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Citation for the published version (APA 6th)

Danner, T., Norden, G., & Justnes, H. (2018). Characterisation of calcined raw clays suitable as supplementary cementitious materials. *Applied Clay Science*, 162, 391-402.

doi:<https://doi.org/10.1016/j.clay.2018.06.030>

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1 **Characterisation of calcined raw clays suitable as supplementary** 2 **cementitious materials**

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10

11 **Abstract:**

12 The potential use of two raw clays (Clay A: kaolin; Clay B: calcareous montmorillonite) as
13 supplementary cementitious material (SCM) in blended cements was investigated. Cement
14 replacement in mortars by 20% calcined Clay A and Clay B resulted in a considerable 28 day
15 compressive strength improvement. The pozzolanic reactivity of Clay A and B is explained by
16 characterization of the structural changes upon calcination with XRD, ICP-MS, FT-IR, 27Al-
17 NMR, Mössbauer spectroscopy and SEM. At the temperature giving highest pozzolanic
18 reactivity, kaolinite and montmorillonite were completely dehydroxylated, while calcite from
19 Clay B was not completely decomposed. FT-IR, 27Al-NMR and Mössbauer spectroscopy
20 revealed considerable structural deformations of kaolinite in Clay A and montmorillonite in
21 Clay B resulting in an amorphous, reactive state. Oxidation of iron in Clay B during calcination
22 contributed to strong distortions of the octahedral sheet in the montmorillonite structure.
23 Additionally, the formation of a glass phase due to reaction of coccoliths (CaCO₃) and
24 montmorillonite was observed.

25

26 Key words: pozzolan, cement, coccolith, Mössbauer spectroscopy

27 Highlights:

- 28 • Calcination of raw calcereous montmorillonite can provide a reactive pozzolanic source
29 for environmentally friendly binders with improved compressive strength.
- 30 • Oxidation of Fe^{2+} to Fe^{3+} in montmorillonite leads to structural disordering and thus to
31 a higher pozzolanic reactivity.
- 32 • Finely intermixed coccoliths in montmorillonite enable the formation of a reactive
33 glass.

34

35 **1. Introduction**

36

37 Cement production is a highly energy intensive process, contributing to about 5-7% of the
38 worldwide carbon dioxide emissions (Ernst Worrell et al., 2001; Mehta, 1999). The biggest step
39 towards reducing CO₂ emissions in the short and long term can be achieved by replacing parts
40 of the cement clinker with supplementary cementitious materials (SCMs) (Damtoft et al., 2008;
41 Ernst Worrell et al., 2001; Schneider et al., 2011). In the long run, the right choice of SCM's
42 is mainly a question of availability (Gartner, 2004), as well as pozzolanic reactivity. Natural
43 pozzolans, especially raw clays are widespread and the most promising source of SCM to serve
44 the cement industry sufficiently for a more sustainable future. Since there is a growing interest
45 of applying calcined clays in the construction industry, many countries started to evaluate the
46 pozzolanic potential of local clay deposits (Al-Rawas et al., 2001; Alujas et al., 2015; Aras et
47 al., 2007; Berriel et al., 2016; Beuntner and Thienel, 2015; Chakchouk et al., 2006; Huenger et
48 al., 2018; Shayma'a et al., 2012; Tironi et al., 2012). Calcining raw clays at temperatures
49 between 600-800°C leads to the formation of an active metastable state with high pozzolanic
50 activity (Fernandez et al., 2011). The pozzolanic reaction of calcined clays and calcium
51 hydroxide during cement hydration results in the formation of more binding phases, reducing
52 the pore space in the cement paste (Davis, 1950; Massazza, 2002; Sabir et al., 2001). This can
53 also lead to improved compressive strength development. The optimum calcination
54 temperature to reach maximum pozzolanic activity depends on the mineralogy of the clays (He
55 et al., 1994, 1996; He et al., 1995). A complete removal of hydroxyl groups upon calcination
56 results in a collapsed and disarranged metastable structure with low crystallinity (Jeans and
57 Bergaya, 2008; Sabir et al., 2001). In a comparative study of calcined illite, montmorillonite
58 and kaolinite using X-Ray diffraction (XRD) and nuclear magnetic resonance spectroscopy (Al
59 NMR), it could be shown that kaolinite undergoes the most significant structural changes upon
60 calcination (Fernandez et al., 2011). Raw clays are often polymineral materials making it

61 difficult to find the optimum calcination temperature. If raw clays are heated at too high
62 temperatures ($> 900^{\circ}\text{C}$) recrystallization can take place, resulting in a decreased reactivity.
63 Ternary blends of cement, metakaolin and limestone have been investigated by many authors
64 (Antoni et al., 2012; Avet and Scrivener, 2018a, b; Bishnoi and Maity, 2018; Cancio Díaz et
65 al., 2017; Favier et al., 2018; Kunther et al., 2015; Nied et al., 2015; Scrivener et al., 2017;
66 Tironi et al., 2015). However, the role of calcium carbonate in raw clays (before calcination)
67 without kaolinite has been paid little attention to. The present authors have previously
68 published extensive studies (Danner et al., 2015; Danner et al., 2012b, 2013; Justnes et al.,
69 2011; Østnor et al., 2015) of what was called calcined "marl" for simplicity, but actually should
70 be categorized as "calcareous mudstone" being a montmorillonite containing 25% calcium
71 carbonate. It was shown that replacing cement with up to 50% "calcined marl" can lead to
72 higher or equal 28 day compressive strength in mortars.
73 In this paper, the pozzolanic reactivity of a kaolin is compared to a calcareous montmorillonite.
74 To explain the pozzolanic reactivity, structural changes upon heating were investigated by
75 Fourier transformed infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy
76 (Al-NMR) and Mössbauer spectroscopy. Phase changes and microstructural changes were
77 documented by X-ray diffraction (XRD) and scanning electron microscopy (SEM).
78 Additionally, changes in specific surface area (BET), and ion release in an approximated
79 concrete pore water was investigated by inductively coupled plasma mass spectrometry (ICP-
80 MS).

81

82 **2. Materials**

83 Table 1 shows the phase composition of the Clay A and B and Table 2 shows the chemical
84 composition of Clay A and B calcined at 800°C . The main mineral phases of Clay A are
85 kaolinite, quartz and orthoclase. Clay B contains high amounts of montmorillonite and 25%

86 calcite. Clay B is a tertiary sediment and was deposited between the middle and late Eocene in
87 a marine depositional environment (Grønbech et al., 2010). The calcite content derives to a
88 large portion from coccoliths (Okkels and Juul, 2008). Pyrite was detected in Clay B, however,
89 the chemical composition showed no SO_3 . Under the SEM the pyrite distribution appeared only
90 very localised in form of pyrite framboids (Figure 10). The non-homogeneous distribution of
91 pyrite in Clay B might be a reason why SO_3 was not detected with XRF in the analysed sample.
92 The cement used in mortar tests was Norcem Standard (CEM I 42.5 R) and the chemical
93 composition is given in Table 2.

94 For ICP-MS investigations, an alkaline solution of pH 13.2 and a KOH:NaOH ratio of 2:1 was
95 prepared. The alkaline solution is an approximated pore water based on analyses from the water
96 of fresh paste from CEM I used in Norway. KOH and NaOH was chosen to achieve a pH value
97 > 13 , representative for concrete pore solution (Moreno et al., 2004; Williamson and Isgor,
98 2016).

99

100 **3. Methods**

101 **3.1. Production of calcined clays**

102 The thermal treatment of Clay A and B was executed at IBU-tec advanced materials AG
103 (Weimar, Germany), using a direct natural gas heated rotary kiln. The kiln is designed for a
104 continuous thermal treatment and was used to simulate trials under industrial conditions. The
105 feed rate was 30 kg/h and the residence time in the kiln was 45 min. Clay A was calcined
106 between 700-800°C as the highest pozzolanic reactivity of calcined kaolinite can be expected
107 in this temperature range. Clay B was calcined at temperatures between 700-1000°C in steps
108 of 50°C, as the temperature range of highest pozzolanic reactivity was unknown. The milling
109 of the calcined clay lumps produced at IBU-tec was performed at UVR-FIA GmbH (Freiberg,
110 Germany). The material was pre-crushed in a laboratory hammer mill equipped with a 1.6 mm

111 grid applying a circumferential speed of 33 m/s, to obtain a material with $d_{95} = 1$ mm. The
112 finish grinding to a $d_{50} < 10$ μm (determined with laser granulometry) was performed with a
113 discontinuous drum mill.

114

115 **3.2. Quantitative mineralogical analysis of the raw clays by X-ray diffraction (XRD)**

116 Bulk mineralogy of Clay A and B was performed on dried and ground samples using the back-
117 loading technique. Followed by that, the ≤ 2 μm fraction (clay fraction) was separated from the
118 bulk sample by means of sedimentation. The ≤ 2 μm fraction was smeared on a glass plate and
119 dried in air. The clay fraction was investigated under three different conditions (a-c); a:
120 untreated, b: after treatment with ethylene glycol vapours in a desiccator for 24 h at 60°C, c:
121 after heating at 500°C for 1 h. For analysis, a PAN Analytical X'Pert Pro MPD equipped with
122 a X'Celerator RTMS detector, an automatic divergence slit and a Cu-K α X-ray source
123 was used. The samples were measured from 2-65° 2 θ using a step size of 0.0170° 2 θ and a
124 step time of 20 sec. Data was collected at 45 kV and 40 mA. More details on the procedure of
125 quantitative mineralogical analysis can be found in (Nielsen, 1994; Nielsen et al., 1989).

126

127 **3.3. X-ray Fluorescence analysis (XRF)**

128 XRF analysis was performed with a Bruker AXS S8 Tiger WDXRF equipped with a 4 kW
129 generator. Dried and powdered clay samples were ignited at 850°C. Then 0.5 g of the dried
130 clay sample was added to 5.0 g of a 2:1 mix of lithium- tetraborate and metaborate and 60 μg
131 of lithium iodide. The mixture was fused in a Pt crucible and moulded to a glass disk.

