

Crystal chemistry of cement-asbestos

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Abstract

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A study of a representative number of cement-asbestos (CA) samples

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removed from different localities in Italy has been accomplished with a

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combination of analytical techniques, including XRF, XRPD, SEM/EDS, micro-

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Raman, and Electron Backscattered Diffraction (EBSD), in order to elucidate the

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mineralogical and chemical variability of such class of building materials on a

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large scale. A complex mineralogy, comprising phases of cement hydration,

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residual non-hydrated components, and a relevant fraction attributed to various

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processes of deterioration, has been described. With the aid of the CaO-MgO-

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SiO₂ compositional diagram, three groups of CAs have been identified on the

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basis of their chemical parameters. This result is considered of importance for

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environmental and waste management issues. Keywords: Cement-asbestos;

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Rietveld method; CaO–MgO–SiO₂; Carbonation; SEM; EBSD

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Introduction

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Cement-asbestos (CA) are undoubtedly the most represented form of

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asbestos-containing materials (ACMs) ever produced worldwide. According to

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recent estimates, in Italy, one of the European countries where ACMs were

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extensively used in the past, approximately 2 billion m² of cement-asbestos

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slates still cover roofs of industrial and civil buildings (D'Orsi 2007). Their

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widespread distribution is obviously matter of great concern even because it has

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been long recognized that CA in open environment undergoes physical-chemical

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degradation eventually leading to the release of breathable fibres (Babic 2006;

51 Dias et al. 2008; Spurny et al. 1989). Therefore, because of human health
52 concerns, substantial effort was devoted to the detection and potential dispersion
53 of asbestos minerals from ACM (Burdett 2007; Sarkar et al. 1987; Spurny et al.
54 1989). Being CA the first fibre reinforced cement composite of modern times,
55 degradation of mechanical properties with time have been extensively studied
56 (Bentur and Mindess 2007), whereas its chemical and mineralogical
57 characterization raised less scientific interest, and has been usually limited to the
58 study of few samples (Dias et al. 2008; Laviano et al. 2002).

59 The chemical and mineralogical variability of CA at a large scale is directly
60 connected with the so-called *asbestos problem*. In Europe, the ban of asbestos,
61 following specific European directives, prompted the problem of safe disposal
62 and/or inertization of ACM. Since then, several industrial processes for thermal
63 transformation of CAs have been proposed (Abruzzese et al. 1998; Borderes
64 2000; Downey and Timmons 2005; Leonelli et al. 2006; Gualtieri et al. 2008);
65 their economic sustainability bears also on the perspective of recycling
66 opportunities for thermally transformed ACMs. In principle, packages of CA
67 materials, and especially slates, from different plants, undergoing the same
68 thermal treatment, may yield different end products. In Italy, before the ban of
69 ACMs in 1992, production of CA was carried out in many geographically distinct
70 plants, employing different processes and raw materials (Fazzo et al. 2012). A
71 preliminary survey, conducted on a limited area of Southern Italy (Laviano et al.
72 2002) evidenced a strong dependence of chemical composition as well as
73 mineralogical assemblage of roof slates upon the production plant.

74 Most of CA products have been manufactured through the Hatschek process
75 and its modifications, in which a very dilute slurry of asbestos fibres (up to about
76 10-15 wt% of solids) and ordinary Portland cement (OPC) was gradually dried,
77 obtaining films of about 0.3 mm which, in turn, were wound up on a roll to a
78 desired thickness, and finally shaped (Bentur and Mindess 2007). Curing of
79 green CA might be accelerated acting on temperature and/or pressure in
80 autoclave. During the process, single layer formation is a critical step in which
81 asbestos fibres play a crucial role. The final product can be roughly described as
82 a cement composite material in which asbestos minerals were employed as
83 reinforcing agent, thanks to the high tensile strength of the fibres. CA was
84 employed in a host of applications including roof tiles, flat sheets for siding,
85 panels for indoor or outdoor use, water and sewer pipes, tanks.

86 A wide range of minerals and/or rocks were also added in different proportion
87 to the cement matrix. Apart from some technical constraints, the choice of
88 suitable aggregates was relatively free, extending the chemical and mineralogical
89 variability of the end product. In general, the mineralogical composition of CA
90 comprises the following components: cement hydration products, asbestos
91 minerals, and inert aggregates. In practice, in aged materials, minor amounts of
92 unreacted cement phases are still found, and, since CA matrix can suffer from
93 deterioration like any other matrix of OPC-based pastes, concrete secondary
94 products will be detected. As a matter of fact, CAs currently removed from the
95 environment, have been in service for at least 20 years, thus, severe
96 deterioration may have occurred (Burdett 2007; Dias et al. 2008; Laviano et al.

97 2002; Sarkar et al. 1987; Spurny et al. 1989). Its extent will be a function of the
98 original chemistry and mineralogy, age, conditions of use, local climate, contact
99 with aggressive fluids.

100 Following Veblen and Wylie (1993), asbestos minerals are divided into two
101 major groups: serpentine and amphibole asbestos, both sharing the same
102 fibrous-asbestiform crystal habit but showing very different structural
103 arrangements at the molecular scale (Bailey 1988). The fibrous and/or
104 asbestiform (according to Zoltai's (1981) definition) variety of serpentine is
105 chrysotile (white asbestos) with ideal chemical formula $Mg_3(OH)_4Si_2O_5$.
106 Chrysotile has been the most commonly used form of asbestos. The amphibole
107 minerals which are considered as asbestos phases are: actinolite
108 $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$, tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$, anthophyllite (Mg,
109 $Fe^{2+})_7Si_8O_{22}(OH)_2$, crocidolite (fibrous and/or asbestiform variety of riebeckite)
110 $Na_2(Fe^{2+},Mg)_3Fe^{3+}Si_8O_{22}(OH)_2$, and amosite (fibrous and/or asbestiform variety
111 of grunerite) $(Fe^{2+},Mg)_7Si_8O_{22}(OH)_2$. Blue and brown asbestos minerals have
112 been widely used for industrial applications.

113 Crystal habit, workability, chemical stability, compatibility between the fibres
114 and the cement matrix, were the reasons for the technical and economic success
115 of asbestos–cement in the past. As a matter of fact, asbestos fibres are stable in
116 the alkaline environment of the cement matrix; furthermore, since in chrysotile
117 the octahedral layer is exposed at the external surface, the fibres are generally
118 hydrophilic and develop high surface potential in contact with water. Unlike other
119 composite cements, in CAs, the matrix composition at the interface with the

120 fibres was the same as that of the bulk, and no weak layers, enriched in
121 portlandite (CH in cement shorthand notation) surrounding the fibres, have been
122 observed (Bentur and Mindess 2007). The affinity of the fibres with the cement
123 matrix has been also confirmed by the observed beneficial effects of chrysotile
124 addition in developing strength in OPC pastes (Feric et al. 1997). Though it is
125 usually assumed that chrysotile was largely the most frequently employed form of
126 asbestos, relevant amount of amphibole have been documented in CA products
127 (Bard et al. 2004). Furthermore, owing to its recognized superior performance,
128 was the major form of asbestos in specific applications like pressure pipes.

129 This work reports for the first time a systematic study on CA with emphasis on
130 its mineralogical and compositional variability at a national scale.

