and BAR2 ceramics (R^2 = 0.60), suggesting that cristobalite gives a contribution to the increase of thermal conductivity, in addition to the densification.

The contribution to thermal conductivity of the γ-Al_2O_3 spinel, which was a distinct newly formed phase in ARG systems in the temperature range from 950 °C to 1150 °C, cannot be discussed at this place as no thermal data about thermal conductivity of this phase are available in literature. The α form of Al_2O_3 is very conductive (k = 35 W/m·K at room temperature) but the thermal conductivity of this phase cannot be assumed for the γ form (Bansel and Zhu, 2005; Bakshi et al., 2008).

Quartz is present in all samples as relic phase. Its effect on the thermal conductivity is described in Figure 5D. Despite the thermal conductivity of quartz (7.2 W/m·K according to Kinugi et al., 1972) is higher than that of clay-based ceramics (0.3 - 1 W/m·K), no positive correlation between the quartz content and the k_{eff}. of the ceramic tests is observed. Looking at Figure 5D, two different situations could be described: 1) ceramics with a quartz content between 50 and 80 wt% (i.e. BAR1 and BAR2 bodies) and 2) ceramics which contain up to 20 wt% of quartz (i.e. ARG and SIF samples). In the first case, the correlation between quartz content and ceramic thermal conductivity is negative (R^2 = 0.55). This can be explained considering two aspects. Firstly, the starting raw materials are poor in clay minerals (20 - 23 wt%) which can fill the spaces between quartz particles and keep them together after sintering. Secondly, quartz undergoes a structural transition from α-to-β-quartz at 573 °C. The reaction takes place with volume expansion and is reversible when the temperature returns below 573 °C. This change in volume produces fractures and fissures in the matrix and detachment zones around quartz particles, which acts as thermal barriers reducing the thermal conductivity of the ceramic (Allegretta et al., 2014; 2015; Bragança et al., 2006; De Noni Jr et al., 2008). In the case of ceramics fabricated from ARG and SIF clays, no correlation can be observed because of the higher densification and the formation of high conductive minerals, such as mullite in ARG ceramics and spinel, pyroxenes and hematite in SIF bodies. Moreover, as reported in literature (Allegretta et al., 2014; García-Ten et al., 2010b) the presence of low percentage of quartz (below 15-20 wt%) can improve the thermal conductivity of the body notwithstanding the occurrence of the α-β quartz phase transition.

The ceramics prepared with the clay sampled from Sifnos are more conductive than other ceramics. SIF clay is less refractory than the others due to the higher content in fluxes (Table 2) and this produces a high densification which can be considered completed (the porosity is 0.04) at 1150 °C while in ARG, BAR1 and BAR2 it starts from this temperature. In fact, the SIF ceramic fired at 950 °C reaches a thermal conductivity (1.03 - 1.07 W/m·K) which is recorded only at 1050 °C for ARG ceramics and at 1250 °C for BAR1 and BAR2 samples. Moreover, in SIF bodies, high conductive minerals form after firing. Spinel and pyroxenes are the main newly formed phases in these ceramics and have a thermal conductivity of 9.5 and 4.3 W/m·K (Horai and Simmons, 1969), respectively, and can give a contribution to the improvement of conductivity of these samples with respect to those prepared with the other kaolinitic clays (Fig. 3D). Hematite, whose content in SIF ceramics increases with increasing of firing temperature, is another mineral which has a high thermal conductivity (11.3 W/m·K according to Horai and Simmos (1969) and may influence positively the overall thermal conductivity of the SIF ceramic bodies. Hematite is also detected as traces in ceramics prepared with BAR1 and BAR2 samples, thus its influence on the thermal conductivity of these ceramics can be considered negligible.

Finally, plagioclase forms in SIF ceramics but its amount (9.5-13.6 wt%) combined with its thermal conductivity (1.7-2.0 W/m·K according to Horai and Simmos (1969)) is not expected to have any significant effect on the overall ceramic thermal conductivity.

4.2 Functional implications

On the base of the results presented in this work, some functional considerations can be done, in particular for the ceramic produced with SIF, BAR1 and BAR2.

Since Siphinian cooking pots were usually fired in the range between 800 and 950 °C (Spataro et al., 2015), a comparison with sample SIF_950 can be done. To fulfill its function, a cooking pot should enable the passing of the heat from outside to inside in order to heat up its content and should withstand its thermal and mechanical loads and possible thermal shocks (Allegretta et al., 2014; Tite et al., 2001; Velde and Druc, 1999).