132

133 **3.4. Compressive strength of mortars**

134 Mortars were prepared by substituting Portland cement (PC) with 20% calcined Clay A and B.
135 The mixing procedure was according to the Norwegian Standard NS-EN 196-1 (2005). The

136 water to binder ratio (w/b) was held constant at 0.5 in all mortar mixes. In mortars with calcined
137 Clay A and B, this was achieved by adding superplasticizer (Dynamon SP 130, Rescon Mapei)
138 with about 0.3% by dry weight of mortar. The consistency of fresh mortar was determined
139 using a flow table and the flow was within $\pm 5\%$ of the reference mortar. The mortar mixes
140 were cast in three 40x40x160 mm molds and stored in a cabinet for 24 hours at $23 \pm 2^\circ\text{C}$ and
141 90% relative humidity (RH). After 24 hours, the mortar prisms were removed from the molds
142 and stored in saturated CH water to avoid leaching, for 28 days. After 28 days storage, the
143 compressive strength was determined according to the Norwegian Standard NS-EN 196-1.

144

145 **3.5. Specific surface area (BET)**

146 BET specific surface area was measured with a Tristar 3000 Surface Area & Porosity Analyzer
147 apparatus from Micromeritics. Prior to analysis the samples were degassed with a SmartPrep
148 degasser (VacPrep 061) to remove adsorbed contaminants from the surface and pores of the
149 samples.

150

151 **3.6. X-ray Powder diffraction (XRD)**

152 Powders of calcined Clay A and B were prepared for XRD measurements using the front
153 loading technique. The samples were measured with a D8 Focus diffractometer from Bruker
154 equipped with a Lynx Eye detector and a Cu-K α X-ray source. A fixed divergence slit
155 of 0.2 mm was used. Measurements were taken from $5-65^\circ 2\theta$ with a step size of $0.2^\circ 2\theta$ and
156 a step time of 1 sec. Data was collected at 40 kV and 30 mA.

157

158 **3.7. Fourier transformed infrared spectroscopy (FT-IR)**

159 FT-IR spectra were taken in the transmittance mode in the middle-IR (MIR) region. Samples
160 of 2 mg were dispersed in 200 mg of KBr and pressed to pellets of 13 mm diameter using a

161 mechanical hand press. Measurements were performed using a Bruker IFS 66v FTIR
162 spectrometer equipped with an IR source, KBr beam splitter, and DTGS KBr detector. For each
163 sample, 200 scans in the 400 – 4000 cm⁻¹ (MIR) spectral range were recorded with a resolution
164 of 2 cm⁻¹. A spectrum of the atmosphere was recorded for background corrections of the
165 samples.

166

167 **3.8. Nuclear magnetic resonance spectroscopy (²⁷Al-MAS-NMR)**

168 The ²⁷Al MAS-NMR spectra have been recorded at 14.1 T, using a 4 mm CP/MAS NMR
169 probe, a spinning speed of $\nu_R = 13.0$ kHz, a 0.5 μ s excitation pulse ($\sim 11^\circ$ pulse) (Garg and
170 Skibsted, 2016), a 2 s relaxation delay, ¹H decoupling during acquisition, and in between 6560
171 and 50300 scans.

172

173 **3.9. Mössbauer spectroscopy**

174 The Mössbauer measurements were carried out at room temperature on a spectrometer with a
175 constant acceleration type of vibrator and a ⁵⁷Co/Rh source. The samples were ground, mixed
176 with BN (boron nitride) and spread out to form absorbers. Calibration spectra were recorded
177 using natural iron foil at room temperature as a reference absorber. Spectra obtained were
178 folded and analysed using the least-squares Mössbauer fitting program Recoil.

179

180 **3.10. Electron probe micro analysis (EPMA)**

181 All samples were cast in epoxy resin, plane polished in iso-propanol and coated with carbon.
182 For analyses, a JEOL JXA-8500F EPMA equipped with 5 wavelength dispersive X-ray
183 spectrometers (WDS) and an energy dispersive X-ray spectrometer (EDS) was used. All
184 samples were investigated in the backscattered electron imaging (BEI) mode with an

185 accelerating voltage of 15 kV. All results from WDX measurements are given in atomic percent
186 (at%).

187

188 **3.11. Inductively coupled plasma mass spectrometry (ICP-MS)**

189 Dispersions of Clay A and B and alkaline solution were prepared in a ratio of 1:30. 3 g of clay
190 were added to 90 mL solution and constantly rotated in a plastic bottle for 3 days. After 3 days
191 the plastic bottle was standing still to enable the clay to settle down on the bottom of the bottle.
192 About 15 mL of the clear solution were taken off with a pipette for ICP-MS analysis. The same
193 was done with a reference sample, composed of only alkaline solution. HR-ICP-MS analysis
194 was performed using a Thermo Finnigan model Element 2 instrument. The samples were
195 introduced using a SC-Fast autosampler with a peristaltic pump. The instrument was equipped
196 with a concentric PFA-ST nebulizer connected to a Scott PFA spray chamber, aluminium
197 sample and skimmer cones, a demountable torch and a quartz injector.

198

199 **4. Results and discussion**

200 **4.1. Compressive strength of mortars**

201 Figure 1 shows the 28 day compressive strength of mortars with 20% replacement of cement
202 by calcined Clay A (left) and calcined Clay B (right). The black line is showing the compressive
203 strength of the reference mortar without cement replacement. The compressive strength of the
204 reference mortar was about 55 MPa. Clay A seemed to be very reactive within the calcination
205 temperature range between 700-800°C. Within the whole temperature range, 20% replacement
206 of cement with calcined Clay A resulted in compressive strength up to about 8 MPa higher than
207 what was achieved with the reference mortar. Calcined Clay B showed a narrower reactivity
208 window. The reactivity with regard to compressive strength development increased from 700-
209 800°C followed by a decrease from 800-1000°C. 20% replacement of cement by Clay B

210 calcined at 800°C resulted in 7 MPa higher 28 day compressive strength compared to the
211 reference mortar. Higher replacement levels of cement up to 50% were tested for Clay A and
212 B at a calcination temperature of 800°C (Danner et al., 2015; Danner et al., 2012a; Danner et
213 al., 2013). It could be shown that even with 50% cement replacement, higher or equal 28 day
214 compressive strength was achieved compared to the reference mortar.

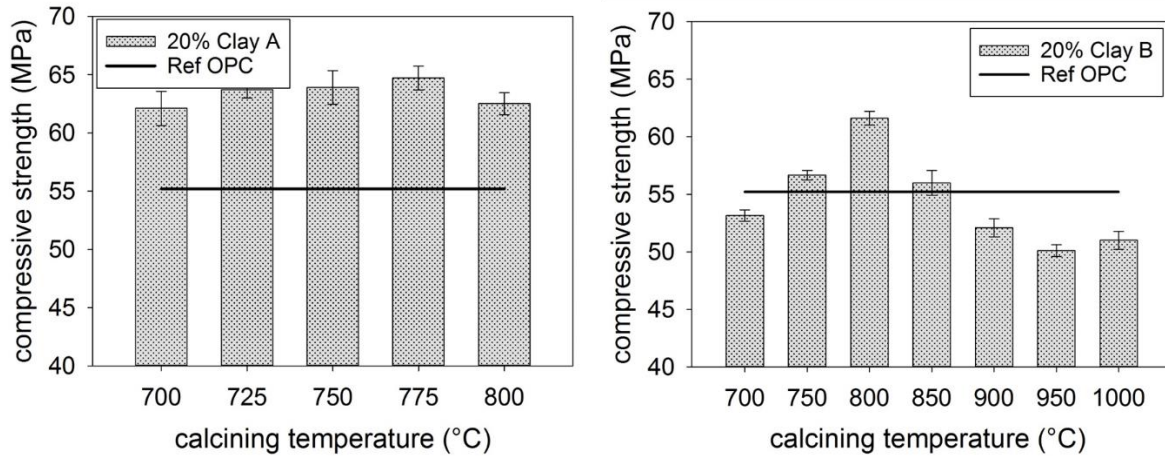
215

216 **4.2. BET specific surface area**

217 Table 3 shows the measured BET surface area of Clay A and B, raw, and calcined at 700 and
218 800°C. While the BET specific surface area of the montmorillonite rich Clay B decreased with
219 increasing temperature, the kaolinite rich Clay A showed no change. When calcined to 700°C
220 the specific surface of Clay B fell from 71.3 to 54.1 m²/g. This is a result of a first collapse of
221 the montmorillonite layers through dehydration of the interlayer spaces reducing the d-spacing
222 of the mineral structure. This was confirmed with XRD presented in section 4.3. Upon further
223 heating to 800°C, the specific surface dropped significantly to 15.1 m²/g. The complete
224 dehydroxylation caused a further decrease of the inner surfaces. Recrystallization was not
225 observed with XRD for Clay B at 800°C. The specific surface of Clay A did not change from
226 100 to 800°C within the error of the measurement. Quartz and orthoclase do not undergo any
227 significant changes when heated to these temperatures. Even the transformation of kaolinite to
228 metakaolinite has only a minor impact on the specific surface (Fernandez et al., 2011; He et
229 al., 1995).

