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# Effects of the secondary minerals of the natural pozzolans on their pozzolanic activity

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ABSTRACT

Natural pozzolans have been widely used as substitutes for Portland cement, because of their binding properties. Some of them are natural volcanic rocks which contain secondary minerals such as clays and zeolites corresponding to products of the alteration of the rock. The objective of this study was to document the potential effect of the secondary minerals on the strength development of pozzolanic mortars. We chose to investigate this effect by thermally destabilising these minerals in three different pozzolanic deposits (poz-1, poz-2 and poz-3). We first did a detailed mineralogical study, to identify the occurrence and the nature of the different secondary minerals. Kaolinite is abundant in poz-1 and different types of zeolite were identified in poz-2 and poz-3. Thermal treatments were monitored by X-ray Diffraction (XRD) analysis, in order to document mineralogical transformations. The effect on the pozzolanic activity has been tested by strength measurements on normalised mortars at 1, 7 and 28 days. Strength of all blended cements is enhanced while destabilising secondary alteration minerals. For kaolinite, we showed that a strength improvement occurs as soon as it is destructured, even if it is not transformed in metakaolin. For zeolites, destabilisation takes place at low temperature (350 °C), but as recrystallisation products are easily formed, activation temperature window is narrow. Endly, we have evidence that the presence of calcite in pozzolans has an effect on early strength. Therefore this study is giving new perspectives for a better use of natural pozzolanic materials in the cement industry.

## 1. Introduction

Natural pozzolans have been widely used as substitutes for Portland cement in many applications because of their advantageous properties which include cost reduction and $CO_2$ emission reduction, decreased permeability and increased chemical resistance [1,2]. However, the most obvious disadvantage for the Portland cement replacement with natural pozzolans is that early strength is normally decreased.

The so called, natural pozzolans, used as an admixture for the production of pozzolanic cements are pyroclastic rocks rich in siliceous or siliceous and aluminous volcanic glass. The origin of the pozzolanic activity lies in this high content of reactive silica in pozzolans [3]. Common silicate minerals are feldspar, mica, hornblende, pyroxene and quartz or olivine depending on the volcanic rock's chemical composition, but most of these minerals are easily alterable and the high porosity and specific surface area of pyroclastic rock enhance the alteration rate. Therefore, it is very common to find secondary minerals resulting from alteration of primary minerals and devitrification of the volcanic glass. Clays, zeolites, calcite and various amphiboles are classic secondary minerals. The effect of these secondary minerals on the pozzolanic activity of the natural pozzolans has already been studied [4–7]. It is mainly accepted that a good pozzolanic material has low quantities of clay minerals and high quantities of zeolite minerals [8,9]. Several techniques have been used to enhance the reactivity of pozzolanic materials and remove unreactive ones, which include calcinations [10], acid treatment [11], and prolonged grinding [12].

## 2. Scope of investigation

The objective of this study was to document the potential effect of the secondary minerals, resulting from the natural alteration of volcanic rocks on their pozzolanic activity. We chose to investigate this effect by thermally removing these minerals. Actually as these are low temperature alteration minerals, they do not resist to very high temperatures. We first did a detailed mineralogical study to investigate composition and textures of the studied samples. Thermal treatments monitored by XRD analysis permit to find destabilisation

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**Table 1**
Chemical analysis of studied samples

| | Vitreous[a] | | | Bulk rock[b] | | |
|---|---|---|---|---|---|---|
| | TZ | TQ | JO | TZ | TQ | JO |
| $SiO_2$ | 60.19 | 67.30 | 51.21 | 62.08 | 66.42 | 43.81 |
| $A1_2O_3$ | 17.82 | 13.25 | 23.73 | 17.84 | 12.74 | 16.64 |
| $Mn_2O_3$ | 0.34 | 0.13 | 0.05 | 0.43 | 0.02 | 0.21 |
| MgO | 0.31 | 0.94 | 3.43 | 0.26 | 1.53 | 8.78 |
| CaO | 0.55 | 2.16 | 2.57 | 0.99 | 3.41 | 4.48 |
| $Na_2O$ | 7.97 | 2.94 | 0.21 | 4.27 | 1.61 | 0.38 |
| $K_2O$ | 5.68 | 3.89 | 1.43 | 3.78 | 1.34 | 0.59 |
| $TiO_2$ | 0.61 | 2.97 | 4.91 | 0.68 | 0.19 | 2.86 |
| $Fe_2O_3$ | 3.56 | 2.40 | 0.95 | 4.24 | 1.42 | 13.62 |
| $P_2O_5$ | – | – | – | 0.03 | – | 0.74 |
| $CO_2$ | 0.91 | – | 0.36 | | | |
| $H_2O$ | 5.18 | 10.78 | 9.55 | | | |
| Volat. [c] | | | | 5.39 | 10.97 | 8.27 |
| Total | 103.12 | 106.76 | 98.40 | 99.99 | 99.65 | 100.38 |

Results come from microprobe and ICP-MS measurements.

[a] Analysis on the vitreous phase with microprobe.

[b] Bulk rock analysis with ICP-MS.

[c] Weight 1oss on heating to 980 °C.

temperatures of the different minerals for each sample. The effect on the pozzolanic activity has been tested by strength measurements on normalised mortars (EN 196-1, [13]).

## 3. Experimental methods

### 3.1. Materials

#### 3.1.1. Natural pozzolans

In this study, representative samples from three natural pozzolanic deposits belonging to the Lafarge cement society were used. These materials were ground, and their fineness was determined so that 10 wt.% was retained by the 100 μm sieve.

#### 3.1.2. Cement

The cement used is an Ordinary Portland Cement (OPC), CEM I 52.5.

#### 3.1.3. Standard sand

The graded standard sand in making the mortar mixtures complied with the EN-196-1.

### 3.2. Test methods

#### 3.2.1. Petrographic examination

In order to make the petrographic identification, thin layers of the samples were prepared and observed under the petrographic microscope. Observations on the washed raw samples were also done with binocular lens.

#### 3.2.2. X-ray Diffraction (XRD)

XRD patterns were done by using an X-ray diffractometer CPS 120 with CoKα radiation. Measures were done on the bulk powdered samples and also on the finest fraction (<5 μm) with the oriented section method in order to identify the clay minerals.

#### 3.2.3. Scanning Electron Microscopy (SEM)

JEOL 6360 Low Vacuum, was used to perform the observations. This microscope is associated with an Energy Dispersive Spectrometry (EDS) from PGT which give the chemical composition of the observed points. All pictures have been done with secondary electrons and an accelerated voltage of 20 kV.

#### 3.2.4. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) measurements were conducted with a DSC 404 from Netzsch from 20 to 1100 °C at a rate of 20°/min.

#### 3.2.5. Chemical analysis

Chemical analyses were done at the Clermond-ferrand laboratory. Microprobe analyses on the vitreous phase are presented in Table 1. Similar results are obtained with ICP-MS analysis on wall rock powder (Table 1).

#### 3.2.6. Thermal treatments

To observe mineral transformations, the samples were heated during 2 h in a Peckly Herrmann-Moritz MF7 oven from 20 to 800 °C. Fast cooling was done at ambient temperature.

#### 3.2.7. Strength testing

Experiments were done on normalised mortars (3 parts of sand, 1 part of cement and 0.5 part of water) in which cement is an OPC (CEM I 52.5). Mortar mixes were made using 30 wt.% pozzolan as a replacement for cement. All sample preparations were processed in a similar manner according to European Standard EN-196 [13]. Water was first introduced into the mechanical blender. The dry mix solids (cement+heated pozzolans) were then added to the water solution and mixed for 30 s at low speed; sand was added and mixed for 30 s. Then, the mixing proceeds in a sequence of three steps: 30 s mix at high speed, 90 s in rest and 60 s mix at high speed. The mortars were then cast into 4×4×16 cm moulds for 24 h and cured with plastic sheet. The hardened mortar was then demoulded and kept at 20 °C under water until tested.

