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This is a pre print version of the following article:

*Original:*

Bernasconi, A., Pellegrino, L., Vergani, F., Campanale, F., Marian, N.M., Galimberti, L., et al. (2023). Recycling detoxified cement asbestos slates in the production of ceramic sanitary wares. CERAMICS INTERNATIONAL, 49(2), 1836-1845 [10.1016/j.ceramint.2022.09.147].

*Availability:*

This version is available <http://hdl.handle.net/11365/1234616> since 2023-06-09T11:53:07Z

*Published:*

DOI:10.1016/j.ceramint.2022.09.147

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# RECYCLING DETOXIFIED CEMENT ASBESTOS SLATES IN THE PRODUCTION OF CERAMIC

## SANITARY WARES

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## ABSTRACT

The recycling of cement asbestos slates (CAS) thermally treated in air at 1100 °C as secondary raw material in the production of Vitreous China (VC) sanitary wares has been investigated. Deactivated cement asbestos powder (DCAP) has been used in individual substitutions (5 wt.%) of quartz and feldspar. The single raw materials, the ceramic technological properties before and after firing, the phases and microstructure evolution during firing, have been investigated with a variety of techniques, including those commonly used for production quality check and instrumental methods for mineralogical analyses. DCAP acts as flux rather than as inert in the firing process,

1 promoting greification. Although the substituted samples show some critical aspects  
2 that need to be addressed before processing, such as the presence of sulphate salts  
3  
4 that increase the dispersant demand and the colour of the fired ceramic body, the  
5  
6 overall technological properties are comparable to those of normal production,  
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8 suggesting the possible reuse of DCAP powder in the production of sanitary wares.  
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20 **KEYWORDS:**

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23 A Slip casting

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26 A Firing

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29 B Microstructural final

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32 C Mechanical properties

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35 D Mullite

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38 D Silicate

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49 **1. INTRODUCTION**

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53 Asbestos, i.e., the fibrous minerals belonging to the serpentine and amphibole groups  
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55 [1] employed as raw material worldwide and then banned in almost all countries since  
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57 90s because carcinogen, is still abundant in many construction materials and therefore  
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59 represents a problem for the human health and the environment. Although many  
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1 processes aiming either at detoxifying asbestos containing material (ACM) and/or  
2 reuse it as secondary raw material have been published (for a summary s. [2,3]), and  
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4 the European Union encourages such strategies (e.g., [4]), they have never turned into  
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7 practice at industrial scale, apart from the only example of the Inertam plant at  
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10 Morcenx, France [5]. The reason is that the solutions currently adopted by law, i.e., i)  
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12 confinement, ii) encapsulation and iii) landfilling are generally preferred because they  
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14 are cost-effective [6].  
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18 However, none of the aforementioned methods is close to ideal. Confinement, i.e.,  
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21 insulating the ACM from the exterior through a physical barrier, may cause the  
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23 environment to be exposed again to asbestos fibres in case of careless maintenance  
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25 operations, extreme natural phenomena, or terrorist attacks. Encapsulation, i.e., the  
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27 application of special resins to the ACM to block asbestos fibres impeding their release  
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29 in the environment, is inexorably subject to degradation over time, requiring periodic  
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31 maintenance. Landfilling does not eliminate the risk that asbestos fibres could be  
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33 released into the environment, especially in the water table, over time.  
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40 It is a fact that the availability of suitable sites for toxic waste confinement becomes  
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42 increasingly difficult, in developed and highly anthropized countries and in a  
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44 worldwide society where free soil is disappearing [7], construction and demolition  
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46 waste increases exponentially [8–10] and natural raw materials are dramatically  
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48 reducing [11]. For all these reasons, environmentally friendly and recycling solutions  
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50 need to be developed, so that the ACM-waste management could include: i) an energy  
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52 sustainable detoxification treatment and ii) a clear recycling route. This would preserve  
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54 the natural environment from pollution, depleting resources and human health from  
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56 hazards.  
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1 On the other hand, processes aiming to the detoxification of ACM still suffer from  
2 critical issues that need to be solved. For instance, the thermal or thermomechanical  
3 treatments are effective but very energy consuming, biological methods are poorly  
4 effective and chemical methods consume large amounts of reagents and produce  
5 highly acidic fluids that require careful disposal [2,3].  
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13 Thanks to a recent patent on thermal inertization of cement asbestos slates (CAS),  
14 energy sustainability seems feasible [12,13], and as regards recycling, many promising  
15 fields have been investigated (e.g., [14–18]and several patents produced [19,20].  
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21 However, the strict protocols characterising many established production pathways  
22 require a deep control of the starting materials and of their behaviour under  
23 processing conditions to confer the suitable technical properties to the final products.  
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29 Among the investigated fields, the ceramic industry appears as one of the most  
30 promising [19,21].  
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34 Typical raw materials used to formulate the ceramic body are quartz, feldspars and  
35 clays [22,23]. Clays give plasticity and mechanical strength to the slip body. Feldspars  
36 act as flux and control the viscous sintering. Quartz is relatively inert and controls the  
37 firing shrinkage and gives dimensional stability. The main processing steps are wet  
38 grinding of raw material mixtures, slip casting and firing at a maximum temperature in  
39 the range of 1100–1250 °C. The final product is composed of a mixture of newly  
40 formed mullite and glass, and residual quartz and feldspar [22,24]. However, the  
41 partial replacement of conventional raw materials may alter the proportion of these  
42 phases in the fired body and even lead to the formation of additional high-  
43 temperature phases and modify the microstructure, which in turn may alter  
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1 mechanical properties, porosity, chemical resistance, colour, and stain resistance of  
2 the product.  
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5 In the present paper, we describe the reuse of CAS thermally treated in air at 1100 °C  
6 in the production of Vitreous China (VC) sanitary ware, a complex ceramic material  
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8 where many parameters like rheology of the slurry, chemical/mineralogical  
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10 composition, particle size distribution and firing conditions strongly affect the  
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12 technological and aesthetic properties of the final products [22,25–30]. Indeed,  
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14 sanitary wares must result in very compact products with extremely low porosity,  
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16 which is essential to impart the material sufficient mechanical properties, low water  
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18 absorption, resistance to chemicals, abrasion and cleaning agents. These make sanitary  
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20 wares robust and easy to clean, and thus perfect for installation where hygiene is of  
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22 primary importance. Finally, even if a glaze is normally applied, the whiteness of the  
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24 fired body is essential.  
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34 The obtained results show that the substitution in the ceramic body of feldspar and  
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36 quartz with thermally treated and deactivate CAS up to 5 wt.% does not alter  
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38 substantially the technological and aesthetic properties of the fired body, therefore  
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40 indicating deactivated CAS as a potentially suitable candidate for the partial  
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42 substitution of these raw materials.  
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## 51 **2. EXPERIMENTAL**

### 52 **2.1. MATERIALS**

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55 The deactivated material used in the experiments comes from the thermal treatment  
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57 in air at 1100 °C of CAS. Before the experiments, the material was deeply investigated  
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1 with a variety of techniques to certify the disappearance of the asbestos fibres and to  
2 characterise the resulting powder (for an exhaustive description of the deactivated  
3 material see [6,12]. Further tests were performed at the Ideal Standard Laboratory of  
4 Trichiana (BL, Italy) with the aim to characterise the deactivated cement asbestos  
5 powder (DCAP) from a ceramic-technological point of view. Quartz and feldspar, which  
6 represent the potential candidates to be partially substituted in the ceramic slip  
7 formulation by the DCAP, have been also characterised. Furthermore, to evaluate the  
8 effect of the introduction of the DCAP in a traditional VC sanitary ware, three slurries  
9 of ball clays, China clays, Quartz, Na-feldspar and DCAP have been prepared at the  
10 laboratory scale (5 Kg of dried material), according with Table 1. Here, sample NP is the  
11 normal production composition, representing the benchmark for further evaluation of  
12 slip behaviour in the ceramic process. Samples S1 and S2 are designed to evaluate the  
13 effect of DCAP introduction in partial substitution (5 wt.%) of filler material like quartz  
14 and fluxing agent like Na-feldspar, respectively. The chemical composition of the  
15 different raw materials is displayed in Table 2.

## 2.2. SINGLE RAW MATERIALS CERAMIC-TECHNOLOGICAL CHARACTERIZATION

DCAP, quartz and feldspar single raw materials have been characterised by several methods:

- *Particle size distribution (PSD)*. Residue of each raw material at 45 and 75  $\mu\text{m}$  have been determined by sieving in humid conditions. Moreover, laser scattering curves have been measured using a Malvern Mastersizer 3000.

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- *pH, Conductivity and Ion Chromatography (IC) test in solution.* These three tests have been performed by means of a Hanna Instruments pH-metre, Hanna Instruments conductivity metre, and Thermo Scientific Dionex Aquion IC system, respectively.

- *Colour after firing.* It has been determined by means of a Konica Minolta CM-700d spectrophotometer using D65 Cielab space. These measurements have been performed after firing in an industrial kiln a pressed sample (around 20 grams) of each single raw material.

- *Upon firing behaviour.* It has been characterised by means of hot stage microscope Camar Microvis. The specimen, a pressed cylinder of about 2 mm diameter and 4 mm height, has been placed on an alumina substrate and fired in the 20-1400°C temperature range, with a ramp-rate of 10°C/min. During the entire ramp, a camera recorded images every minute to monitor the specimen shape evolution (i.e., sintering, softening and melting).

### 2.3 SLIP CERAMIC-TECHNOLOGICAL CHARACTERIZATION

NP, S1 and S2 slip compositions have been characterised by several methods:

- *Density and rheology of the slurry.* Density has been measured by weighing each slurry into a 500-cc capacity pycnometer. Rheology has been measured by means of a Brookfield viscometer using spindle n.3. In particular, the Bingham method [31] has been applied to quantify the plastic viscosity and the yield stress by collecting data at five different shear rates (130, 110, 80, 50 and 30 rpm for 10 s/each).



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- *Particle size distribution (PSD)*. For each slurry, the laser scattering curve has been measured using a Malvern Mastersizer 3000.

All the following tests have been performed on samples fired in an industrial tunnel kiln according to the firing cycle reported in Figure 1.

- *Total shrinkage (T<sub>s</sub>)*. For each slip it has been quantified on fired rod by means of equation 1:

$$T_s = (L_0 - L_f) / L_0 * 100 \quad \text{Eq.1}$$

where L<sub>0</sub> is the length of the mould in mm and L<sub>f</sub> is the length of the fired rod in mm.