230

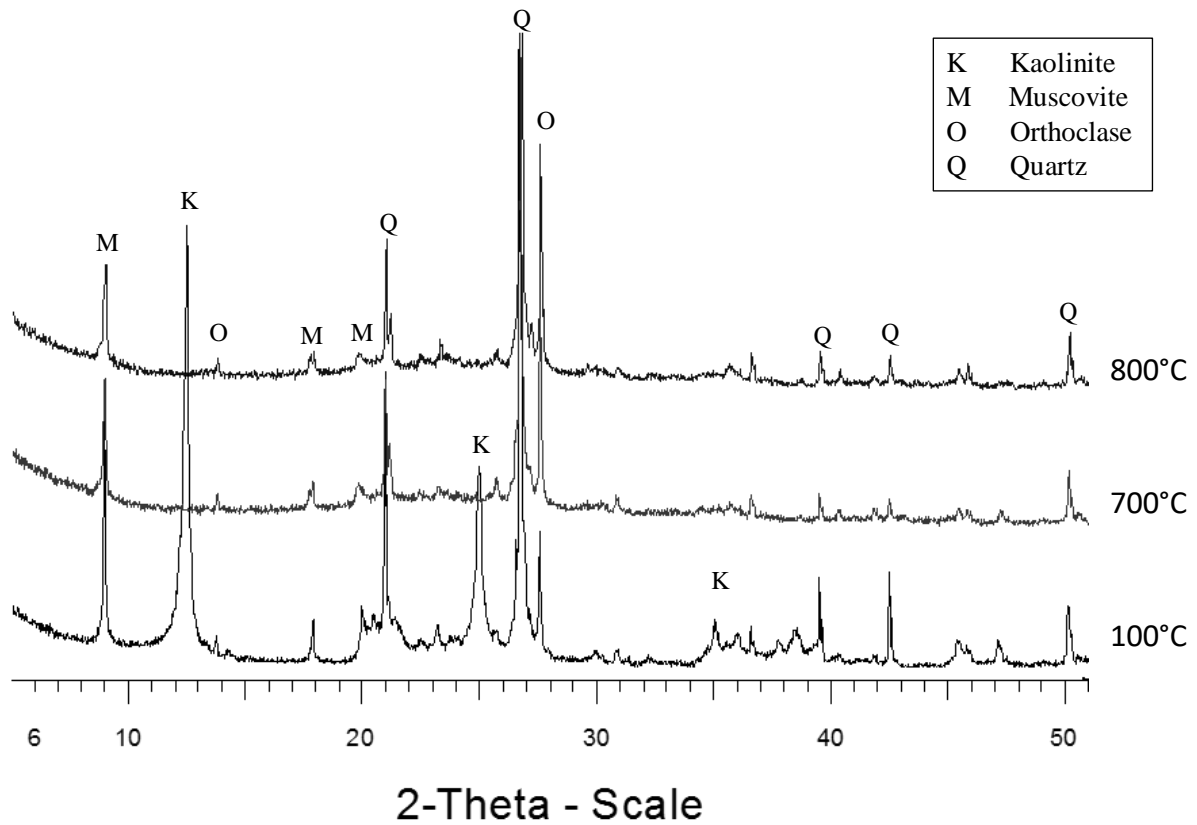
231 **XRD**



232

233 *Figure 1: 28 day Compressive strength of mortars with 20% replacement of cement by calcined Clay A (left) and calcined*
 234 *Clay B (right).*

235



236

237 Figure 2 shows the XRD diffractograms of Clay A, raw and calcined at 700 and 800°C. When
 238 calcined at 700°C, the kaolinite reflections disappeared due to dehydroxylation of the kaolinite
 239 structure, i.e transformation of kaolinite to X-ray amorphous metakaolinite. This is visible in
 240 the increased background of the diffractograms from Clay A calcined at 700 and 800°C. Quartz
 241 and orthoclase minerals were not affected by the heat treatment. Muscovite reflections were

242 still visible at a calcination temperature of 800°C. The dihydroxylation of muscovite takes
243 place between 850°C and 900°C (2003; Meyers and Speyer, 2003). The phase assemblage as
244 visible in the XRD diffractograms did not change between 700-800°C. There is no
245 recrystallization to expect in kaolin when burned at such relatively low temperatures. At
246 temperatures above 1100°C, the formation of mullite may occur (Mota et al., 2009; Sperinck
247 et al., 2011). The good pozzolanic reactivity of Clay A calcined at 700 and 800°C in mortar
248 tests is coherent with the identical XRD diffractograms at 700 and 800°C. Already at 700°C,
249 the transformation to metakaolin is complete and the pozzolanic reactivity does not increase
250 further.

251 In Figure 3, the phase changes during the calcination of Clay B between 700-1000°C are
252 presented. Raw Clay B was dried at 100°C so that the interlayer space of montmorillonite
253 decreased due to dehydration. This caused a shift of the 001 montmorillonite reflection from
254 about 6° 2θ to 9° 2θ resulting in an overlapping with the illite reflection at 8.9° 2θ. At a
255 calcination temperature of 700°C the kaolinite reflection at 12.4° 2θ disappeared due to
256 transformation to metakaolinite. Calcite was not completely decomposed until 850°C.
257 Montmorillonite was visible until 800°C. It appeared from the background of the
258 diffractograms that the highest amount of amorphous phases was present between 800-850°C.
259 The main phases detected at temperatures above 850°C were anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$),
260 wollastonite (CaSiO_3) and diopside ($\text{CaMgSi}_2\text{O}_6$). Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) appeared as an
261 intermediate phase at 850 and 900°C. When coexisting with quartz or other SiO_2 minerals,
262 gehlenite becomes unstable and reacts further to anorthite and wollastonite (Duminuco et al.,
263 1998; Rathossi et al., 2004; Trindade et al., 2009). With regard to the compressive strength
264 results obtained in the mortar tests, the beginning recrystallization of new stable and unreactive
265 phases at 850°C explains the decreasing reactivity of Clay B at temperatures above that and
266 hence the decrease in compressive strength of the mortars.

267

268 **4.3. FT-IR spectroscopy**

269 The FT-IR spectra of the raw and calcined Clay A are shown in Figure 4. Kaolinite showed
270 four OH stretching bands at 3696, 3670, 3670, 3620 cm⁻¹ (Chakchouk et al., 2009; Madejova
271 and Komadel, 2001; Tironi et al., 2012). Additionally, three well-resolved Si-O stretching
272 bands at 1114, 1032, 1008 cm⁻¹, typical for kaolinite were observed. The absorption band at
273 696 cm⁻¹ was assigned to Si-O stretching of kaolinite or quartz. The absorption band observed
274 at 912 cm⁻¹, is related to the Al-O-H deformation band of the octahedral sheet in the structure.
275 Absorption bands observed at 538 and 469 cm⁻¹ are attributed to Al-O-Si and Si-O-Si
276 deformation bands respectively. The first describing the connection of octahedral and
277 tetrahedral sheet in the kaolinite structure and the second reflecting the bonding of tetrahedra
278 in the tetrahedral sheet. These signals were also visible in Clay B (Figure 5). Quartz and
279 orthoclase was detected in the absorption bands at 795 and 755 cm⁻¹ respectively.

280 Calcination at 700°C resulted in the disappearing of the OH stretching bands between 3600-
281 3700 cm⁻¹ and the Al-O-H deformation band at 912 cm⁻¹. This indicates complete
282 dehydroxylation of kaolinite. All samples appeared to adsorb water from the atmosphere visible
283 in the bands at 3400 cm⁻¹ and 1635 cm⁻¹. The well-resolved Si-O stretching bands transformed
284 into one wide peak with a maximum at about 1080 cm⁻¹ upon calcination. This was explained
285 with the formation of a 3 dimensional amorphous silica network (Madejová, 2003). The
286 disappearing of the Al-O-Si deformation band at 538 cm⁻¹ and the shifting of the Si-O-Si
287 deformation band at 469 to a higher wavenumber has been observed by several authors
288 (Madejová, 2003; Tironi et al., 2012). Additionally, new absorption bands appeared at 570 and
289 870 cm⁻¹. These can most likely be ascribed to the amorphous metakaolinite structure.

290 Especially the disappearance of the Al-O-Si deformation band and the shift and broadening in
291 the Si-O-Si deformation band potentially imply significant structural changes in the local

292 environment of the Al and Si atoms in the octahedral and tetrahedral sheet. Increasing the
293 calcination temperature from 700 to 800°C did not result in a change of the FT-IR spectra. The
294 higher intensities of most of bands at a calcination temperature of 800°C, are explained by a
295 potential higher sample saturation in the KBr disk.

296 Figure 5 shows the FT-IR spectra of the raw and calcined Clay B. The band observed at 3620
297 cm⁻¹ is typical for dioctahedral montmorillonites with a high amount of aluminium in the
298 octahedra (Madejová, 2003). The absorption band at 3699 cm⁻¹ reflects the presence of
299 kaolinite. The OH stretching band of H₂O molecules at 3439 cm⁻¹ is found in almost all clay
300 minerals, especially when smectite is dominating. Common for all smectites is the broad
301 complex Si-O stretching band at 1030 cm⁻¹ (Madejová, 2003). Within this broad band a
302 shoulder was observed at around 1100 cm⁻¹ which can be assigned to kaolinite. The Al-O-H
303 deformation band observed at 911 cm⁻¹ is typical for dioctahedral smectite minerals
304 (Madejová, 2003). Calcium carbonate absorption bands were found at 713, 874, 1428 and 2514
305 cm⁻¹. The absorption band at 1799 cm⁻¹ is typical for several carbonate minerals and could
306 potentially be due to the small amounts of siderite found in Clay B (Table 1). The presence of
307 quartz was visible in the Si-O stretching bands at 796 cm⁻¹ and 696 cm⁻¹. Small amounts of
308 organic material showed bands at 2877 cm⁻¹ and many smaller peaks at higher frequencies.

309 When calcined at 700°C the OH stretching band of kaolinite at 3699 cm⁻¹ disappeared while
310 the OH stretching band of the montmorillonite at 3621 cm⁻¹ was still visible. At 800°C
311 montmorillonite became dehydroxylated as well, also visible by the disappearing of the Al-O-
312 H deformation band at 911 cm⁻¹. With increasing calcination temperature, the Si-O stretching
313 bands around 1030 cm⁻¹ broadened indicating the presence of amorphous silica (Madejová,
314 2003). Potential distortion in the montmorillonite layers and modified bonding of the bridging
315 oxygen atoms was visible in the diminishing intensities of the Al-O-Si and Si-O-Si deformation
316 bands at 534 and 469 cm⁻¹. The Si-O-Si band broadened, decreased in intensity and shifted to

317 higher frequencies. This confirms a lower crystallinity in the tetrahedral sheet and distortions
318 in the arrangement of the tetrahedra. The completely disappearing Al-O-Si deformation band
319 might reflect a decreasing content of octahedral cations (Madejová, 2003). The disappearance
320 of the band at 534 cm⁻¹ and the displacement of Si-O-Si band at 469 cm⁻¹ was confirmed for
321 kaolinite to metakaolinite transformation in several papers as a sign for the presence of an
322 amorphous reactive phase (Chakchouk et al., 2009; Tironi et al., 2012). Calcium carbonate was
323 not completely decomposed at 800°C confirming results from XRD. The partly decomposition
324 of calcite was reflected in a peak broadening and a decreasing intensity of the band at 1428 cm-
325 1. The higher intensities of some absorption bands in the sample calcined at 700°C are
326 explained by a potential higher sample saturation in the KBr disk.