131

132 **Experimental procedure**

133 **Materials and sample preparation**

134 The CA samples used in this study were collected from sealed packages
135 removed from 29 different locations in Italy (Table 1). The majority of the samples
136 (26) came from corrugated CA slates, and few others belonged to water tanks,
137 pipes and partition boards. As far as corrugated CA slates are concerned, their
138 original sizes, when known, were also reported. Protocols for ACM removal
139 commend sealing of the packages on site. Usually, each package is
140 compositionally homogeneous, as it contains material from a single removal site,
141 and thus, was likely produced in the same plant. It follows that samples taken
142 from a single slate can soundly be considered representative of the entire

143 package. Figure 1 depicts a typical ACM package. Fragments approximately
144 25cmx10cm wide were all collected from individual packages, and placed in
145 sealed plastic bags prior to analyses. Because they were produced a long time
146 ago, no details about original production plant, age and conditions of
147 conservation are available.

148 ACM samples prior to analyses were milled for 10 s in a steel shatterbox. All
149 samples and powders were kept under dry atmosphere in order to inhibit
150 carbonation, until measurement or further sample preparation.

151

152 **Analytical methods**

153 Chemical analyses were conducted on pelletized powdered samples of raw
154 CA using the X-rays fluorescence method (XRF). Prior to pelletization, the
155 powders underwent a prolonged annealing in oven at 1100 °C in order to
156 independently determine the loss on ignition (L.O.I.). The spectrometer used was
157 an ARL-Advant XP. Apart from existing calibration curves, matrix effects were
158 also checked against known standards, measured along with the samples.
159 Sulphur was determined separately using a Leco CS 230 instrument equipped
160 with an induction furnace (allowing conversion of sulphur into sulphur dioxide),
161 and an infrared detector. Measurements were conducted in triplicate for each
162 sample, and the mean values were taken. About 0.15 g of powder annealed at
163 1100 °C was employed in each run.

164 Mineralogical quantitative phase analyses (QPA) were performed through X-
165 ray powder diffraction (XRPD). Data were collected using a Bragg–Brentano θ - θ

166 diffractometer (PANalytical X'Pert PRO, Cu K α radiation, 40 kV and 40 mA)
167 equipped with a real time multiple strip (RTMS) detector. Divergence and anti-
168 scattering slits of $\frac{1}{2}^\circ$ and $\frac{1}{2}^\circ$, respectively, were mounted in the incident beam
169 pathway. The pathway of the diffracted beam included a Ni filter, a soller slit
170 (0.02 rad) and antiscatter blade (5 mm). The virtual step scan of the
171 measurement was $0.0167^\circ 2\theta$. QPAs were performed using the Rietveld method
172 (Rietveld, 1969). Refinements were accomplished with the GSAS (Larson and
173 Von Dreele 1999) package and its graphical interface EXPGUI (Toby 2001). The
174 determination of both crystalline and amorphous content was calculated using
175 the combined Rietveld–RIR method (Gualtieri and Brignoli 2004). Whenever the
176 samples showed the presence of more than the maximum number of 9 phases
177 available to the program, the procedure described by Winbur et al. (2000) was
178 used. Although samples were prepared with the side loading technique to
179 minimize *a priori* preferred orientation of crystallites, during the refinement, any
180 residual preferred orientation effect was modelled with the March model (Dollase
181 1986). Structural models used for alite M₃, β -belite, cubic aluminate, ferrite,
182 portlandite, calcite, dolomite, quartz, gypsum, bassanite, anhydrite, were taken
183 from Le Saoût et al. (2011). The structural model for the following phases were
184 used: chrysotile (Falini et al. 2004), riebeckite (Hawthorne 1978), vaterite (Kamhi
185 1963), aragonite (Antao and Hassan 2009), plagioclase (Wenk et al. 1980), albite
186 (Downs et al. 1994), microcline (Ribbe 1979), orthoclase (Prince et al. 1973),
187 leucite (Palmer et al. 1997), wollastonite (Hesse 1984), illite (Birle 1968), jarosite
188 (Basciano and Peterson 2008), ettringite (Hartman and Berliner, 2006),

189 hydrogarnet (Lager and Von Dreele 1996), monocarbonate aluminate hydrate
190 (Renaudin et al. 1999).

191 Micro-Raman measurements were performed on selected samples with a
192 Jobin Yvon HR800 LabRam m-spectrometer equipped with an Olympus BX41
193 microscope, an HeNe 20 mW laser working at 632.8 nm and a CCD detector.
194 The use of the microscope allowed for the collection of spectra of bundles of
195 asbestos fibres (Rinaudo et al. 2004).

196 Scanning electron microscopy (SEM) study of samples was accomplished with
197 a Philips XL-40 instrument equipped with an energy dispersive X-rays
198 fluorescence spectrometer (EDS). For the observations, performed using
199 secondary electrons, a tiny amount of sample was loaded on an aluminium stub
200 and coated with a gold 10 nm thick film. Furthermore, examination on polished
201 surface was accomplished on selected samples. In this case, samples were
202 embedded in epoxy resin and put under vacuum in order to facilitate
203 impregnation. Transversal sections were then exposed and carefully polished.
204 Observations were conducted in backscatter mode.

205 Possible permanence of a residual fraction of non-reacted clinker phases in
206 the cement used for CA manufacturing, was investigated through micro-
207 mineralogical analyses on selected samples by means of the electron
208 backscatter diffraction (EBSD) technique (Schwartz et al. 2009). EBSD analyses
209 were performed using a LaB₆ Camscan MX2500 SEM, equipped with a Nordif
210 CCD camera, Argus 20 (Hamamatsu) image processor and CHANNEL 5
211 software (HKL Technology) to detect and process the EBSD signal. The

212 analytical conditions were as follows: accelerating voltage = 30 kV; filament
213 emission = 160 mA; working distance = 25 mm; stage tilting: 70°.

214 The structural models of β -belite, ferrite, cubic and orthorhombic aluminate
215 used for the creation of the reference EBSD reflector data were taken from Le
216 Saoût et al. (2011).

217

218 **Results and discussion**

219 The chemical composition of the samples investigated is reported in Table 2,
220 while Table 3 reports the quantitative mineralogical compositions. Phases
221 detected whose phase fractions was too low to be refined were indicated in Table
222 3 as < 0.5 wt%.

223 Agreement factors of the Rietveld refinements, as defined in Larson and Von
224 Dreele (1999), were in the range: $R_{wp} = 5.3 - 8.3 \%$, $R_p = 3.9 - 6.5 \%$, $\chi^2 = 2.7 -$
225 7.2. The complex matrix of CAs is well illustrated by the example of Rietveld
226 graphical outputs showed in Figure 2. In Figure 3 and 4 representative set of
227 high-resolution SEM images of CA are depicted.

228 Example of Raman spectra of selected CA are reported in Figure 5. Detailed
229 interpretation of the main features will be given in due course.

230 The results of EBSD analyses on three representative samples are reported in
231 Figure 6, 7 and 8. For each sample, a low-magnification backscatter electron
232 image (BEI) is reported (a), together with an high-resolution BEI of a relict clinker
233 grain (b), with representative electron backscatter diffraction patterns (EBSP) of
234 the analyzed minerals, both raw and indexed (c, d, e ,f).

235 As far as accuracy of XRPD is concerned, the results reported hereby using
236 the Rietveld method should be more accurate than those recently reported using
237 other qualitative and semi-quantitative X-ray diffraction methods (Bassani et al.
238 2007; Dias et al. 2008; Laviano et al. 2002).