## 4. Results

### 4.1. Mineral characterisation

#### 4.1.1. Binocular lens and petrographic microscope

The three pozzolans have very different chemical compositions (Table 1), from an acid sodic rock (poz-1) or sodi-calcic (poz-2) to a

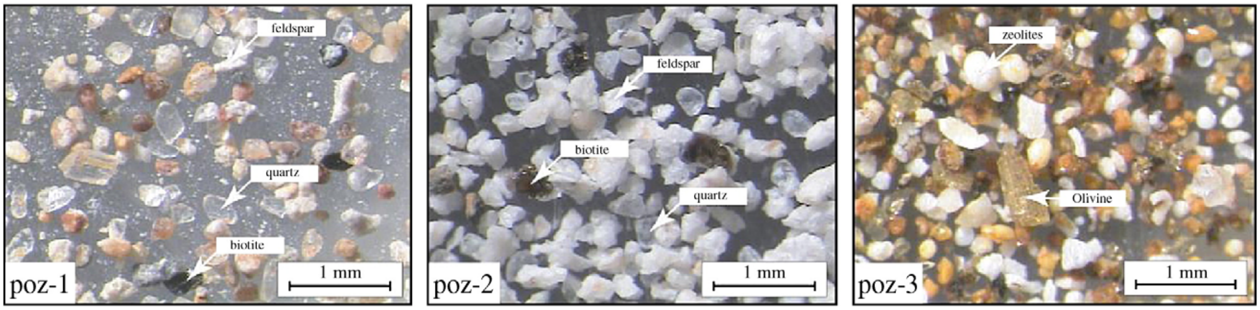

**Fig. 1.** Pictures with the binocular lens of the three pozzolanic materials. The scale bar on pictures represents 1 mm.

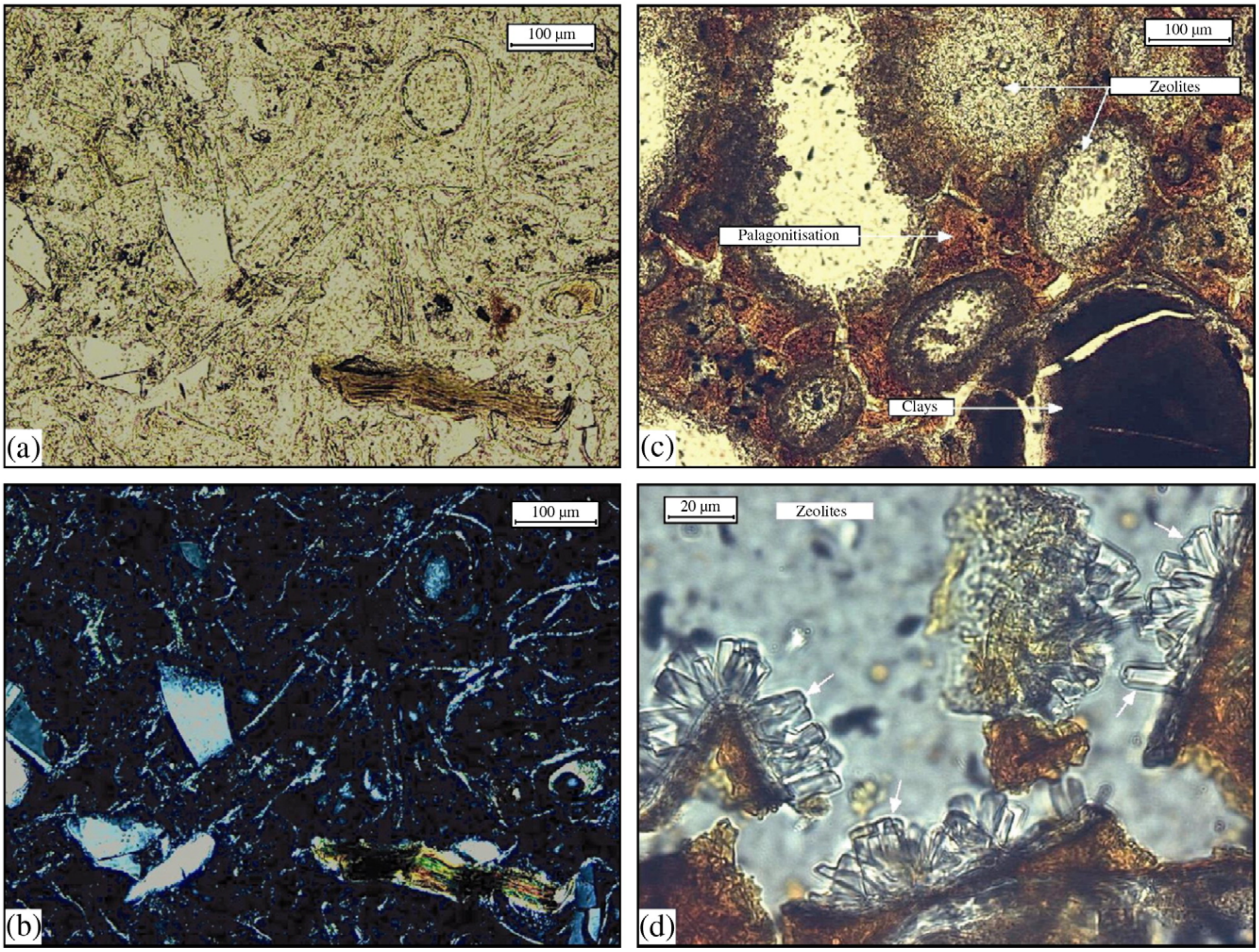

**Fig. 2.** Pictures of thin sections through the poz-2 and the poz-3 samples. Picture b is taken with crossed polarisers on a petrographic microscope. For the other pictures plane polarised light has been used. Scale bars on pictures represent 100 µm, except for picture d where it represents 20 µm.

basic pyroclastic deposit (poz-3). Therefore, minerals expected in the samples are different. Observations with the binocular lens (Fig. 1) show a relative homogeneity between grains in poz-1 and poz-2 samples. Quartz and feldspars and biotite appear to be the main minerals in those deposits. The grains from the poz-3 deposit are more differentiated, but we can separate them in two main classes: olivine crystals and white round-shaped grains that we have identified as clusters of zeolites with petrographic microscope observations (Fig. 2).

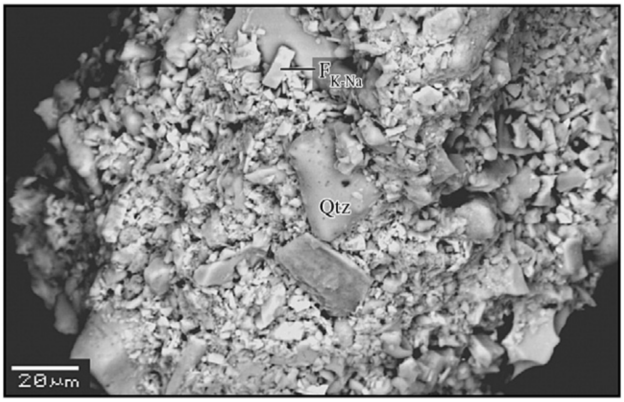

**Fig. 3.** Scanning electron micrograph of a grain from the poz-1 sample. Voltage is 20 kV. The scale bar indicates a length of 20 µm.

Observations with a petrographic microscope on samples poz-2 and poz-3 are presented in Fig. 2. Pictures under natural and polarised lights (Fig. 2a and b) highlight the presence in the poz-2 sample of a

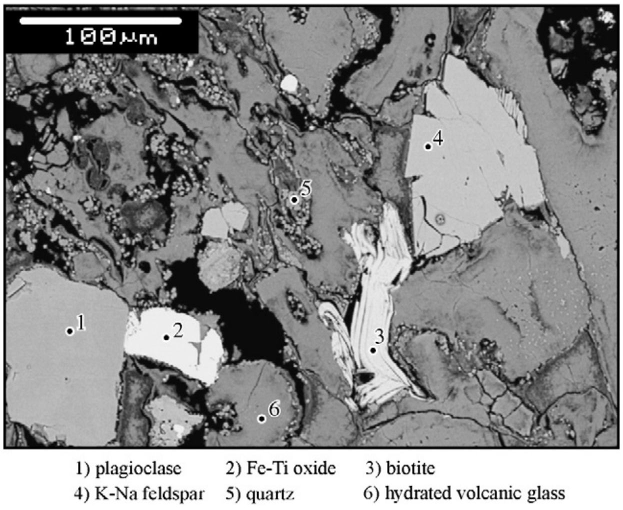

**Fig. 4.** Scanning electron micrograph of a polished section of the poz-2 sample. Voltage is 20 kV. The scale bar indicates a length of 100 µm. Identification of minerals comes from microprobe analysis, see Table 2 for details.