327

328 **4.4. ²⁷Al MAS NMR**

329 Figure 6 shows the ²⁷Al MAS NMR spectra of the raw and calcined Clay A. Spinning side
330 bands are marked with asterisks. The chemical shifts at 71.4 ppm and 56.9 ppm originate from
331 Al in tetrahedral coordination, and are typical for Al sites in layered clay mineral structures
332 (70.8 ppm) and fully condensed Al(OSi)₄ sites (59.3 ppm) (Brown et al., 1987b; Drachman et
333 al., 1997; Fernandez et al., 2011; Jeans and Bergaya, 2008; Skibsted, 2011). Al in tetrahedral
334 coordination might represent the substitution of Al for Si in the tetrahedral sheet of muscovite.
335 However, orthoclase present in Clay A also contains Al entirely in tetrahedral coordination and
336 exhibits a chemical shift in the same region between 56-60 ppm (Zhou et al., 1997). The most
337 intense chemical shift observed at 4.9 ppm reflects Al in octahedral coordination, i.e. octahedral
338 sheets in kaolinite. The relative intensities were 2.6% (71.4 ppm), 11.9% (56.9 ppm) and 85.5%
339 (4.9 ppm), confirming that most of the aluminium was present in octahedral sheets of the
340 kaolinite structure.

341 The ^{27}Al MAS NMR spectrum of Clay A calcined at 800°C showed chemical shifts for Al in
342 tetrahedral (57.2 ppm), five-fold (29 ppm) and octahedral (4.2 ppm) coordination (Fernandez
343 et al., 2011; Rocha and Klinowski, 1990). An estimation of the relative intensities for the
344 different sites, by spectral integration, gave relative intensities of 37.3% (57.2 ppm), 40.3% (29
345 ppm), and 22.4% (4.2 ppm). This indicates that Al was mainly present in 4 and 5-fold
346 coordination in Clay A, calcined at 800°C . 4-fold coordinated Al was observed before in
347 calcined kaolinite (Fernandez et al., 2011) but it cannot be excluded that a significant amount
348 of the intensity of this peak derives from the orthoclase. The change in coordination and
349 especially the presence of 5-coordinated Al clearly indicates a disordering and loss of
350 crystallinity of the structure.

351 ^{27}Al MAS NMR spectra of the raw and calcined Clay B (800°C) are shown in Figure 7. The
352 spectrum of the raw Clay B showed three chemical shifts at 70.8 ppm, 59.3 ppm, and 4.3 ppm
353 with the following relative intensities 5.4%, 16.0%, and 78.7%, respectively. As expected, Al
354 was mainly present in the octahedral sheet of the montmorillonite. The spinning sidebands
355 closest to the central-transition region are marked by asterisks.

356 The ^{27}Al NMR spectrum of Clay B calcined at 800°C showed two chemical shifts at 59.6 ppm
357 and 3.7 ppm with the relative centre-band intensities of 95.1% and 4.9%, respectively.
358 Octahedral Al in the raw montmorillonite has been almost completely converted to Al in
359 tetrahedral coordination. The signal at 3.7 ppm in the calcined sample might represent residual
360 octahedrally coordinated aluminium from montmorillonite (Drachman et al., 1997) or from
361 kaolinite and illite (Fernandez et al., 2011). The dehydroxylation accompanied with the change
362 in coordination for Al must result in significant structural alterations. The reorganizing
363 octahedral sheet will induce distortions in the tetrahedral silicon sheet as well, from changing
364 bond lengths and angles up to a complete separation (Drachman et al., 1997). This was

365 confirmed with FT-IR spectroscopy where a disappearing Al-O-Si band was observed upon
366 calcination.

367

368 **4.5. Mössbauer spectroscopy**

369 Mössbauer spectroscopy was only used to study Clay B. The iron content of Clay A was too
370 low to be studied by this method. Representative Mössbauer spectra of the raw and calcined
371 Clay B are shown in Figure 8. Data points and fitting are marked with crosses and black lines,
372 respectively. The individual red and blue lines correspond to the absorption of the Fe^{2+} and
373 Fe^{3+} components, respectively. The lines marked black in Figure 8a are the inner lines of the
374 six-line patterns emanating from the magnetic part. In the fitting procedure, both Fe^{2+} and Fe^{3+}
375 are represented by two absorption lines with equal intensities (doublets). The isomer shift (δ)
376 taken as the centre of the doublet, is referred to α -Fe as standard absorber. The electric
377 quadrupole splitting (Δ), is the splitting of the doublet. In the fitting, the isomer shift,
378 quadrupole splitting, doublet intensity (I) and the line width (Γ) were kept as varying
379 parameters. Both spectra showed strong resonances at around 0 - 2 mm/s as it is typical for clay
380 minerals (Murad and Wagner, 1998). The calcined Clay B showed furthermore resonances at
381 higher velocities (Figure 8b). These resonances are parts of six-line patterns originating from
382 a magnetic part of the sample. These outer lines representing the magnetic phases are rather
383 symmetric. The isomer shift (δ) was 0.36 (1) mm/s and the quadrupole coupling constant (ϵ)
384 was about - 0.11 (3) mm/s. The high fields are representative for hematite (α - Fe_2O_3). The field
385 distribution potentially derives from solid solutions of corundum-hematite (α - $\text{Fe}_{2-x}\text{Al}_x\text{O}_3$)
386 (Brown et al., 1987a; Majzlan et al., 2002). The substitution of Fe with Al would result in a
387 lowering of the field. With this interpretation, the whole magnetic signal comes from Fe^{3+} . The
388 intensities of these magnetic patterns showed, within error, 30 mass% of Fe in the calcined
389 sample to be present in the magnetic part.

390 The analysis of spectra, recorded with lower velocity scale, (Figure 8a) were performed with
391 varying number of quadrupole split doublets. The spectrum of the raw montmorillonite
392 consisted mainly of a slightly split doublet and wider doublets (marked blue in the figure).
393 From the fitting of the doublets in the raw montmorillonite, Fe^{3+} and Fe^{2+} were detected. In
394 Table 4 averaged hyperfine interaction values for the ferric and ferrous patterns of raw and
395 calcined Clay B are given. The isomer shifts and quadrupole splitting's found are characteristic
396 for clay minerals, like kaolinite, illite and montmorillonite (Murad and Cashion, 2011). The
397 values for the isomer shift of Fe^{3+} and Fe^{2+} indicated octahedral coordination for both (Takeda
398 et al., 1979). Fe^{3+} and Fe^{2+} were thus substituted for Al^{3+} and Mg^{2+} in the octahedral layer of
399 montmorillonite. All changes recorded for the iron species are therefore representative for any
400 change in the octahedral layer of the structure, i.e. the Al environment. The allowed quadrupole
401 splitting versus isomer shift combinations for ^{57}Fe were investigated in (Murad and Cashion,
402 2011). Different combinations result in different coordination for Fe^{3+} and Fe^{2+} . The
403 coordination of Fe^{3+} seemed to change towards 5 and 6 upon calcination as the quadrupole
404 splitting increased. Increasing quadrupole splitting may also be due to changes in the ligand
405 structure for Fe caused by dehydroxylation. The isomer shift of Fe^{2+} decreased from the raw to
406 the calcined Clay B and so did the quadrupole splitting, indicating a change in coordination
407 towards 4. The values obtained for isomer shift and quadrupole splitting are in agreement with
408 literature and were interpreted as the result of strong distortions in the octahedral layer of
409 calcined clay mineral structures (MacKenzie and Rogers, 1977; Takeda et al., 1979).
410 During the calcination process the Fe^{2+} was expected to be oxidized mostly to Fe^{3+} at 800°C
411 since the calcination takes place in air. The relative amounts (I) of different Fe valences are
412 presented in Table 4 and show that almost all the iron was oxidized in the calcined Clay B.
413 Induced stresses and distortions leading to a highly disorganized calcined montmorillonite

414 structure due to the oxidation of iron accompanied with increasing quadrupole splitting values
415 was partly confirmed by (Miller et al., 1963; Simopoulos et al., 1975; Tichit et al., 1988).

416

417 **4.6. SEM**

418 Figure 9a-b shows images of the raw Clay A. In the fine-grained kaolin matrix, larger grains
419 of orthoclase and quartz were observed. Only small kaolinite crystallites with lamellar texture
420 were found in the matrix. The presence of kaolinite was verified by WDX analysis. In contrast
421 to that, large crystallites of muscovite with a size up to 50 μm were found (Figure 9b). When
422 calcined at 700-800°C the kaolinite matrix showed only a slightly modified microstructure
423 (Figure 9c-f). The kaolinites lamellar texture appeared to widen up upon calcination. In point
424 1 & 2 in Figure 9c-d, the element composition was analysed by WDS (wavelength dispersive
425 spectra). The composition was similar in both points with about 20% Al and 20% Si (both in
426 atomic percent). A composition with Al/Si ratio of 1/1 is typical for metakaolinite with the
427 formula $\text{Al}_2\text{Si}_2\text{O}_5$. Figure 9e-f show two metakaolinite particles with a size of about 5 μm .

