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1 Evaluation of marine dredged sediment as reactive powder compared to ground 2 basaltic pyroclastic materials for the development of eco-friendly lime-pozzolan 3 binders

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10

11 **Abstract**

12 The combination of lime with natural pozzolans for the production of binders in masonry
13 construction dates back to ancient times. These were largely ignored with the industrialization of
14 the building sector even though their use for specific applications is of interest. The use of lime-
15 pozzolan binders with the least amount of lime is a relevant opportunity to reduce carbon
16 emissions due to the decarbonation of limestone for the production of quicklime but also to
17 introduce new alumino-silicate materials. In this context, the present investigation intends to relate
18 marine dredged sediment to pyroclastic materials and to mix it with hydrated lime without any
19 thermal treatment but after micronization. The blends were moist cured either at 20°C or 50°C
20 and the paper will discuss the pozzolanic reactivity through the study of compressive strength and
21 reaction kinetics from 3 days to 180 days. Reaction product assemblage, microstructure, and
22 porosity refinement were also addressed after advanced curing ages. Results have well illustrated
23 the long-term pozzolanic reactivity of the marine sediment cured at 50°C through the whole
24 combination of initially available lime after 60 days and the compressive strength development
25 providing 12 MPa after 180 days.

26

27 **Key-words:**

28 Marine dredged sediment;
29 Basaltic pyroclastic materials;
30 Pozzolanic reactivity;
31 Low-carbon binder;
32 Curing temperature;
33 Hydration kinetics.

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36 **1. Introduction**

37 After World War II, in a context of industrialized and quick production of new buildings,
38 embodied carbon and energy efficiency are relegated to the background. From the mid-1970s,
39 interior insulation of buildings using mineral wools or polystyrene with concrete blocks and other
40 masonry units (such as burnt clay bricks) is widely used in France. These design practices are not
41 the most effective to deal appropriately with moisture condensation and summer thermal comfort
42 which can imply an excessive use of air conditioning. However, these issues were better
43 addressed with ancestral buildings using traditional methods (earth-straw, building stones, etc.). In
44 addition, as a result of successive thermal regulations, a significant part of the overall carbon
45 footprint of buildings is due to the production of materials.

46 The combination of hydrated lime with natural pozzolans (i.e. pyroclastic fall deposits) goes back
47 to the Greco-Roman period [1]. Unfortunately, the use of lime-pozzolan binders was strongly
48 reduced following the advent of ordinary Portland cement. Furthermore, most natural pozzolans
49 do not present the appropriate properties for specific applications owing to their low reactivity or
50 unstable quality [2]. Nevertheless, some research studies dealing with the use of lime-pozzolan
51 binders for the design of Bio-aggregate-based Building Materials (BBMs) are available [3,4].
52 Nozahic et al. [3] used trachytic pumice as a natural pozzolan with hydrated lime and some
53 authors [4] used metakaolin (an artificial pozzolan) with various limes bearing in mind the goal of
54 reducing the carbon impact of the binder that will be mixed with plant aggregates (like hemp
55 shives). As a matter of fact, the extraction of raw materials and the production of the lime-based
56 binder are reported to heavily contribute to the carbon footprint of hemp concrete [5,6]. Since
57 carbon emissions are mainly due to the decarbonation of limestone for the production of
58 quicklime, the use of lime-pozzolan binders with the least amount of hydrated lime is relevant.

59
60 Vitruvius (30-20 B.C.) described Roman building materials using zeolitic tuff and pumices
61 originated from Italy in the Vesuvius area. The term “pozzolan” comes from an Italian city called
62 Pozzuoli and is originally associated to trachytic fall deposits [7]. However, depending on the
63 geological context, other lithologies may be considered as pozzolans. The latter are actually
64 defined as raw materials that are able to provide cementation when combined with lime and water.
65 According to Pichon [8,9], the hardening of lime-pozzolan blends occurs through the dissolution
66 of silica and alumina within the volcanic glassy phase by calcium hydroxide attack. In addition,
67 the vesicular nature of pyroclastic materials contribute to their reactivity [10]. Most of the
68 traditionally used natural pozzolans are of trachytic or rhyolitic composition with a silica content
69 of 60 – 70 wt.% and are reported to present a better reactivity compared to basic and ultrabasic
70 pyroclastics (i.e. basaltic) for which the silica content is under 45 – 50 wt.% [3,7,10]. However,
71 along French lines and more specifically in the French Massif Central, pozzolans only refer to
72 scoria of basaltic composition and are well-known in the field of quarrying. These basaltic
73 pyroclastics are mainly used for winter road sanding, water drainage or road engineering but not
74 in the cement industry [7]. Only a few old research studies about the mixing of these pyroclastics
75 with lime for road applications were published in the 1970s [11,12].

76
77 Furthermore, the building sector is also challenged by a growing shortage of non-renewable
78 mineral resources and has to find meaningful alternatives to quarry materials. In addition, natural
79 pozzolans are not locally available in the North of France (Hauts-de-France area) and there is
80 limited access to deposits for environmental reasons. Instead, dredged sediments are abundant in
81 this area, deposited as well in waterways as on the seafloor of coastal ports (e.g. port of Dunkirk).
82 The composition of marine dredged sediments is partly provided by terrigenous sources resulting
83 from physical and chemical weathering of crustal rocks. The main resulting solid products are
84 quartz sand and clay minerals, due to winds and water current flows over lands composed of
85 sandstone, mudstone, etc. Since quartz is the most stable form of silica in the earth’s crust, this
86 mineral is often predominant [13]. Marine sediments can also contain biogenic deposits in the
87 form of calcite in addition to alumino-silicates. Although pozzolanic reactivity is regularly
88 assigned to the glass content of materials, the ability of some mineral components to bind lime
89 was found to be non-negligible [14]. Some authors showed a subsequent pozzolanic reactivity of
90 crystallized quartz after an accurate micronization and a curing temperature of 100°C [15]. Thus,
91 they defined a critical median diameter of 5 micrometers below which quartz particles show an
92 interesting reactivity. Moreover, Diamond et al. [16] investigated the reactivity and the hardening
93 of mixtures with 30 wt.% of lime and 70 wt.% of pure quartz or clays (kaolinite and
94 montmorillonite). The blends were stored under endogenous conditions for 55 days at 60°C. In
95 these specific curing conditions, calcium hydroxide was consumed and the reaction products were
96 C-S-H but also calcium aluminate hydrates in the case of lime-clay blends, especially hydrogarnet

97 (C₃AH₆). Hence, these results lead one to believe that cementation of mixtures made out of
98 marine sediments and hydrated lime could occur.

99 The objective of this paper is to provide a new insight into the development of lime-pozzolan
100 binders using marine dredged sediment as reactive powder in combination with hydrated lime.
101 The marine dredged sediment will be used without any thermal treatment (i.e. calcination) but
102 following micronization by air jet milling. In some previous investigations, sediments were used
103 only as supplementary cementitious materials (SCMs) in the field of waste recovery in cement
104 binders. Conversely, several studies about lime-pozzolan binders revealed that the optimal lime
105 content to achieve the best strength performances was in the range of 15 to 30 wt.%
106 [3,7,8,11,17–19]. Hence, this is an opportunity to include a substantial amount of marine
107 sediment in the mix design. The marine dredged sediment that will be used herein is from the port
108 of Dunkirk in the North of France. It will be related to basaltic pyroclastic deposits from the
109 Devès plateau in the French Massif Central. Following mechanical treatment (micronization or
110 grinding), the raw materials will be mixed with 20 wt.% of hydrated lime. The pozzolanic
111 reactivity should be claimed if the different variables of the function in Eq. 1 follow on from each
112 other. Therefore, this paper deals with an evaluation of reaction kinetics, reaction products,
113 microstructure, porosity and compressive strength development until 180 days.

$$114 \text{ Pozzolanic reactivity} = f(\text{Fixed Lime} \rightarrow \text{Reaction products} \rightarrow \text{Porosity} \rightarrow \text{Hardening}) \quad (1)$$

115
116 Since high curing temperature is known to significantly increase the pozzolanic reaction rate due
117 to accelerated reaction kinetics following the Arrhenius law [20,21], two curing temperatures will
118 be considered i.e. 20°C and 50°C.

120 2. Materials and methods

121 2.1. Raw materials

122 2.1.1. Pyroclastic deposits

123 Weakly consolidated basaltic pyroclastic deposits (tephras) were collected in the Devès basaltic
124 plateau (French Massif Central) in 2019. The geological context of this environment is linked to
125 Strombolian eruptions of the Pleistocene time (~ 2.5 Ma) [22]. Lava flows occur simultaneously
126 with incandescent ejections that undergo a sudden cooling in the atmosphere. The pyroclastic fall
127 deposits (i.e. bombs, lapilli and cinders) build up around the vent to form the volcanic edifice.
128 Almost 150 scoria cones are counted over this basaltic plateau (Fig. 1a). Samples were taken from
129 different sites in the middle part of the plateau (see the different geographic locations on the map
130 of Fig. 1a). Fig. 1b shows one of the quarry faces. The pyroclastics used in this investigation
131 (thereafter noted SDA, MTB, COS and BZ depending on the site) were composed of highly
132 vesiculated lapilli-size millimetric fragments (Fig. 1c).

134 2.1.2. Marine dredged sediment

135 The marine sediment (thereafter noted MS) was dredged in the port of Dunkirk (North of France)
136 in 2019 and stems from an active lagooning process (Fig. 1d). The fines content of the raw
137 sediment (illustrated in Fig. 1e) was determined by wet sieving at 63 micrometers and was 40
138 wt.%. The particle size distribution of clay and silt grades by laser diffraction is reported in Fig.
139 2a. For the sand fraction, it was performed by mechanical sieving and the result is shown in Fig.
140 2b. The marine sediment can be considered non-hazardous and non-inert based on heavy metals
141 and organic contents in eluates in accordance with criteria and procedure for waste acceptance at
142 landfills (99/31/EC).

144 2.1.3. Hydrated lime

145 A commercial hydrated lime (SuperCalco[®]97 from Carmeuse) with 94 wt.% of calcium hydroxide
146 (Ca(OH)₂) and 1.2 wt.% of calcite (CaCO₃) was employed.