These two quantities have been measured by a high precision calliper.

- *Water absorption (W<sub>A</sub>)*. For each slip it has been determined on the fired rod, following UNI-EN 997 normative. The procedure requires initially weighing the rod (w<sub>d</sub>) after drying for 12 h at 110°C. Then, the rod is immersed and boiled in water for 2 h, then cooled in situ for 12 h and then re-weighed (w<sub>w</sub>). The W<sub>A</sub> value is calculated by equation 2:

$$W_A = (w_w - w_d) / w_d * 100 \quad \text{Eq.2}$$

The W<sub>A</sub> value represents a technical requirement of the sanitary-ware vitreous body to be accepted in the warehouse, being its limit value equals to 0.5.

- *Mechanical tests*. They have been performed by means of a Monsanto Tensiometer 2000 instrument to measure the Flexural strength (in kg/cm<sup>2</sup>) and the Young modulus (in GPa). For each slip, 8 different bars have been tested to improve statistics.

- *Linear thermal expansion measurements*. They have been carried out using a Netzsch Dilatometer 402 ED in the 20°C-650°C temperature range, with a heating ramp of

10°C/min. The linear thermal expansion coefficient ( $\alpha$ ) has been then calculated by Proteus software (from Netzsch) in the desired temperature range following equation 3:

$$\alpha = L_n (1+ d_L/L_0)/(T-T_0) \quad \text{Eq.3}$$

with  $d_L$  equals to  $L(T)-L(T_0)$ , where  $L(T)$  and  $L(T_0)$  correspond to the measured lengths of the specimen at  $T$  and  $T_0$ , respectively, being the latter set at 30°C. The specimen is a bar of 5 x 5 x 50 mm cut from the total shrinkage fired rod.

- *Colour after firing*. It has been determined by means of a Konica Minolta CM-700d spectrophotometer using D65 Cielab space. These measurements have been performed on the total shrinkage fired rod.

- *Gradient kiln test*. NP and S2 slips have been also characterised using a gradient kiln from Kiln & Furnaces to further investigate their greification behaviour at 6 different peak programmed temperatures (1140, 1160, 1180, 1200, 1220 and 1240 °C, 1 h of soaking time each). Once cooled down, the  $W_A$  have been measured for each sample, following the procedure described above in order to draw the greification curve (i.e. Temperature vs.  $W_A$  curve).

#### 2.4. X-RAY POWDER DIFFRACTION (XRPD)

Fragments of S2 and NP samples fired at temperatures of 1160, 1180, 1200 and 1220 °C were grinded in agate mortar, back loaded into an Al sample holder and analysed by a Bragg–Brentano PANalytical X’Pert-Pro PW3060 diffractometer ( $\theta$ – $\theta$  geometry;  $\text{CuK}\alpha$  radiation). XRPD data were collected in the 5–80°  $2\theta$  range, with step size of 0.02°, at

1 room temperature, and operating conditions of 40 mA and 40 kV. Qualitative phase  
2 analysis was carried out with the PANalytical X'Pert High Score software, using the  
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4 ICSD PDF2-2004 database. Quantitative phase analysis (QPA) was performed with the  
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6 Rietveld method [32] using the GSAS II package [33] . To determine the amorphous  
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8 content, 20 wt.% of  $\alpha$ -alumina was added as an internal standard. In order to eliminate  
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10 any possible amorphous content in the standard that could adversely affect the QPA  
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12 results [27], corundum was previously annealed at 900 °C for 36 hours in a furnace.  
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14 The weight fraction of each crystalline phase ( $W_{\alpha}'$ ) in the studied samples was  
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quantified according to equation 4:

$$W_{\alpha}' = W_{\alpha} * (W_c' / W_c) * [1 / (1 - W_c')] \quad \text{Eq. 4}$$

where  $W_{\alpha}$  and  $W_c$  are the refined weight fractions of phase  $\alpha$  and of the internal corundum standard, respectively, and  $W_c'$  is the actual added weight of the internal standard (20 wt.%). The actual weight fraction of the amorphous material ( $W_g'$ ) is then calculated as  $W_g' = 1 - \sum_i W_{\alpha i}'$ .

## 2.5. SCANNING ELECTRON MICROSCOPY (SEM)

SEM investigations were performed at the Platform of Microscopy of the University of Milano-Bicocca with a Tescan VEGA TS 5136XM and a Zeiss Gemini 500, both equipped with an energy dispersive system (EDS). Backscatter electron (BSE) images and EDS analyses were acquired on DCAP-bearing samples (S2) and normal production samples (NP) fired at different temperatures (1160, 1180, 1200 and 1220 °C). Fired samples

1 were prepared as parallelepipeds about 4 x 2 x 0.5 cm with a 4 x 2 cm polished face  
2 and carbon coated to avoid electrostatic charging during the observations.  
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6 Particle Analysis was carried out to determine the porosity and shape of voids of the  
7 NP and S2 samples using the java-based open-source ImageJ/Fiji software. For each  
8 sample, four BSE images taken at fixed magnification (200x) and resolution (768x840  
9 pixels), leading to 0.64 pixel/ $\mu\text{m}$ , were investigated. A pixel-based segmentation was  
10 made using the Fiji plugin 'Trainable weka segmentation', a machine learning tool for  
11 pixel classification [34]. This plugin was used to recognize and distinguish the pores  
12 and to apply the same conditions to all images. Once the binary images were obtained,  
13 the porosity (%) of each image was measured, together with the number of pores and  
14 their area and shape (circularity) using the Imagej/Fiji particle analysis tool. For  
15 porosity, all pores with an area less than 5  $\mu\text{m}^2$  (~2 pixels) were excluded. The final  
16 porosity (%) represents the average of the four images in each sample (Table 6). For  
17 circularity, all pores with an area less than 22  $\mu\text{m}^2$  (~9 pixels) were excluded, to limit  
18 the contribution of smaller pores that statistically have circularity of ~1, this because  
19 the samples studied in this work show a dimension of the smallest pores which is too  
20 close to one pixel at 768x840 resolution.  
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### 50 **3. RESULTS AND DISCUSSION**

#### 51 **3.1. CERAMIC TECHNOLOGICAL CHARACTERIZATION**

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53 Sanitary ware production follows established protocols which optimise workability of  
54 the slurry and technical and aesthetic properties of the final products. Any substitution  
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1 of conventional raw materials must not alter these standards. Table 3 summarises the  
2 results of single raw materials ceramic technological characterization. The DCAP has a  
3 larger average grain size than the substituted raw materials, as demonstrated by the  
4 higher residue at 45 and 75  $\mu\text{m}$  and the higher d90 value. Several authors have  
5 established a clear relationship between the grain size of filler (inert) material and the  
6 final mechanical properties of the fired sanitary body (e.g., [22,28,35]). However, in  
7 the present case, as will be shown in the following sections, the DCAP acts as a fluxing  
8 agent rather than as inert, and it is completely consumed at the highest firing  
9 temperatures. Bernasconi [27] demonstrated that the grain size of feldspar affects the  
10 greification process: the finer the grain size, the faster the process. Therefore, it seems  
11 that exploiting the interplay between feldspar and DCAP with a suitable selection of  
12 their respective grain sizes, the fine tuning of the greification process would be  
13 possible.

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34 The conductivity of the DCAP is much higher for the substituted materials, probably  
35 related to the higher electrolytes content, i.e., sulphate but also iron and other metals  
36 [6]. The colour of DCAP tend to dark and red if compared with the colour of feldspar  
37 and quartz, as inferred by the lowest  $L^*$  and the highest  $a^*$  values, respectively. The  
38 resulting ochreous colour of the DCAP is probably due to oxidation of iron in the  
39 starting material during heat treatment in air.

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50 The hot stage microscopy single raw material characterization is reported in Figure 2.  
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52 The behaviour of the DCAP is in between the fully inert behaviour of quartz and the  
53 fluxing role of feldspar. This observation justifies our choice of partially replacing with  
54 DCAP these two traditional ceramic raw materials.

1 Table 4 summarises the results of ceramic slips technological characterization. The  
2 high value of sulphates in the DCAP (Table 3) directly affect the slip rheological  
3 behaviour, being the presence of soluble salts in solution responsible for flocculation  
4 of clay minerals, which increases the slurry viscosity [22,36]. In fact, to reach similar  
5 plastic viscosity and yield stress in NP, S1 and S2, the dispersant addition in the case of  
6 DCAP-substituted samples is ten times higher than for the NP sample.  
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10 The mechanical properties of the DCAP-substituted samples are in line with those of  
11 the NP samples in the terms of Young moduli, while the flexural strength is lower than  
12 in NP samples (see discussion in the following sections). Both S1 and S2 samples show  
13 very low  $W_A$  values, suggesting that the DCAP is actively contributing to the greification  
14 of the slip upon firing. Moreover, the total shrinkage of both DCAP-substituted  
15 samples is in line with the NP sample, suggesting that the partial introduction of the  
16 DCAP in the slip formulation would not require modification in the mould modelling.  
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34 The fired slip colour is clearly connected with the single raw material after firing  
35 colour: both S1 and S2 slips are darker than normal production. This result must be  
36 further evaluated when glazing the slip, being the fired glaze colour affected by several  
37 parameters like, for example, the colour of the slip below. Both S1 and S2 slips have a  
38 lower thermal expansion in the 30-600°C range compared to the normal production.  
39 These results need to be carefully considered in parallel with the glaze thermal  
40 expansion. This is because the thermal expansion of these two bodies (slip and glaze)  
41 need to match, or at least the latter kept lower than the former, being the compressive  
42 resistance of glaze higher than its tension resistance.  
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In light of the promising greification behaviour, the S2 and NP slips were further investigated by gradient kiln in a wider temperature range, to better constrain how the addition of 5 wt% of DCAP may affect the ceramic mixture in comparison to NP. Figure 3 displays the greification curve of the S2 and NP slips in the 1140°C-1240°C temperature range. It must be noted that, although NP has much lower water absorption at 1140 and 1160°C than S2, at the highest investigated temperature the difference between the two slips disappears, suggesting a very similar greification level. That also fulfils the UNI-EN 997 normative, being the water absorption values less than 0.5 by mass at a temperature equals or higher than 1180°C. These results confirm previous results at industrial kiln conditions, indicating that the DCAP acts as a good fluxing agent.

### 3.2. PHASE EVOLUTION WITH TEMPERATURE

It is universally acknowledged that the physical properties of fired ceramic bodies rely on the constituent phases resulting from i) the high temperature reactions involving the starting materials and ii) the developed microstructure (e.g. [22,24,37–40]). In this and the following section these two aspects will be evaluated, in the order.