428 Clay B originates from marine sedimentation and contains calcareous microfossils. The
429 calcium carbonate content in Clay B derives to a large extent from coccoliths, observed all over
430 the raw Clay B (Figure 10a). Coccoliths are the exoskeletons of a group of plant plankton called
431 coccolithophores which belong to the algal division Haptophyta (Young and Henriksen, 2003).
432 Pyrite was found only locally in form of pyrite framboids (Figure 10b) (Lauf et al., 1982). Clay
433 B calcined at 700°C is presented in Figure 10c-d. Coccoliths appeared still stable at this
434 temperature. However, it appeared that the dense matrix widened up. When calcined at 800°C
435 the morphology was altered significantly (Figure 10e-f). The coccoliths were decomposed
436 leaving cavities in the montmorillonite matrix. At the same time the matrix appeared more
437 vitreous (Figure 10e). Moreover, new larger glassy particles were found all over calcined Clay
438 B (Figure 10f). The lower BET specific surface area measured in the calcined Clay B is most

439 likely the result of these new formed glassy phases. The formation of a liquid phase in calcite
440 bearing clays has also been observed by other authors (Duminuco et al., 1998; Nodari et al.,
441 2007; Trindade et al., 2009). The composition of this new formed phase was measured with
442 WDS analysis. The average composition of 3 particles in atom% was 19% Si, 8% Al, 8% Fe,
443 5% Ca, 2% Mg, 2% Na+K and 55% O. The result obtained in atom% of the elements was
444 recalculated in weight% of the respective oxides. The calculated oxide composition was similar
445 to the chemical composition measured with XRF of the initial raw Clay B (Danner, 2013).
446 However, the analysis was performed on a limited amount of particles and might not be
447 representative for the whole calcined Clay B. The glassy phase potentially contributes to the
448 good pozzolanic reactivity of the calcined Clay B shown in mortar tests.

449

450 **4.7. Inductively coupled plasma mass spectroscopy (ICP-MS)**

451 ICP-MS analysis was performed to investigate the release of ions from the raw and calcined
452 Clay A and B in an approximated concrete pore water. Of particular interest was the release of
453 silicon, aluminium and alkalis as these are the main elements contributing to the pozzolanic
454 reaction. The results are given in Table 5. In the raw Clay A, the release of silicon and
455 aluminium was about equal. This can be explained by the mineral structure of kaolinite, having
456 the octahedral and tetrahedral sheet exposed equally. Due to that, the aluminium release of
457 Clay A was considerably higher than for Clay B where montmorillonite dominates. In the
458 layered structure of montmorillonite, the octahedral sheet is located between two tetrahedral
459 sheets. When calcined at 800°C, both the release of silicon and aluminium increased
460 considerably. Calcined Clay A released higher amounts of silicon and aluminium than Clay B,
461 indicating higher pozzolanic reactivity in cementitious binders. In the raw Clay B, the release
462 of silicon was higher than the release of aluminium. As explained above, the tetrahedral sheets
463 of montmorillonite are more exposed to the alkaline solution while the octahedral sheet is

464 shielded between the tetrahedral sheets. When calcined at 800°C the release of silicon
465 decreased while the release of aluminium increased. This might be explained with structural
466 rearrangement of the metastable structure. The release of calcium from Clay B increased upon
467 calcination. Calcium release in Clay B derives probably from calcite and montmorillonite.
468 For potassium and sodium, negative values were measured. That means that higher amounts of
469 potassium and sodium were measured in the pure reference solution (alkaline solution without
470 Clay A or Clay B). Reason could be higher alkali ad- and absorption than what was released
471 from Clay A and B. Especially potassium was reduced in much higher magnitude than sodium
472 in the solution. The potassium ion with its ionic radius of about 1.38 Å fits perfectly in the
473 cavity of the pseudo-hexagonal rings of oxygens of the adjacent silica tetrahedral sheet of illite
474 or smectite minerals (Murray, 1999).

475

476 **5. Conclusions**

477 In this paper the potential use of two raw clays (Clay A: kaolin; Clay B: calcareous
478 montmorillonite) as supplementary cementitious materials in blended cements is investigated.
479 The pozzolanic reactivity of Clay A and B is explained by characterizing the structural changes
480 upon calcination with XRD, , FT-IR, Al-NMR, Mössbauer spectroscopy, SEM and ICP-MS.
481 The main conclusions are listed below.

- 482 • Compressive strength of mortars with 20% replacement of cement by calcined Clay A
483 and B resulted in more than 10% strength increase after 28 day curing.
- 484 • At the temperature of highest pozzolanic reactivity (Clay A: 700-800°C; Clay B:
485 800°C) kaolinite and montmorillonite were completely dehydroxylated. However, the
486 calcite in Clay B was not completely decomposed.

- 487 • FT-IR indicated changes in the connectivity of tetrahedral and octahedral sheets of the
488 kaolinite and montmorillonite structure and showed the formation of 3-dimensional
489 amorphous silica networks.
- 490 • In Clay A, most of the octahedral coordinated Al changed to 5-fold coordination upon
491 calcination. In calcined Clay B, the coordination of Al was changed to tetrahedral
492 coordination.
- 493 • Oxidation of iron during calcination resulted in strong distortions of the
494 montmorillonite structure in Clay B. The coordination of Fe³⁺ was changing to 5-fold
495 while the coordination of Fe²⁺ was changing towards 4-fold.
- 496 • Under the SEM, reactive metakaolinite particles were observed in Clay A. In Clay B,
497 the formation of a glass phase due to reaction of coccoliths (CaCO₃) and
498 montmorillonite was observed.
- 499 • When calcined at 800°C, Clay A and B showed increased release of Al in concrete pore
500 water. Clay A did also show increased release of Si. This contributes to the pozzolanic
501 reaction forming more binding phases in cementitious systems.

502

503 **Acknowledgements:**

504 Saint-Gobain Weber is acknowledged for initiating and financing this research project.
505 SINTEF Building and Infrastructure is acknowledged for the cooperation, support with mortar
506 testing and discussing the results of this research. Prof. Jørgen Skibsted (University of Aarhus,
507 Denmark) and Prof. Ole Bjørnslev Nielsen (University of Aarhus, Denmark) are acknowledged
508 for performing NMR analysis and the mineralogical analysis of the raw clays, respectively.
509 Lennart Häggström (University of Uppsala, Sweden) is acknowledged for performing
510 Mössbauer analysis.

511

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693

694

695 **Table 1: Mineralogical composition of Clay A and B before calcination**

Phase (mass%)	A	B
Kaolinite	47	8
Montmorillonite	—	54
Illite		4
Muscovite	2	—
Quartz	18	4
Orthoclase	34	—
Calcite	—	25
Siderite	—	3
Pyrite	—	1

696

697 **Table 2: Chemical composition of Clay A and B calcined at 800°C and the cement used in mortar tests**

Oxide (%)	A	B	Cement
SiO₂	60.6	48.7	19.9
Al₂O₃	30.0	17.8	4.8
Fe₂O₃	3.4	10.4	3.3
CaO	0.1	13.8	61.9
K₂O	3.2	2.4	1.0
Na₂O	—	0.7	0.5
MgO	0.4	2.8	2.7
MnO	0.0	0.2	
P₂O₅	0.10	0.2	0.2
TiO₂	0.4	1.0	
SO₃			3.3
Total	98.2	98.0	97.6
LOI	1.8	2.0	2.4

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699 **Table 3: BET specific surface area of raw and calcined Clay A and Clay B**

Sample Name	BET Surface Area (m ² /g)		
	raw	700°C	800°C
Clay A	18	20	19
Clay B	71	54	15

700

701 **Table 4: Mössbauer averaged results. Isomer shift δ , quadrupole splitting Δ and line width at half**
 702 **maximum Γ are given in mm/s, while the intensities I are given in %. The errors in the parameters are: δ**
 703 **(± 0.01 mm/s), Δ (± 0.05 mm/s), I ($\pm 1\%$) and Γ (± 0.02 mm/s).**

Sample	Fe³⁺				Fe²⁺			
	δ	Δ	I	Γ	δ	Δ	I	Γ
raw Clay B	0.39	0.52	77	0.24	1.12	2.20	23	0.17
calcined Clay B	0.33	1.21	63	0.31	0.95	1.90	7	0.33

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Table 5: Ion release from raw and calcined Clay A and B dissolved in approximated concrete pore water (0.132 M, pH = 13.2, KOH/NaOH = 2/1)

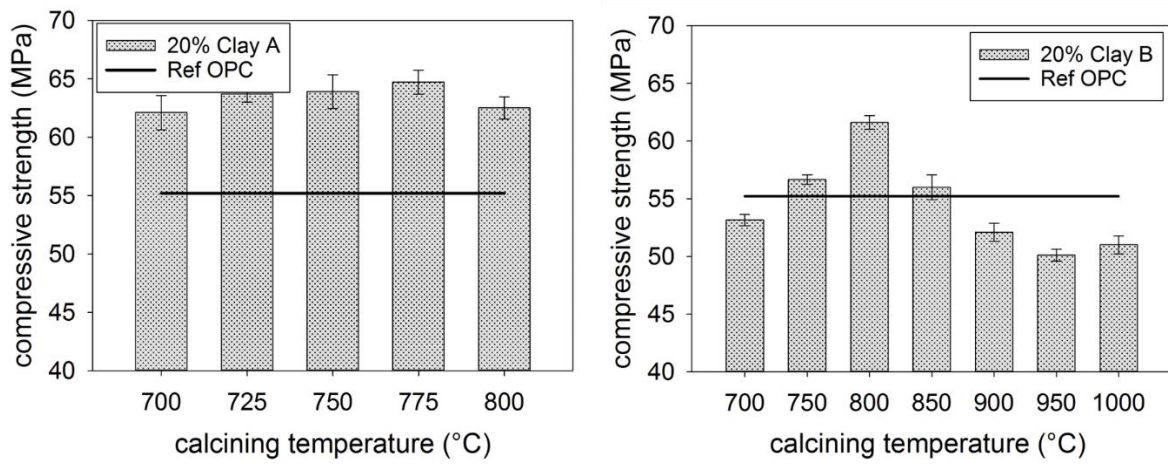
	Si 30 [mg/L]	Al 27 [mg/L]	Ca 44 [mg/L]	Fe 56 [mg/L]	Na 23 [mg/L]	K 39 [mg/L]	P 31 [mg/L]	Cl 35 [mg/L]
Clay A raw	41.9	43.9	1.0	0.0	-158.2	-1302	2.3	0.0
Clay A 800	106.2	154.1	0.0	0.2	-126.3	-798.3	6.0	0.0
Clay B raw	66.7	1.9	2.9	0.0	-13.0	-752.2	0.1	0.0
Clay B 800	20.9	29.4	15.7	0.0	-40.7	-165.5	0.0	0.0