239 As expected, a quite complex mineralogy is showed by the samples under
240 study. As a matter of fact, chemical analyses and mineralogical phase
241 compositions, reported in Table 2 and 3 respectively, reflect both the complexity
242 of the original CA matrix and the results of degradation processes. Similarly to
243 other aged CA samples, calcite is the most abundant crystalline phase detected,
244 being considered the main product of weathering of the cement matrix (Bassani
245 et al. 2007; Dias et al. 2008; Laviano et al. 2002, Sarkar et al. 1987). The weight
246 fraction of the amorphous fraction, usually not determined in XRPD analyses of
247 hardened cement pastes and old cement based products, is quite variable,
248 ranging from 9.5 to 66.6 wt%, and inversely correlates with carbonates. This is
249 not surprising, since the most of the amorphous/ paracrystalline phases are
250 formed during hydration of the cement matrix, while carbonates and other
251 crystalline deterioration products grow later on, mainly at their expenses.

252

253 **Asbestos minerals**

254 Weight fraction of asbestos minerals employed in CA production have been
255 usually considered highly variable, however, no reliable mineralogical
256 quantitative phase analyses of asbestos minerals in CA materials were made
257 available so far. Samples 3, 18, 23 and 25, show values <5 wt%, while samples

258 1, 13,15, 27 and 28 >12 wt%. Due to the uptake of CO₂ to form calcite during
259 weathering, it's possible to infer that their original weight fractions were
260 somewhat higher. A typical example of a chrysotile bundle on a fresh fractured
261 surface is depicted in Figure 3a, while corresponding EDS point analysis is
262 reported in Supplementary Data Figure S1. In Figure 5 two typical micro-Raman
263 spectra collected pointing the laser beam onto the asbestos fibres of CA samples
264 are depicted: numbers correspond to chrysotile band wavenumbers in Figure 5a,
265 and crocidolite band wavenumbers in Figure 5b (Bard et al. 2004).

266 With respect to chrysotile, amphibole asbestos fibres are more brittle and
267 usually exhibit a more straight, needle-like crystal habit, as well exemplified by
268 the crocidolite SEM image reported in Figure 5b. Corresponding EDS point
269 analysis is reported in Supplementary Data Figure S1.

270 Though chrysotile was undoubtedly the most employed form of asbestos in CA
271 production, its use was not exclusive, and amphibole asbestos has been
272 detected in 17 out of 29 samples. For three samples (14, 15, 27), the determined
273 weight fractions exceed 3 wt%. It has been suggested that amphiboles in most
274 cases were not intentionally added, but were present as impurities (Bassani et al.
275 2007). We are inclined to think that, at least for our samples, this hypothesis can
276 be ruled out for a number of reasons. First of all, in Italy, due to a surplus of
277 internal production, all the asbestos employed in the past was mined locally. The
278 Balangero mine, near Turin, was by far the main chrysotile extraction site for CA
279 production and it was deprived of amphibole. Secondly, the chrysotile to
280 amphiboles ratio is highly variable from sample to sample, and this is

281 incompatible with a natural resource. On the other hand, the use of blends of
282 asbestos fibres was a well established practice in cement-asbestos industry
283 (Berntur and Mindess, 2007). Chrysotile has in fact some drawback when
284 considering the performance of the fibres at the wet stage. Amphibole fibres
285 perform better in relation to solid retention and water drainage, and help in
286 producing products with better strength. Sample 14, corresponding to a water
287 pipe, seems to confirm this view. Here, amphibole is even more abundant than
288 chrysotile. It should be noted that crocidolite was banned in Italy since June
289 1986, six years before chrysotile. This means that the amphibole-containing
290 samples are presumably older than 26 years.

291

292 **Fillers and aggregates**

293 Quartz is the most common mineral filler detected, it can be considered
294 ubiquitous, with amounts as high as 19.0 wt% (as in sample 12). The frequent
295 association of quartz with feldspars further suggests that granitic rocks have
296 seemingly been employed (see samples 1, 10-13, 16, 17, 20, 22, 24, 26, 27). In
297 few cases, less common crystalline phases were detected, see for example
298 wollastonite in sample 14, or leucite in sample 19. In Figure 3c and 3d, examples
299 of quartz and feldspar grains are shown, respectively. The corresponding EDS
300 point analyses are reported in Supplementary Data Figure S1.

301 Amongst mineral fillers, finely ground crystalline silica has been extensively
302 employed in materials undergoing autoclave processes (Berntur and Mindess,
303 2007; Sarkar et al. 1987). Substituting up to 40 wt% of OPC, it plays an important

3 0 4 role during hydration because of its pozzolanic activity. In general, pozzolanic
3 0 5 fillers, reducing the CH content of the matrix, with some exception, improve
3 0 6 durability of the end product. To be effective in this respect, silica should be
3 0 7 highly reactive (like fly ash) or finely ground. Any excess to the amount needed to
3 0 8 react with the CH available to the system, acts as a simple aggregate. It is not
3 0 9 always straightforward to discern the origin of quartz detected in CA. In case of
3 1 0 samples showing feldspars and quartz coexistent (i.e. samples 1, 10-13, 16, 17,
3 1 1 22, 24, 27), it is reasonable to suppose that at least a fraction of crystalline silica
3 1 2 has been introduced with the granitic aggregate. In theory, if a correct amount of
3 1 3 quartz has been added, all the available CH will be consumed, and both phases
3 1 4 will not be detected in the sample. Any excess or defect will result in a quartz or
3 1 5 CH residue. This seems in accordance with the observation that in the less
3 1 6 altered samples, showing the lowest carbonates and the highest amorphous
3 1 7 weight fraction (samples 3, 9, 12, 14, 16, 26), at a significant amount of CH
3 1 8 corresponds a low quartz content. SEM investigation of sample 9 revealed the
3 1 9 presence of blast furnace slag relics, confirming the use of composite cements
3 2 0 (EN Type III cements). An example of such material is depicted in Figure 4c.
3 2 1 Reaction rims are clearly visible. Corresponding EDS point analysis spectrum is
3 2 2 reported in Supplementary Data Figure S2.

3 2 3 Calcite deserves special attention, as major deterioration product of CAs. It is
3 2 4 hard to say whether calcium carbonate was used as mineral filler or not. Calcite
3 2 5 has been detected in a qualitative XRPD of a sample of CA roof slate, described
3 2 6 as unaltered (Sarkar et al. 1987). However, secondary origin cannot be excluded,

327 since it is known that, under ordinary conditions, carbonation of the cement
328 matrix is a relatively fast process. Blended limestone cements in Europe were
329 produced as early as 1960's, and in principle they could have been employed as
330 cement binders in CA fabrications. In limestone cements, calcite is not only an
331 inert filler, but reacts with aluminates leading to the formation of various
332 carboaluminate phases (Matschei et al. 2007). However, the presence of
333 carboaluminates is not exclusive of this process, as will be explained below.

334 Unlike other inert aggregates, isolated calcite crystals, were never observed
335 with SEM. This seems to support the view that micro-crystalline calcium
336 carbonate finely dispersed into the matrix of CAs materials is of secondary origin
337 (Lagerblad 2005). Dolomite, whose significant amounts have been found in
338 sample 8, 25 and 28, has been reported to be frequently added as inert filler
339 (Dias et al. 2008; Sarkar et al. 1987). However, being a common mineral in
340 limestones, it may testify the use of blended limestone cements.