The thermal conductivity of SIF_950 is higher than that measured in other ceramics fired at the same temperature and comparable thermal conductivities are recorded in ARG ceramics at 1050 °C and BAR1-BAR2 bodies fired at 1250 °C. SIF_950 is also more conductive than other traditional ceramics prepared with different raw materials which fired at 1000 °C (Dondi et al., 2004; García-Ten et al., 2010a; 2010b; Lassinantti Gualtieri et al, 2010; Michot et al., 2008). This is mainly due to the higher densification of the matrix and, in second instance, by the formation of spinel, pyroxenes and hematite which do not form in the other systems. Since, SIF_950 is more conductive than other ceramics, the thermal energy transfer through the pot walls is easier and heat up its content. If fired at higher temperature, SIF ceramics are 50% more conductive than SIF_950, which is particularly suitable for directly heating foodstuff in an oven or on a fire. On the other hand high thermal conductivity might be a disadvantage for sustaining heat inside a cooking pot, once it is removed from the heat source, even though in this case also the heat capacity of the material has to be considered.

A high thermal conductivity improves the thermal shock resistance (R_{ci}) which is given by:

$$R_{ci} = k\sigma_f(1-\mu)/E\alpha$$

where k is the thermal conductivity, σ_f is the fracture strength, μ is the Poisson ratio, E is the Young's modulus and α is the linear thermal expansion coefficient of the ceramic (Kingery et al., 1976; Tite et al., 2001). A further improvement of the thermal shock resistance is given by the consistent amorphous content, the ceramic porosity, the shape of pores, and the particle size of the clay. The amorphous phase has a very low linear thermal expansion coefficient compared with that of mineral phases (Kingery et al., 1976). The presence of 53.8 % of amorphous phase, combined with a moderate amount of quartz (15.1 %), makes these ceramics less sensible to thermal gradients than other materials, such as BAR1 and BAR2 ceramics, where the consistent amount of quartz can cause some problems due to differential expansion or shrinkage (De Noni Jr et al., 2009; 2010). The high sintering level, favored by the complex chemical composition of the clayey matrix, improves both the fracture strength and the Young's modulus of the ceramic body (Allegretta et al., 2015). The low open porosity with respect to that reported for other ceramics in literature (Dondi et al., 2004; García-Ten et al., 2010a; 2010b; Lassinantti Gualtieri et al, 2010) could contribute to the improvement of these material properties. According to the Griffith's mechanical theory, the elongated shape of the pores in SIF_950 (Fig. 1) should reduce the entity of the stress in the proximity of the flaw. Moreover, porosity could improve the toughness of the ceramic. This means that the ceramic could fail under a critical mechanical load in a stable or semi-stable way and the fracture will propagate through the body step by step avoiding an instant break. There is also a correlation between toughness and the thermal shock resistance by minimizing crack propagation which is very important for technical ceramics that are used in contact with a heating source (Tite et al., 2001). All these characteristics can explain why SIF clay was and is still used as raw material for the production of cooking pots on the island of Sifnos (Greece) and, in particular, why Sifinian ceramics were exported to other Aegean islands, where, however, emigrated Sifinian potters produced ceramics with local clay (Kyriakopoulos, 2015).

The exploitation of BAR clays as refractory earth in the Berner Jura has historical and archaeometrical evidences (Amweg, 1941; Eramo, 2006a; Gerber et al., 2012). Such clayey sands provided a good refractory behaviour in service conditions for crucibles and refractory elements of the forest glass melting furnaces (Eramo, 2005; 2006a). Purest clayey sands have bulk chemical compositions of SiO_2 and Al_2O_3 up to 99 %, with an eutectic of about 1600 °C (Aramaki and Roy, 1962). The main function to fulfil for the refractory elements and the glass melting crucibles is to

withstand to high temperatures (1300 and 1500 °C) of operative conditions, without melting or break. Such high temperatures implied thermal transfer essentially by heat radiation and low thermal conductivity of the crucible body and the furnace structure was necessary to hinder heat dissipation (Eramo, 2005; 2006c). Instead of cooking pots, crucibles are not subjected to high thermal gradients in operative conditions, thus resistance to thermal shock was not determinant. The analysis of BAR1 and BAR2 fired at 1350 °C shed light on some important aspects.
BAR1 and BAR2 fired at 1350 °C show open porosity of about 10% and thermal conductivity reaches 1.13 W/m·K, a value lower than that of other kaolinite-based ceramics fired at the same temperature (e.g. ARG_1350). Even though quartz content was around 75 wt.%, it does not improved the thermal conductivity. The diffused presence of secondary porosity significantly affected the conductivity of the body "isolating" the high conductive quartz grains, as inferred by the closeness of measured k values of the body to amorphous phase (about 1 W/m·K). It should be considered that the conductivity determined at 370 °C is not comparable with those existing at temperatures above 1200 °C and close to the solidus of the ceramic body, where the heat transfer occurs mainly by electromagnetic radiation. The thermal conductivity for fire-clay refractories in the temperature range between 1300 and 1500 °C may vary from 1.2 to 1.5 W/m·K (Aliprandi, 1987). Although the high amount of quartz does not allow an extensive and complete densification even at 1350 °C, its fine size give more stability to the ceramic body, minimising the thermal expansion stresses.
Few impurities of carbonates or Fe oxides and hydroxides in the ceramic body of the glass melting crucibles may compromise the functionality of the ceramic, lowering the eutectic point of the refractory materials or contaminating the molten glass. Some impurities, as in the case of BAR1 and BAR2, can be tolerated in the refractory elements of the furnaces, not in contact with the molten glass.