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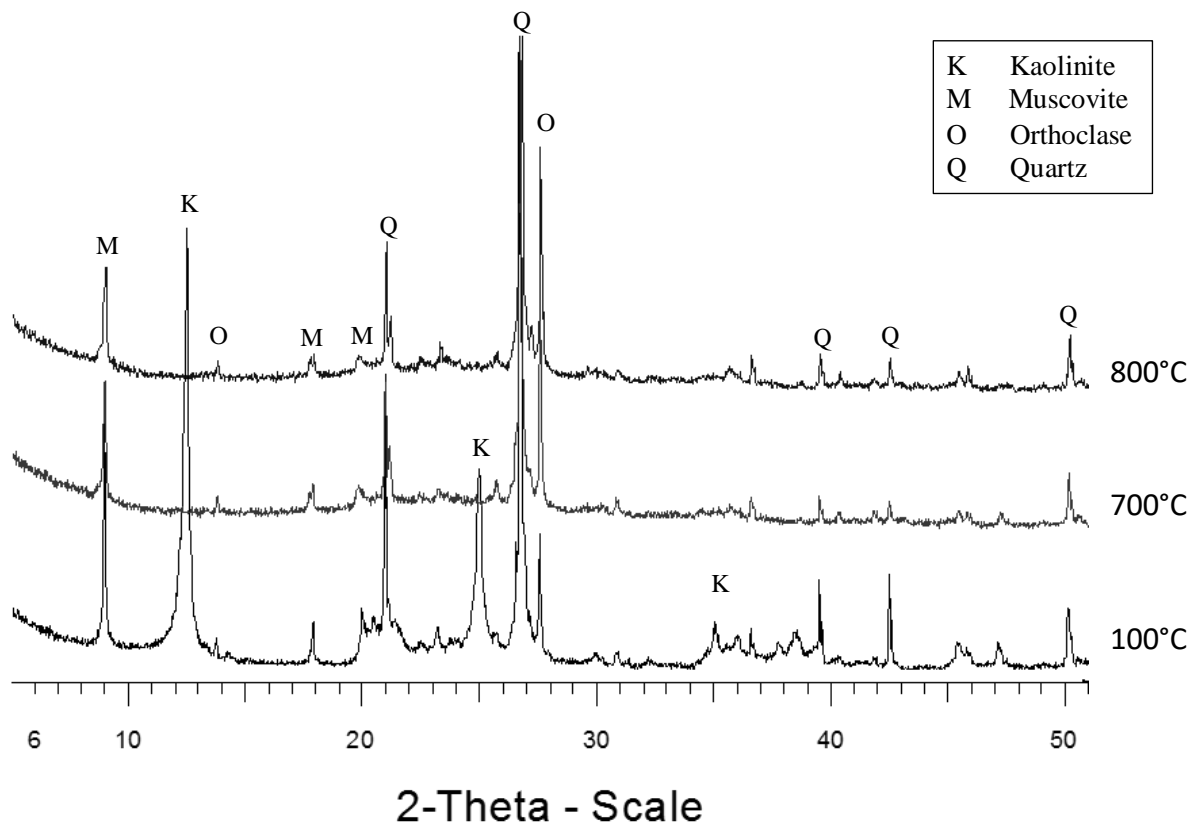
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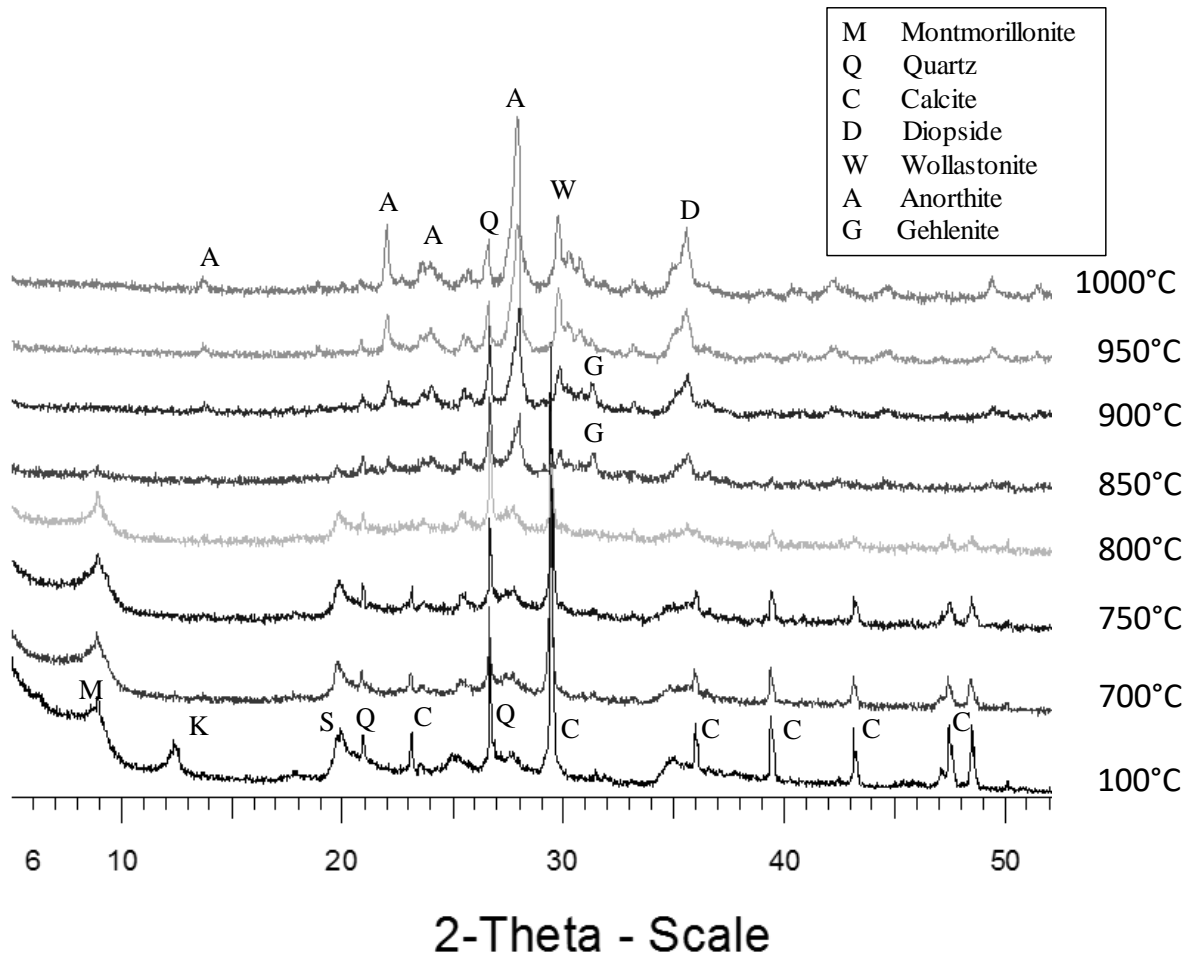
714 *Figure 1: 28 day Compressive strength of mortars with 20% replacement of cement by calcined Clay A (left) and calcined*
715 *Clay B (right).*

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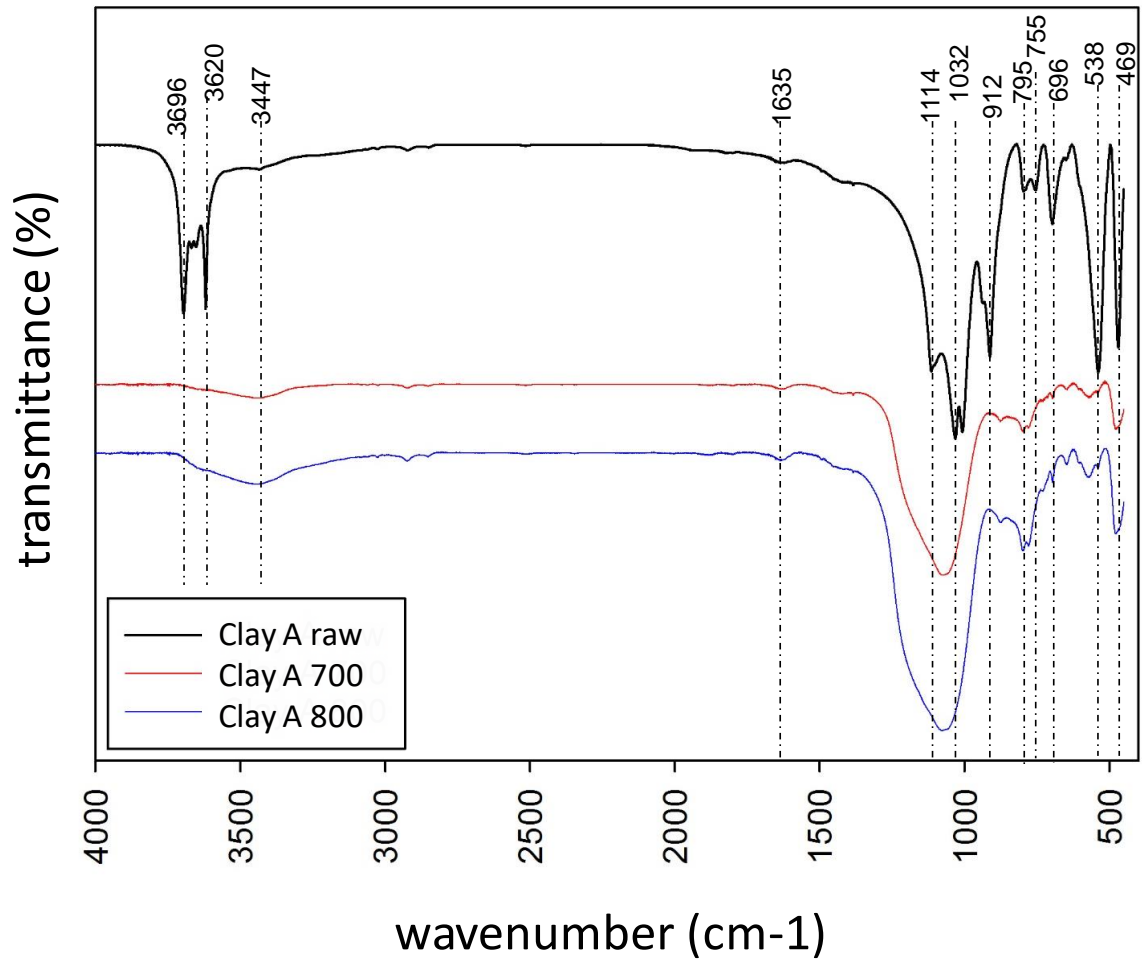
718 *Figure 2: XRD diffractogram of raw and calcined Clay A*