**Table 2**
Microprobe analysis from the poz-2 sample

| Point | K | Na | Ca | Mg | Mn | Ti | Fe | Al | Si | P | Total | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pt_1 | 0.01 | 7.90 | 6.02 | 0.07 | 0.08 | 0.26 | 0.55 | 23.60 | 60.54 | 0.96 | 99.99 | Plagioclase |
| pt_2 | 0.00 | 1.40 | 0.30 | 0.84 | 1.89 | 3.94 | 88.20 | 1.37 | 1.51 | 0.56 | 100.01 | Oxide |
| pt_3 | 8.25 | 0.82 | 0.57 | 15.03 | 0.59 | 4.52 | 16.16 | 13.84 | 39.44 | 0.78 | 100.00 | Biotite |
| pt_4 | 11.47 | 3.29 | 0.47 | 0.00 | 0.00 | 0.09 | 0.19 | 18.95 | 64.41 | 1.13 | 100.00 | Feldspath (K–Na) |
| pt_5 | 0.00 | 0.90 | 0.62 | 0.31 | 0.00 | 0.37 | 0.50 | 2.08 | 93.99 | 1.22 | 99.99 | Quartz |
| pt_6 | 0.14 | 0.95 | 4.95 | 1.39 | 0.00 | 0.10 | 0.74 | 13.79 | 77.08 | 0.87 | 100.01 | Hydrated glass |

The dot numbers correspond to the plotted dots on Fig. 4.

high fraction of volcanic glass. Thin sections through the clusters of zeolites from the poz-3 deposit (Fig. 2c and d) show that zeolite minerals have crystallised from the border to the interior of these holes which were probably initially volcanic gas vacuoles. The poz-3 deposit is also composed of hydrated volcanic glass (palagonite) and clay minerals which have been further identified with XRD analysis.

### 4.1.2. SEM and EDS

The use of EDS, give the chemical composition of the observed phases. The identification is therefore easier. Poz-1 grains (Fig. 3) are mainly composed of quartz and sodi-potassium feldspar (anorthoclase). Poz-2 grains have a granitic composition with sodi-calcic plagioclase, anorthoclase, quartz, iron-titane oxide and biotite (Fig. 4, Table 2). The small dots all over the picture of Fig. 4 may be zeolites (see XRD session for details). Fig. 5 presents the observations from the poz-3 pozzolan. Zeolites have been identified on Fig. 5a, and olivine and volcanic glass on Fig. 5b. Fig. 5c presents a general view of a grain which supports the fact that zeolites are very abundant and represent at least 50% of the deposit. Zeolite crystals are spread all over the surface of the grains, which is a common way of deposit for crystal resulting from alteration process. Two different zeolite types have been identified. The most abundant zeolite belongs to the phillipsite group (Fig. 6a) and the other to the heulandite one (Fig. 6b).

### 4.1.3. XRD

From the XRD study of the samples it is concluded that the main secondary minerals are kaolinite, zeolites from the heulandite group and zeolite from the phillipsite group for respectively poz-1, poz-2 and poz-3.

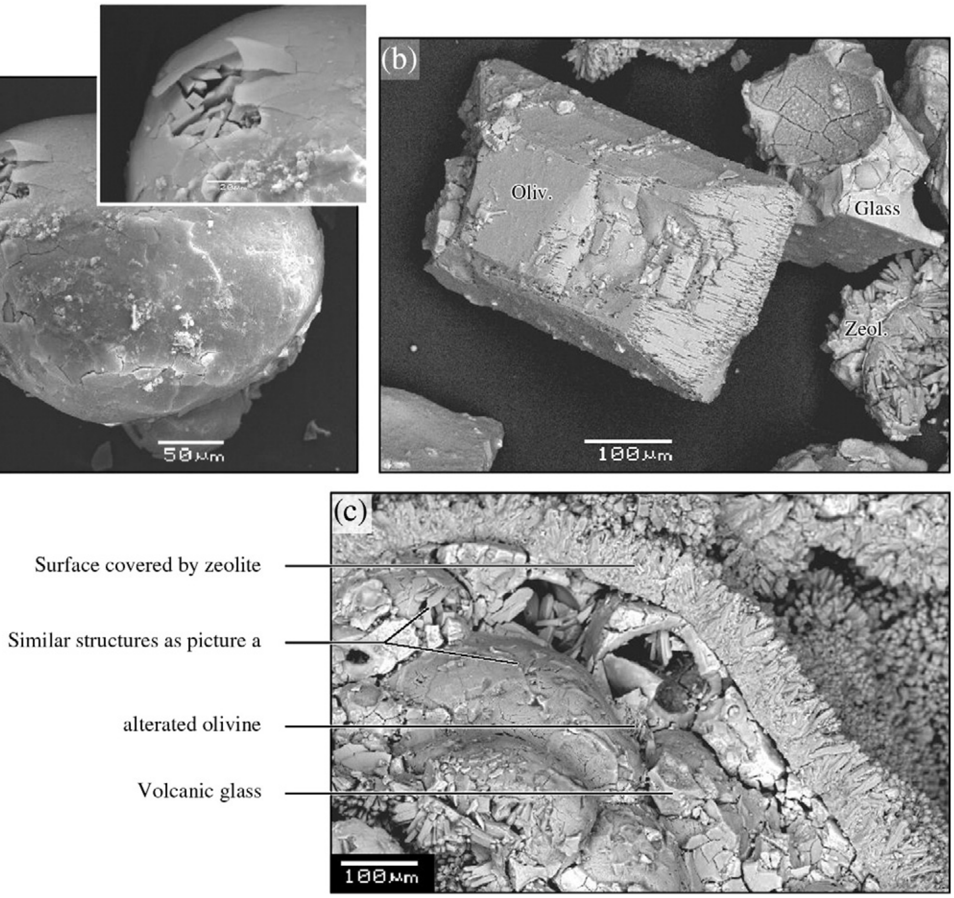

**Fig. 5.** Scanning electron micrograph of the poz-3 sample. Voltage is 20 kV. a) Picture of a grain composed of zeolites. The scale bar indicates a length of 50 μm. A magnification of 2.5 is presented in the upper right corner. b) Picture of an olivine crystal. Grains composed of volcanic glass and zeolites are also present. The scale bar indicates a length of 100 μm. c) General view of the surface of a grain. The scale bar indicates a length of 100 μm.

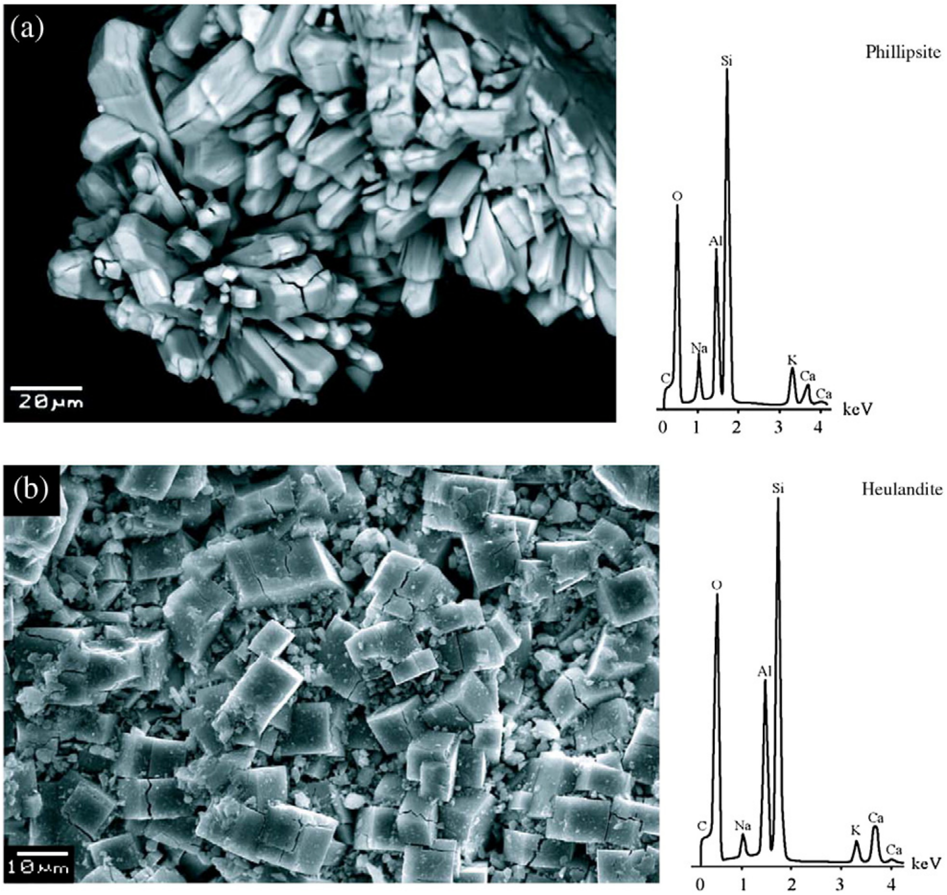

**Fig. 6.** Scanning electron micrograph of the two zeolite types from the poz-3 sample. Spectra from the EDS analysis are represented. a) Zeolites from the phillipsite group and b) zeolites from the heulandite group. The scale bars indicate respectively a length of 20 and 10 μm.