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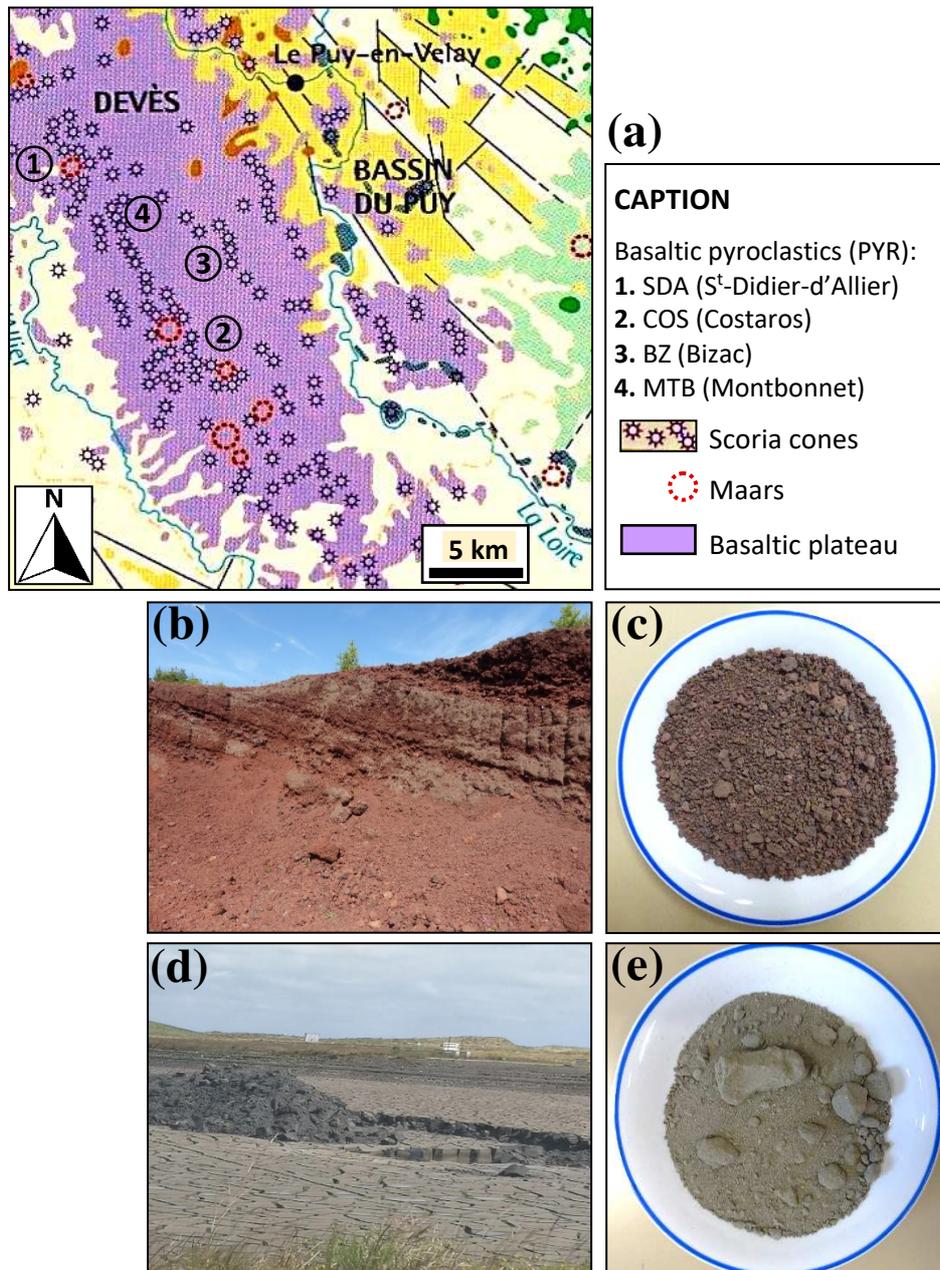
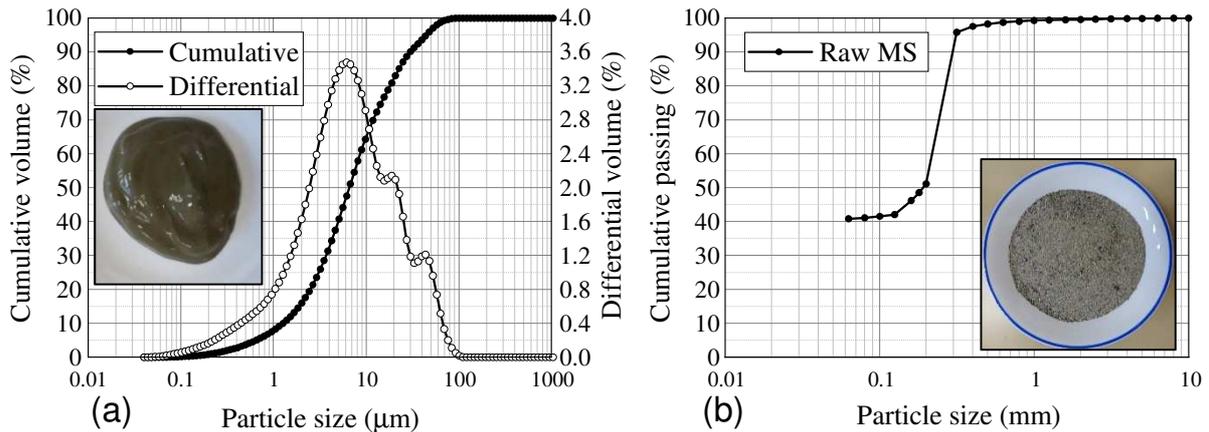


Fig. 1. (a). Geological map of the Devès plateau [22], (b) Quarry face, (c) Pyroclastics in the form of millimetric aggregates (lapilli), (d) In-situ dehydration of the marine sediment after dredging, (e) Raw marine dredged sediment

2.2. Experimental methods

2.2.1. Preparation of materials

Following receipt in the laboratory, the raw materials (pyroclastics and marine dredged sediment) were dried at 50°C. The pyroclastics were ground using a cross beater mill (maximum diameter of 250 micrometers) followed by a more intensive grinding with a vibratory disc mill at 700 rpm for 5 minutes. The marine dredged sediment was ground using a rotor beater mill (maximum diameter of 500 micrometers) with a speed of 10,000 rpm in order to get the suitable maximum particle size for the use of air jet milling. The equipment was set up to micronize the sediment powder at a median diameter (D_{50}) of 2.3 micrometers.



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Fig. 2. Size distribution of (a) wet-sieved particles under 63 μm, (b) sand fraction over 63 μm for the raw marine dredged sediment

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2.2.2. Mix design and curing conditions

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Based on past experiences with regard to lime-pozzolan blends [3,7,8,11,17–19], the pastes studied in this paper were made up of 80 wt.% of ground pyroclastics or micronized sediment mixed with 20 wt.% of hydrated lime. The water-on-powder mass ratio (W/P) of the pastes combining each of the materials with hydrated lime were determined using a flow spread test [23]. The mixtures were cast into cylindrical molds (2.7 cm in diameter and 5.4 cm in height) under the effect of vibration and the molds were placed in hermetically sealed vials to ensure endogenous conditions (RH higher than 95%) and avoid carbonation of hydrated lime for the curing time. Immediately after casting and sealing, samples were cured either under standard moist curing at room temperature (20°C) or under elevated temperature (50°C).

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2.2.3. Compressive strength test

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The tests were conducted on the cylindrical specimens with an electromechanical standard press (Instron). A load cell of 10 kN was used to provide a suitable accuracy for low strength materials and the loading rate was 1.5 kN.min⁻¹. The compressive strength was tested from 3 to 180 days. For each testing age, samples were polished and the strength reported is an average of 3 to 5 specimens. Although kneading water plays a significant role in strength loss during early ages [24], the samples were tested with their water saturation degree since drying of pastes would result in shrinkage cracks, especially when the hydration degree is high.

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2.2.4. Method for hydration stoppage

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The characterization of reaction kinetics, reaction products, microstructure, and porosity after a given degree of reaction require the removal of capillary water while preserving at the most the physical and chemical state of the samples [25,26]. As such, a drying method by solvent exchange with IPA (Isopropyl alcohol or 2-propanol) was used. A representative sample of the cylinders was reduced to powder for TGA and XRD analyses and immersed in IPA for 7 days. IPA was renewed twice (each time for 48 hours) to facilitate the diffusion process. In the end, IPA was evacuated by a vacuum filtration process and completely removed by vacuum drying until constant mass, using a desiccator with silica gel and hydrated lime. Samples were actually kept under vacuum until analysis to avoid carbonation as far as possible. The same protocol was followed for little cubic samples that were carefully cut from cylinders for MIP and SEM.

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2.2.5. Bound water and fixed lime by TGA

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TGA (Mettler Toledo) was performed under nitrogen atmosphere from 25°C to 950°C with a heating rate of 10°C.min⁻¹. Chemically bound water in hydrates was estimated from mass loss in

220 the range 80°C – 400°C [27]. Free lime (CH) and calcium carbonate (CC) were quantified by the
221 tangential method [28] respectively in the range 400 – 500°C and 500°C – 800°C using the
222 following equations (Eq. 2&3):

$$\text{Free CH (\%)} = \text{WL}_{\text{CH}} (\%) \times \frac{m(\text{CH})}{m(\text{H}_2\text{O})} \quad (2)$$

$$\text{CC (\%)} = \text{WL}_{\text{CC}} (\%) \times \frac{m(\text{CC})}{m(\text{CO}_2)} \quad (3)$$

225 where WL_{CH} and WL_{CC} are respectively the weight losses due to dehydroxylation of CH and
226 decarbonation of CC with a normalization to the anhydrous binder and m is the molecular mass of
227 CH (74 g.mol⁻¹), H₂O (18 g.mol⁻¹), CC (100 g.mol⁻¹) and CO₂ (44 g.mol⁻¹).

228
229 The amount of fixed CH by the pyroclastics or the sediment over time (until 180 days of curing)
230 was calculated as percent of the initially available CH as follows (Eq. 4):

$$\text{Fixed CH (\%)} = [(\text{CH}_i (\%) - \text{Free CH (\%)} - \text{Carbonated CH (\%)}) / \text{CH}_i (\%)] \times 100 \quad (4)$$

233 where $\text{CH}_i (\%)$ is the amount of CH initially introduced into the blend and carbonated CH (%) is
234 the free lime that underwent carbonation.

235 2.2.6. Reaction products (DTG, XRD) and microstructure (SEM-EDS)

236 Analysis of newly formed phases was done using DTG curves and XRD (Bruker D2 phaser) with
237 Cu K α radiation, 2θ from 10 to 80° and step size of 0.02°.

238 The microstructure of pastes after 90 days of hardening was investigated using Scanning Electron
239 Microscopy (SEM Schottky emission Hitachi, Model S-4300Se/N). Prior to observations, cubic
240 samples need to be embedded in epoxy resin, polished and coated with a carbon film.

241 Images were acquired in backscattered electron imaging mode (BSE) and the acceleration voltage
242 was 20 kV. Semi-quantitative chemical analysis was also performed by means of Energy
243 Dispersive X-ray Spectroscopy (EDS Silicon drift detector, Thermo Electron Corporation)
244 coupled with SEM with the aim of studying the composition of hydrated phases (Ca, Si, Al).
245 Elemental compositions were recorded for 60 seconds live time at 20% dead time.

246

247 2.2.7. Porosity (MIP)

248 The samples were subjected to porosity measurement after 90 and 180 days of hardening. The
249 equipment was an AutoPore V 9600 Mercury porosimeter (from Micromeritics). Paste samples
250 were inserted in a penetrometer for solids with a cup volume of 5 cm³ (and capillary tube of 1.8
251 cm³). The measurement included one intrusion-extrusion cycle and was carried out until maximal
252 pressure of 200 MPa, corresponding to a minimal pore radius of about 6 nm. The step mode was
253 used for the increase in pressure and the equilibrium time between each pressure increment was
254 20 seconds. The surface tension of mercury is 0.485 N.m⁻¹ and its contact angle with the sample
255 was 130°.

256 The curve of cumulative pore volume was plotted from the volume of intruded mercury under
257 pressure and gives the total volume of connected pores in the whole sample. Then, the differential
258 intrusion distribution was calculated from the cumulative mercury intrusion. With these two
259 curves illustrated in Fig. 3, it was possible to examine the pore size distribution, the critical pore
260 diameter which corresponds to the recorded diameter for the maximum value of differential
261 intrusion, and the median pore diameter calculated at 50% of cumulative pore volume [29].

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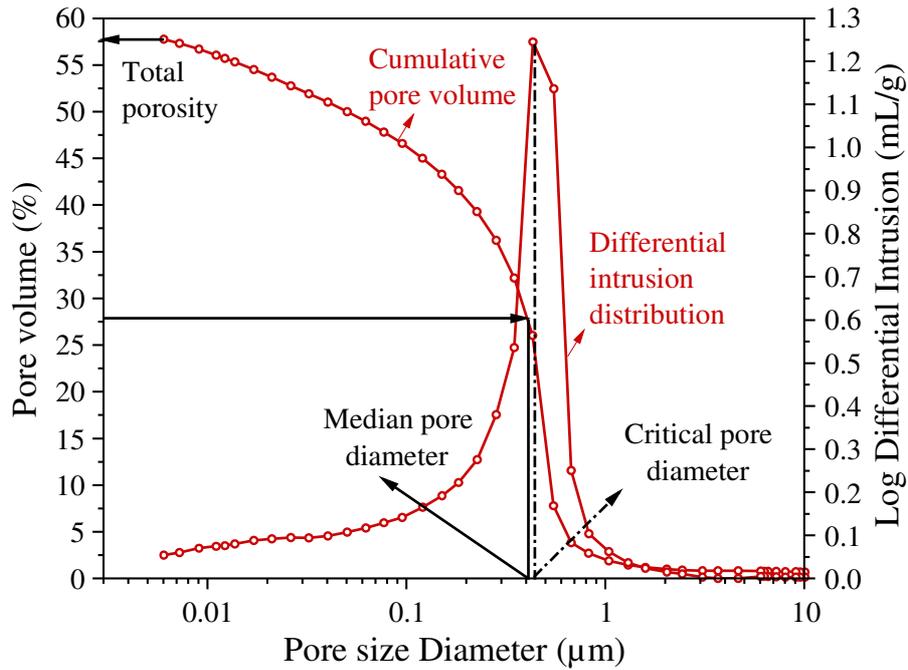