341

342 **Products of cement hydration**

343 The most abundant fraction in non-degraded samples is expected to be
344 represented by cement hydration products.

345 Our discussion of hydration and alteration of the cement component will be
346 focused on OPC, since basic concepts hold, with minor modifications, for other
347 Portland-based binding materials, such as CEM II-V, as well.

348 Cement hydration processes have been the object of intense study, and have
349 been recently reviewed (Scrivener and Nonat 2011). OPC usually reacts with

350 water producing a variety of hydrated compounds (Taylor 1997; Scrivener and
351 Nonat 2011). In general, hydration of calcium silicates prompts to the formation
352 of calcium silicate hydrates (C-S-H) and CH. In the presence of gypsum, the
353 calcium aluminates react with water producing ettringite
354 ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\times 26(\text{H}_2\text{O})$), calcium monosulphate hydrate
355 ($\text{Ca}_4\text{Al}_2\text{O}_4(\text{SO}_4)\times 12\text{H}_2\text{O}$) and later calcium aluminate hydrates with different
356 compositions (generally indicated as Afm in cement shorthand notation). Since
357 variable fractions of C-S-H, CH and Afm are reported to possess a low degree of
358 crystallinity, a reliable quantification of each single cement hydration product
359 through XRPD, is usually precluded; however, the weight fraction of the
360 amorphous component can be successfully assessed with the aid of the
361 combined Rietveld-RIR method. In our samples, CH, the Afm phase
362 hydrocalumite ($\text{Ca}_2\text{Al}(\text{OH})_6[\text{Cl}_{1-x}(\text{OH})_x]\cdot 3(\text{H}_2\text{O})$) and hydrogarnets of the katoite-
363 hibschite series ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$) are the most represented hydrated
364 crystalline phases detected. Hydrogarnets usually do not form in modern OPC,
365 but are commonly found in cement materials cured at high temperature or
366 autoclaved like CAs (Ramlochan et al. 2004; Taylor 1997). In cement pastes with
367 addition of pozzolana, fly ash or slags, formation of monocarboaluminate (Afmc)
368 have been detected after heat-curing (Ramlochan et al. 2004). The weight
369 fraction of carboaluminate in our samples was usually $< 1\%$. In general, we may
370 speculate that, with few exceptions, only tiny amounts of crystalline phases of
371 hydration may have survived many years of exposure to weathering.
372 C-S-H, observed by electron microscopy (Figure 3h), was difficult to be

373 detected by XRPD because of its amorphous/paracrystalline nature. It is evident
374 from Table 3 that the amorphous fraction is more abundant when the content of
375 crystalline cement hydration products and residual clinker phases (occurring
376 often in conjunction) is high. When this happens (see for example, samples 9,
377 and 14), the carbonate fraction is low. Considering that carbonates are the main
378 deterioration products of the cement matrix, this is consistent with a lower degree
379 of alteration experienced by these samples. Accordingly, sample 14 showed the
380 highest weight fraction of hydrogarnet, CH and amorphous phase.

381

382 **Unreacted clinker phases**

383 Despite the common assumption that OPC can be considered virtually fully
384 hydrated within few years (Taylor 1997), evidence of unreacted clinker phases
385 (mainly belite and ferrite) have been reported for concretes several decades old,
386 or even intensely altered (Gao et al. 1999; Gebauer and Harnik 1975; Hearn et
387 al. 1994; Scrivener and Nonat 2011; Taylor et al. 2010). Occurrence of small
388 quantity of unreacted ferrite have been discussed in the literature (Hearn et al.
389 1994; Scrivener and Nonat 2011) suggesting that it is impossible to
390 unequivocally discern the crystalline nature of ferrite in hydrated samples by
391 means of EDS. Our results clearly indicate that the presence of unreacted clinker
392 phases is quite common in the matrix of CA. Their cumulative weight fraction
393 occasionally exceed 7 wt% (i.e. samples 2, 9, 12, 14, 21). Because of the
394 analytical technique employed, these findings are indisputable and refer to a
395 representative amount of sample.

396 In Figure 4a and b, residual round shaped belite crystals surrounded by
397 interstitial phase (ferrite and aluminate), and of ferrite as appearing in a polished
398 surface of sample 4, respectively, are depicted. The corresponding EDS point
399 analysis spectrum is reported in Supplementary Data Figure S2.

400 Before EBSD investigations, conducted on three representative samples (9,
401 12 and 14), preliminary explorative analyses by means BEI, showed a diffuse
402 presence of relict clinker grains in the CA matrix (Figure 6a, 7a and 8a). At
403 greater magnifications (Figure 6b, 7b and 8b), these relicts showed a peculiar
404 microstructure constituted by a nearly white skeleton of apparently totally non-
405 hydrated interstitial phase, enclosing dark grey areas of euhedral to subhedral
406 shape, suggesting a substitution pseudomorphosis of hydration products after
407 calcium silicates (alite and belite). The skeletal microstructure often showed
408 some small chemical heterogeneities at the micro-metric scale indicated by
409 different intensities in the backscattered electron emission, with areas appearing
410 slightly wither than the others due to the presence of heavier atoms. The
411 compositional heterogeneity was confirmed by micro-fluorescence analyses on
412 such relicts, being the slightly darker areas constituted mainly by calcium and
413 aluminum plus traces of alkalis, with an overall stoichiometry close to the one of
414 aluminate, while the slightly wither areas appear to be mainly constituted by
415 calcium, aluminum and iron, with an overall stoichiometry close to the one of
416 ferrite. The enclosed dark grey subhedral areas are mainly constituted by
417 calcium and silicon with a heterogeneous stoichiometry, typical of C-S-H phases.

418 The chemical data therefore seem to confirm the long permanence of the

419 interstitial phase in the anhydrous state, although only micro-mineralogical
420 analyses evidencing the crystal structure of the clinker phases would prove
421 unequivocally their nature, excluding pseudomorphosis or other substitutional
422 phenomena of AFm phases after aluminate and ferrite. In fact, EBSD analyses
423 on selected clinker relicts proved the crystalline nature of the white skeletal
424 portion, which gave sharp EBSP (Figure 6c-e, 7c-e, 8c-e). On the contrary, no
425 EBSP were observed from the dark grey subhedral areas, proving the
426 amorphous/paracrystalline nature of the constituting phases. All the EBSP
427 acquired from the white interstitial phase were successfully indexed with an
428 orthorhombic aluminate cell (Figure 6d, 7d, 8d) in the slightly darker areas, and
429 with while an orthorhombic ferrite cell for the whiter ones (Figure 6f, 7f, 8f): thus,
430 the analytical results confirmed unequivocally the mineralogical nature of the
431 analysed phases.