In the poz-1 sample, quartz and sodi-potassic feldspars are the main primary minerals and illite is also present in minor amount (Fig. 7).

The zeolite present in the poz-2 deposit belongs to the heulandite group which is a solid solution between heulandite ((Na,K)$Ca_4(Al_9Si_{27}O_{72})\cdot 24H_2O$), and clinoptilolite or "high silica" heulandite ((Na,K)$_6Al_6(Si_{30}O_{72})\cdot 20H_2O$) end members. In heulandite, the higher peak is attributed to the (020) reflection (8.99 Å; 11.42° 2$\theta$), while in clinoptilolite, the higher peak is attributed to the (004) reflection (3.98 Å; 25.98° 2$\theta$). The XRD pattern from oriented section on fine minerals (Fig. 8b) defends the argument that zeolites are closer to the heulandite pole. However the presence of a second type of zeolite cannot be excluded as the peaks on the XRD trace from bulk powder are just as high. Another way to identify the type of zeolite is to examine their thermal behaviour. Actually clinoptilolite is thermally stable at a temperature above 450 °C, while heulandite undergoes structural collapse below 450 °C. The thermal treatments that we did (Fig. 12) confirm the fact that most of the zeolites are destabilised below 500 °C, but that a small amount of zeolites are still present at higher temperatures. The XRD study of poz-2 sample supports the presence of calcite and montmorillonite in a minor amount. Quartz and feldspars are also present.

XRD data from the poz-3 deposit confirm that it is mainly composed of zeolite (phillipsite) and olivine crystals (Fig. 9). The presence of calcite and montmorillonite is also pointed out. Dolomite appears to have crystallised in very fine grained minerals detected exclusively by the trace from the crystals with a diameter below 5 μm. The presence of the second zeolite type that we identified with the SEM study, is barely highlighted with the XRD observations.

## 4.2. Mineral transformation during heating

### 4.2.1. DSC

The DSC curves for the studied samples are presented in Fig. 10.

For the poz-1 sample, an endothermic reaction at 70 °C indicates the evaporation of absorbed moisture. The exothermic reaction at 300 °C is attributed to a phase transformation of feldspars. Dehydroxylation of kaolinite takes place at 480 °C as observed by Kakali et al. [14]. An S-shaped endothermic/exothermic reaction at 900 °C indicates the decomposition of metakaolin and the formation of mullite.

For the poz-2 and poz-3 samples dehydration of minerals is marked by a broader curve from 70 to 220 °C. This indicates the presence of bound water probably in the zeolitic cages from phillipsite and heulandite minerals. In the poz-3 sample, the departure of the zeolitic water is clearly supported by the endothermic reaction at 180 °C. At 500 °C, an endothermic reaction indicates the dehydroxylation of clay and zeolite minerals. A strong reaction at 750 °C corresponds to the decarbonation of calcite. Lastly, a small S-shaped endothermic/exothermic reaction just below 900 °C marks the crystallisation of new high-temperature phases such as feldspars.

### 4.2.2. XRD

Phase transformations in the samples upon calcinations were monitored by XRD of the cooled products. Results are presented only

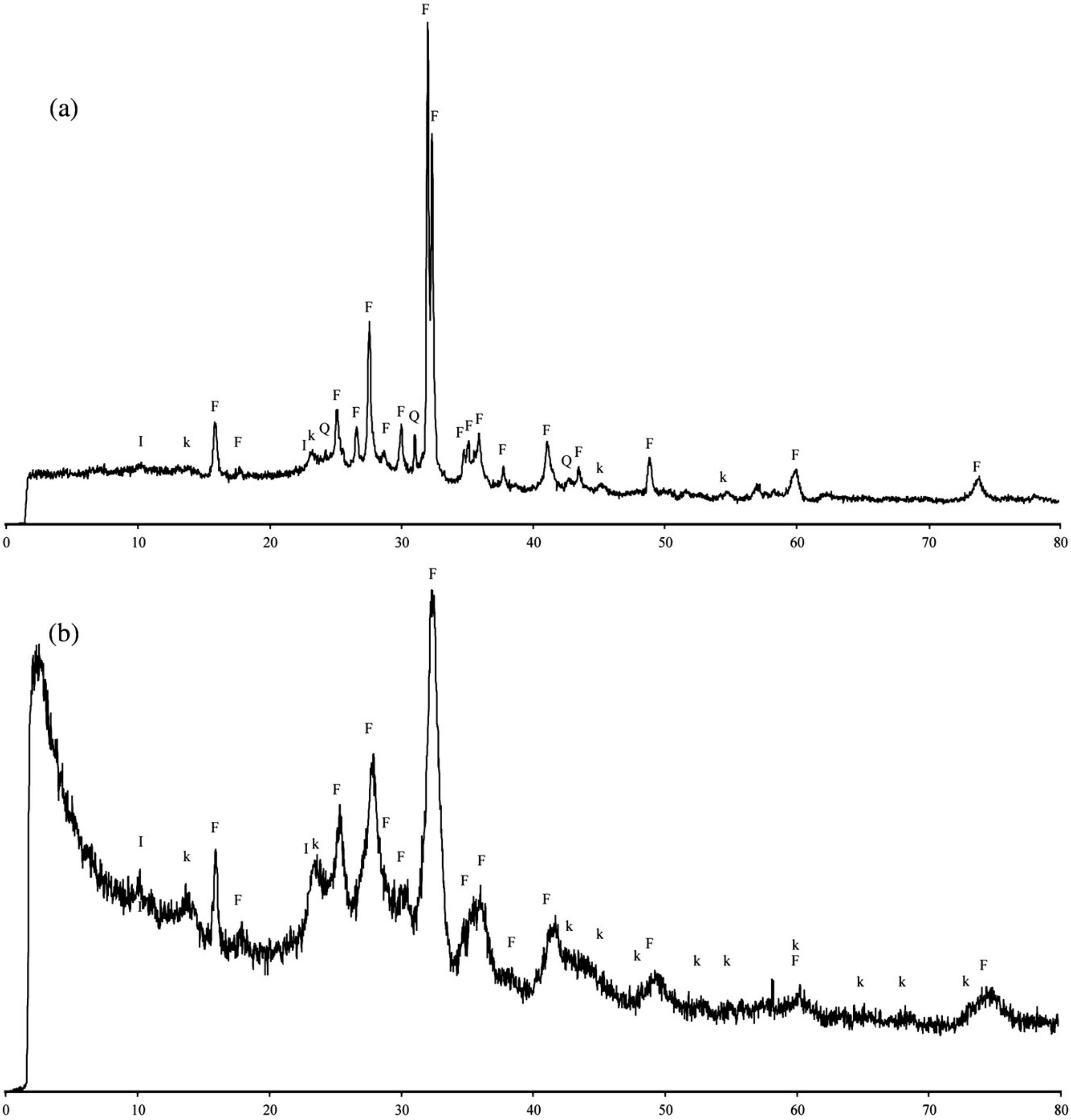

**Fig. 7.** XRD powder pattern of the raw studied sample poz-1. Analysis is conducted from: a) bulk powder, b) the fine grained fraction (<5 μm) on oriented section. Feldspar (F), illite (I), kaolinite (k) and quartz (Q) have been identified.

for a range of 2$\theta$ angles between 5 to 45° because it is the main active part of the spectra.

The kaolinite peaks at 7.01 and 3.42 Å (respectively 14.66° and 23.35° 2$\theta$) decreases in the poz-1 sample from 350 °C and completely disappears at 500 °C (Fig. 11). Illite is still present at temperatures above 500 °C, but its low content makes it difficult to follow. It probably survives to calcinations up to 800 °C, as it has already been shown [15]. The main reflections of anorthoclase (Na,K-feldspar) at 3.21 Å (32.35° 2$\theta$) and quartz 3.34 Å (31.03° 2$\theta$) are not affected by thermal treatments.

XRD patterns of the poz-2 sample are presented in Fig. 12. The heulandite main peaks at 8.99 and 3.98 Å (11.42° and 25.98° 2$\theta$) are smoothed after calcinations above 270 °C, and the main collapse occurs above 400 °C. At 500 °C, the peaks from zeolite are barely discernible, and could result from the second type of zeolite (clinoptilolite) that we identified in finest fraction and that resist to temperature higher than 450 °C. They finally completely disappear at 800 °C. The calcite peak at 3.03 Å disappears between 500 and 600 °C. The main reflection of anorthoclase at 3.21 Å becomes more pronounced with increasing calcination temperatures.