XRPD results of samples S2 and NP are reported in Table 5. The main difference is represented by feldspar (anorthite 62-66%), present only in the S2 samples, whereas quartz, mullite and abundant amorphous phase are present in both samples at all temperatures. Relative phase abundances and variations with increasing temperature are plotted in Figures 4 and 5.

1 The S2 samples show a progressive increase with temperature of the amorphous  
2 phase (49.1-71.3 wt.%) with a relative decrease of the crystalline phases, in particular  
3 feldspar (22.1-11.6 wt.%) and quartz (16.6-8.6 wt.%), as expected. Instead, the newly  
4 formed mullite remains in the range 8.5-12.2 wt.%, showing a small increment at 1200  
5 °C and then decreasing again (Table 5), although the differences are probably within  
6 the experimental error. No trace of the crystalline phases typical of DCAP (akermanite-  
7 gehlenite, bredigite, merwinite and larnite;[6]) were detected in sample S2, probably  
8 because they were resorbed during firing or remained in a concentration too low to be  
9 detected (< 1 wt.%).

10 Compared to the S2 samples, NP samples show important differences. At all firing  
11 temperatures, NP samples are characterised by lack of feldspar. The remaining phases  
12 show a seesaw behaviour, even if quartz generally decreases with increasing  
13 temperature (23.2-16 wt.%), and mullite and glass increase. Mullite (12.8-21 wt.%)  
14 shows the maximum value at 1200 °C and on average is more abundant than in  
15 samples S2. The amorphous phase oscillates around 57.7-66.6 wt.%, showing the  
16 lowest value at 1200 °C (Table 5).

17 The average lower value of mullite in S2 samples in comparison to NP samples offers a  
18 possible explanation of the lower value of flexural strength observed in the former.  
19 Indeed, according to the “mullite hypothesis” e.g., [22,24], the interlocking network of  
20 mullite needles is the major contributor to the mechanical strength. However, other  
21 hypotheses and explanations also need to be considered (see ahead).

22 Overall, the addition of DCAP seems to saturate the melt respect to feldspar,  
23 promoting its preservation at expense of quartz and induces lower production of



1 mullite and higher amount of melt. In other words, it acts as a fluxing agent in place of  
2 feldspar and makes quartz less inert. Moreover, it seems to provide a more regular  
3 thermal evolution of phase development. These findings open to the possibility for  
4 some optimization of the DCAP/feldspar ratio in order to minimise the presence of  
5 residual fluxing agent, following two different ways: 1) as a more conservative  
6 approach, reducing the amount of DCAP in the slip in order to maintain an upon firing  
7 behaviour closer to the NP one; on the other side, the design of a more challenging  
8 formulation by further increasing the amount of DCAP in the slip, after previous  
9 amelioration of the above mentioned rheological issues.  
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### 28 3.3. MICROSTRUCTURE EVOLUTION WITH TEMPERATURE

29 As outlined above, the developed microstructure plays a prominent role in the  
30 determination of the sanitary ware bodies after firing properties. For this reason, the  
31 microstructure was investigated by SEM-EDS and particle analysis. Quartz, feldspar and  
32 mullite were identified based on the chemical composition, glass since its interstitial  
33 nature and silica- and alkali-rich composition, non-reconcilable with any expected  
34 crystalline phase. In addition, Ti- and Fe-oxides were detected by SEM-EDS, not  
35 detected by XRPD probably because of their low concentration.  
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50 All samples are porous, with porosity ranging from ~5 to ~20% (Table 6). In addition,  
51 the S2 samples fired at 1160 and 1180 °C show bright regions more than 100 µm in  
52 diameter, with ill-defined contours (Figs. 6) and identified as clusters of very fine  
53 particles of Ca-Mg-Al silicates. These particles probably derive from the powder of the  
54 DCAP admixed to the slip and not reabsorbed during firing at low temperature. They  
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1 were not detected either in samples fired at 1200 and 1220 °C, or by XRPD, suggesting  
2 that their concentration is very low or that they are completely reabsorbed in the melt  
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5 at higher temperature.  
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8 Quartz grains stand up in BSE images by their intermediate grey colour and subhedral  
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10 to anhedral habit. Most grains are sub-rounded, with dimensions from few  $\mu\text{m}$  to  
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12 more than 50  $\mu\text{m}$  (Fig. 6). Feldspar, mullite and glass tend to get confused at low  
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14 magnification because they are intimately intermixed (Figs. 7 and 8). At higher  
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16 magnification, after fine tuning brightness and contrast, feldspar appears in relatively  
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18 large ( $>10 \mu\text{m}$ ) ghost crystals, partially melted, and reabsorbed (Fig. 7). Mullite forms  
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20 small (few  $\mu\text{m}$ ), randomly oriented, acicular crystals, brighter than the surrounding  
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22 glass (Fig. 7). Fe- and Ti-oxides, distinguished by the highest BSE yield, form crystals  
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24 from  $\sim 1 \mu\text{m}$  to less than 15  $\mu\text{m}$  in size, dispersed in the matrix.  
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32 The matrix can therefore be described as a microcrystalline irregular network of BSE-  
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34 lighter phases in a BSE-darker amorphous groundmass (Fig. 6). Within the groundmass,  
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36 the micro-scale mullite grains can be distinguished from feldspar and glass thanks to  
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38 their higher content of Al and much lower Ca, Na and K, as shown in the elemental X-  
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40 ray map of Figure 8. Overall, for both sample types (NP and S2), the matrix seems to  
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42 increase with respect to quartz and the remaining porosity (darker features in Fig. 6, s.  
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44 ahead) with increasing temperature, consistently with XRPD results.  
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51 The fact that mullite forms small acicular crystals embedded in the melt, suggests an  
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53 origin from recrystallization and dissolutions of aluminosilicates in the melt (secondary  
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55 mullite). Fine, feltlike interlocking mullite needles as those observed in these samples  
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57 are believed to confer strength (mullite hypothesis) to the porcelain body [22,41–43].  
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In a few cases, annular fractures around quartz grains were observed (Fig. 8). These fractures are due to different thermal expansion coefficients between the particle and the matrix and have this peculiar form when the particle contracts more than the matrix. Conversely, when the matrix contracts more than the particle, radial fractures are formed within the particle, which is a worse situation since the fractures can easily connect and cause deleterious strength and higher water absorption [22]. However, even if annular fractures represent the “normal” situation, their concentration must be contained since they may also cause deleterious strength. Warshaw and Seider [44] have demonstrated that the quartz grain size controls the development of annular fractures. In particular, fractures form easily around quartz grains with dimensions in the range of 50-150  $\mu\text{m}$  (which is the case of Fig. 8), instead they are much less abundant around quartz grains of 25-50  $\mu\text{m}$  and form only occasionally around quartz grains lower than 10  $\mu\text{m}$ .

#### 3.4. PORE PARTICLE ANALYSIS

The pore structure in porcelain sanitary wares is a very important physical property since it determines critical characteristics such as mechanical strength and water absorption. In comparison to NP samples, S2 samples result more porous at all temperatures, although both decrease with increasing firing temperature (Table 6 and Fig. 6). In the S2 samples, the porosity is initially very high (22%) and suddenly decreases with increasing temperature, stabilising at ~9%. In the NP samples, the porosity is low at the lower firing temperatures (6.7%) and oscillates between 4.8 and 7.4% with increasing temperature, confirming the same seesaw behaviour seen with XRD for phase evolution.

1 Figure 9 shows the normal and cumulative distribution of the pores' area of all samples  
2 at each firing temperature. In all samples, the porosity is dominated by pores with area  
3 <40  $\mu\text{m}^2$  (about 70-90% of the total pores' area; Tables 1S-3S in the supplementary  
4 material). This percentage is always slightly higher in the NP samples, so that in the S2  
5 samples pores' area result larger on average. All samples show a similar trend on both  
6 normal and cumulative distribution, except that S2 samples show small percentages of  
7 pores with area >500  $\mu\text{m}^2$ , which reaches ~3% at 1220 °C, absent in the NP sample  
8 (Table 1S-3S in the supplementary material). These data on porosity parallel the  
9 observations on water absorption only in part. Indeed, porosity decreases with  
10 increasing firing temperature, in the S2 samples faster than in the NP samples, but  
11 stabilises at higher porosity values in S2 samples, contrary to water absorption, which  
12 results lower in S2 samples. This further suggests that the observed porosity is not  
13 interconnected, therefore limiting water absorption. The higher porosity of S2  
14 samples, however, could be responsible for the lower flexural strength observed.  
15 Indeed, it is believed that the predominant factor affecting the strength of porcelain  
16 bodies is the density of flaws, here represented by pores [22].

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42 To better understand porosity data, the variation of the cumulative distribution of  
43 circularity with increasing temperature has been reported in Figure 10. As a general  
44 trend, for both samples, circularity increases with increasing temperature, with few  
45 exceptions. For instance, the curves of samples NP\_1180 and NP\_1200 and of samples  
46 S2\_1200 and S2\_1220 exchange their relative position. Moreover, for sample S2, less  
47 regular and comparable trends are observed, with the S2\_1160 curve showing a  
48 markedly lower average circularity. In spite of these minor oddities, which may be  
49 intrinsic of the measuring method (i.e., limited number of investigated samples, image  
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1 quality, etc.), and in part reflects the seesaw trends observed for other measured  
2 properties (i.e., phase abundances), the observed circularity increase with  
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4 temperature indicates that the pore structure changes from irregular, interconnected  
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6 pores at low temperature to isolated, sealed, round pores at high temperature, and  
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8 explains the lower water absorption of the investigated materials. That is a very  
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10 important property of sanitary ware ceramic bodies, which results in more stain-  
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12 resistant and are easier to clean.  
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#### 22 **4. CONCLUDING REMARKS**