432

433 **Degradation of CA**

434 Despite the peculiar nature of CA, deterioration of the cement matrix has been
435 recognised similar to that reported for analogous matrices of other OPC-based
436 products (Bentur and Mindess, 2007; Dias et al. 2008; Spurny et al. 1989). Water
437 containing CO₂ brings Ca²⁺ ions into solution, dissolving cement hydration
438 products (Carde and Francois 1999, Faucon et al. 1996, 1998). Soft water may
439 also attack mineral fillers. Because of variation in the chemical environment,
440 calcite and ettringite re-precipitate inside the degraded layer (Faucon et al.
441 1998). CH and C-S-H also react with atmospheric CO₂, yielding calcium

442 carbonate (Johannesson and Utgennant 2001). Acid rain and/or aggressive
443 conditions are the cause of acid attack (Beddoe and Dorner 2005; Xie and Zhou
444 2004), leading to a progressive release of Ca^{2+} from CH and C–S–H. As pH
445 decreases, even the dissolution of ferrite or aluminate hydrates occurs,
446 prompting the release of Fe^{3+} and Al^{3+} . Ettringite and hydrogarnets can be
447 decomposed until a silica gel residue is obtained (Zivica and Bajza 2001). In
448 case of SO_x rich water, like acid rain, gypsum and sulphates precipitate with a
449 resulting increase in volume. Ettringite is formed initially at the expenses of Afm,
450 and later of gypsum, but, frequently both can occur at the same time (Brown and
451 Badger 2000), due to concentration gradients within the sample. The extent of
452 acid attack is ultimately controlled by the resulting pH values and by the
453 mineralogy of the system. For example, gypsum may be formed by reaction of
454 sulphuric acid with calcium carbonate. Gypsum, anhydrite and calcium sulphate
455 hemihydrate (bassanite) were frequently detected in CAs, but at concentration
456 usually less than 1 wt%. Other conditions, like abundance of chloride ion (e.g.
457 near to the sea) or the material being continuously wet (e.g. in cooling towers of
458 power stations) have been reported to increase weathering of CA (Sarkar et al.
459 1987). Alteration of organic nature, due to mushrooms and/or lichens, increases
460 the chemical dissolution of the surface layer and of chrysotile as well (Spurny et
461 al. 1989). Though the effect of Ca leaching may have masked that of other less
462 abundant elements (Wang et al. 2011), a depletion of Mg from the asbestos
463 fibres at the surface layers of CA, cannot be excluded (Spurny et al. 1989). EDS
464 point analyses did not clarify this point, but it should be noted that access at the

465 fibres lying at surface of samples, was prevented by the protective coating
466 applied during the removal procedures.

467 The main product of weathering observed in CA samples is calcite, its
468 presence is due to the carbonation of the cement matrix, a pervasive process in
469 which atmospheric CO₂ reacts with the cement fraction at the pore level, after
470 dissolution into the aqueous phase of the concrete pore solution. This means that
471 conditions of relative humidity >50% and/or presence of water are necessary for
472 the process to occur.

473 In 13 out of 29 samples, other forms of calcium carbonate were found to
474 coexist with calcite. Aragonite was frequently detected, with weight fractions
475 always lower than 3.5 wt%, but more frequently lower than 1.5 wt%. Precipitation
476 of aragonite has been related to carbonation of calcium-poor C-S-H phases, in
477 presence of amorphous silica (Grattan-Bellew 1996).

478 Vaterite, the least thermodynamically stable form of calcium carbonate, was
479 detected in sample 6. It is not clear whether the presence of calcium sulphates
480 could have favoured its precipitation (Black 2009). Vaterite has been recognized
481 to crystallize preferentially upon carbonation of a poorly crystalline CH and/or C-
482 S-H gel with high CaO/SiO₂ (C/S) ratio (Black et al. 2007). In aged samples,
483 vaterite is however thought to transform to calcite. Nonetheless, findings in old
484 CA slates have been documented (Dias et al. 2008; Sarkar et al. 1987).

485 Carbonation of ettringite has been inferred to be at the origin of calcium
486 sulphate dehydrate (anhydrite) in degraded CA (Dias et al. 2008), and the same
487 mechanisms have been invoked for the occurrence of anhydrite in old concrete

488 (Faucon et al. 1998). This may be an explanation for the absence of ettringite
489 and the occurrence of anhydrite in nearly all the samples investigated.

490 Jarosite ($\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$), in old concrete is scarcely documented (De
491 Ceukelaire 1991; Gregerova and Vsiansky 2009; Tazaki et al. 1992). Oxidation of
492 pyrite, introduced with the aggregate material, has been considered the plausible
493 source of iron. At completion, the process leads to precipitation of jarosite,
494 gypsum and amorphous ferric hydroxide (De Ceukelaire 1991). Owing to the
495 scarce mobility of iron, this mineral association is usually discovered near the
496 original pyritic material. In sample 12, containing 1.5 wt% of jarosite, no gypsum
497 was detected. This can be due to the fact that part of SO_4^{2-} needed for jarosite
498 crystallization, may have been supplied by the gypsum itself (De Ceukelaire
499 1991). Potassium may have been provided by the alteration of K-feldspar in the
500 same chemical environment. Sample 29 shows the concurrent presence of
501 jarosite and ettringite, suggesting the intervention of sulphate fluids during the life
502 history of this sample. At the same time, the high amorphous content, and a
503 fraction of CH, indicate a moderate degree of carbonation.

504 Alkali-silica reaction (ASR), involves systems containing aggregates potentially
505 reactive with alkaline fluids. They may undergo degradation to variable extent,
506 leading to expansion and cracks. A necessary condition for the process to occur,
507 is the presence of reactive aggregates, high content in alkali oxides and water
508 (Stark 2006; Taylor 1997). One of the effects of ASR, is the corrosion of quartz.
509 Examples were sometimes observed on quartz grains of CA. In Fig 4d, a
510 corroded quartz surface, resembling similar findings in concrete (Fernandes et al.

511 2004), is depicted. Feldspars, detected in this sample, may have been the source
512 of alkalis for the reaction (Stark 2006).

513 A correct identification of the alteration processes occurring in cement-
514 asbestos materials is a complicated task, also because the same microstructural
515 features and/or reaction products could be the result of different deterioration
516 mechanisms or sample history (Dias et al. 2008; Grattan-Bellew 1996). In spite of
517 this, a few indicators of the degree of alteration can be identified. Besides the
518 already discussed inverse correlation of carbonates with cement hydrated
519 phases, a further example is the positive correlation between the weight fractions
520 of carbonates and calcium sulphates. As showed in Table 3, when carbonates
521 are less than 30 wt%, no calcium sulphates are present; on the contrary, calcium
522 sulphates are at maximum in samples high in carbonates (i.e. samples 10 and
523 11).

524 In CAs, deterioration products other than calcite have been detected only at
525 low concentration, suggesting that carbonation was by far the prevalent
526 mechanism of weathering. Gypsum and ettringite, found in other CAs (Dias et al.
527 2008; Sarkar et al. 1987), are scarcely represented in our samples. The invoked
528 carbonation of ettringite (Dias et al. 2008), should have produced the
529 corresponding amounts of anhydrite, but anhydrite was always less than 1 wt%.
530 Nonetheless, as already noted, there are evidences supporting the view that, for
531 most samples, more than a single deterioration process has been involved. At
532 the level of the present investigation, no unique model for the mechanism of
533 deterioration can be proposed.

534 The chemistry of the investigated system (see Table 2) is dominated by Si,
535 Ca, and Mg but remarkable differences between samples exist. The observed
536 mineralogy can easily explain some of them. As an example, sample 12 is the
537 highest in silica because of its high initial quartz content; similarly, sample 18 is
538 low in magnesium because chrysotile content is negligible. In the case of sodium,
539 a rather good relationship is showed by sodium content and weight fraction of the
540 main Na-bearing phase: the feldspar albite ($\text{NaAlSi}_3\text{O}_8$). However, the same
541 rationale does not hold for other important elements like calcium, silicon and iron.
542 With the analytical methods employed, explaining their concentration in terms of
543 the observed mineralogy is largely prevented, because the chemical composition
544 of many phases, like ferrite, C-S-H, Afm, is variable from sample to sample and
545 within the same sample, depending upon a number of factors (age of sample,
546 initial composition, sample degradation, surrounding mineralogy). Moreover,
547 owing to their low degree of crystallinity, many phases were necessarily detected
548 as amorphous in XRPD, thus, no direct information on their chemical composition
549 can be obtained.