Fig. 3. Typical cumulative and derivative MIP curves for the lime-sediment binder. Adapted from Berodier et al. [30]

3. Results and discussion

3.1. Characterization of materials

3.1.1. Chemical and mineralogical composition

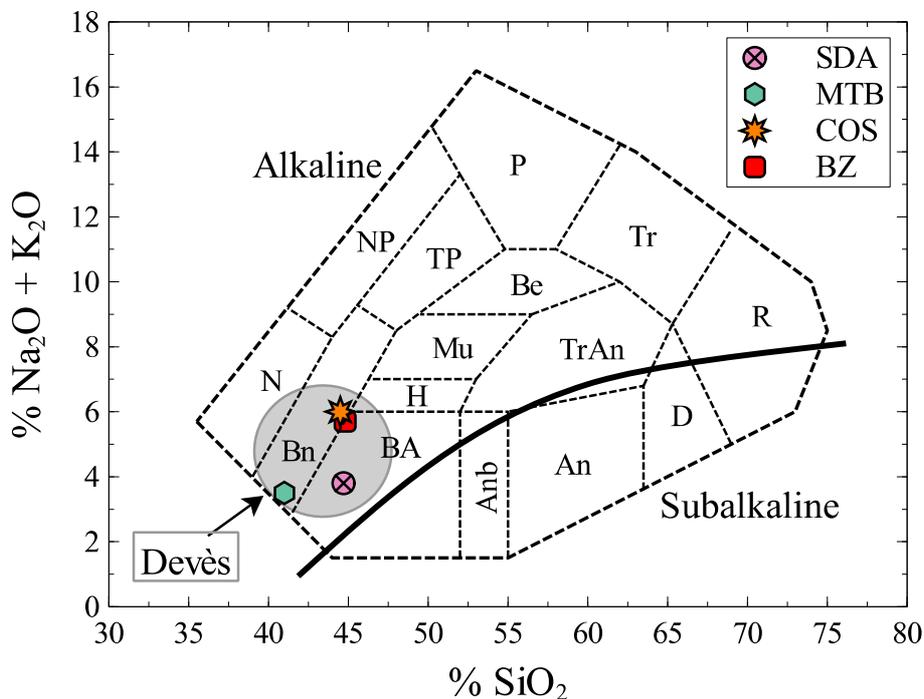
The chemical compositions of pyroclastics are presented in Table 1 and are representative of basaltic or basanite deposits from the alkaline series according to the Total Alkali-Silica (TAS) diagram (Fig. 4) [31]. The pyroclastics were silica-undersaturated (SiO_2 content of 41 – 45 wt.%) with 3.5 – 6 wt.% of Na-K feldspars and their Al_2O_3 and Fe_2O_3 contents were relatively close together. The XRD patterns of pyroclastics are reported in Fig. 5. The main mineralogical phase was augite (monoclinic pyroxene) as well as plagioclase feldspars (anorthite or labradorite) and forsteritic olivine. Alkali basalts never contains free silica (quartz) since the latter is not consistent with the presence of olivine. However, nepheline (feldspathoid, $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$) was clearly identified for BZ and COS, linked to their higher alkali content (~ 6 wt.%) compared to other pyroclastics. In addition, analcime ($\text{NaAl}(\text{Si}_2\text{O}_6)_2 \cdot \text{H}_2\text{O}$) was only detected for SDA. This mineral belongs to the family of zeolites but is also very close to some feldspathoids and quite common in silica-undersaturated basaltic materials. The presence of hematite (accessory mineral) is linked to iron oxide providing the red colour.

Table 1. Chemical composition of materials (previously calcined at 550°C) by XRF (in wt.%)

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	SO_3	LOI
SDA	44.7	13.6	11.8	10.5	11.3	3.2	0.6	2.6	0.6	0.2	—	0.34
MTB	41.0	12.1	12.4	10.7	11.6	2.1	1.4	2.6	0.5	0.2	—	4.8
COS	44.5	13.8	11.3	9.4	8.9	4.4	1.6	2.5	0.6	0.2	—	2.4
BZ	44.8	13.2	11.5	8.5	9.3	4.2	1.5	2.2	0.6	0.2	—	3.4
MS	73.4	3.0	1.9	8.3	0.5	1.0	0.9	0.1	0.1	—	1.1	9.3

XRD patterns have not shown a clearly visible amorphous halo, suggesting a low content of uncrystallized volcanic glass, as was evidenced in literature with around 5% of vitreous phase in basaltic pyroclastics of same origin (Devès) [32]. Nevertheless, some authors [33 – 35] argue that feldspars could be involved in the pozzolanic reaction. According to Dron and Brivot [35], the

292 glass content of pozzolans that contain a high proportion of calcium-rich feldspars (i.e. anorthite)
 293 is likely to be low. Hence, the authors suggest to calculate the difference $\text{SiO}_2 - \text{CaO}$ (wt.%) with
 294 a threshold around 34% under which the glassy phase is not present. For the pyroclastics studied
 295 in this work, this difference is in the range 34 – 36 %, with the exception of MTB (~ 30%).
 296



297
 298 **Fig. 4.** Total Alkali-Silica (TAS) diagram. (N: Nephelinite, NP: Nephelinite - Phonolite, P: Phonolite, Bn:
 299 Basanite, BA: Basalt, TP: Tephrite - Phonolite, Be: Benmoreite, Mu: Mugearite, H: Hawaiiite, An:
 300 Andesite, Anb: Andesite - Basalt, Tr: Trachyte, TrAn: Trachyandesite, D: Dacite, R: Rhyolite) [31]
 301

302 The oxide composition of the sediment following micronization is reported in Table 1. It shows a
 303 very high content of SiO_2 (73%) compared to pyroclastics. This is due to the predominance of
 304 quartz sand. In contrast, it can be observed a poor amount of aluminum, iron, and magnesium
 305 oxides. These XRF results are consistent with the XRD pattern (Fig. 6) where the presence of
 306 quartz is significant whereas clay minerals are more difficult to track. However, albite
 307 (plagioclase feldspar), gypsum, and calcite were detected. The amount of calcium carbonate was
 308 calculated to be 19 wt.% by TGA.
 309

310 3.1.2. Physical properties

311 The particle size distribution of the sediment compared to pyroclastics following micronization
 312 and grinding processes is shown in Fig. 7. It is interesting to see that the size range of SDA and
 313 MTB was the same and their median diameter (noted D_{50} in Table 2) was similar (5 – 5.5 μm).
 314 However, COS and BZ exhibited coarser particles, especially BZ for which the median diameter
 315 was about 55 μm . The other physical properties are also reported in Table 2. The BET specific
 316 surface area showed the highest values for the finest pyroclastics (SDA and MTB). The true
 317 density was found to be very close to that of basalt (~ 3 $\text{g}\cdot\text{cm}^{-3}$) and LOI at 550°C was in the range
 318 0.35 – 1.61%, except for MTB for which it was less than 4%.
 319

320 It can be observed a higher BET specific surface area for SDA and MTB compared to the marine
 321 sediment. In view of the particle size distribution illustrated in Fig. 7 and median diameters (Table
 322 2), this result is probably due to the porosity within powdered grains of pyroclastics. Indeed, the
 323 BET method is especially valuable for revealing the large internal pore structure of these vesicular
 324 materials. The true density of the sediment (2.65 $\text{g}\cdot\text{cm}^{-3}$) was close to that of sand and LOI at
 550°C was 5% (Table 2).