For the poz-3 deposit (Fig. 13), the zeolite (phillipsite) undergoes a complete structural collapse at 350 °C. The main peaks at 7.16 and 3.2 Å (14.35° and 32.40° 2$\theta$) suddenly disappear between 270 and 350 °C. New broad peaks indicating a neo-crystallisation are noticed as soon as 350 °C. The main one is located at 3.25 Å

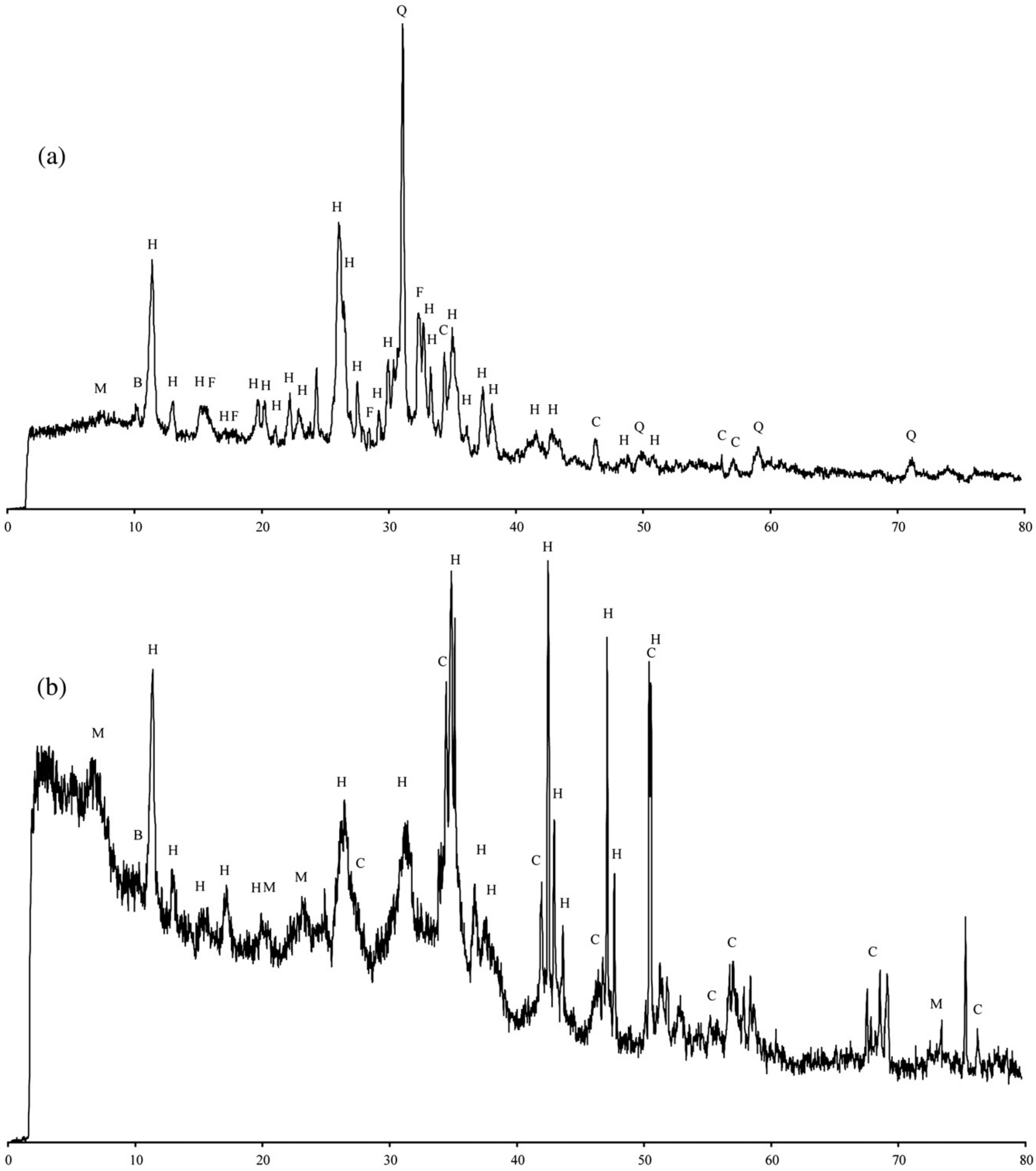

**Fig. 8.** XRD powder pattern of the raw studied sample poz-2. Analysis is conducted from: a) bulk powder, b) the fine grained fraction (<5 μm) on oriented section. Biotite (B), calcite (C), feldspar (F), heulandite (H), montmorillonite (M) and quartz (Q) have been identified.

(31.95° 2$\theta$). These new reflections are getting more pronounced with increasing temperature particularly between 500 and 600 °C. The position of the peaks also slightly moves indicating changes in the composition of this new mineral. The main peak is moving from 3.25 to 3.22 Å. Based on the trace from the 800 °C calcinations temperature, we have identified this neo-crystallisation as a calcium aluminium silicate, referenced in the PCPDFWIN program as Svyatoslavite with the following cell parameters: $a$ = 8.232 Å, $b$ = 8.606 Å, $c$ = 4.852 Å [16]. The slight changes in the position of the peaks probably come from a solid solution with a more sodic pole.

The calcite peak at 3.03 Å decreases above 500 °C and completely disappears at 700 °C. The decarbonation of the calcite leads to the formation of oxidized calcium (CaO). However, because of the sample storage conditions before analyses, a hydration has occurred which has transformed slaked lime (CaO) in portlandite ($Ca(OH)_2$). Portlandite is marked by peaks at 4.90 and 2.62 Å (21.04° and 39.80° 2$\theta$). For the montmorillonite, destabilisation occurs at 500 °C.

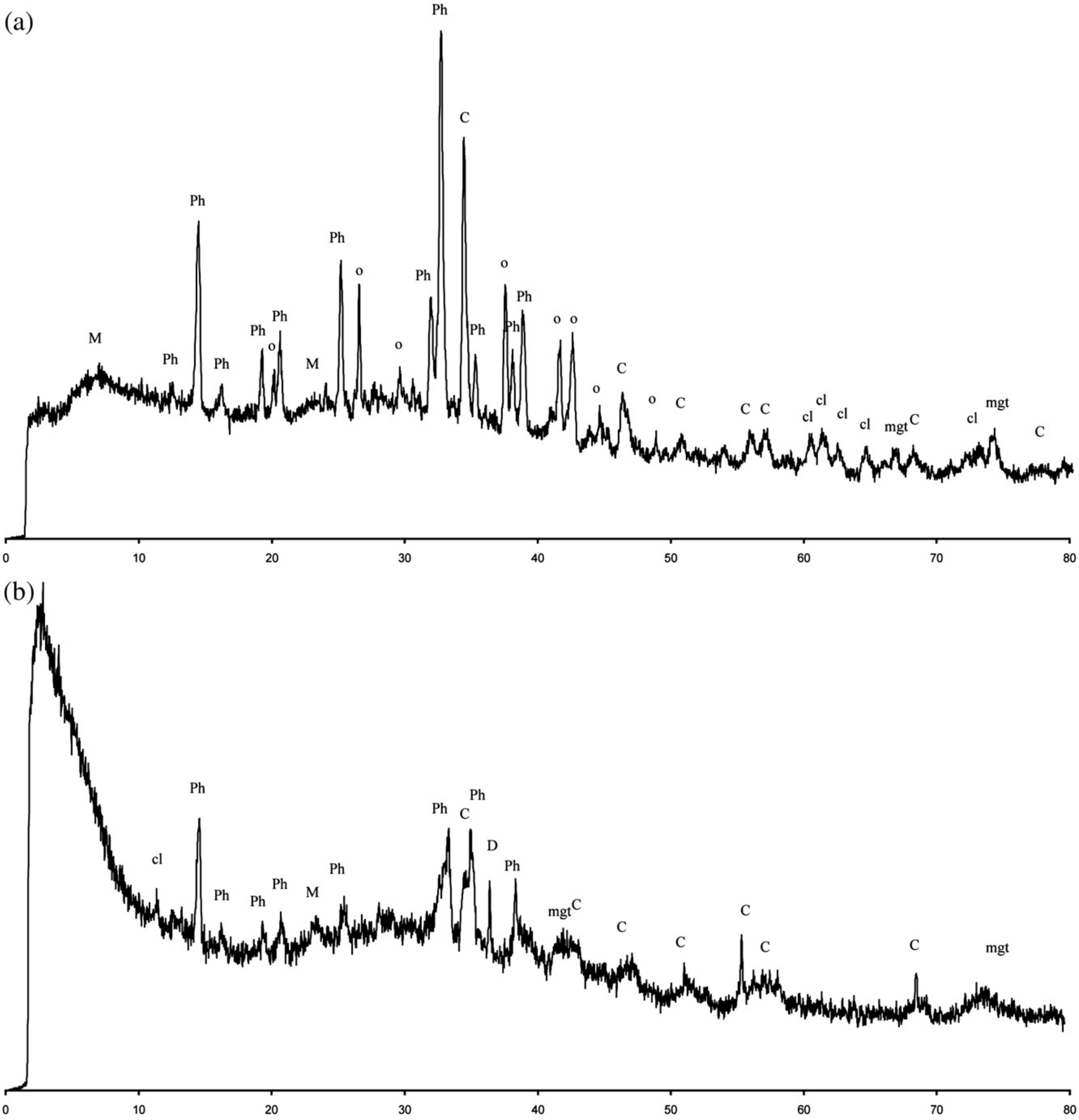

**Fig. 9.** XRD powder pattern of the raw studied sample poz-3. Analysis is conducted from: a) bulk powder, b) the fine grained fraction (<5 μm) on oriented section. Calcite (C), clinoptilolite (cl), dolomite (D), magnetite (mgt), montmorillonite (M), olivine (o) and phillipsite (Ph) have been identified.