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25 The reuse of DCAP in sanitary ware vitreous china in substitution of 5 wt.% of quartz or  
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27 feldspar presents some advantages and disadvantages as compared to normal  
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29 production. The DCAP secondary raw material presents an ochreous colour due to  
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31 oxidation of Fe-bearing phases during the deactivation process, which determines a  
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33 darker fired slip colour of DCAP-substituted samples. Since the colour of the slip affects  
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35 the fired glaze colour, the final aesthetic properties in case of sanitary whitewares  
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37 must be preventively assessed. No major problems are envisaged in case of coloured  
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39 sanitary wares.  
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47 Although the reasons that determine the colloidal stability of clays is a complex  
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49 matter, we retain the large amount of sulphates in the DCAP responsible for clay  
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51 minerals flocculation, which in turn determines a critical increase of slurry viscosity.  
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53 This effect is clearly undesired in the ceramic process because it hinders slip  
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55 preparation procedure as well as casting into plaster and/or resin moulds. To avoid  
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57 this, a large amount of dispersant must be added, which affects the production costs.  
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1 Since sulphates are highly soluble in water, a washing pre-treatment of the DACP  
2 before usage should quickly leachate soluble salts avoiding abnormal addition of  
3 dispersant, saving money and lengthening only marginally the process time.  
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8 It has been observed that DCAP acts as a fluxing agent more than as inert. Its addition  
9 limits feldspar consumption and mullite formation. This in turn affects mechanical  
10 properties of the slip, with a decrease of flexural strength, but still within acceptable  
11 limits. Overall, important technological properties such as water absorption are as  
12 good as (or even better than) in normal production. This is due to a high level of  
13 greification of the DCAP-substituted samples and consequent low and sealed porosity.  
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18 In conclusion, the recycling of DCAP as secondary raw material in sanitary ware  
19 production, as for other similar ceramics (stoneware), appears feasible, providing  
20 some critical aspects such as soluble salts content and colour of the DCAP, could be  
21 properly managed.  
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## 24 **5. ACKNOWLEDGEMENTS**

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27 This paper is an outcome of the projects DEAR, “Deattivazione Efficiente dell’Amianto e  
28 Riutilizzo, funded by the Italian Ministry of the Ecologic Transition and A-FIRE, “Asbestos  
29 Fast Inertization and Recycling”, funded by Fondazione Cariplo within the call “Cariplo  
30 2020 – Circular Economy for a Sustainable Future”.

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## Captions to figures and tables

**Figure 1:** Industrial firing cycle used for after firing behaviour characterization.

**Figure 2.** hot stage microscopy curves of DCAP (red line), quartz (blue line) and feldspar (green line).

**Figure 3.** Greification curves of NP slip (green squares) and S2 slip (red circles).

**Figure 4.** Plot of the relative phase abundances determined in sample S2 at different firing temperatures

**Figure 5.** Plot of the relative phase abundances determined in sample NP at different firing temperatures.

**Figure 6.** BSE images of NP (left column) and S2 (right column) samples fired at 1160 °C, 1180 °C, 1200 °C, 1220 °C. Qtz = quartz. Arrows indicate Ca-Mg-Al silicates clusters of admixed deactivated CA slates powder. For explanation see text. Scale bar: 50 µm.

**Figure 7.** BSE image of sample S2\_1200. Quartz grains (Qtz) appear fragmented and rounded; feldspar (Fsp) partially melted and strongly resorbed. We also observe a widespread irregular network with a brighter BSE signal embedded in a BSE-darker groundmass. Part of the BSE-brighter part consists of a microcrystalline acicular mullite (arrows); the darker one of glass.

**Figure 8.** BSE image (A) and related X-ray map (B) of a portion of sample S2\_1200. The major element map (Si, Al, Ca, Na, K) shows that the microcrystalline grains in the matrix are separated into two geochemically distinct domains, i.e. an Al-rich (alkali absent)

1 domains in red and an alkali-rich (Al-poor) domains in blue. Quartz grains are highlighted  
2 in green (Si-rich). Note the annular fracture around the large quartz grain on the left.  
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6 **Figure 9.** Comparison of the normal and cumulative distribution of the pores' area for  
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8 S2 and NP samples at 1160, 1180, 1200, and 1220 °C.  
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12 **Figure 10.** NP vs S2 cumulative distribution of circularity with increasing temperature.  
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18 **Table 1.** Raw materials composition of the prepared slurries.  
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22 **Table 2:** Elemental composition of the raw materials used for the initial slip  
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24 composition. Average uncertainty about 1%.  
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28 **Table 3.** Results summary of the raw material ceramic technological characterization.  
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40 **Table 6.** Porosity (%) affecting the studied samples as measured through particle  
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42 analysis image processing.  
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**Declaration of interests**

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

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



Table 1. Raw materials composition of the prepared slurries.

Sample ID	Ball clay (wt.%)	China clay (wt.%)	Quartz (wt.%)	Na-Feldspar (wt.%)	DCAP (wt.%)
NP	26.5	25	19	29.5	0
S1	26.5	25	14	29.5	5
S2	26.5	25	19	24.5	5

NP = normal production; S1 = quartz DCAP-substituted formulation; S2 = feldspar DCAP-substituted formulation.

Table 2: Elemental composition of the raw materials used for the initial slip composition. Average uncertainty about 1%

Raw materials (wt.%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	TiO <sub>2</sub>	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	LOI (%)
Ball clay*	50.8	32.6	1.21	-	0.25	0.95	0.2	1.72	0.21	-	12.07
China clay*	48.23	36.68	0.95	-	0.05	0.15	0.19	1.77	0.08	-	11.9
Quartz*	99.37	0.4	0.04	-	0.01	0.01	0.02	0.05	0.05	-	0.05
Na-Feldspar*	69.9	18.1	0.12	-	0.2	0.25	0.5	0.3	10.3	-	0.33
DCAP**	30.41	3.9	5.94	0.43	7.68	0.23	47.38	0.42	0.17	3.11	0.32

\* From the datasheet of the provider. \*\* EDXRF data (major components) from [6].

Table 3. Results summary of the raw material ceramic technological characterization.

	DCAP	Feldspar	Quartz
Residue at 45 $\mu\text{m}$ (wt.%)	33	8	10.7
Residue at 75 $\mu\text{m}$ (wt. %)	19.7	1.1	1.8
d10 ( $\mu\text{m}$ )	1.55	1.6	2.1
d50 ( $\mu\text{m}$ )	12.4	11.4	16.5
d90 ( $\mu\text{m}$ )	142	42.4	52.3
pH	10	8	9.8
Conductivity ( $\mu\text{S}$ )	10000	82	40
Sulphate (ppm)	10238	221.9	124.3
Chloride (ppm)	62.9	42.6	36
L*	62.86	73.95	94.68
a*	9.71	1.58	1.35
b*	23.44	19.65	3.97

Table 4. Results summary of the ceramic slips technological characterization.

	NP	S1	S2
Density (g/l)	1850	1848	1849
Plastic viscosity (cP)	541	476	484
Yield stress (dyn/cm <sup>2</sup> )	73	85	108
d10 (μm)	1.6	1.6	1.6
d50 (μm)	10.4	10	10.3
d90 (μm)	47.8	46.6	47.1
Total shrinkage (%)	10.6	10.3	10.6
WA (%)	0.15	0.02	0.01
Flexural strength (kg/cm <sup>2</sup> )	630	586	537
Young modulus (GPa)	21	23	23
α from 30 to 600°C (1/°C)	7.21	6.65	6.76
L*	80.87	70.01	70.58
a*	0.9	1.1	1.1
b*	9.6	9.04	8.62

Table 5. Quantitative phase analysis for sample S2 and NP detected at different firing temperatures

	S2_1160	S2_1180	S2_1200	S2_1220
Qtz	16.6	13.7	12.6	8.6
Mul	12.2	9.1	10.8	8.5
Fsp	22.1	17.3	15.4	11.6
Glass	49.1	59.9	61.2	71.3