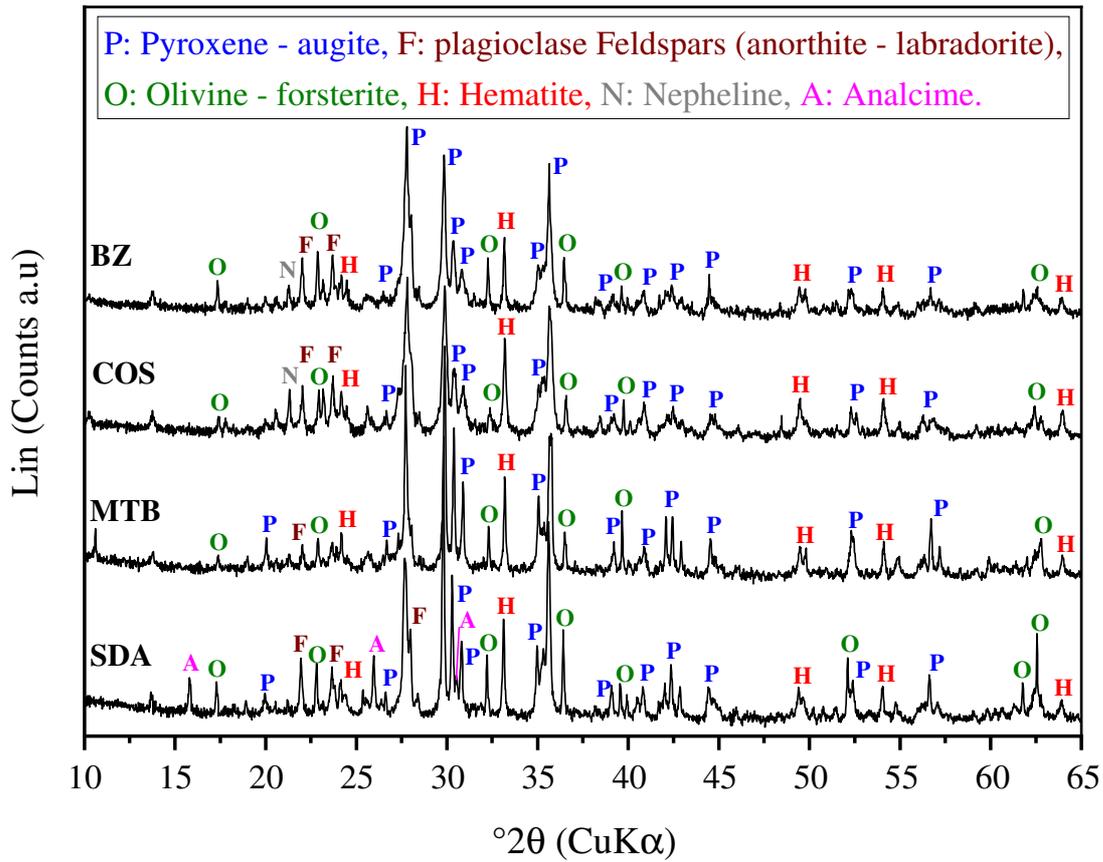


Fig. 5. XRD patterns of pyroclastics

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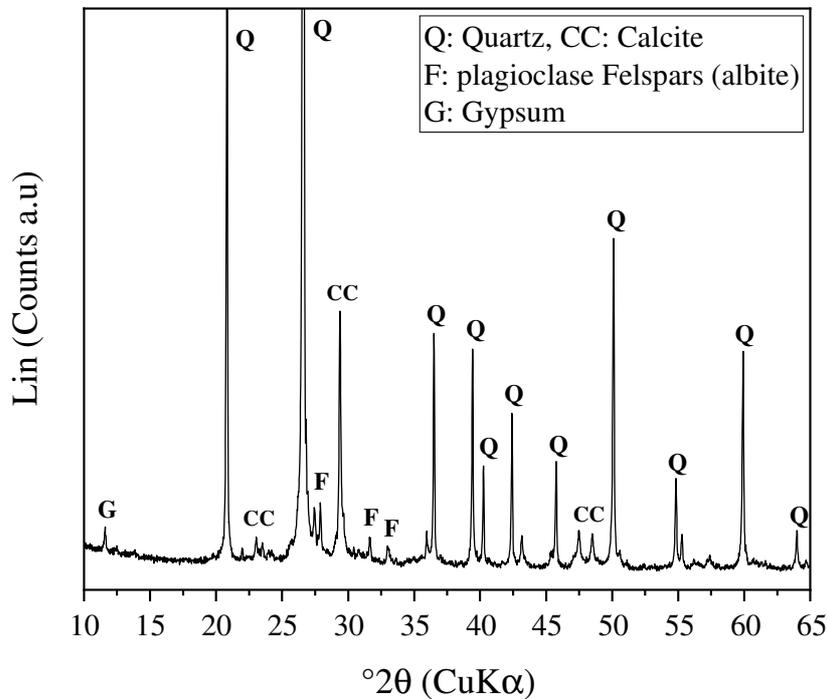
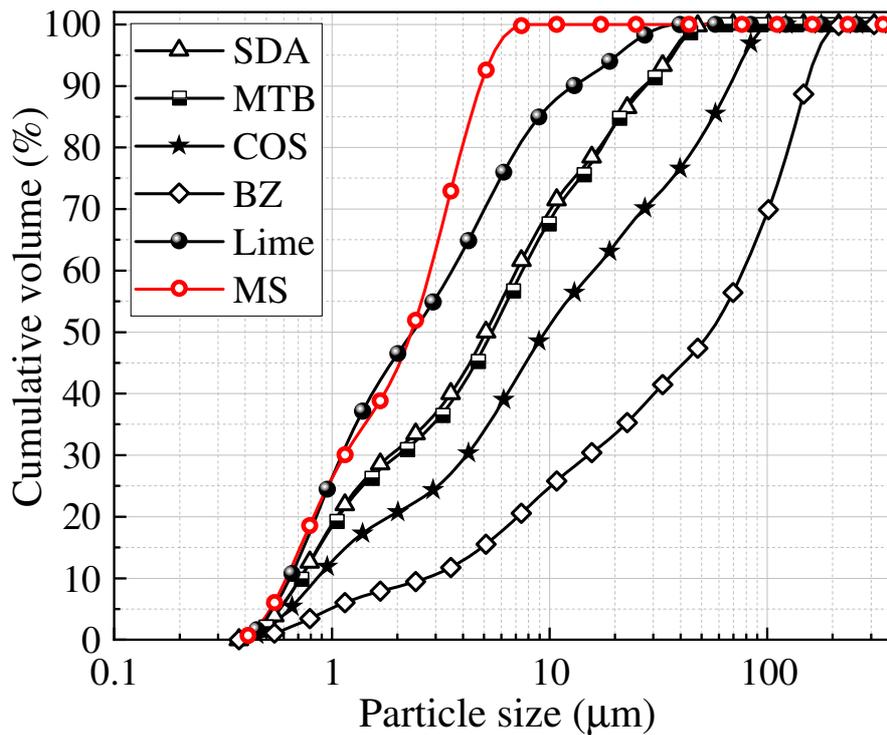


Fig. 6. XRD pattern of the marine dredged sediment

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Fig. 7 also presents the particle size distribution of hydrated lime. It can be seen that its size range is similar to that of the micronized marine sediment up to 2.5 micrometers but the maximum size diameter of hydrated lime was around 12 micrometers. In addition, the huge BET specific surface area of hydrated lime should be noted (less than $18 \text{ m}^2 \cdot \text{g}^{-1}$, see Table 2).



335
336
337
338 **Fig. 7.** Particle size distribution of powders after grinding processes

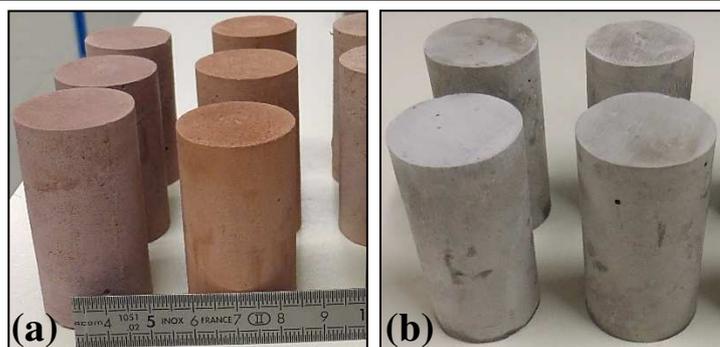
Table 2. Physical properties of ground pyroclastics, micronized sediment and hydrated lime

Materials	SDA	MTB	COS	BZ	MS	Lime
D ₅₀ (µm)	5.11	5.44	9.65	54.78	2.32	2.36
BET-SSA (m ² .g ⁻¹)	6.06	9.67	2.46	1.07	4.54	17.66
True density (g.cm ⁻³)	3.06	3.05	3.09	3.01	2.65	2.33
LOI – 550°C (wt.%)	1.61	3.73	0.47	0.35	4.99	–

339
340 Related to these physico-chemical properties, the water-on-powder mass ratios (W/P) of pastes
341 determined from the flow spread test are reported in Table 3. As expected, the water demand was
342 strongly linked to particle size distribution and specific surface area of powders.
343 The wet bulk density of hardened pastes was around 1.8 for lime-pyroclastics pastes (L–PYR)
344 and around 1.55 for the lime-sediment paste (L–MS). The specimens are pictured in Fig. 8. It
345 should be noted that blends of lime and SDA will be named L–SDA and the same designation
346 will be used for other pyroclastics.

347
348 **Table 3.** Water demand of pastes (W/P ratio)

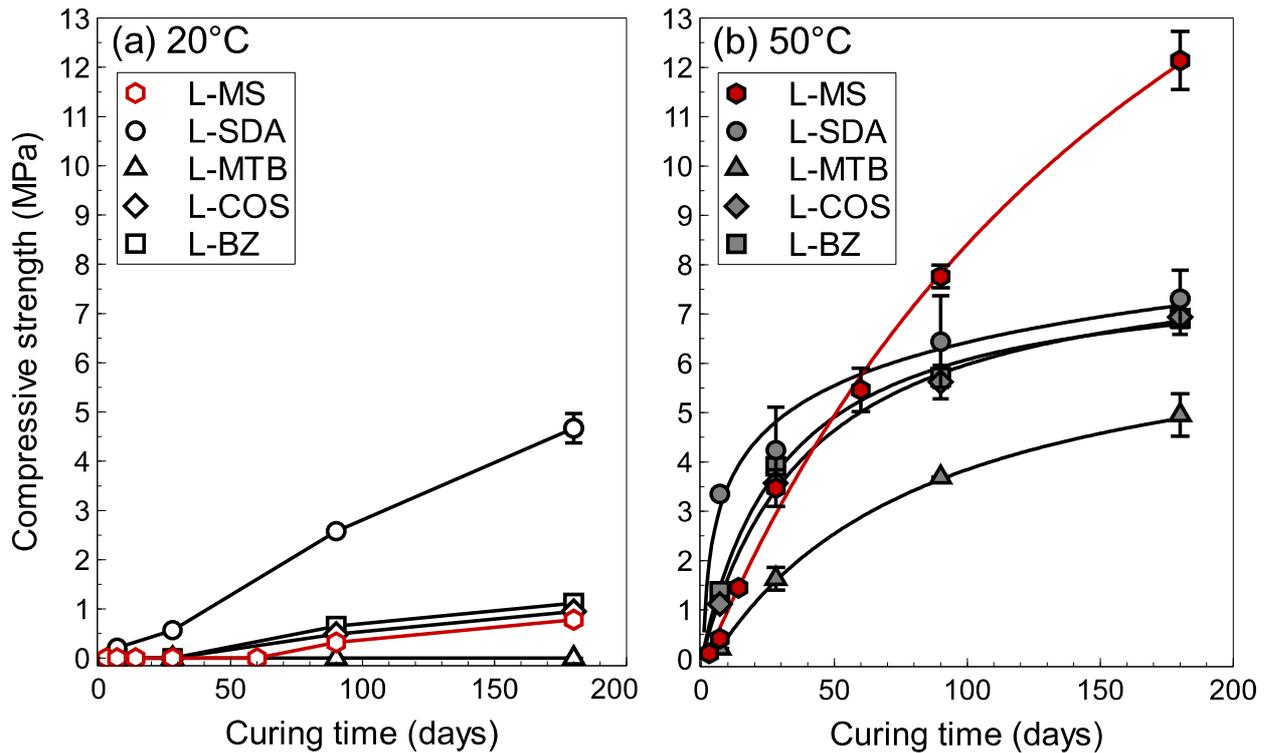
Blends	L–SDA	L–MTB	L–COS	L–BZ	L–MS
W/P (80 PYR or MS + 20 L) wt.%	0.46	0.49	0.42	0.38	0.73



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356
357 **Fig. 8.** Cylindrical specimens (a) L–PYR or (b) L–MS

358 3.2. Compressive strength development

359 The compressive strength development of pastes is reported in Fig. 9a for room temperature
 360 (20°C) and Fig. 9b for elevated temperature (50°C). At 20°C, L–MTB did not harden until 180
 361 days. On the opposite, a compressive strength of 4.7 MPa was reached for L–SDA after 180 days.
 362 The L–MS paste was able to show an initial hardening from 90 days and finally reached 0.8 MPa
 363 after 180 days. The absence of hardening at 20°C within a reasonable time shows that an increase
 364 of curing temperature is needed. It should be noted that blends including lime and natural
 365 pozzolans often require high temperature (38°C in the work of Pichon [8]) or chemical activators
 366 [17] to achieve a suitable hardening.
 367



368
 369 **Fig. 9.** Compressive strength development of pastes over time depending on the curing temperature
 370 (a) 20°C, (b) 50°C

371 Strength results at 50°C were markedly different. Regarding the pyroclastics for which the
 372 hardening of pastes at 20°C was low or non-existent (MTB, BZ, and COS), the rise in curing
 373 temperature has obviously resulted in a higher compressive strength from 7 to 180 days. The
 374 compressive strength of L–MTB was 5 MPa after 180 days while the paste did not show
 375 measurable strength at this date for a curing at 20°C. It is interesting to note the same strength
 376 development for the pastes designed with COS and BZ. Those pyroclastics were very different in
 377 terms of size distribution (see Fig. 7) but their specific surface area was quite similar compared to
 378 SDA and MTB. Moreover, the chemical composition of COS and BZ was almost identical as
 379 shown in the TAS diagram (Fig. 4). Ultimately, the compressive strength at 180 days was in the
 380 range 6.9 – 7.3 MPa for the pastes with BZ, COS and SDA. For the most reactive pyroclastic
 381 material from a mechanical point of view (i.e. SDA), it can be seen that the rise in curing
 382 temperature accelerated the early age strength (3.3 MPa at 50°C versus 0.2 MPa at 20°C after 7
 383 days). However, since the strength tended to level off after 90 days, the compressive strength after
 384 180 days at 50°C (7.3 MPa) was not so far from that reached at 20°C (4.7 MPa).
 385 The measurable strength of L–MS at 50°C was extremely low until 7 days and it was 1.45 MPa
 386 after 14 days. This is partly explained by the high water-on-powder mass ratio used for this blend
 387 (0.73) compared to the others. However, the strength development of L–MS at 50°C beyond 7
 388 days was of great significance. It is readily seen that the effect of curing temperature became

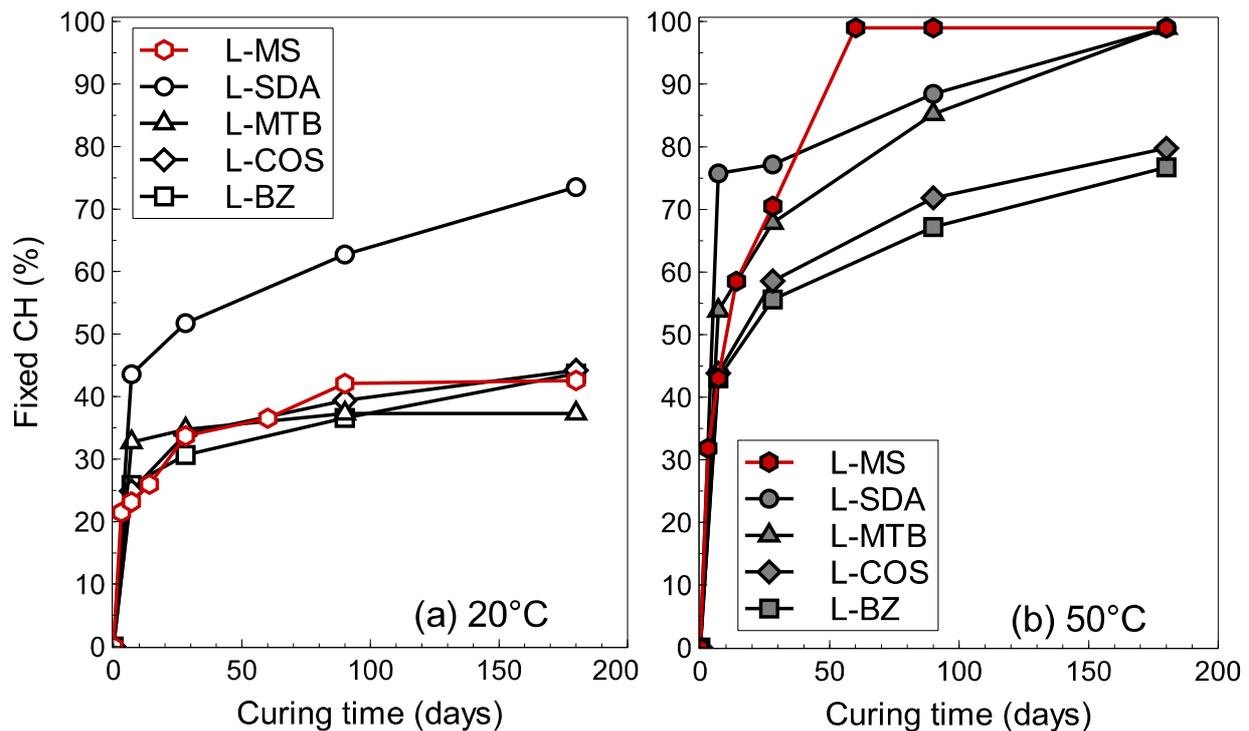
389 increasingly remarkable with time. After 90 days, the compressive strength of L-MS exceeded
 390 those achieved with L-PYR. From 90 days to 180 days, the compressive strength of L-MS kept
 391 going up to reach 12.1 MPa. The gap between this performance and the compressive strength
 392 recorded at 20°C (0.8 MPa) shows that the apparent activation energy of the micronized marine
 393 sediment is very high.