550

551 **Classification of CAs**

552 Classification of CAs has been attempted by means of the chemical
553 parameters. Owing to their peculiar mineralogy with respect to ordinary concrete
554 materials, the CaO-SiO₂-MgO (CMS) triangular diagram, reported in Figure 9,
555 has been chosen. Bulk compositions are plotted as molar fraction of each oxide.
556 Points representing stoichiometric compositions, together with stability fields of

557 phases at equilibrium (Jung et al. 2005), are indicated. This information is of
558 crucial importance when considering the already studied inertization of ACMs via
559 thermal treatment at 1200 °C (Gualtieri et al. 2008).

560 In the ternary phase diagram, points representing our samples can be viewed
561 as scattered along a line of roughly constant Mg molar fraction, crossing in turn
562 the stability fields of diopside ($\text{CaMgSi}_2\text{O}_6$), akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), merwinite
563 ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$), belite and periclase. Different positions along this line
564 correspond to different values of C/S molar ratio.

565 Three classes, identified by different symbols, having different C/S ratio and
566 dominant mineralogy have been recognized:

567 -Samples laying at the boundary between the stability field of belite and periclase
568 or well into the belite field (e.g. samples 18 and 21), and showing high C/S.

569 Corresponding points are depicted as grey dots in Figure 9.

570 -Samples falling prevalently into the stability field of merwinite, depicted as empty
571 triangles in Figure 9.

572 -Samples whose corresponding points lay inside the stability field of akermanite,
573 and diopside, with C/S below 1 (samples 10, 12, 16, 22, 24). They are
574 depicted as black squares in Figure 9.

575 Through this diagram, the chemistry of CAs can be linked to the mineralogical
576 character of CA after thermal treatment, allowing for a correct management, at
577 the industrial scale, of any high temperature inertization process of ACM (Viani et
578 al. 2013).

579

580

Conclusions

581 For the first time, a representative number of CA samples removed from
582 various locations in Italy, have been thoroughly characterized under their
583 mineralogical and chemical aspects. QPA conducted with the combined Rietveld-
584 RIR method evidenced that the amount of asbestos added during product
585 manufacturing, was highly variable. In 17 out of 29 samples, besides chrysotile
586 asbestos, the amphibole asbestos has been detected. Experimental evidence
587 confirmed the intentional addition of amphibole asbestos as a consolidated
588 practice in CA industry. Mineralogical composition revealed that various mineral
589 fillers have been added to the mix. In addition to ordinary OPC, composite
590 cements containing silica or blast furnace slags were certainly employed.

591 The presence of unreacted cement phases is confirmed using EBSD
592 combined with SEM observations, despite the long time since hydration and the
593 extensive occurrence of alteration. The detected amounts are as high as 7 wt%
594 by XRPD.

595 Several processes are recognized to have interested the samples to various
596 extent, with carbonation of the cement matrix being the most intense and
597 ubiquitous. However, owing to the different sample histories, definition of a
598 common model for the mechanism of deterioration was prevented.

599 Chemical parameters have been found useful for classify CA material. With
600 the aid of the CMS ternary phase diagram, chemical parameters were linked to
601 the mineralogy of the corresponding product of thermal inertization. XRF analysis
602 conducted on only three chemical elements, allows for a classification of CA.

603 These analyses, are an invaluable tool for the assessment of the sustainability of
604 every CA inertization process involving a thermal treatment.

605

606

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612

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819 **Figure Captions**

820 **Figure 1.** Picture of one sealed ACM package prior to sampling.

821

822 **Figure 2.** Example of Rietveld refinement of one of the CA samples studied.

823 Angular regions corresponding to Al sample holder reflections have been
824 excluded. Observed (crosses), calculated (continuous line), and difference
825 (bottom line) curves are reported. Vertical bars mark Bragg reflection positions
826 corresponding to the following phases: from top to bottom: corundum (internal
827 standard), hydrocalumite, quartz, calcite, amphibole, gypsum, belite β , chrysotile,
828 portlandite. In the enlarged portion of the low angle region of the powder
829 spectrum, from left to right, amphibole, hydrocalumite, gypsum and chrysotile
830 reflection peaks are shown.

831

832 **Figure 3.** High resolution SEM images of selected CA slate samples. (a)
833 chrysotile, Chr; (b) crocidolite, Cro; (c) quartz, Qz; (d) plagioclase, Plag; (e)
834 portlandite, CH; (f) gypsum C-SH₂; (g) lamellar portlandite crystals and acicular
835 ettringite crystals; (h) Calcium silicate hydrate (CSH) growing on a grain.

836

837 **Figure 4.** High resolution SEM images of selected CA slate samples: (a) round
838 shaped belite crystals (Bel); (b) ferrite crystal (C₄AF); (c) blast furnace slags
839 relics, reaction rims at the grain-matrix boundary are visible; (d) corrosion of
840 quartz surface likely due to the action of alkaline fluids.

841 **Figure 5.** Micro-Raman spectra of minerals from selected CA samples. Images

842 depict crystals onto which the laser beam has been focused. Band attribution
843 explained in the text.

844

845 **Figure 6.** Sample 9: low magnification BEI of the sample (a); high magnification
846 BEI of a relict clinker grain (b, tricalcium aluminate (C3A) and ferrite (C4AF)
847 phases are arrowed); EBSP, both raw (c) and indexed (d), of the arrowed
848 aluminate phase; EBSP, both raw (e) and indexed (f), of the arrowed ferrite
849 phase.

850

851 **Figure 7.** Sample 12: low magnification BEI of the sample (a); high magnification
852 BEI of a relict clinker grain (b, tricalcium aluminate (C3A) and ferrite (C4AF)
853 phases are arrowed); EBSP, both raw (c) and indexed (d), of the arrowed
854 aluminate phase; EBSP, both raw (e) and indexed (f), of the arrowed ferrite
855 phase.

856

857 **Figure 8.** Sample 14: low magnification BEI of the sample (a); high magnification
858 BEI of a relict clinker grain (b, tricalcium aluminate (C3A) and ferrite (C4AF)
859 phases are arrowed); EBSP, both raw (c) and indexed (d), of the arrowed
860 aluminate phase; EBSP, both raw (e) and indexed (f), of the arrowed ferrite
861 phase.

862

863 **Figure 9.** Points corresponding to samples under study in the CaO-MgO-SiO₂
864 system. Stability fields of phases are depicted. Ak, akermanite; Crs, cristobalite;

865 Di, diopside; Fo, forsterite; Bel, belite; Mnt, monticellite; Mrw, merwinite; Opx,
866 orthopyroxene; Per, periclase; Pig, pigeonite; Ppx, protopyroxene; Pwo,
867 pseudowollastonite; Tri, tridimyte; Wo, wollastonite. Empty circles mark points
868 corresponding to pure compositions.

869

870 **Supplementary Data Figure S1**

871 EDS spectra of minerals as showed in Figure 4. Arrows in inset images depicts
872 the point of analysis.

873 **Supplementary Data Figure S2**

874 EDS spectra of minerals as showed in Figure 5. Arrows in inset images depicts
875 the point of analysis.

876

Tables

Correction date January 18th 2013

Table 1. Nature and origin of cement-asbestos samples used in this study. Known dimensions of corrugated slates as follows: Samples 1-10, 15 = 1x1x2 m; Samples 11, 13, 16 = 1x1x1.5 m.