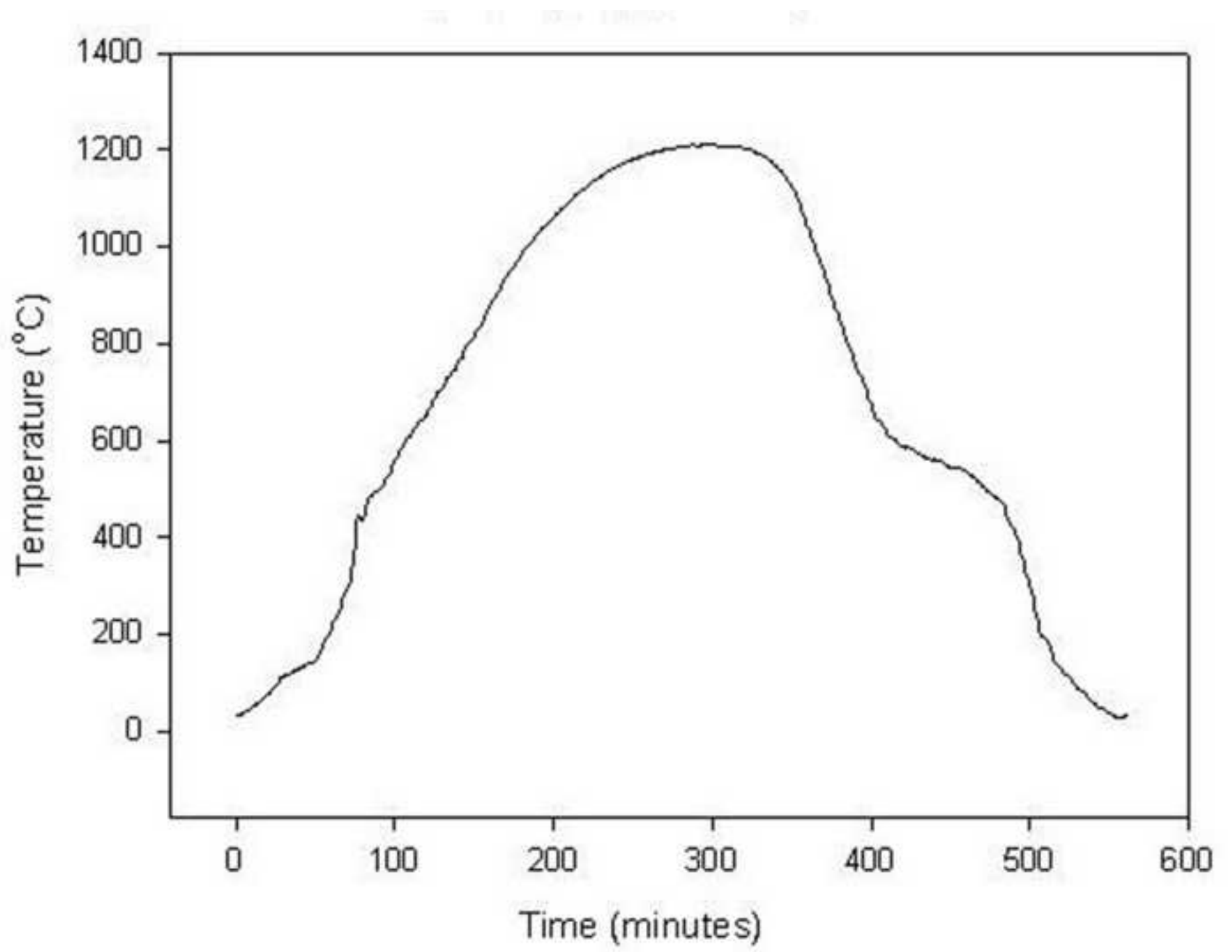
  

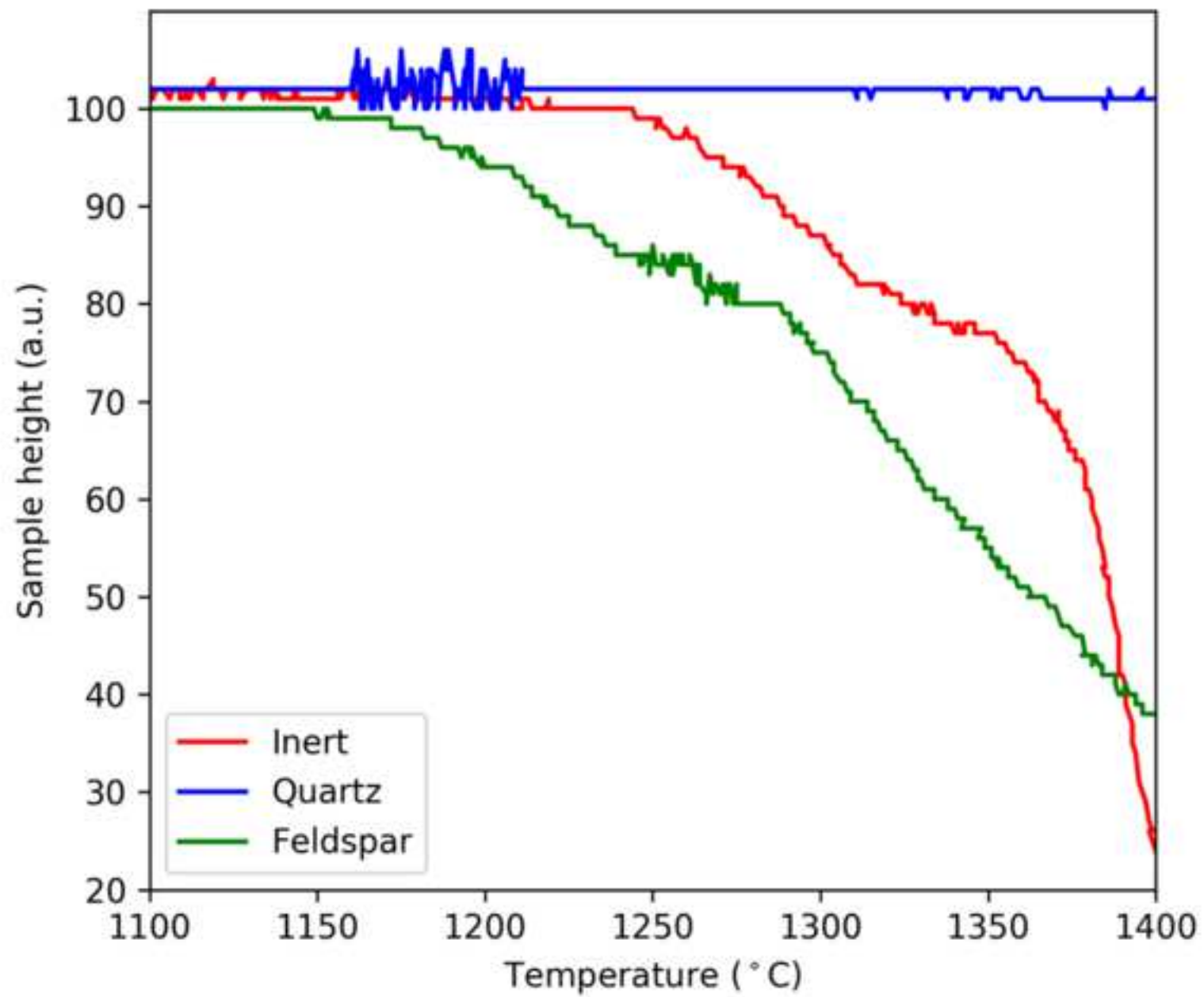
	NP_1160	NP_1180	NP_1200	NP_1220
Qtz	23.2	20.6	21.3	16
Mul	13.4	12.8	21	17.5
Fsp	0	0	0	0
Glass	63.4	66.6	57.7	66.6

Table 6. Porosity (%) affecting the studied samples as measured through particle analysis image processing