394

395 3.3. Reaction kinetics

396 The amount of fixed CH by the studied materials as percent of the initially available CH is
 397 illustrated in Fig. 10a for 20°C and Fig. 10b for 50°C.

398



399
 400 **Fig. 10.** Evolution of fixed CH over time depending on the curing temperature
 401 (a) 20°C, (b) 50°C
 402

403 For both curing temperatures, CH was consumed very quickly during the first days and much
 404 more slowly thereafter. This trend is consistent with literature regarding especially natural
 405 pozzolans [19,21,27,36,37]. The initial reaction rate of natural pozzolans can be higher than that
 406 of some fly ashes and with time, the reverse trend occurs [38]. This was attributed to their higher
 407 specific surface area giving a high initial rate of lime combination [39]. At 20°C, this combination
 408 rate was noted to be low from 28 days (or even 7 days) to 180 days and after six months of curing,
 409 the percentage of fixed CH did not exceed 45%, except for L-SDA. However, at 50°C, the
 410 combination rate increased at the early age and until 180 days. For L-BZ and L-COS, the
 411 amount of fixed CH after 180 days at 50°C was less than 80%, namely twice the rate reached at
 412 20°C. This result is even stronger with L-MS for which the combination rate at 50°C was very
 413 significant from 3 days to 60 days, rising from 32% to the whole content of initially available CH.
 414 This observation obviously highlights the effect of curing temperature on the reaction rate.

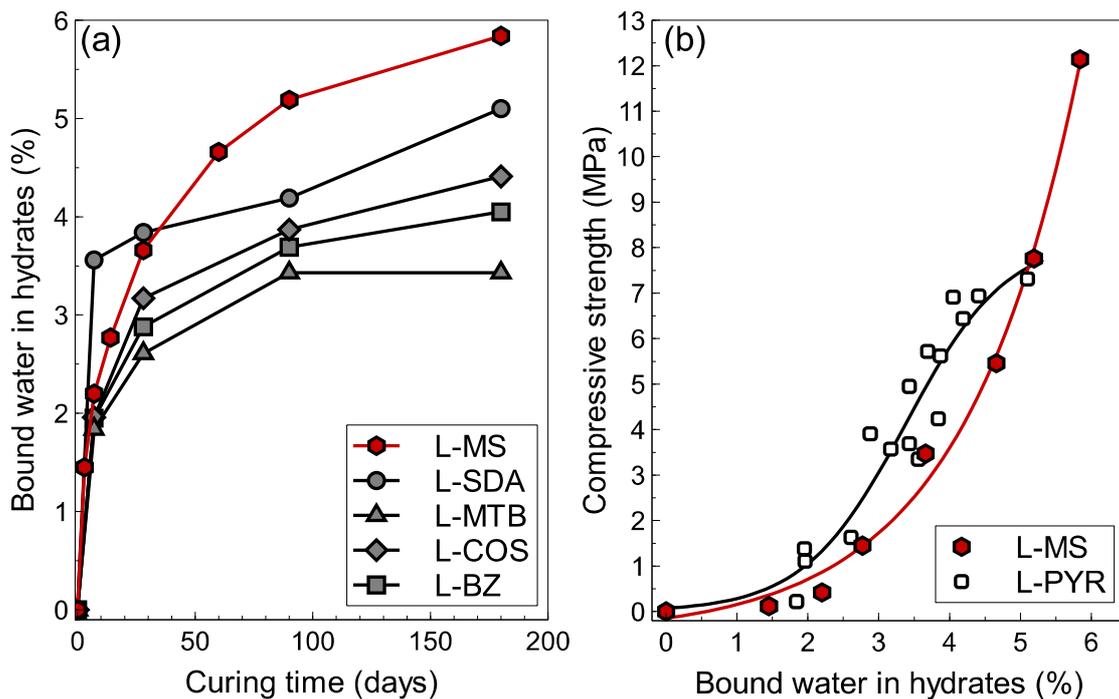
415

416 In the study of Millet and Hommey [12], the reactivity of some basaltic pyroclastics was found to
 417 be very low at 20°C and a chemical equilibrium was reached only after one year. In their work,
 418 Diamond et al. [16] also found a considerable amount of unreacted CH after a long reaction
 419 period of 6 months between lime and clay at 23°C whereas most of the CH had disappeared for a
 420 curing at 60°C with clay and pure quartz. In the case of SDA, the combination rate at 20°C was

421 higher than those recorded for the other pyroclastics. It can be seen that the percentage of fixed
 422 CH, especially in the long term, is well correlated with the compressive strength development.
 423 SDA was the only one able to fix more than 70% of CH after 180 days at 20°C. In addition, the
 424 amount of fixed CH after 7 days was clearly improved at 50°C (more than 75% versus less than
 425 45% at 20°C).

426
 427 More generally speaking, for a given curing temperature, the rate of lime combination is reported
 428 to be strongly linked to the specific surface area of pozzolanic materials and to the water-on-
 429 powder mass ratio [21]. Hence, at 50°C, it is interesting to note that higher amounts of fixed lime
 430 were calculated for pyroclastics exhibiting the higher specific surface area i.e. MTB ($9.7 \text{ m}^2.\text{g}^{-1}$)
 431 and SDA (about $6 \text{ m}^2.\text{g}^{-1}$). Overall, at 50°C, CH combination was found to be strongly correlated
 432 with the specific surface area of ground pyroclastics. However, it must be noted that MTB should
 433 be able to fix more CH than SDA due to its very high specific surface area (and the higher W/P)
 434 but this was not the case at 20°C. Since the long-term activity is more related to the nature and the
 435 content of reactive phases [21,40], MTB could present a deficiency in these phases or include
 436 some harmful components (see LOI in Table 2) due to potential alteration [41].

437
 438 The strength development of lime-pozzolan binders is not only dependent on the amount of fixed
 439 lime but also, and above all on the type of hydration products. As a matter of fact, while the
 440 sediment was able to fix 34% of lime after 28 days at 20°C, this has not resulted in a suitable
 441 hardening of the paste. From there, it is interesting to study the chemically bound water in
 442 hydrates over the curing time as illustrated in Fig. 11a for 50°C.
 443



444
 445 **Fig. 11.** (a) Evolution of bound water in hydrates over time at 50°C, (b) Relationship between bound water
 446 and compressive strength at 50°C

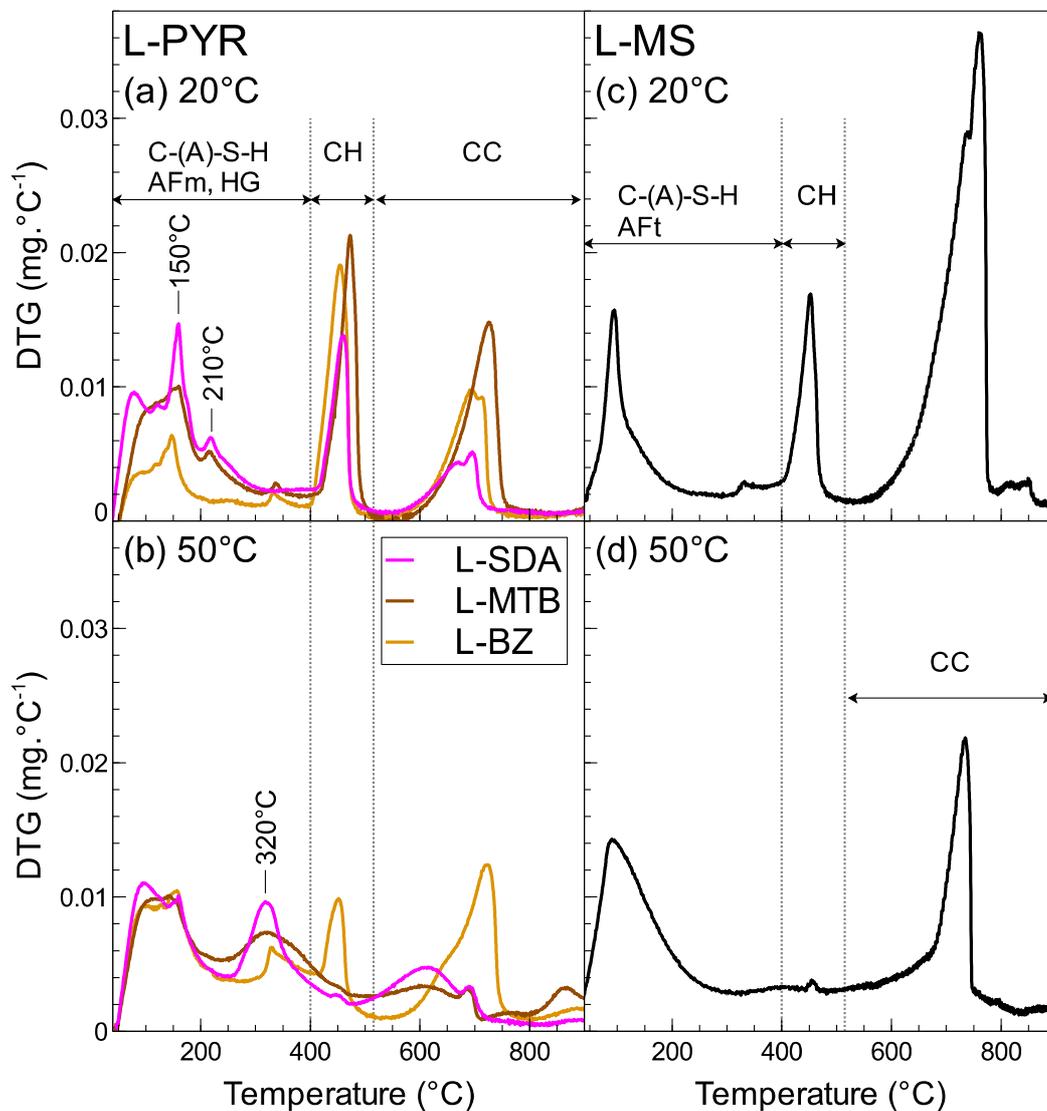
447 A very good correlation was found between the combination of CH and bound water. The highest
 448 amount of bound water over time was reported for L-MS and L-SDA. It is also noted that L-BZ
 449 and L-COS were very close to each other as was the case for fixed CH and compressive strength
 450 development. The only exception was L-MTB for which the amount of bound water was the
 451 lowest whereas the percentage of fixed lime after 180 days of curing was 100% as well as for
 452 L-SDA and L-MS (Fig. 10b). The ratio of bound water to fixed CH was in the range 0.27 – 0.28
 453 for L-SDA, L-COS and L-BZ, 0.31 for L-MS and only 0.19 for L-MTB. Even if MTB was

454 able to fix all the CH due to its huge specific surface area, the resulting reaction product
 455 assemblage was probably affected [42]. Fig. 11b reports the relationship between compressive
 456 strength and bound water. For the pyroclastics, the S-shape of the curve fitting all the points was
 457 also found by Fournier and Geoffray [11]. The same trend was observed for the marine sediment
 458 but the stabilization did not occur within the allotted time. For all materials, the results suggest
 459 that the reaction products formed at the early age exhibit poor binding properties and this could be
 460 related to their Ca/Si ratio or their small size leading to insufficient interconnection as is also the
 461 case at 20°C. High curing temperature is needed for CH to be sufficiently depleted giving rise to
 462 hydrates further contributing to the strength over a lengthy period of time, as suggested in some
 463 research works [42–44]. Since the water content of hydration products (C-S-H) is expected to
 464 decrease with hydration time [38], this could explain the slope of the curve that becomes
 465 increasingly important.