### *4.3. Strength development*

The compressive strength of cement–pozzolan mortars is one of the most important parameters for evaluating a pozzolanic material. The results are presented in Table 3 and Fig. 14. They show that all samples have a better compressive strength than a mortar with OPC mixed with an inert component in the same replacement percentage as for the tested pozzolans (assumed to be equal to 63% of pure reference OPC) [17]. It appears that dehydroxylation of kaolinite in the poz-1 sample calcined at 500 °C substantially improve the resistance of mortar at 28 days, but early strength is decreased. A calcination at 800 °C slightly decreases the strength resistance at 28 days. For the poz-2 sample, a good early strength resistance is reached when the sample is calcined at 600 °C. At 28 days, the increase in the compressive strength can be noticed at 500 °C and does not decreased with higher calcinations temperature. The poz-3 pozzolans has a high pozzolanic activity as soon as 350 °C. This temperature is the optimal temperature for this sample as higher calcinations contribute to decrease the compressive strength resistance.

## 5. Discussion

### *5.1. Strength and secondary mineral transformations*

The results presented in this study show a strong correlation between transformations of the secondary minerals and compressive

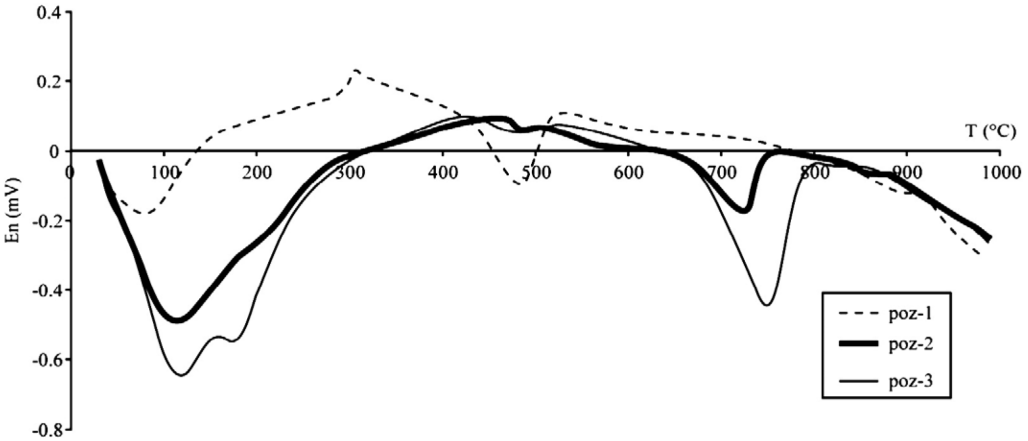

**Fig. 10.** DSC of the poz-1, poz-2 and poz-3 samples. Heating rate: 20 °C/min.

strength evolution of the pozzolan deposits. Fig. 15 summarises this relationship.

### 5.1.1. The clay minerals

In the poz-1 sample, destabilisation of kaolinite minerals at 500 °C considerably enhances 28 days strength. At 500 °C, this destructured kaolinite cannot be considered as metakaolin, for which activation temperature is closer to 700 °C [14,18]. The water demand for mortars with clay minerals is higher, when clays are not heated, which reduces the workability of the pozzolanic mortars compared to the 100% OPC mortars. Therefore, the strength increase at 500 °C could be due to a better workability of the mortar more than a higher pozzolanic activity of the binder. We did not make experiments to discriminate these effects.

### 5.1.2. The zeolites

Different studies conclude that the presence of zeolite positively influences the pozzolanic activity of natural tuffs [4,6,8]. Our results disagree with those conclusions. Actually, even if zeolite rich pozzolans develop interesting strength, our results clearly support that it is when zeolites are destabilised that activity is enhanced. The compressive strength of mortar made with 500 °C heated poz-2 pozzolans is higher than with 100% OPC. This increase of strength is clearly correlated with the destructuration of the heulandite minerals. In a similar way, the destructuration of phillipsite at 350 °C in the poz-3 sample leads to higher strength than with pure Portland cement. In the poz-2 sample, zeolites are microcrystallised. Neocrystallisation are therefore difficult to be observed with XRD study., Phillipsite recrystallises in a calcium aluminium silicate close to a feldspar structure which is weakly reactive. The fact that the recrystallisation of zeolites into an inert phase reduces the strength of mortar confirms the common observations that the zeolites minerals had a pozzolanic activity by themselves. However, this study shows also that the highest compressive strength is reached when zeolites have been destructured and are not already recrystallised. We should then use the term metazeolite, as metakaolin is used to describe the amorphous phase created from the thermal activation of kaolinite and before its recrystallisation into mullite [19].

### 5.1.3. The calcite

Decarbonation of calcite in the poz-2 sample occurs at 600 °C, and seems to enhance the early strength of mortar. Degradation of calcite minerals activates the dissolution of $Ca^{2+}$ in the cementitious solution which enhances the precipitation of the calcium silicate hydrate (CSH). In the poz-3 sample, few variations in early strength can be noticed except at 800 °C. This can be explained by the fact that calcite is not completely decarbonated at 600 °C, and that the highest content of $Ca^{2+}$ between all poz-3 experiments is therefore reached at 800 °C.

## 5.2. Temperature of destabilisation

The temperature of destruction of many minerals was not the same as what is expected by thermal evolution study of the pure mineral. This is specially the case for the calcite minerals which are expected to disappear at 800 °C. This observation is very common in geological study of metamorphic rocks, and is attributed to the properties of the mineral assemblage which are different from those of each mineral observed separately.

## 5.3. Water percent and workability

We have worked at constant water to cementitious material ratio and it is well known that pozzolanic mortars have a lower workability than 100% OPC one. Actually, the water demand increases with zeolites and clay minerals content in mortars. These variations of workability may have lead to variations in the compressive strength as we expect to have higher porosity in mortars with lower workability. This effect can be particularly strong in mortars with raw material substitution as secondary minerals are not destructured. Our results indicate strong correlations between mineral transformation and strength development (Fig. 15) but we cannot evaluate the respective part of the pozzolanic activity enhancement of substitution material and the increase of compressive strength due to a better workability during heating.

## 6. Conclusion

This study shows that the pozzolanic activity of natural pozzolans can be enhanced by a thermal treatment. Treated pozzolans are then a powerful substitution material for cement-based mortars. Low temperature thermal treatment considerably improves performance of pozzolanic cements when pozzolans contain significant amount of secondary minerals like clays and zeolites. These results are giving new perspectives for natural pozzolan uses, but they also show that systematic mineralogical study need to be done for new deposit exploitation as mineral transformations depend on the composition of the mineral but also on its mineral environment.