Sample	Location	Type
1	Sicily	c.*slab
2	Sicily	c.slabs
3	Sicily	c.slabs
4	Sicily	c.slabs
5	Sicily	c.slabs
6	Sicily	c.slabs
7	Lombardy	c.slabs
8	Lombardy	c.slabs
9	Piedmont	c.slabs
10	Piedmont	c.slabs
11	Lombardy	c.slabs
12	Lazio	board
13	Lombardy	c.slabs
14	Tuscany	pipe
15	Piedmont	c.slabs
16	Lombardy	c.slabs
17	Piedmont	c.slabs
18	n.a.	c.slabs
19	Campania	water tank
20	Campania	c.slabs
21	Campania	c.slabs
22	Campania	c.slabs
23	Campania	c.slabs
24	Lazio	c.slabs
25	Lazio	c.slabs
26	Emilia Romagna	c.slabs
27	Emilia Romagna	c.slabs
28	Emilia Romagna	c.slabs
29	Lombardy	c.slabs

*c. = cement

Table 2. Results of chemical analyses for the samples studied (values in wt%). Relative standard deviations were within 0,1%-0,6%.

Abbreviations used: L.O.I., loss on ignition.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	L.O.I.
1	30.5	0.21	4.36	2.38	0.07	5.71	27.2	0.73	0.68	0.08	0.70	27.4
2	24.0	0.16	3.08	1.19	0.03	6.24	35.4	0.08	0.10	0.15	1.05	28.6
3	24.2	0.22	3.22	1.33	0.05	6.69	33.7	0.00	0.00	0.10	2.83	27.7
4	22.6	0.22	2.58	1.39	0.03	5.91	32.0	0.18	0.44	0.13	2.39	32.1
5	23.4	0.23	3.01	1.43	0.04	6.15	33.1	0.00	0.04	0.13	2.17	30.4
6	25.3	0.35	4.53	2.56	0.05	5.09	30.1	0.61	0.29	0.12	1.08	29.9
7	26.8	0.12	2.83	1.45	0.11	7.00	35.8	0.00	0.02	0.08	1.38	24.5
8	22.1	0.11	1.85	0.91	0.04	8.21	31.5	0.07	0.33	0.03	1.67	33.1
9	28.7	0.15	3.66	1.03	0.13	7.15	34.7	0.03	0.09	0.08	1.57	22.8
10	34.3	0.14	3.24	1.97	0.06	4.75	26.7	0.49	0.74	0.08	1.41	26.1
11	28.3	0.13	2.89	1.51	0.04	6.00	28.6	0.29	0.49	0.11	1.79	29.8
12	45.2	0.20	2.50	2.08	0.04	7.19	27.2	0.15	0.04	0.26	0.53	14.6
13	28.8	0.16	3.30	2.38	0.04	6.05	28.1	0.21	0.20	0.15	0.60	30.0
14	27.9	0.13	2.77	2.36	0.04	7.69	37.0	0.25	0.03	0.14	0.87	20.9
15	27.6	0.13	2.74	2.21	0.08	5.62	29.5	0.20	0.45	0.08	0.81	30.6
16	32.9	0.15	3.55	1.38	0.06	6.79	28.0	0.39	0.48	0.07	0.87	25.3
17	26.2	0.19	4.06	1.95	0.07	4.55	29.2	0.46	1.04	0.10	4.16	28.0
18	21.8	0.13	2.70	1.26	0.15	2.45	34.6	0.11	0.36	0.11	3.18	33.1
19	21.9	0.14	2.80	1.71	0.08	5.38	34.1	0.02	0.04	0.10	3.27	30.4
20	29.2	0.15	3.20	1.61	0.04	7.01	28.3	0.27	0.23	0.08	0.50	29.5
21	25.6	0.13	2.60	1.45	0.07	4.38	38.4	0.18	0.14	0.10	1.12	25.9
22	31.5	0.15	3.06	1.99	0.04	5.39	28.1	0.52	0.54	0.09	0.58	28.0
23	24.8	0.15	3.66	1.59	0.09	5.74	36.8	0.00	0.01	0.05	1.96	25.1
24	31.5	0.14	3.41	3.23	0.09	5.13	26.7	0.58	0.49	0.08	0.28	28.5
25	22.7	0.12	2.14	1.21	0.04	5.70	36.5	0.02	0.06	0.04	1.94	29.5
26	25.7	0.15	2.63	1.08	0.04	6.27	32.7	0.15	0.34	0.03	4.41	26.4

27	28.3	0.14	2.93	2.62	0.04	5.48	27.9	0.61	0.60	0.17	1.65	29.6
28	22.1	0.12	1.9	0.64	0.04	7.86	32.3	0.01	0.11	0.04	0.59	34.4
29	23.6	0.14	2.4	0.88	0.04	7.72	35.2	0.03	0.03	0.07	1.27	28.7

Table 3. Results of the quantitative phase analyses of the ACM samples studied (values in wt%). Abbreviations used: AFmc, calcium monocarboaluminate hydrate.

	1	2	3	4	5	6	7
Chrysotile	10.9 (3)	11.1 (4)	4.9 (4)	11.6 (4)	8.9 (3)	5.6 (3)	8.5 (4)
Amphibole	1.9 (2)	-	-	-	-	1.4 (2)	2.0 (1)
Calcite	54.3 (1)	46.9 (1)	37.9 (1)	67.0 (1)	58.7 (1)	43.6 (1)	49.9 (1)
Vaterite	-	-	-	-	-	13.8 (2)	-
Aragonite	-	1.7 (1)	0.4 (1)	1.5 (1)	1.4 (1)	1.2 (1)	1.3 (1)
Dolomite	-	-	-	-	-	-	-
Quartz	7.2 (1)	1.4 (1)	0.8 (1)	5.0 (1)	1.1 (1)	-	1.4 (1)
Plagioclase	5.3 (2)	-	-	-	-	5.2 (1)	-
K-Feldspar	1.6 (1)	-	-	-	-	-	-
Leucite	-	-	-	-	-	-	-
Wollastonite	-	-	-	-	-	-	-
Mica + Illite	0.9 (2)	-	-	-	-	-	-
Belite β	1.0 (2)	7.1 (2)	4.2 (1)	1.6 (2)	2.2 (1)	-	3.3 (1)
Alite M_3	-	-	-	-	-	-	-
Ferrite	-	1.1 (1)	-	1.7 (1)	0.9 (1)	1.0 (2)	-
Aluminate	-	0.7(1)	0.8(1)	-	-	1.3(1)	-
Gypsum	< 0.5	-	0.4 (1)	1.6 (1)	-	-	-
Bassanite	< 0.5	0.9 (1)	-	-	0.9 (1)	1.1 (1)	-
Anhydrite	-	-	-	0.4 (1)	-	-	-
Portlandite	-	-	0.5 (1)	-	-	-	2.0 (1)
Jarosite	-	-	-	-	-	-	-
Hydrocalumite	-	-	1.5 (1)	-	-	-	-
Ettringite	-	-	-	-	-	-	-
Hydrogarnets	-	-	-	-	-	-	-
AFmc	-	-	< 0.5	< 0.5	0.5 (1)	-	0.5 (1)
Amorphous	16.8 (5)	29.1 (5)	48.9 (5)	9.5 (5)	25.4 (4)	25.8 (4)	31.1 (4)