3.4. Reaction products and microstructure

3.4.1. TGA-XRD

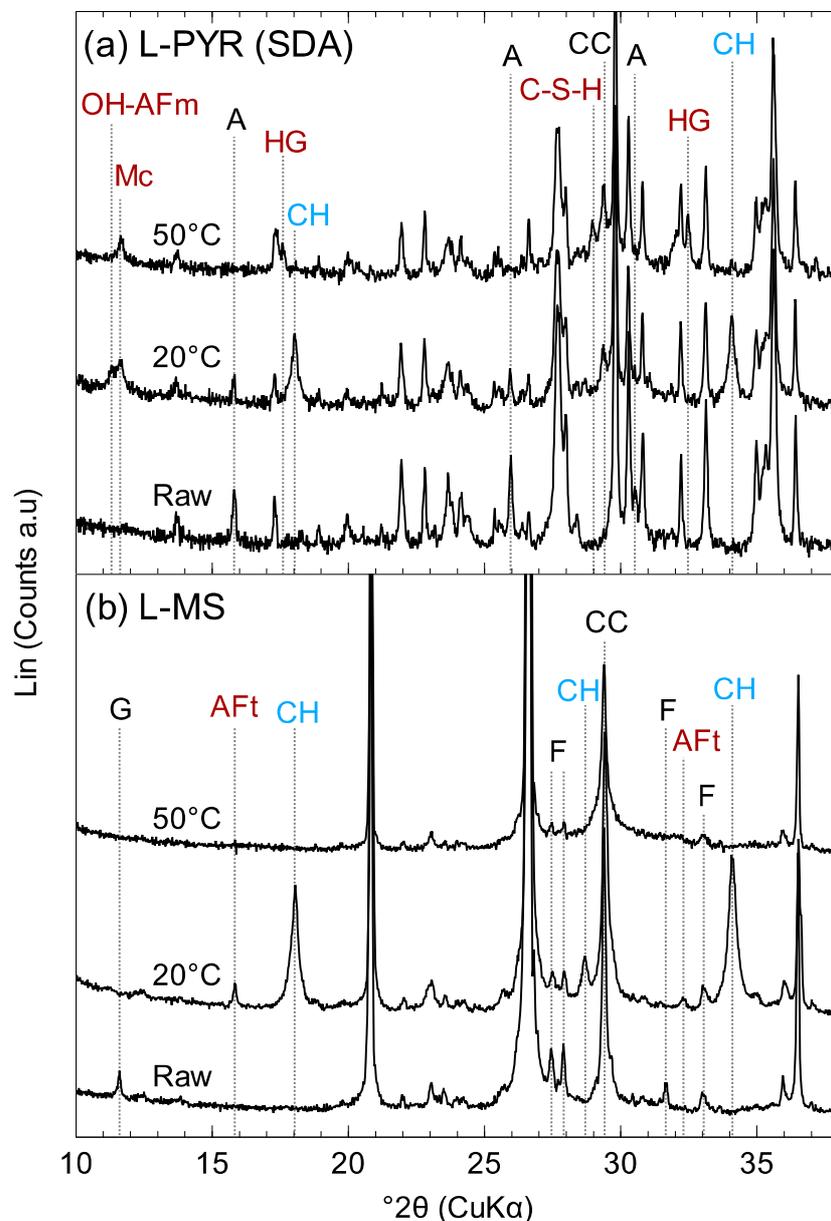
469 Newly-formed hydrated phases were identified by means of DTG curves illustrated in Fig. 12 and
 470 XRD patterns reported in Fig. 13. The results are presented after 90 days of curing.
 471



472

473 **Fig. 12.** DTG curves after 90 days of curing (a) L–PYR at 20°C, (b) at 50°C, (c) L–MS at 20°C, (d) at
 474 50°C. Note: L–COS is not reported since the signal was identical to L–BZ.

475 In the case of L-MS, the single mass loss up to about 240°C (Fig. 12) is due to the dehydration of
 476 C-S-H and C-A-S-H (i.e. C-S-H with the inclusion of Aluminum) [45]. C-S-H could not be
 477 detected by XRD due to an important overlapping with the diffraction peak of calcite (CC in Fig.
 478 13b). However, at 20°C, AFt (ettringite, C₆As₃H₃₂) was found as a new phase by XRD (Fig. 13b).
 479 This is consistent with the disappearance of gypsum that was present in the marine sediment. At
 480 50°C, AFt was present after 28 days but not after 90 days (see Fig. 13b) suggesting that it was
 481 destabilized. In view of the very low SO₃ content in the sediment (Table 1), AFt should transform
 482 into AFm quickly [46] but this could not be shown conclusively herein. Beyond this, the alumina
 483 content of the sediment was also low compared to that of the pyroclastics (3% versus 12-14%)
 484 thus justifying the absence of calcium aluminate hydrates. On another note, the absence of CH on
 485 the XRD pattern at 90 days is consistent with the whole combination of initially available CH
 486 after 60 days of curing at 50°C (Fig. 10b). Furthermore, XRD results show that albite was
 487 apparently involved in the pozzolanic reaction since the diffraction peak for 2θ = 31.6° has
 488 disappeared for both curing temperatures by comparison with the raw material.
 489



490
 491 **Fig. 13.** XRD patterns after 90 days of curing at 20°C or 50°C.
 492 (a) L-PYR, (b) L-MS. OH-AFm: Hydroxy-AFm (C₄AH₁₃), Mc: Monocarboaluminate, HG: Hydrogarnet,
 493 A: Analcime, G: Gypsum, F: Feldspar – Albite

494 In the case of L-PYR, a peak at $2\theta = 29^\circ$ revealing the presence of C-S-H was clearly identified
495 for all pyroclastics but only at 50°C (Fig. 13a). The two DTG peaks noted at 150°C and 210°C in
496 Fig. 12a are attributed to the dehydration of AFm phases. The diffraction peaks of C_4AH_{11} and
497 monocarboaluminate (carbonated form $\text{C}_4\text{AcH}_{11}$) are very close together [12]. However, due to
498 the presence of CC and according to literature, the presence of monocarboaluminate (Mc) is
499 advanced [8,10,47,48]. The presence of Mc (TG mass loss around 150°C and XRD peak for $2\theta =$
500 11.6°) was found for all pyroclastics, both curing temperatures and from 7 to 180 days. Matschei
501 et al. [49] have reported the good thermodynamic stability of Mc until 70°C . The DTG peak at
502 210°C was observed for L-SDA and L-MTB only at 20°C and from 90 days. It is attributed to
503 the dehydration of C_4AH_{13} [50,51] and was confirmed by the presence of a XRD peak for $2\theta =$
504 11.2° . At 20°C , C_4AH_{13} can decompose to hydrogarnet (HG) and CH at long term ages [49], this
505 probably explaining the absence of this phase on the DTG signal for L-BZ and L-COS. At 50°C ,
506 an important mass loss was detected around 320°C (Fig. 12b). The latter is assigned to
507 hydrogarnet series $\text{C}_3\text{AS}_x\text{H}_{6-2x}$ ($\text{C}_3\text{AH}_6 - \text{C}_3\text{AS}_2\text{H}_2$) [21,52,53]. HG are typical hydration products
508 formed under hot water curing, especially above 40°C , and originate from the conversion of
509 metastable C_4AH_{13} [10,51,54]. For L-PYR, HG mass loss occurred as of 7 days and was stable
510 until 180 days. HG was also identified by XRD (Fig. 13a). Furthermore, a very interesting result
511 of XRD is the disappearance of the diffraction peak of analcime for L-SDA at 50°C . This
512 mineral is known to present a significant pozzolanic activity [55]. The lime-binding capability of
513 analcime was reported to be intermediate between the glassy phase and the feldspars of trass (a
514 natural pozzolan) [14]. This is consistent with the higher amounts of fixed CH for L-SDA (Fig.
515 10). In addition, there was a strong decrease in the diffraction peak of nepheline for L-COS and
516 L-BZ cured at 50°C . Accordingly, the involvement of crystalline minerals (analcime, nepheline,
517 and albite) in the pozzolanic activity of the materials studied in this paper was highlighted.

518

519 3.4.2. SEM-EDX

520 BSE-SEM pictures of microstructures after 90 days of hardening are reported in Fig. 14. The first
521 point is the comparison between L-PYR (Fig. 14a) and L-MS (Fig. 14b) at 20°C . In the case of
522 L-MS, a large number of sharp-edged quartz grains (i.e. pure white in the back-scattered mode)
523 were spread across the section. The grain size was clearly lower compared to that of ground
524 pyroclastics due to the micronization of the marine sediment. At 20°C , lime clumps were
525 frequently observed as illustrated in Fig. 14a. However, it was more difficult to identify the C-
526 (A)-S-H phases for this curing temperature. According to Taylor [44], reaction of lime with quartz
527 surface initially gives a lime-rich substance like C-S-H (II) with a Ca/Si ratio from 1.5 to 2. At
528 20°C , some phases in the interstitial mass displayed high Ca/Si ratios (i.e. more than 2). It is quite
529 likely that an intermixing occurred between free CH and C-S-H phases as this phenomenon has
530 been well described in the research of Rossen and Scrivener [56].

531 However, it was possible to observe the calcium aluminate phases of L-PYR for both curing
532 temperatures. Fig. 14c and Fig. 14d report pictures with calcium aluminate phases at 50°C . These
533 phases were well crystallized and from Fig. 14c, it can be seen that the cauliflower-shaped
534 aluminous phases were embedded in C-(A)-S-H gel. These observations are in line with what had
535 been described by Pichon [8] for whom the late formation of C-A-S-H comes to cover the
536 aluminous frame. Fig. 15e shows another typical micrograph of L-PYR at 50°C in which the
537 interstitial mass (between crystals) was fulfilled with C-(A)-S-H phases. At 20°C , Fig. 14f shows
538 an interesting micrograph of CC surrounded by an AFm phase (Al/Ca ~ 0.5) assumed to be
539 monocarboaluminate.

540 The microstructure of L-MS at 50°C is illustrated in Fig. 14g and Fig. 14h. Compared to 20°C
541 (Fig. 14b), the interstitial mass (between the quartz crystals) was much denser. The higher
542 magnification of Fig. 14h made easier to see that quartz grains were trapped in a massive gel-like
543 microstructure. In addition, a lot of large-sized areas interpreted as former lime particles that
544 converted to C-(A)-S-H were observed.