5 Conclusions

The effective thermal conductivity of the ceramics analysed in the present study is affected by three main factors: the porosity, the amorphous phase and the crystalline phases. Porosity is subject to the starting clay mixture and firing conditions and it implies different pore structures in terms of shapes, sizes and distributions. In all the ceramics samples, the impact of porosity on thermal conductivity is quantitatively higher than that cohering with amorphous and crystalline phases. The formation of the amorphous phase improves the ceramic thermal conductivity since it closes pores and spaces between particles which act as thermal barriers. The formation of crystalline phase affects the thermal conductivity of the ceramic body according to the system taken into account. In fact, both mullite and cristobalite form in ARG, BAR1 and BAR2 ceramics. But, in the case of ARG samples, the only mullite improves the thermal conductivity, while in BAR1 and BAR2 the crystallization of cristobalite is directly correlated to the improvement of ceramic thermal conductivity. Regarding to SIF samples, the formation of high conductive mineral phases like spinel, pyroxenes and hematite make these ceramics more conductive than the others. For this reason, probably, traditional cooking pots made with SIF clays were traded through the whole Eastern Mediterranean region, even if Sifinian potters lived in these islands and produced the same pots with local clay (Kyriakopoulos, 2015). The temperatures used to test the thermal conductivity of BAR1 and BAR2 samples cannot be comparable to those used to glass production, even if the thermal conductivities reported in the range 1300-1500 °C (Aliprandi, 1987) do not bias from those measured on 1350 °C-fired samples (0.99-1.13 W/m·K). However, the study of their thermal conductivity combined with the mineralogical and microstructural data allowed to understand the importance of some aspects such as the role of quartz and cristobalite in the thermal conductivity of these materials. Further tests on BAR1 and BAR2 ceramics are planned at higher temperatures, comparable to those used in the glass production, in order to investigate the role of ceramic characteristics, such as porosity, mineralogy and microstructure, in operation conditions at which a larger contribution of heat transfer processes, like radiation and convection, can be expected.

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Table caption list

Table 1 Mineralogical composition (wt%) of the investigated clays as determined by XRPD data and Rietveld refinements.

Footnotes: Mineral abbreviations after Whitney and Evans (2010): quartz (Qz), illite (Ilt), kaolinite (Kln), glaucophane (Gln), epidote (Ep), calcite (Cal), smectite (Sme), plagioclase (Pl), hematite (Hem), K-feldspar (Kfs), rutile (Rt), alunite (Alu), anatase (Ant), garnet (Grt), dolomite (Dol). E.s.d with a 3-sigma correction are in parenthesis.

Table 2 Chemical composition and loss of ignition (LOI) of the clay used for the production of ceramic disks. Data are reported in wt%.

Table 3 Particle size distribution of the studied clay samples. Data are reported in wt%.

Table 4 Mineralogical composition (wt%) of the fired ceramic bodies as determined by XRPD data and Rietveld refinements

Table 5 Open porosity (p) and effective thermal conductivity (k_{eff}) of the fired ceramics.

Footnotes: Mineral abbreviations after Whitney and Evans (2010): quartz (Qz), calcite (Cal), plagioclase (Pl), hematite (Hem), rutile (Rt), anatase (Ant), mullite (Mul), cristobalite (Crs) garnet (Grt), dolomite (Dol), spinel (Spl), pyroxene (Px), amorphous phase (Am). E.s.d with a 3-sigma correction are in parenthesis.

Figure caption list

Figure 1. Back-scattered electron micrographs of the ceramic prepared with ARG, BAR1 and BAR2 fired at 950, 1150 and 1350 °C and with SIF clay fired at 950, 1050 and 1150 °C.

Figure 2. Back-scattered electron (BS) image and silicon (Si), aluminium (Al) and calcium (Ca) distributions in BAR2 fired at 1350 °C which put in evidence the formation of trydimite in the glassy part around quartz particles.

Figure 3 Evolution of mineralogy, porosity and thermal conductivity with firing temperature in ceramic prepared with BAR1 (A), BAR2 (B), ARG (C) and SF (D) clays.

Figure 4 Correlation between thermal conductivity and the porosity of the ceramics fired at different temperatures.

Figure 5 Correlations between thermal conductivity and the amount of amorphous (A), mullite (B), cristobalite (C) and quartz (D).