719

720 *Figure 3: XRD diffractogram of raw and calcined Clay B*

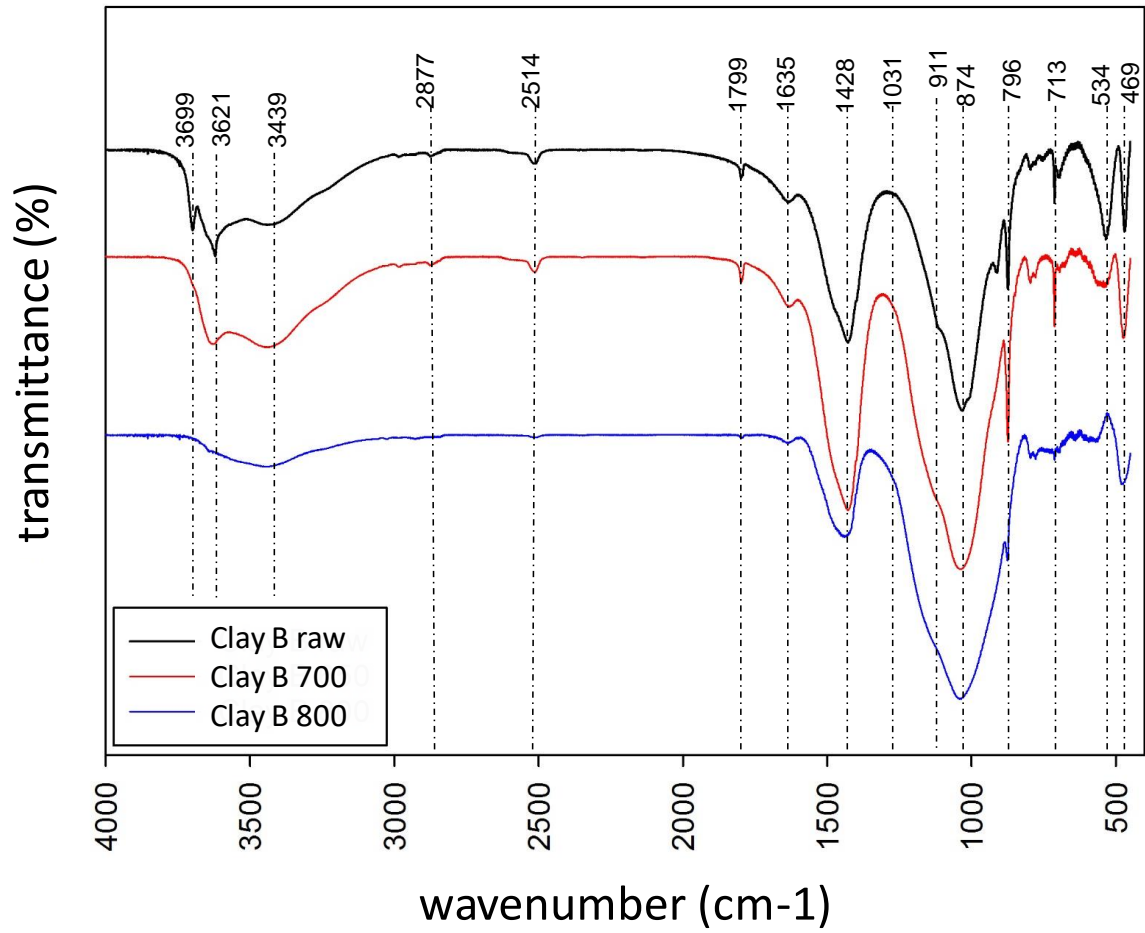
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723 *Figure 4: FT-IR spectra of raw and calcined (700 and 800°C) Clay A*

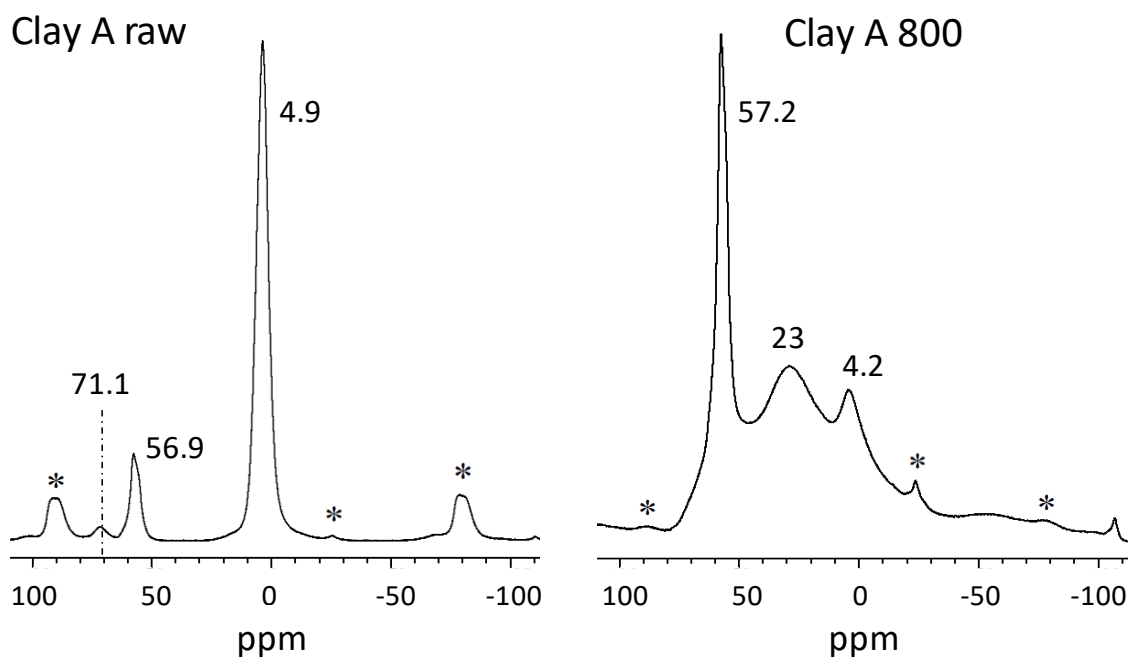
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726 *Figure 5: FT-IR spectra of the raw and calcined (700 and 800°C) Clay B*

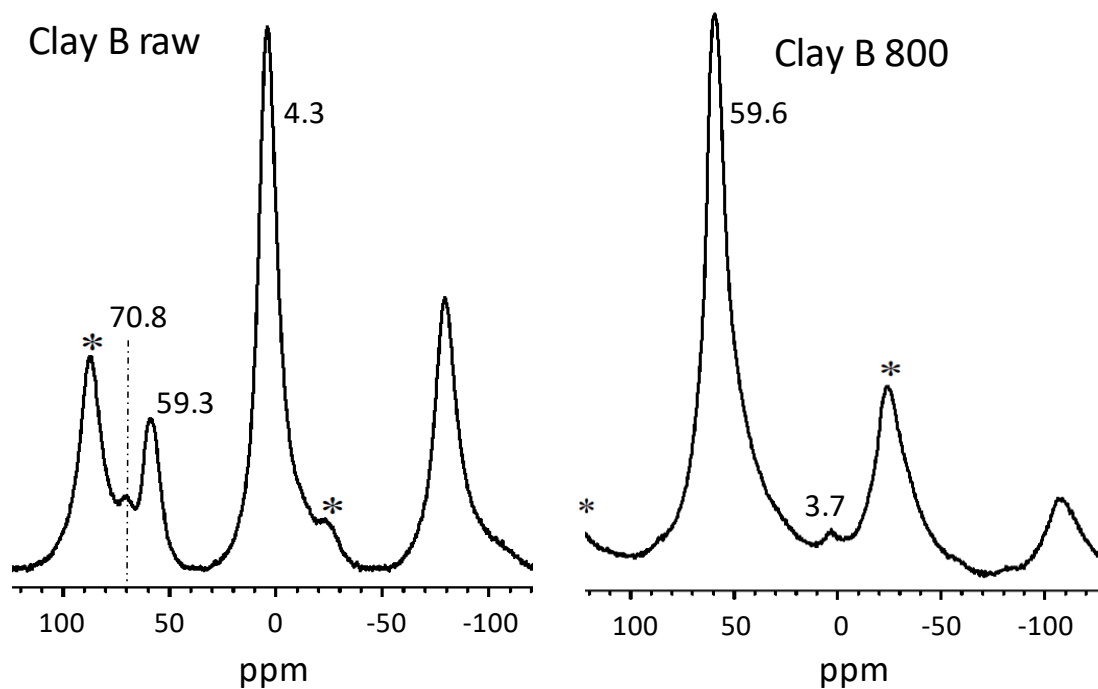
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729 *Figure 6: ²⁷Al MAS NMR spectra of raw and calcined Clay A*