	1160	1180	1200	1220
S2	22%	9.50%	9.60%	9.20%
NP	6.70%	7.40%	4.80%	5.40%

Figure 1







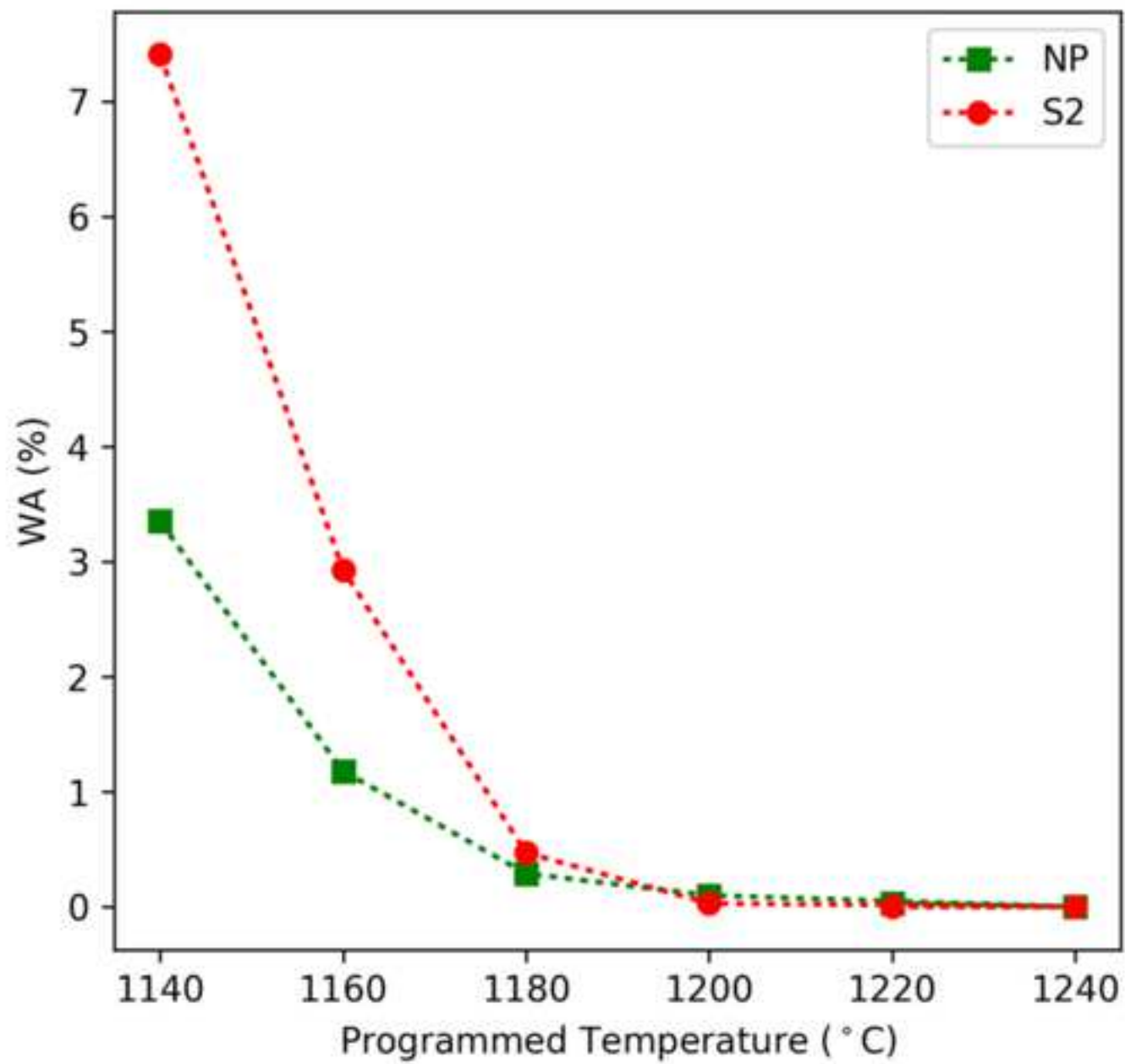


Figure 4

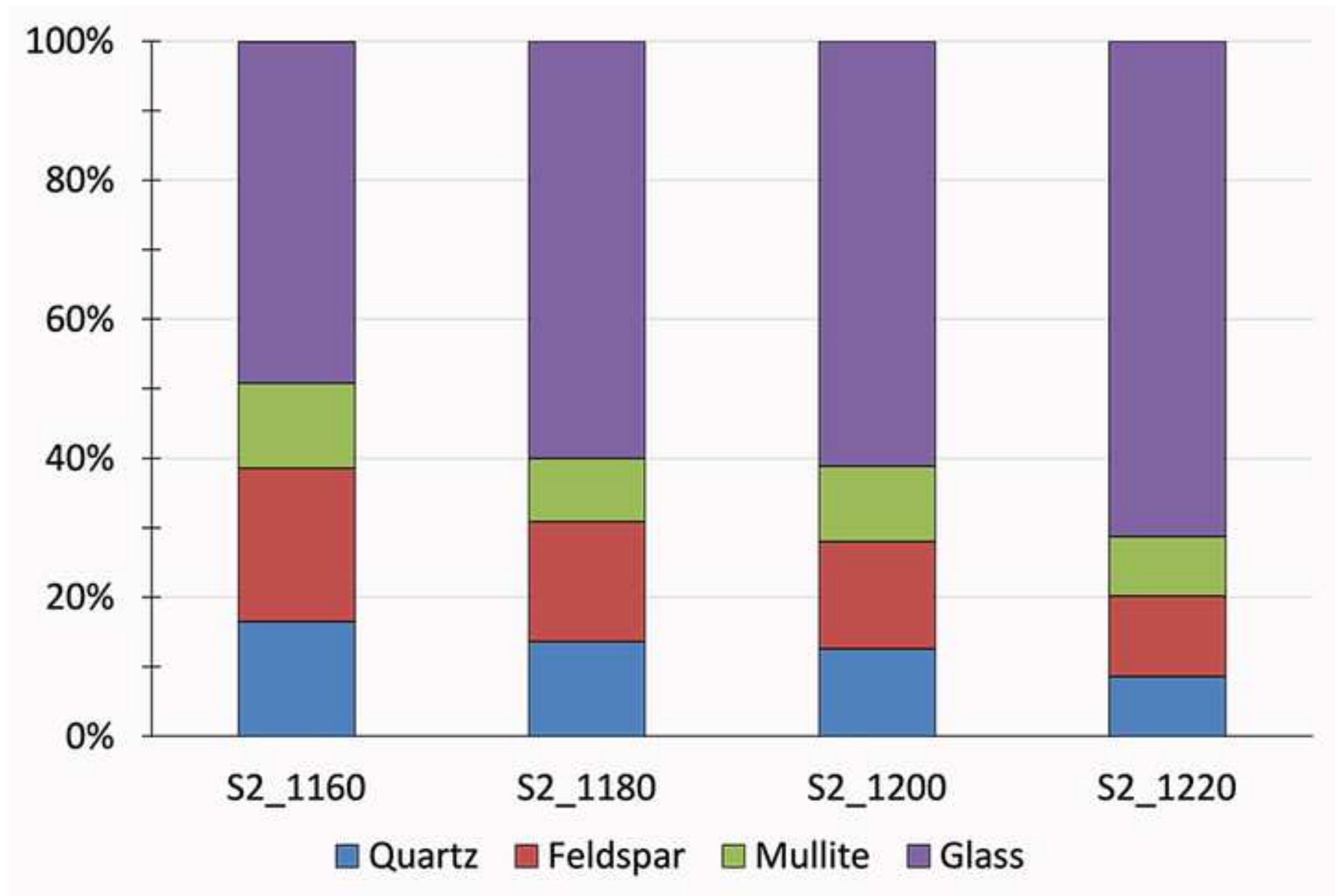
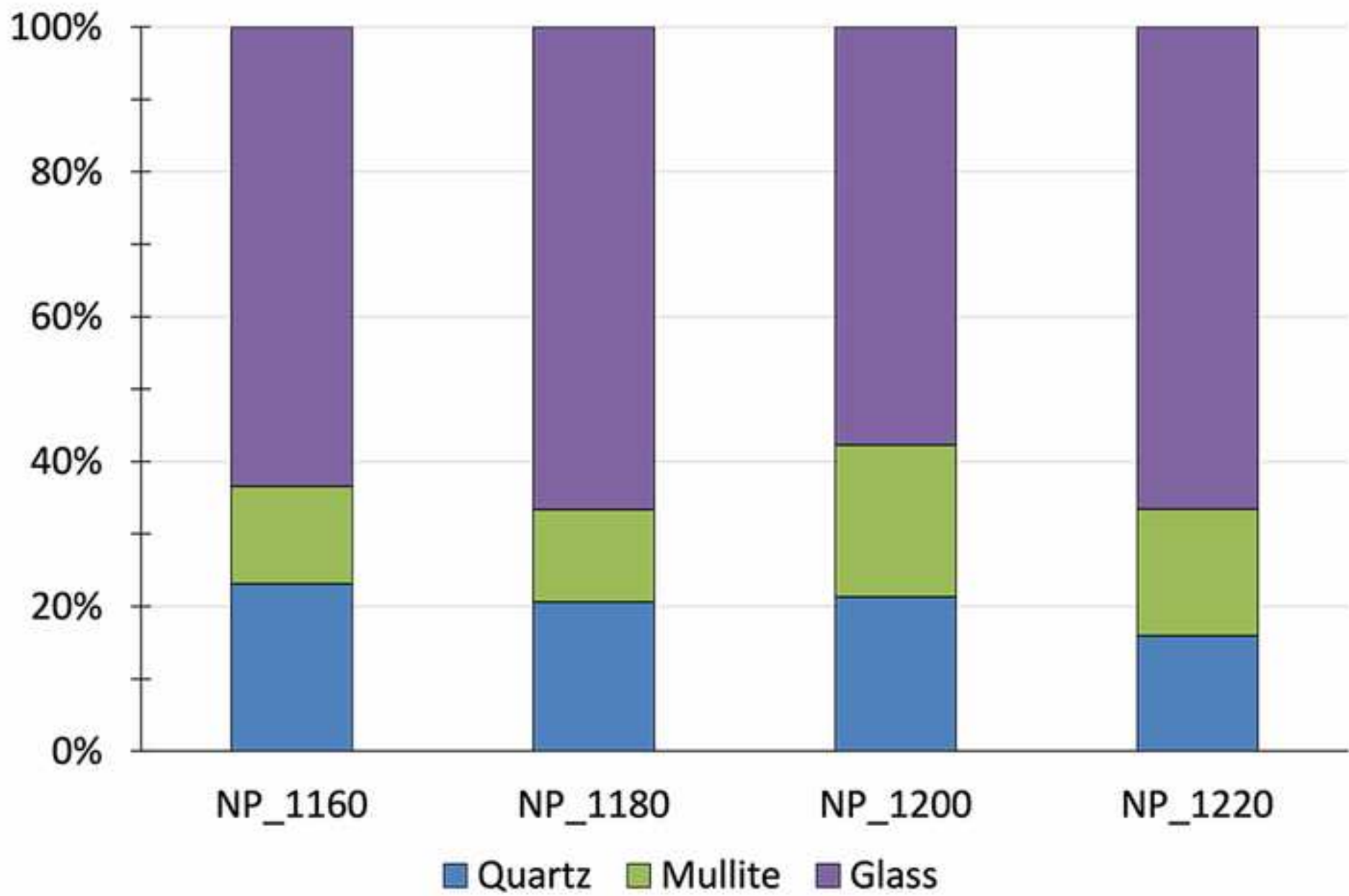
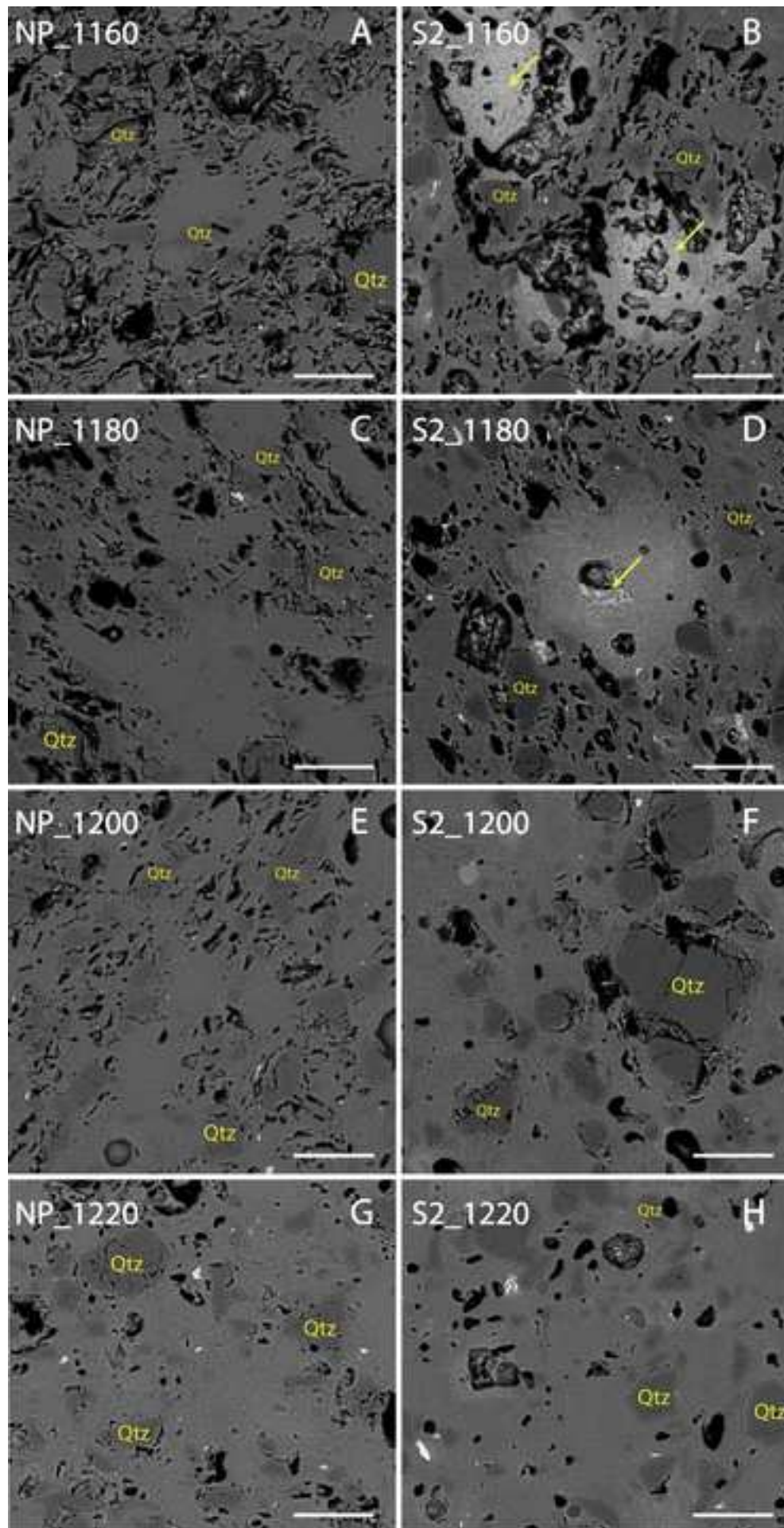
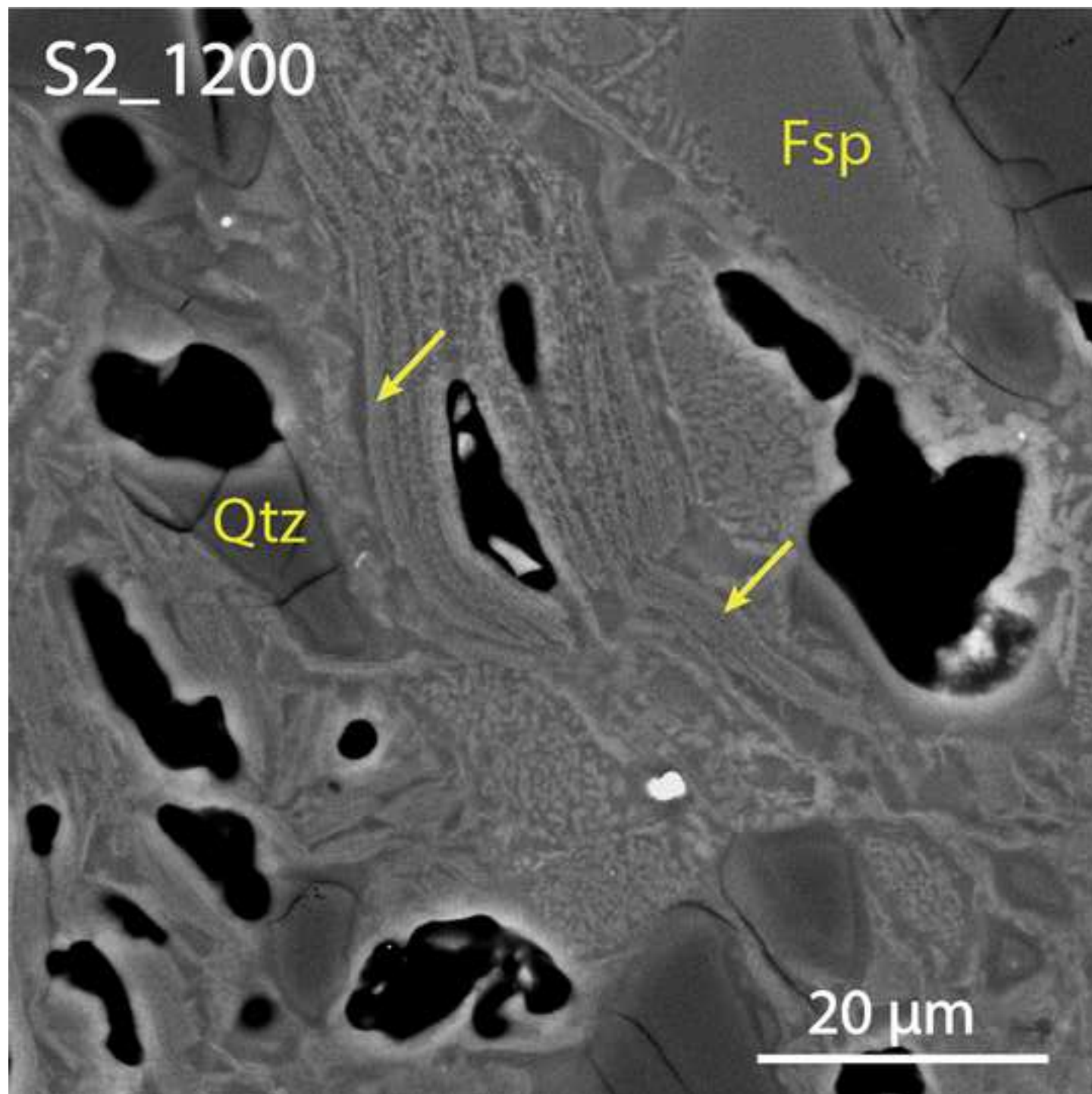