	8	9	10	11	12	13	14
Chrysotile	12.0 (3)	4.9 (5)	8.9 (4)	7.2 (4)	9.5 (6)	11.1 (4)	3.4 (4)
Amphibole	-	-	1.4 (2)	-	-	1.5 (2)	6.5 (3)
Calcite	61.6 (1)	24.2 (1)	49.3 (1)	48.9 (1)	3.8 (4)	53.6 (1)	3.0 (1)
Vaterite	-	-	-	-	-	-	-
Aragonite	1.5 (1)	0.6 (1)	-	-	-	-	-
Dolomite	2.3 (1)	-	-	-	-	-	-
Quartz	0.2 (1)	1.2 (1)	14.2 (1)	3.3 (1)	19.0 (1)	4.5 (1)	-
Plagioclase	-	-	2.8 (2)	0.7 (1)	-	1.4 (1)	-
K-Feldspar	-	-	2.9 (4)	1.8 (2)	2.5 (3)	-	-
Leucite	-	-	-	-	-	-	-
Wollastonite	-	-	-	-	-	-	0.9 (2)
Mica + Illite	-	-	< 0.5	-	-	-	-
Belite β	2.2 (1)	5.5 (1)	-	-	5.4 (2)	-	2.0 (2)
Alite M_3	-	1.6 (1)	-	-	2.4 (1)	-	2.8 (2)
Ferrite	-	-	-	0.8 (1)	1.0 (1)	-	2.5 (1)
Aluminate	0.6(1)	0.3(1)	-	-	1.1(2)	-	-
Gypsum	-	-	-	-	-	-	-
Bassanite	0.6 (1)	-	3.3 (2)	5.2 (1)	-	0.6 (1)	-
Anhydrite	-	-	-	-	-	-	-
Portlandite	-	4.0 (1)	-	-	-	-	10.9 (1)
Jarosite	-	-	-	-	1.8 (1)	-	-
Hydrocalumite	-	< 0.5	-	-	-	0.3 (1)	< 0.5
Ettringite	-	0.4 (1)	-	-	-	-	-
Hydrogarnets	-	0.5 (1)	-	-	-	-	2.0 (1)
AFmc	-	-	< 0.5	-	-	-	-
Amorphous	19.2 (4)	56.8 (6)	17.4 (5)	32.1 (5)	53.9 (8)	26.9 (4)	66.6 (9)

	15	16	17	18	19	20	21
Chrysotile	13.2 (4)	11.3 (5)	10.3 (4)	1.4 (2)	10.6 (4)	8.9 (3)	5.3 (4)
Amphibole	3.2 (3)	-	1.9 (3)	-	1.6 (3)	0.8 (1)	1.7 (2)
Calcite	60.5 (1)	39.5 (1)	58.6 (1)	57.0 (1)	65.6 (1)	51.2 (1)	42.4 (1)
Vaterite	-	-	-	-	-	-	-
Aragonite	0.2 (1)	-	-	-	-	1.2 (1)	2.7 (1)
Dolomite	0.1 (1)	-	-	1.0 (1)	-	-	-
Quartz	1.8 (1)	9.2 (1)	4.4 (1)	0.1 (1)	2.2 (1)	4.1 (1)	1.4 (1)
Plagioclase	-	1.9 (3)	2.4 (2)	-	-	2.1 (1)	-
K-Feldspar	-	1.4 (1)	-	-	-	-	-
Leucite	0.3 (1)	-	0.5 (1)	-	-	-	-
Wollastonite	-	-	-	-	-	-	-
Mica + Illite	-	0.6 (2)	1.5 (2)	-	1.1 (1)	2.2 (2)	-
Belite β	-	2.7 (1)	-	2.9 (1)	-	-	7.1 (2)
Alite M_3	-	-	-	-	-	-	3.6 (1)
Ferrite	0.8 (1)	-	-	0.7 (1)	1.5 (1)	-	-
Aluminate	-	-	-	0.5(1)	-	-	-
Gypsum	-	-	-	-	< 0.5	-	-
Bassanite	-	-	1.3 (1)	-	-	-	-
Anhydrite	-	-	-	0.3 (1)	-	-	-
Portlandite	-	0.8 (1)	-	-	-	-	1.9 (1)
Jarosite	-	-	-	-	-	-	-
Hydrocalumite	< 0.5	< 0.5	-	-	-	-	-
Ettringite	-	-	-	-	-	-	-
Hydrogarnets	-	-	-	-	-	-	-
AFmc	-	-	< 0.5	-	-	2.0 (1)	-
Amorphous	20.0 (4)	32.7 (6)	19.1 (5)	36.1 (3)	17.4 (4)	27.6 (4)	33.9 (5)

	22	23	24	25	26	27	28	29
Chrysotile	8.3 (4)	3.9 (4)	8.2 (4)	2.9 (5)	5.1 (5)	11.8 (4)	13.3 (3)	5.9 (4)
Amphibole	2.0 (3)	1.5 (3)	2.8 (3)	0.7 (1)	-	3.1 (3)	-	2.7 (2)
Calcite	58.3 (1)	43.9 (1)	52.5 (1)	44.6 (1)	34.3 (1)	55.7 (1)	68.8 (1)	45.4 (1)
Vaterite	-	-	-	-	-	-	-	-
Aragonite	-	-	< 0.5	-	-	-	3.6 (2)	-
Dolomite	-	-	-	2.5 (1)	-	-	2.5 (1)	0.9 (2)
Quartz	5.8 (1)	1.6 (2)	5.2 (1)	0.3 (1)	2.6 (1)	5.1 (1)	0.1 (1)	0.3 (1)
Plagioclase	0.9 (2)	-	2.9 (1)	-	0.8 (1)	2.0 (1)	-	-
K-Feldspar	1.2 (2)	-	-	-	-	-	-	-
Leucite	-	-	-	-	-	-	-	-
Wollastonite	-	-	-	-	-	-	-	-
Mica + Illite	1.8 (2)	-	1.8 (2)	-	1.6 (2)	1.7 (2)	-	-
Belite β	-	4.3 (1)	-	5.6 (1)	4.1 (1)	-	0.5 (1)	2.7 (1)
Alite M ₃	-	-	-	-	-	-	-	-
Ferrite	-	-	-	-	-	1.1 (1)	-	-
Aluminate	-	0.8(1)	-	-	0.4(2)	-	-	0.3 (1)
Gypsum	-	0.6 (1)	-	-	-	-	0.3 (1)	< 0.5
Bassanite	-	-	-	-	1.8 (1)	-	-	-
Anhydrite	0.3 (1)	-	-	-	-	-	0.3 (1)	-
Portlandite	-	2.2 (1)	-	3.6 (1)	1.6 (1)	-	-	1.5 (1)
Jarosite	-	-	-	-	-	-	-	0.5 (1)
Hydrocalumite	-	1.1 (1)	-	< 0.5	< 0.5	< 0.5	-	-
Ettringite	-	-	-	-	-	-	-	2.5 (1)
Hydrogarnets	-	-	0.3 (1)	0.2 (1)	-	0.2(1)	-	-
AFmc	-	-	1.0 (1)	-	0.7 (1)	-	-	-
Amorphous	21.4 (5)	40.1 (5)	25.2 (5)	39.7 (6)	47.1 (6)	19.4 (5)	10.7 (4)	37.2 (5)

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