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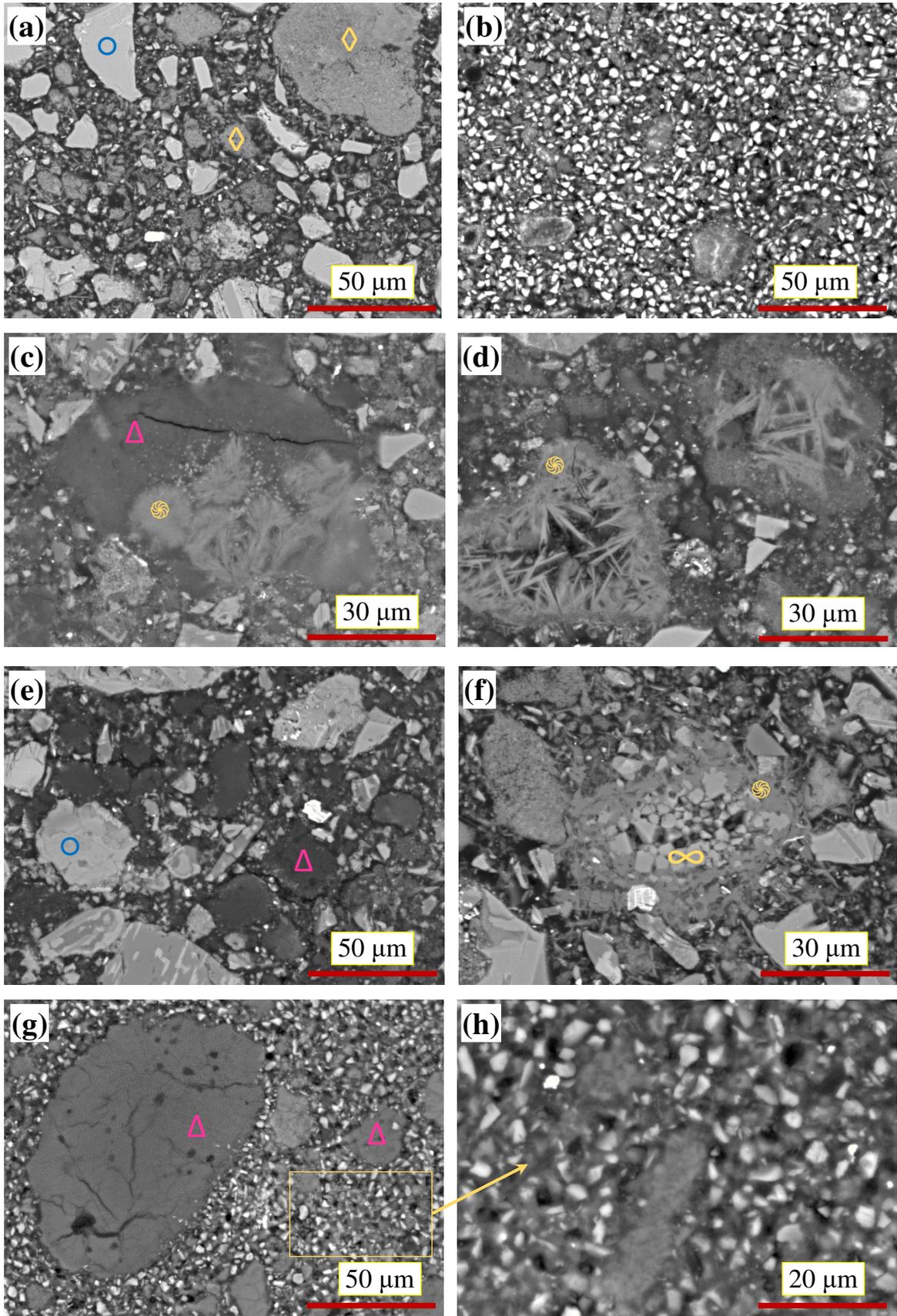
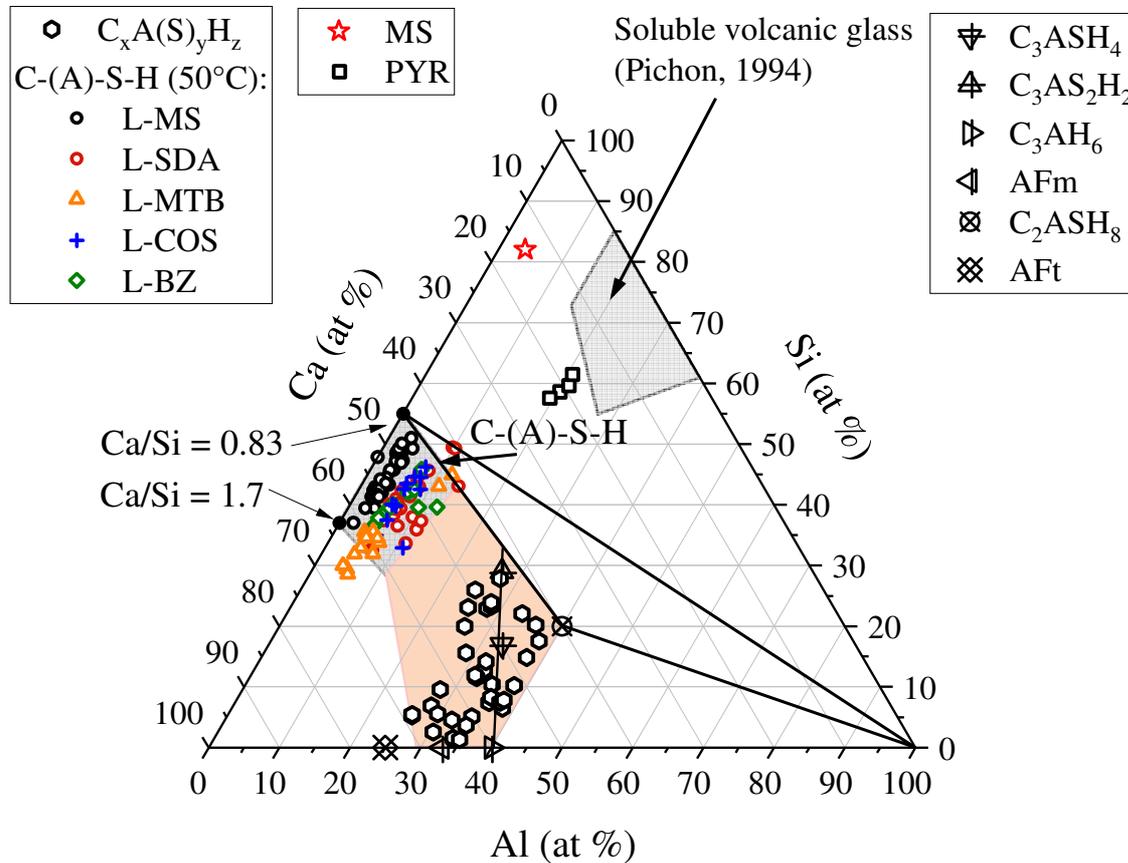


Fig. 14. BSE-SEM pictures of hardened pastes at 90 days
 (a, f) L-PYR at 20°C, (b) L-MS at 20°C, (c, d and e) L-PYR at 50°C, (g, h) L-MS at 50°C
 ○ Crystal fragments, ◇ Lime cluster, ∞ Calcium carbonates, ☉ AFm or HGs, Δ C-(A)-S-H gel

579 The punctual EDX analysis results are reported in the Ca-Si-Al ternary diagram illustrated in Fig.
 580 15. The presence of siliceous hydrogarnets is confirmed, especially around C_3ASH_4 (katoïte). The
 581 latter is in the form of hexagonal plates (using topographic images with secondary electrons) and
 582 might justify what appeared to be needle-shaped units on polished cross sections. Some points are
 583 also more around AFm (C_4AHx) as clearly shown in Fig. 15.
 584



585 **Fig. 15.** Ca-Si-Al ternary phase diagram with raw materials (PYR: pyroclastics and MS: marine sediment),
 586 theoretical reaction products and pinpoint EDX analysis after 90 days of curing
 587

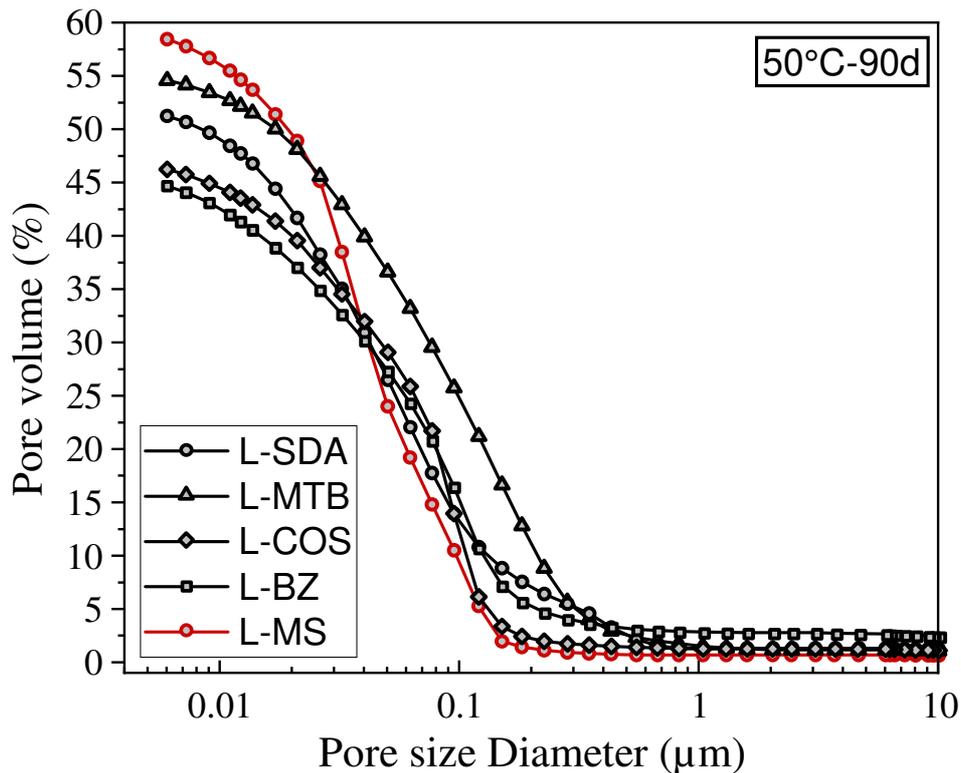
588
 589 EDX analysis showed a linear trend when plotting the Al/Ca ratio against the Si/Ca ratio of C-
 590 (A)-S-H as suggested in some works [56,57]. In other words, when the Ca/Si ratio decreased, the
 591 amount of incorporated aluminum increased. According to Lothenbach et al. [58], the area of C-
 592 (A)-S-H corresponds to Ca/Si ratios between 0.83 (i.e. tobermorite-like) and 1.7 (i.e. jennite-like).
 593 Only the results on samples cured at 50°C are reported for C-(A)-S-H phases since the
 594 intermixing with lime at 20°C made that task difficult. For L-SDA, L-BZ and L-COS, their
 595 mean composition was $(CaO)_{1.3} SiO_2 (Al_2O_3)_\beta (H_2O)_z$. It was possible to identify some C-(A)-S-H
 596 with a Ca/Si ratio around 0.8 in the case of L-SDA. On the contrary, for L-MTB, the mean
 597 Ca/Si ratio was more around 1.7. The Ca/Si ratio of calcium silicate hydrates is known to be
 598 variable in time since more and more silica is introduced into the pore solution [8,44]. It seems
 599 clear that the best compressive strength was reached for the lowest Ca/Si ratios. This was also
 600 found in the case of lime-clay mixtures [40]. For L-MS, the mean composition of C-(A)-S-H was
 601 calculated to be $(CaO)_{1.1} SiO_2 (H_2O)_z$. The Ca/Si ratio of ~ 1.1 is consistent with the study of
 602 Benezet and Benhassaine [15] about the reactivity of quartz powders. As expected, the aluminum
 603 content was almost insignificant as seen in Fig. 15.
 604 Furthermore, it is interesting to note that points resulting from EDX on C-(A)-S-H phases were on
 605 the line between the composition of raw materials and CH (lower left corner of the ternary
 606 diagram, Fig. 15).

607 Since C_4AcH_{11} was quickly formed (after 7 days) for both curing temperatures, it can be assumed
 608 a zero contribution of it to the strength. The contribution of siliceous hydrogarnets highlighted by
 609 TGA, XRD and EDX is more uncertain but the conversion of C_4AH_{13} into C_3AH_6 may lead to an
 610 increase in porosity and loss of strength. In the present paper, their early formation did not prevent
 611 the L-SDA to reach 3.3 MPa after 7 days at 50°C. The strength development is mainly provided
 612 by the growth of C-S-H. However, it is necessary to consider the calcium aluminate phases for the
 613 lime combination.

614
 615 3.5. Porosity investigation

616 The pore size distribution of pastes after 90 days of hardening at 50°C is reported in Fig. 16.

617



618

619 **Fig. 16.** Pore size distribution of hardened pastes after 90 days of curing at 50°C

620

621 The total porosity was in the range of 45 to 55 vol.% for L-PYR and slightly less than 60 vol.%
 622 for L-MS. A strong correlation between the water-on-powder mass ratio and the total porosity is
 623 clearly observed in Fig. 16. This is due to a higher capillary porosity when the water content
 624 increases [29,30,59]. It is well known that the water-on-powder mass ratio is an important
 625 parameter for which a little variation can induce large changes in the total porosity [60].