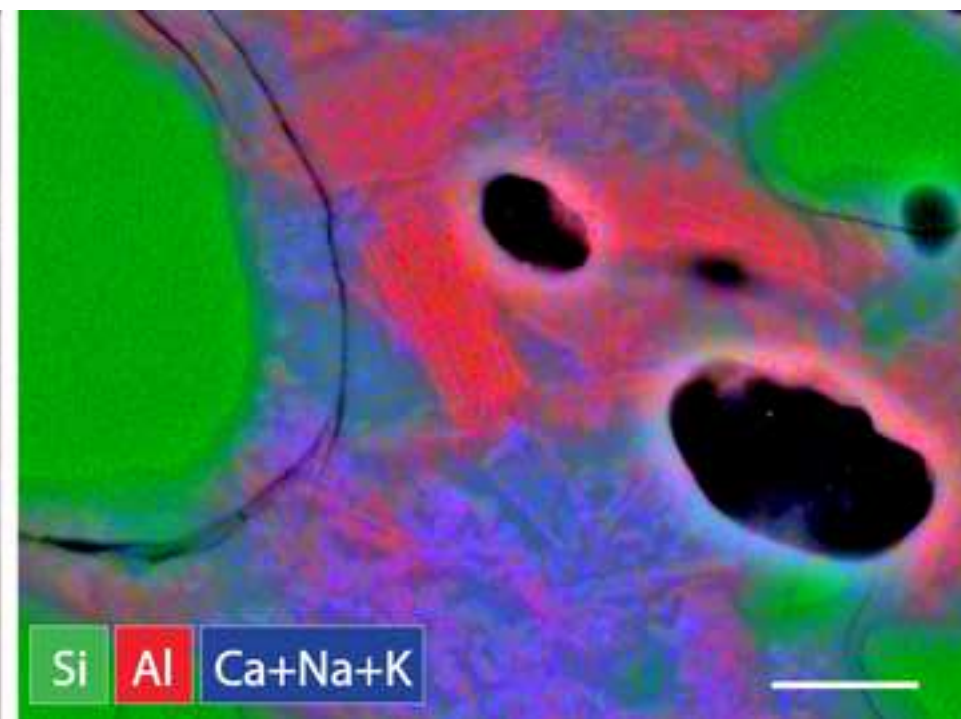
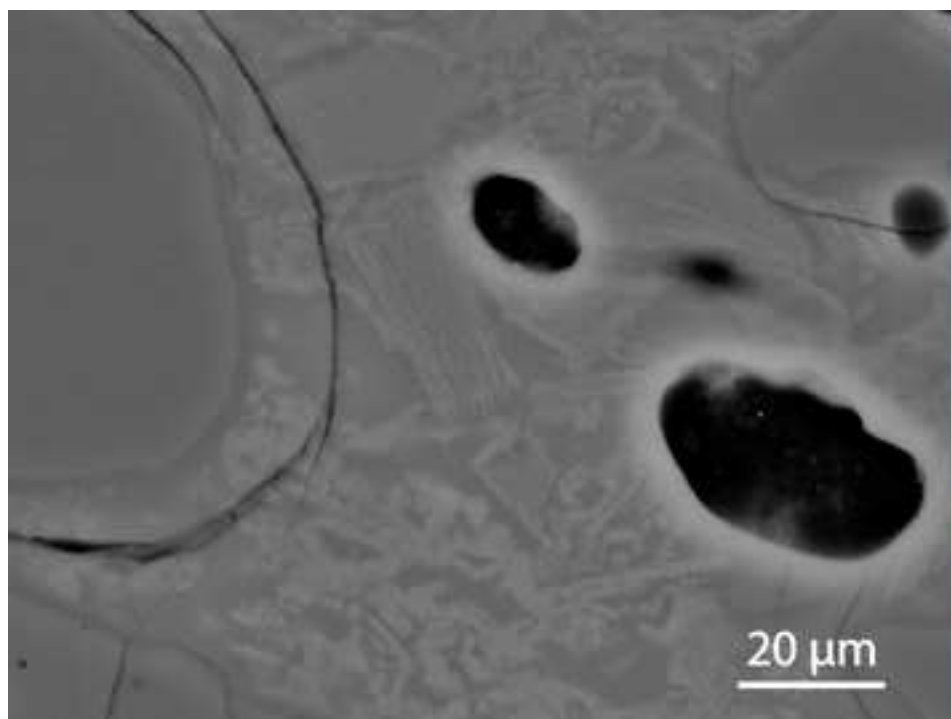
Figure 5