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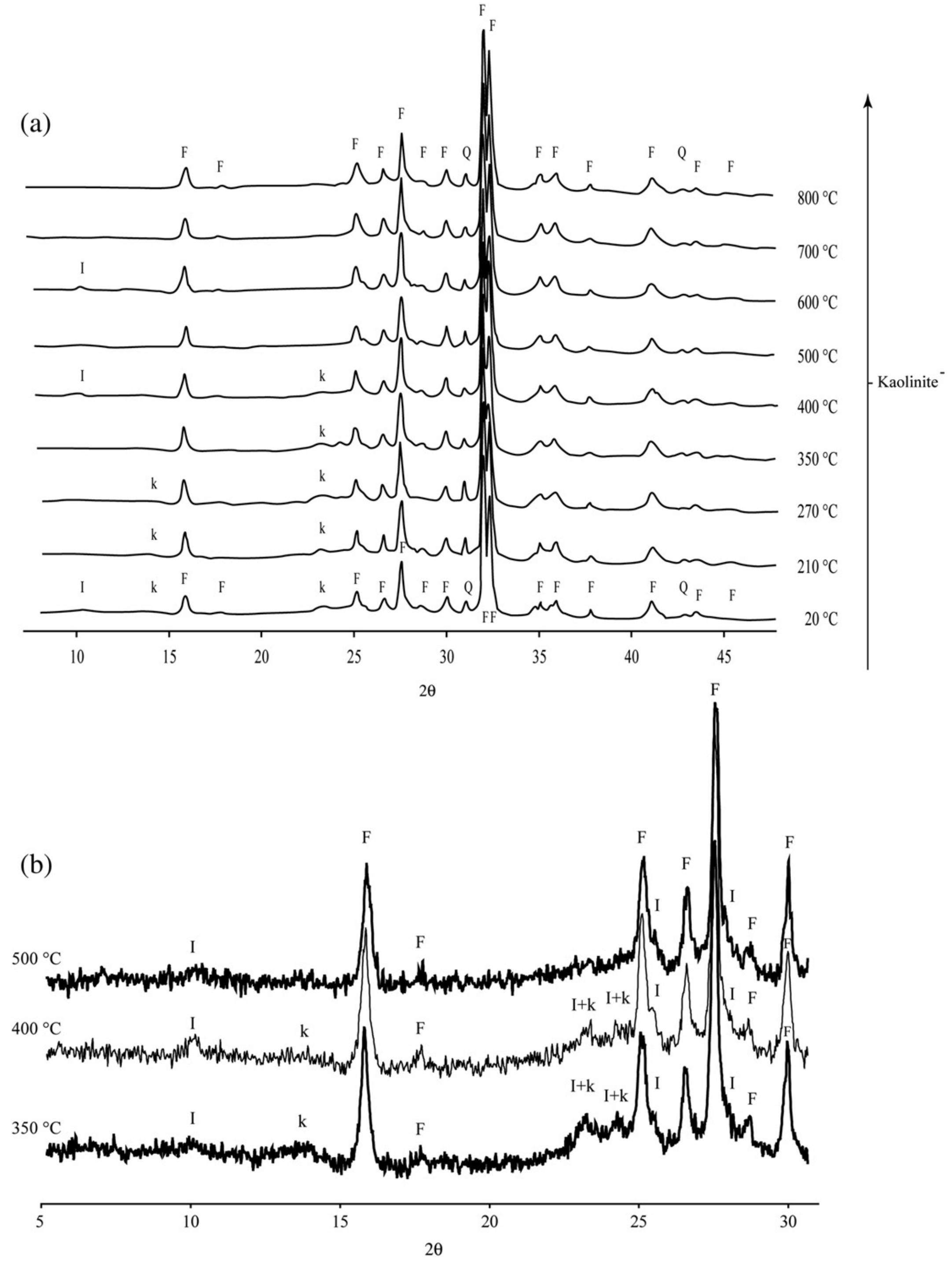

**Fig. 11.** XRD powder pattern of the poz-1 sample thermal transformations. Analysis is conducted from: a) bulk powder, b) the fine grained fraction (<5 μm) on oriented section. Feldspar (F), illite (I), kaolinite (k) and quartz (Q) have been identified.

casting and compressive strength measurements which were conducted at the LMDC (Toulouse, France). The authors wish to thank M. Thibaut and T. Aigouy for their help on DRX and SEM respectively, F. De Parseval and J.F. Mena for grinding procedures. Comments on drafts on the manuscript by A. Haricot are acknowledged.

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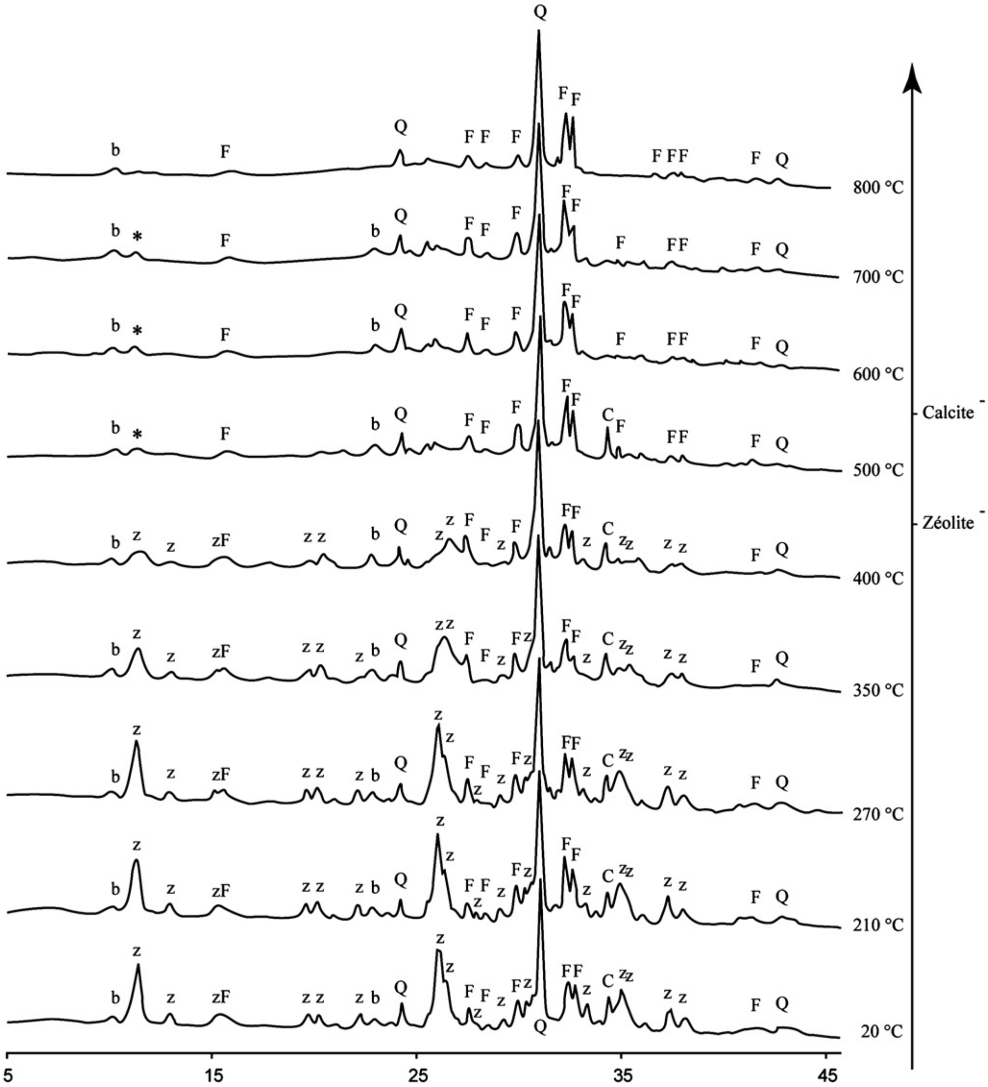

**Fig. 12.** XRD powder pattern of the poz-2 sample thermal transformations. Analysis is conducted from bulk powder. Biotite (b), calcite (C), Feldspar (F), quartz (Q) and zeolite (z) have been identified.