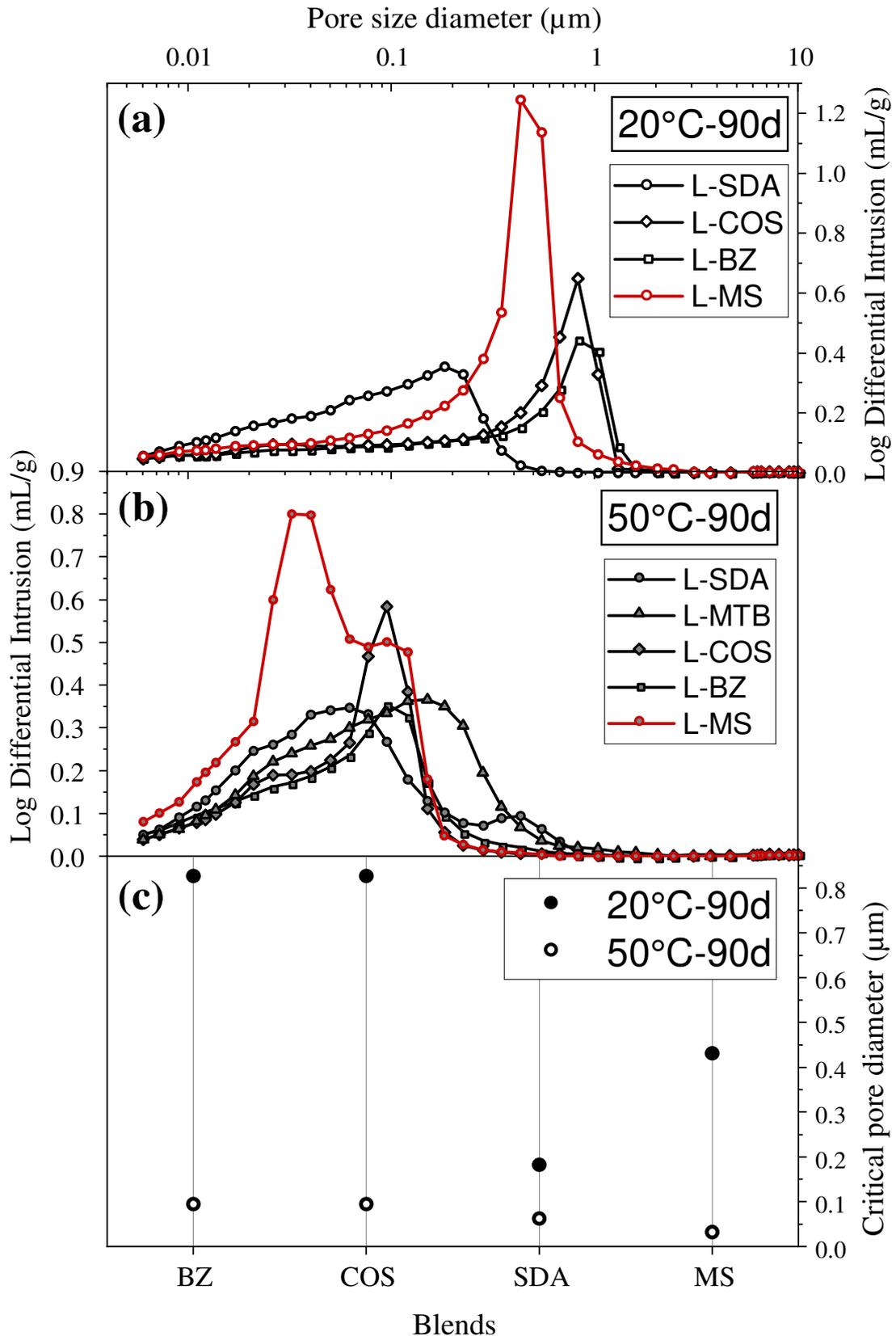
626 The total porosity may be affected by many factors such as curing conditions, age and degree of
 627 hydration [60]. The absolute strength of lime-pozzolan pastes do not only depend on their total
 628 porosity but also on the phase constitution (kind and relative volume of hydration products,
 629 unreacted phases, etc.) [61]. For instance, in the case of L-MS, the total porosity was 57.8 vol.%
 630 at 20°C and 58.4 vol.% at 50°C whereas the compressive strengths of pastes were 0.8 MPa and
 631 12.1 MPa respectively. This result is attributed to the different nature of the reaction products
 632 (density, microstructure) depending on the curing conditions.

633

634 To investigate the effect of curing temperature, differential distributions are reported in Fig. 17.

635 The latter shows the porosity refinement for the pastes cured at 50°C (Fig. 17b) compared to those
 636 cured at 20°C (Fig. 17a).

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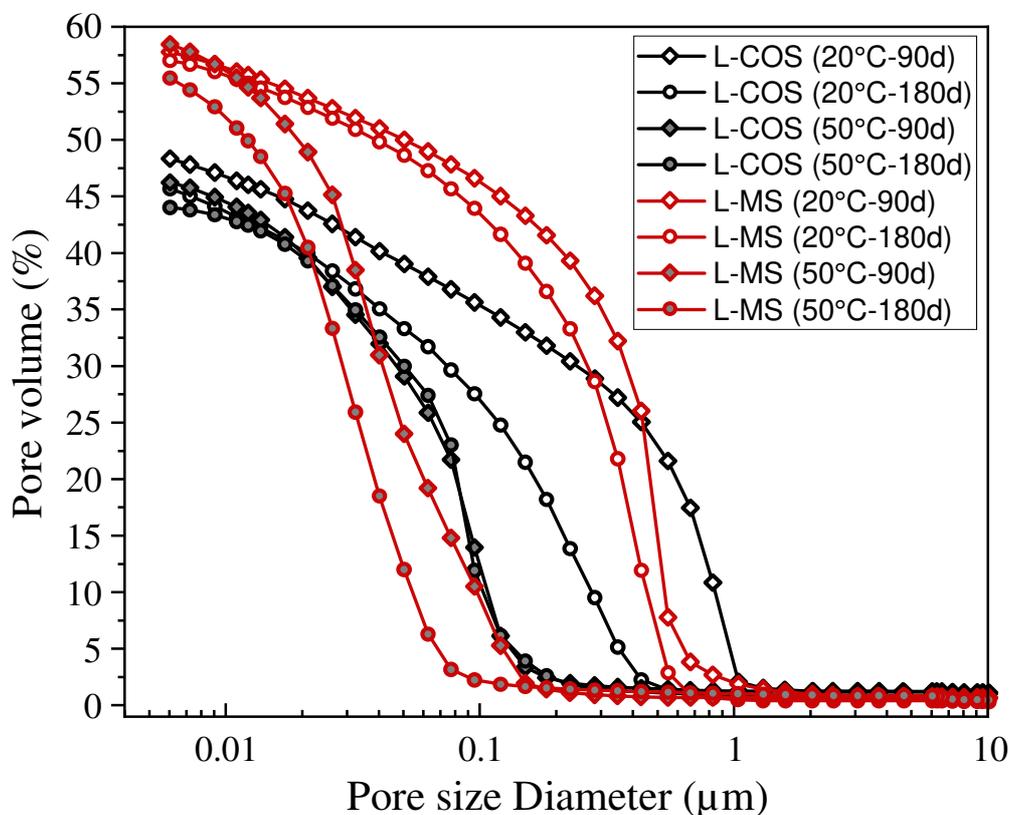
Fig. 17. Differential distribution of mercury intrusion after 90 days of curing (a) 20°C, (b) 50°C (c) Critical pore diameter reported for the different blends depending on the curing temperature

The porosity moved towards smaller sizes. This porosity refinement contributes to the densification of the granular skeleton and consequently to the compressive strength. According to

644 Cheng et al. [62], a pore size over 0.2 μm would correspond to so-called harmful pores. It can be
 645 seen in Fig. 17 that the amount of these coarse pores was significantly reduced for pastes cured at
 646 50°C compared to those cured at 20°C. The porosity refinement is indeed confirmed in Fig. 17c
 647 where the critical pore diameter is reported for each blend. The results clearly show a lower
 648 critical pore diameter for the pastes cured at 50°C, highlighting the infilling of pores by the
 649 hydration products. Furthermore, it is interesting to note that in the case of L–SDA, the difference
 650 between the two critical pore diameters (at 20°C and 50°C) was significantly lower compared to
 651 the pastes including the other pyroclastics. This is consistent with the compressive strength results
 652 since SDA has always been the most reactive at 20°C. The porosity refinement of L–MS should
 653 not be compared to that observed in the case of L–PYR since the total porosity and the pore size
 654 distribution depend on the origin and the nature of the material. However, it is still possible to
 655 underline the denser microstructure of L–MS in relation to its smallest critical pore diameter.
 656 L–MTB is not reported in Fig. 19c since no hardening was observed at 50°C.

657
 658 Fig. 18 shows the pore size distribution of pastes combining lime and either one of the
 659 pyroclastics (COS) or the marine sediment after 90 and 180 days of curing depending on the
 660 curing temperature. The variation of the total porosity between 90 days and 180 days of curing for
 661 a given blend is expected to be low since it was shown that the total porosity of cement pastes
 662 does not change a lot beyond 14 days with a much faster reaction kinetics [29,30]. At 20°C, the
 663 curve of cumulative pore volume for L–COS was strongly shifted to the left from 90 days to 180
 664 days whereas at 50°C the pore size distributions were nearly overlapped. This confirms that the
 665 reaction proceeds very slowly at 20°C and suggests that porosity refinement came to an end at
 666 50°C. For L–MS, there is scope for greater refinement beyond 180 days at 20°C. In addition, an
 667 evolution of the median pore diameter can be observed at 50°C (i.e. 0.045 μm after 90 days versus
 668 0.03 μm after 180 days). Therefore, the porosity refinement of L–MS continues to develop
 669 beyond 90 days of curing.

670



671

672 **Fig. 18.** Pore size distributions of L–COS and L–MS after 90 days and 180 days of curing at 20°C and
 673 50°C

674 **4. Conclusion**

675

676 Based on the different findings, the following conclusions can be drawn:

677 (1) The percentage of fixed lime at 50°C is clearly improved compared to that at 20°C and this
678 applies for the marine dredged sediment as well as for the basaltic pyroclastics. At 50°C, lime
679 combination is found to be strongly correlated with the specific surface area of ground
680 pyroclastics.

681 (2) At 20°C, the percentage of fixed lime tends to level off at about 40%, except for one of the
682 pyroclastics for which analcime was involved. It is found that fixation of lime does not necessarily
683 lead to the hardening of the binders and this is related to the poor binding properties of reaction
684 products formed at 20°C and at early age for heat cured samples.

685 (3) At 50°C, the micronized marine sediment is able to fix a substantial amount of lime. However,
686 the hardening kinetics at the early age is very slow with a compressive strength of only 1.45 MPa
687 after 14 days. The higher water-on-powder mass ratio and the presence of organic matter within
688 the marine sediment should be considered. After 180 days, the compressive strength reached with
689 this quartz-rich sediment (~70 wt.% SiO₂) is more than 12 MPa and it keeps going up. This is
690 consistent with the porosity refinement that is still growing from 90 to 180 days. This remarkable
691 strength gain suggests a huge apparent activation energy.

692 (4) By referring to [Eq. 1](#), the micronized marine sediment shows an interesting pozzolanic
693 reactivity under specific curing conditions i.e. saturated humidity and 50°C. Hence, it would be
694 wrong to consider raw sediments (i.e. without calcination) as non-pozzolanic materials. In these
695 suitable curing conditions and for advanced curing times, the reactivity of the quartz-rich
696 micronized sediment studied herein is even of a higher intensity compared to French basaltic
697 pyroclastics.

698

699 The next investigations will focus on the use of other marine sediments with different
700 mineralogical compositions (different fractions of sand and fines). The ratio of lime to sediment
701 will also be studied in a forthcoming study.

702

703 **Declaration of competing Interest**

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

706

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713

714 **CRedit autorship contribution statement**

715 **S. Kourtaa:** Investigation, Methodology, Data curation, Writing – original draft

716 **M. Chabannes:** Conceptualization, Methodology, Investigation, Data curation, Resources,
717 Writing – original draft, Writing – Review & editing, Validation, Supervision

718 **F. Becquart:** Resources, Writing – Review & editing, Co-supervision

719 **N.-E. Abriak:** Co-supervision

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