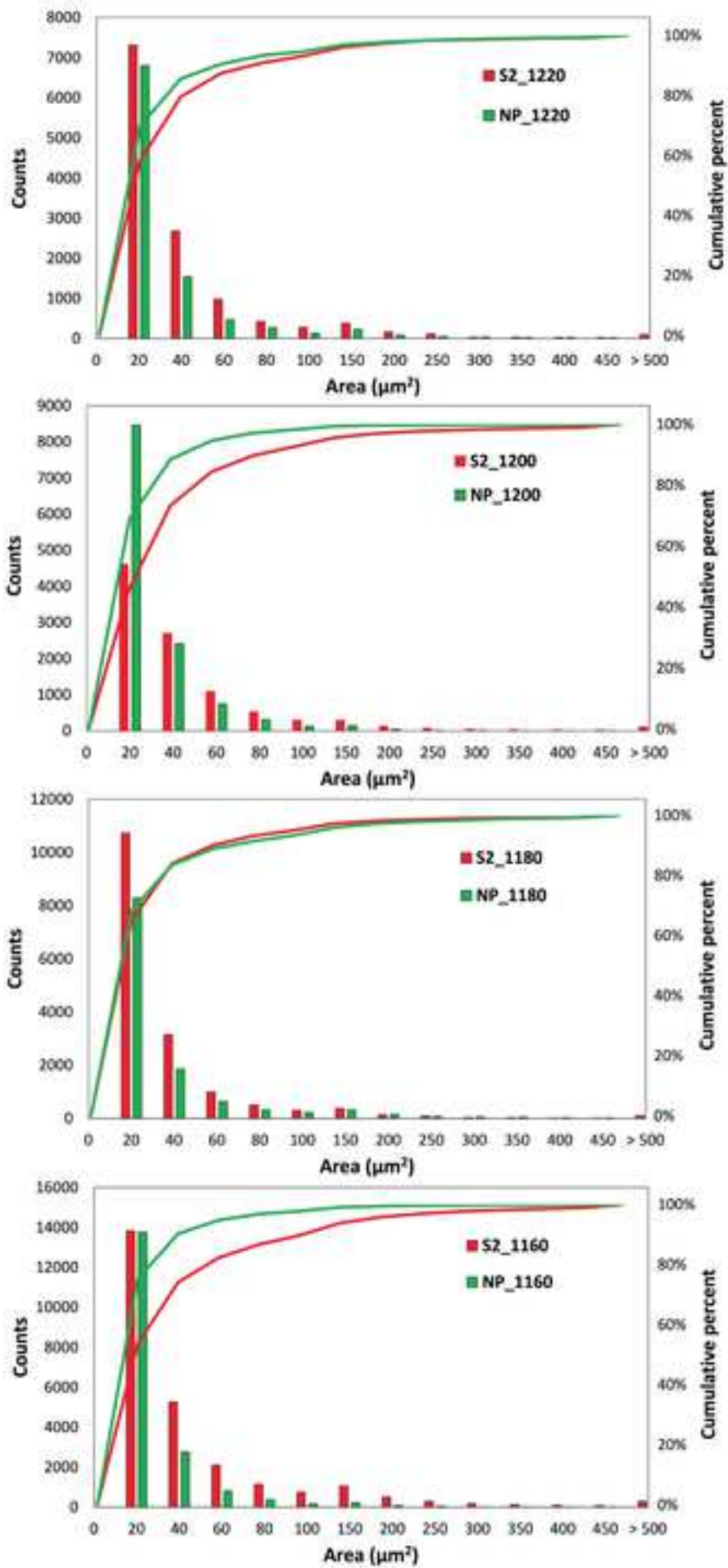












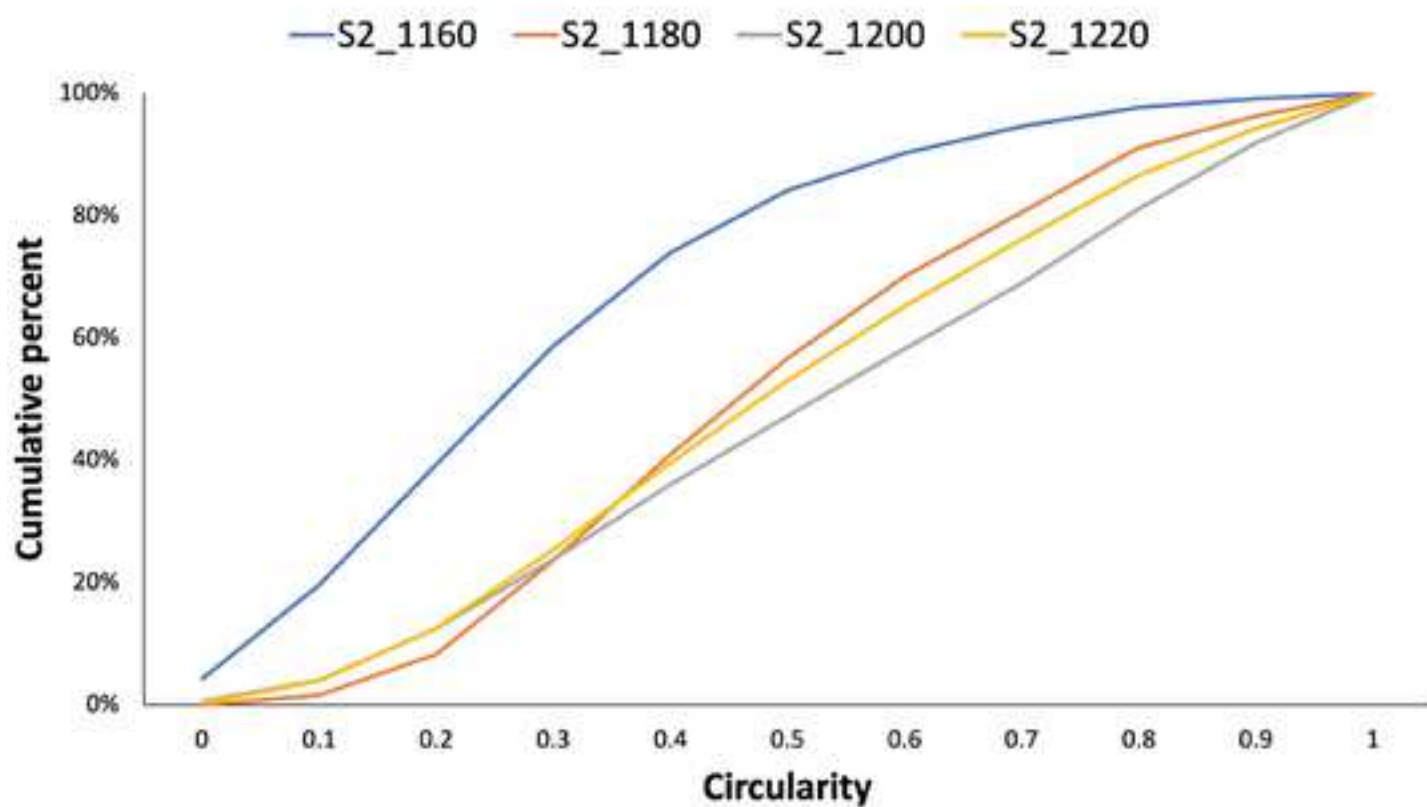
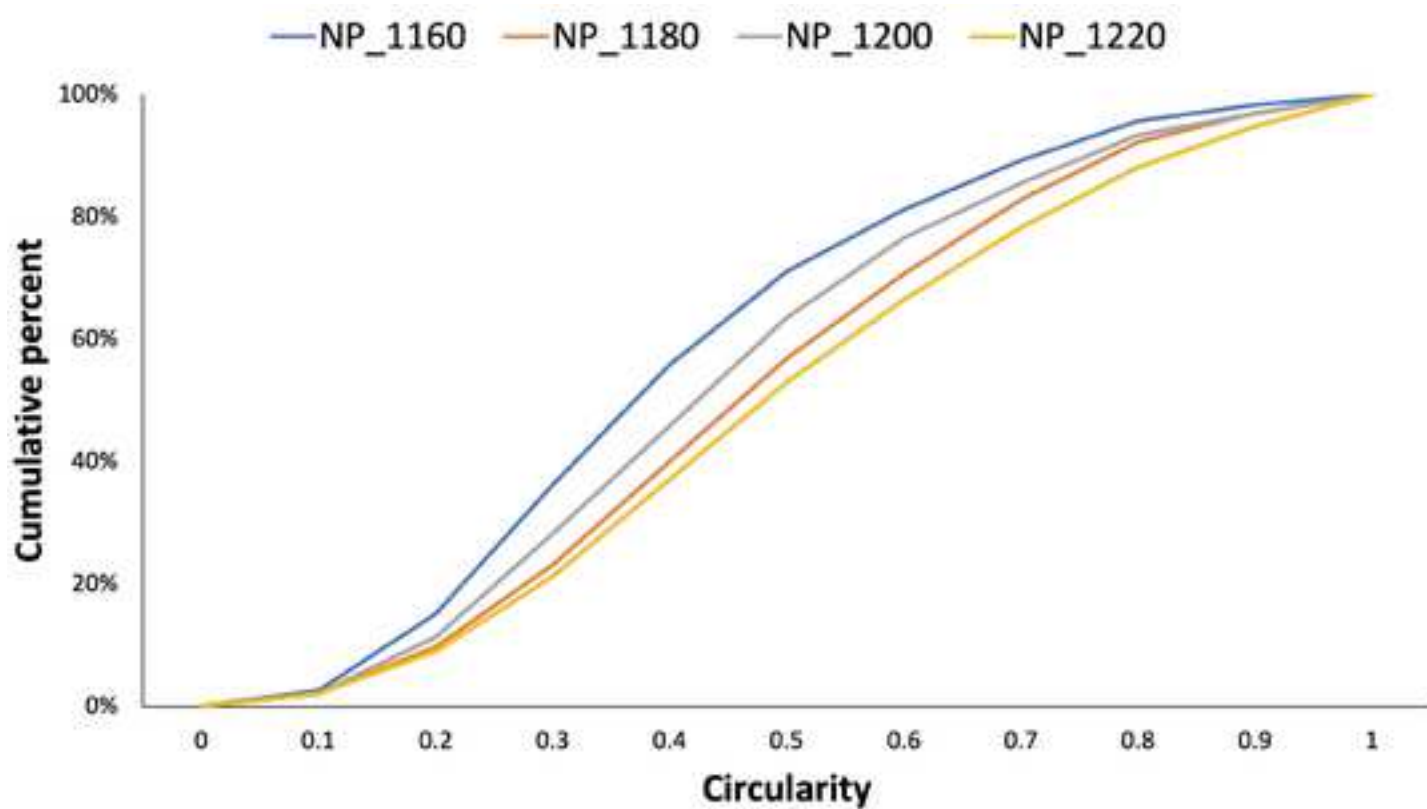




Table 1S. Number of pores > 5 $\mu\text{m}^2$  and their distribution in the chosen bin limits.

bin limits	1220	1220NP	1200	1200NP	1180	1180NP	1160	1160NP
20	7313	6805	3755	8463	10728	8294	13838	13766
40	2678	1546	1357	2410	3148	1864	5267	2765
60	981	474	578	747	1002	640	2107	816
80	431	274	337	309	509	319	1153	377
100	280	128	188	133	303	225	760	175
150	379	226	340	142	378	319	1055	230
200	163	84	178	35	141	154	516	82
250	112	50	120	14	94	75	305	34
300	35	40	51	9	44	61	188	15
350	35	24	41	7	34	51	130	8
400	24	21	48	5	17	31	98	9
450	22	17	29	5	16	24	71	8
> 500	100	66	198	7	102	99	297	19
<b>SUM</b>	12553	9755	7220	12286	16516	12156	25785	18304

Table 2S. Percentage of pores > 5 $\mu\text{m}^2$  and their distribution in the chosen bin limits.

bin limits	1220	1220NP	1200	1200NP	1180	1180NP	1160	1160NP
20	58.26%	69.76%	52.01%	68.88%	64.96%	68.23%	53.67%	75.21%
40	21.33%	15.85%	18.80%	19.62%	19.06%	15.33%	20.43%	15.11%
60	7.81%	4.86%	8.01%	6.08%	6.07%	5.26%	8.17%	4.46%
80	3.43%	2.81%	4.67%	2.52%	3.08%	2.62%	4.47%	2.06%
100	2.23%	1.31%	2.60%	1.08%	1.83%	1.85%	2.95%	0.96%
150	3.02%	2.32%	4.71%	1.16%	2.29%	2.62%	4.09%	1.26%
200	1.30%	0.86%	2.47%	0.28%	0.85%	1.27%	2.00%	0.45%
250	0.89%	0.51%	1.66%	0.11%	0.57%	0.62%	1.18%	0.19%
300	0.28%	0.41%	0.71%	0.07%	0.27%	0.50%	0.73%	0.08%
350	0.28%	0.25%	0.57%	0.06%	0.21%	0.42%	0.50%	0.04%
400	0.19%	0.22%	0.66%	0.04%	0.10%	0.26%	0.38%	0.05%
450	0.18%	0.17%	0.40%	0.04%	0.10%	0.20%	0.28%	0.04%
<b>SUM</b>	100%	100%	100%	100%	100%	100%	100%	100%
>100	9.16%	6.72%	16.52%	2.91%	6.84%	8.55%	13.26%	3.17%
<60	79.59%	85.61%	70.80%	88.50%	84.02%	83.56%	74.09%	90.31%