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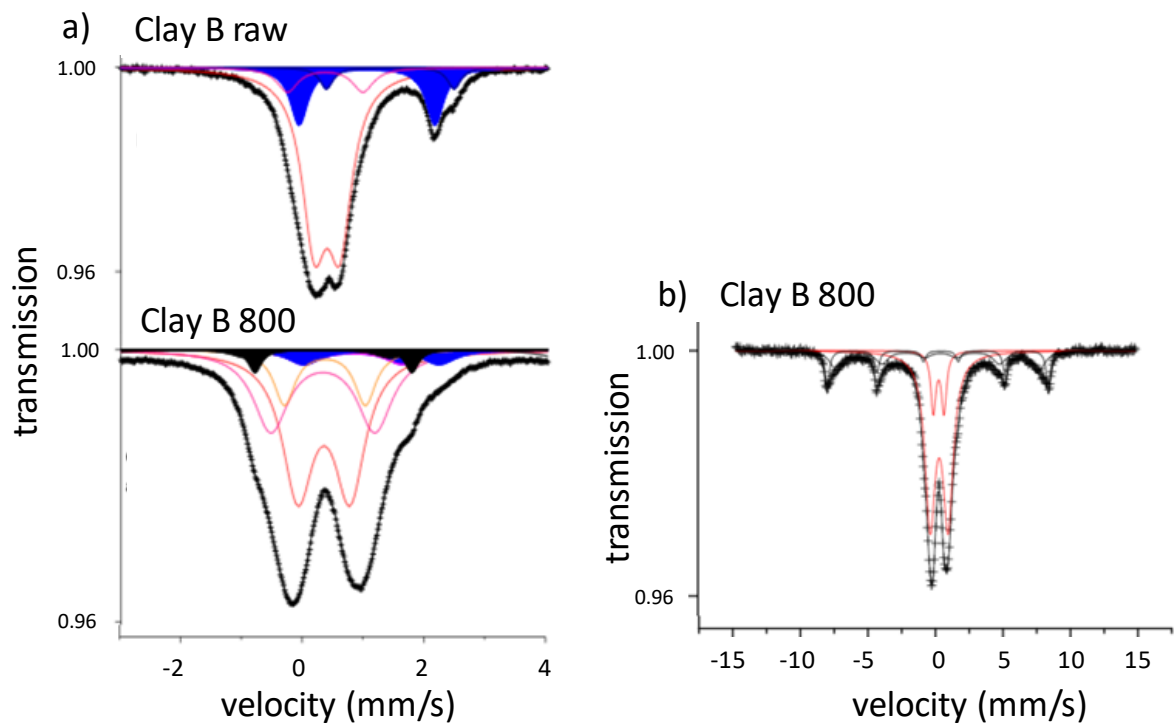


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732 *Figure 7: ²⁷Al MAS NMR spectra of raw and calcined Clay B*

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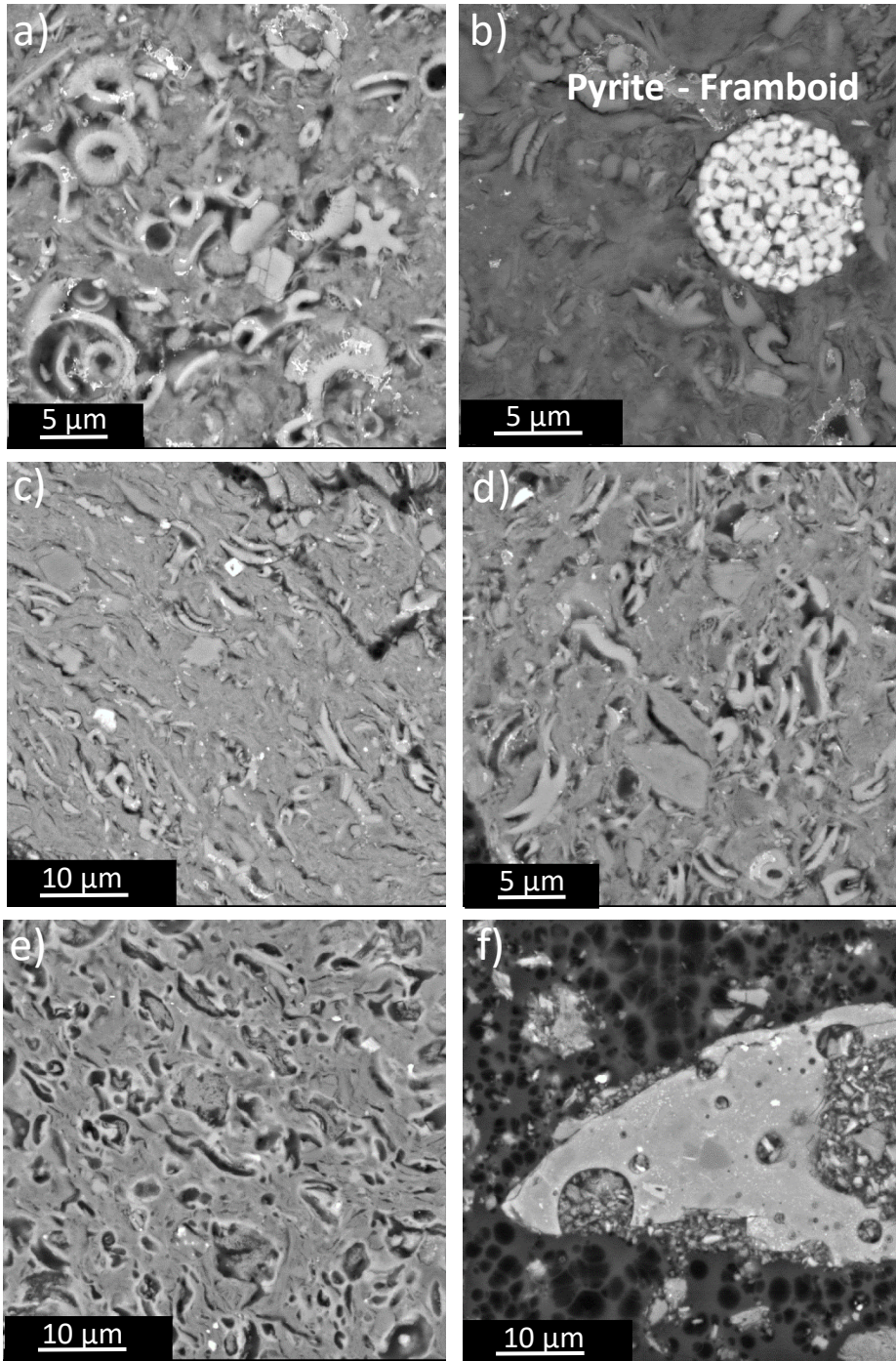
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736 *Figure 8: Mössbauer spectra of the raw and calcined Clay B sample with low (a) and high (b) velocity scales*

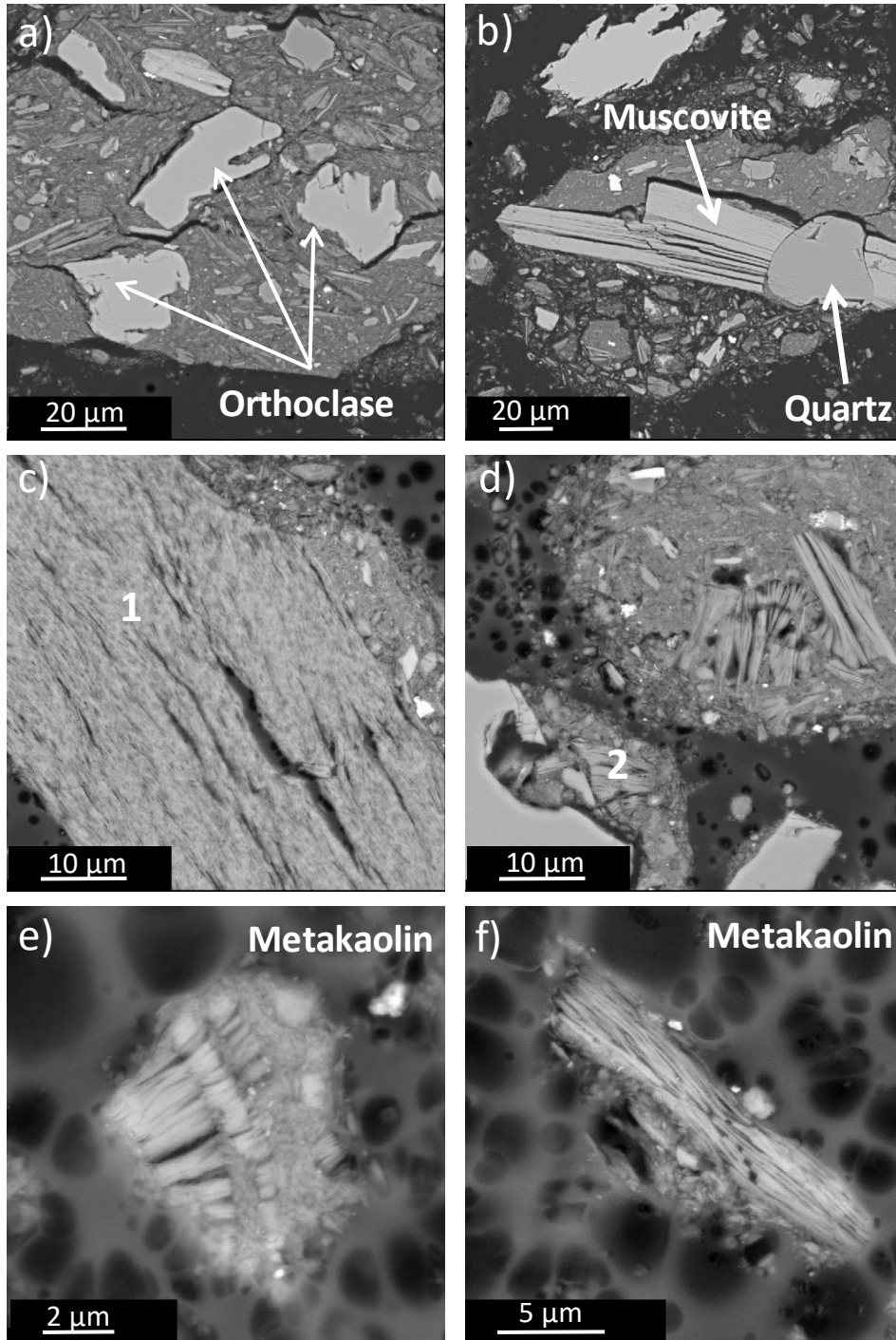
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739 *Figure 9: BSI images of the raw Clay A (a-b), calcined at 700 °C (c-d) and calcined at 800 °C (e-f). 1 and 2 indicate points*
 740 *for WDS analysis referred to in text.*

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Figure 10: BSI images of raw Clay B (a-b), calcined at 700(c-d) and 800°C (e-f)