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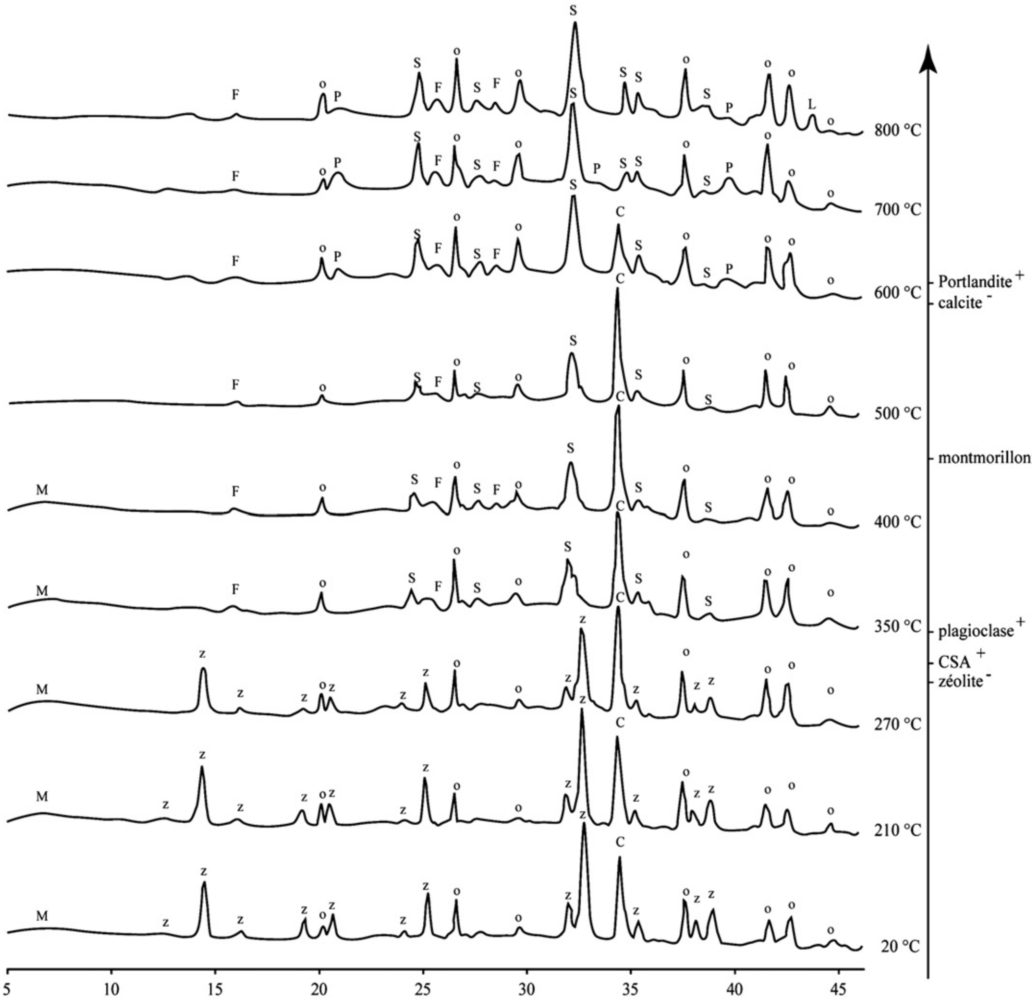

**Fig. 13.** XRD powder pattern of the poz-3 sample thermal transformations. Analysis is conducted from bulk powder. Calcite (C), plagioclase (F), montmorillonite (M), olivine (o), portlandite (P), Svyatoslavite (S) and zeolite (z) have been identified.

**Table 3**
Compressive strength of calcined pozzolan–cement mortars

| TZ | Compressive strength (MPa) | | | | |
|---|---|---|---|---|---|
| Curing days | 20 °C | 400 °C | 500 °C | 800 °C | Ref. OPC |
| 1 | 17.35 | 17.06 | 15.85 | 18.10 | 23.09 |
| 7 | 31.18 | 32.56 | 34.39 | 35.07 | 44.92 |
| 28 | 42.42 | 44.00 | 47.42 | 46.72 | 52.90 |

| TQ | Compressive strength (MPa) | | | | |
|---|---|---|---|---|---|
| Curing days | 20 °C | 400 °C | 500 °C | 600 °C | 800 °C |
| 1 | 12.02 | 13.90 | 14.75 | 17.11 | 15.61 |
| 7 | 29.90 | 32.01 | 34.82 | 35.34 | 34.48 |
| 28 | 48.07 | 48.37 | 54.11 | 54.10 | 54.37 |

| JO | Compressive strength (MPa) | | | | |
|---|---|---|---|---|---|
| Curing days | 20 °C | 350 °C | 500 °C | 600 °C | 800 °C |
| 1 | 14.66 | 14.78 | 15.36 | 14.51 | 17.56 |
| 7 | 35.55 | 37.32 | 36.74 | 36.76 | 33.49 |
| 28 | 48.80 | 53.72 | 50.23 | 51.77 | 46.42 |

RILEM prisms; 30 wt.% replacement of OPC by calcined material; cured in water at 25 °C. Each value is an average of 3 measurements; the mean coefficient of variation is 2.6%.

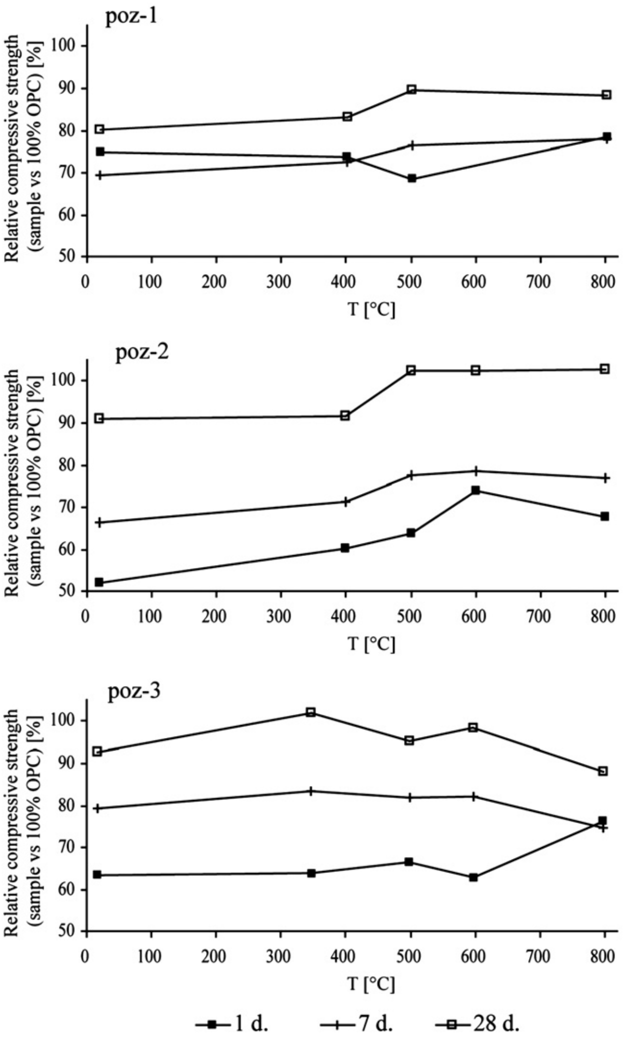

**Fig. 14.** Temporal compressive strength evolution of mortars containing calcined samples at different temperatures. Normalised prisms; 30 wt.% of cement was replaced by pozzolans; cured in water at 25 °C.

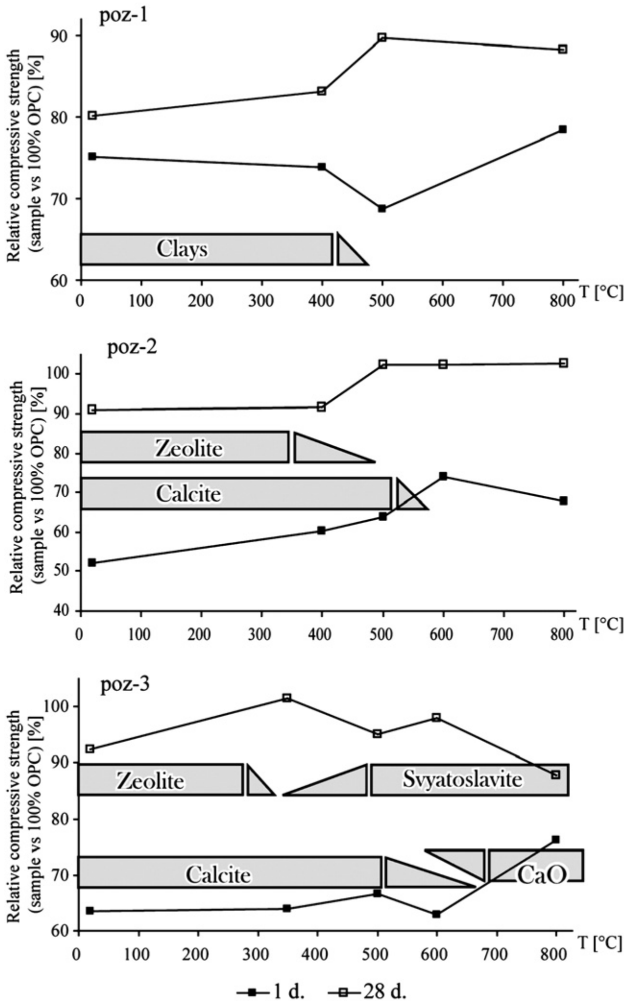

**Fig. 15.** Relation between the compressive strength of pozzolanic mortars after 28 days of curing and the mineral composition of the thermal activated pozzolan substitute.