

1 **Characterization of halloysite (North East Rif, Morocco): evaluation of**
2 **its suitability for ceramic industry**

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17 **ABSTRACT:** Halloysite from Nador (NE Morocco) has been studied to
18 evaluate their suitability in ceramic industry. Cross-section involving all the
19 Messinian facies was performed in the Melilla Neogene basin, at the foot of
20 the Gourougou volcano, in order to understand the origin of the halloysite
21 and appreciate its reserves. White layers of halloysite and red clays rich in

22 smectite occurred in contact with basal reef limestone, were characterized
23 by mineralogical (XRD, IR), textural (SEM) and physico-chemical analyzes
24 (grain-size, Atterberg limits, ATD/TG, XRF and specific surface area).
25 Ceramic proprieties were evaluated for fired halloysite from 500 to 1100°C
26 in order to appreciate technical processing for ceramic production.

27 The halloysite consists of fine particles with a high plasticity and a large
28 specific surface area. XRD results revealed the presence of 7Å non-hydrated
29 halloysite with the presence of gibbsite, alunite, K-feldspar plus other minor
30 phases, and traces of smectite and illite.

31 Infrared spectroscopy confirms the occurrence of characteristic bands of
32 halloysite at 3695 and 3618 cm^{-1} . SEM observations confirmed the
33 predominance of tubular facies typical of halloysite. The chemical analysis
34 revealed high aluminum content linked to the presence of some aluminous
35 phases (gibbsite and alunite). ATD/TG and XRD results of fired clay
36 sample evidenced halloysite dehydroxylation and a rearrangement of
37 metakaolinite to form mullite and spinel from 975°C.

38 Moroccan halloysite has good properties for refractory ceramic application.
39 However, quartz sand addition is required to avoid any cracks development
40 at firing as well as to reduce the plastic behaviour of raw halloysite and
41 minimize shrinkage during sintering.

42 **Keywords:** Halloysite, Morocco, Nador, Messinian, physico-chemical
43 properties, ceramic, mullite.

44

45 INTRODUCTION

46 Halloysite is typically formed by hydrothermal alteration of aluminosilicate
47 minerals. It occurs in association with dickite, kaolinite, montmorillonite
48 and other clay minerals (El Amrani El Hassani & Sadic, 2016). According
49 to Blanc et al., (2006), kaolinite would be the most stable clay ($\Delta H_f = -$
50 4115.30 kJ/mol, $\Delta G_f = -3793.93$), followed by dickite ($\Delta H_f = -4099.80$
51 kJ/mol, $\Delta G_f = -3777.30$) and halloysite ($\Delta H_f = -4092.93$ kJ/mol, $\Delta G_f = -$
52 3771.95); this might explain the scarcity of halloysite. Hollow tubular
53 structure constitutes the predominant and chemically stable form of
54 halloysite. Depending on humidity, halloysite occurs naturally in two
55 different forms (Joussein et al., 2005): the hydrated form ($n = 2$), in which
56 the sheets are separated by water molecules layer, with an equidistance
57 (d_{001}) close to 10\AA and meta-halloysite, which is the most common of the
58 halloysite, with an interfoliar distance close to 7.15\AA similar to kaolinite.
59 The latter is obtained by irreversible dehydration of the 10\AA halloysite
60 between 60 and $100\text{ }^\circ\text{C}$ (Ruiz-Hitzky et al., 2008). Decipher between
61 kaolinite and halloysite forms based only on XRD spectra is challenging,
62 and request some morphological observations (Singer et al., 2004; Joussein

63 et al., 2005). The halloysite has a tube-like shape, which is different from
64 the hexagonal platelets of kaolinite, gives it the capability to retain water
65 (Giese, 1988, Caillère et al., 1982, Pasbakhsh et al., 2013; Bain, 1971). The
66 tubes have multi-layer walls with positively charged Al-OH on the inner
67 surface and negatively charged Si-OH on the outer surface (Shchukin et al
68 2005).

69 Halloysite has several industrial applications (Zhou & Keeling, 2013,
70 Schroeder & Erickson, 2014, Churchman et al., 2016), particularly in
71 ceramics industry. A growing demand for this raw material is in general
72 observed (Detellier & Schoonheydt, 2014, Pracejus et al., 2017). Recently,
73 due to its specific morphology and properties, several studies have aimed to
74 widen its application fields, to high technology application as support for
75 catalysts and other functional materials (Lu et al., 2016). It is also capable of
76 storing a large quantity of hydrogen molecules (Jin et al., 2014), drugs for
77 medical purposes (Lvov et al., 2008, Tan et al., 2014, Yuan et al., 2012), to
78 form antibacterial biological membranes (Chen et al., 2012; Zhang et al.,
79 2013; Jin et al., 2014) and polymer-based composites (Abdullayev et al.,
80 2013; Pan et al., 2011; Zhou et al., 2010). Halloysite is also a major
81 absorber for cationic and anionic molecules (Zhao et al., 2010a, Abdullayev
82 & Lvov, 2010, Luo et al., 2010, Zhao et al., 2010b). It also applied in nano-
83 composites (Tan et al., 2014), like in other technological uses (Williams &
84 Hillier, 2014).

85 In Morocco, the halloysite deposit is located only in the North Eastern in the
86 Nador region (El Amrani El Hassani & Sadic, 2016). Within the Gourougou
87 area, a large volcanic deposit dated from middle-Miocene to late Pliocene, is
88 located the Maaza valley (Fig. 1). The halloysite occurs in thin layers
89 (decimetric) in contact with the reefal limestone, cinerites and volcanic
90 gravels. Despite the scientific and economic interest of this natural resource,
91 in comparison with other countries, Moroccan's halloysite investigations are
92 still lacking. Several geological studies were undertaken in this region
93 (Jeannette, 1958; Vivaldi & Vilchez, 1958; Vilchez, 1961; Azdimousa,
94 1991). In the point of view of sedimentology, Martin Vivaldi (1961)
95 outlined that Maaza deposits is composed of a mixture of endellite,
96 halloysite, gibbsite, montmorillonite and alunite, probably of hydrothermal
97 origin.

98 The main aim of this study was to promote these halloysite deposits as well
99 as to update the state of knowledge on its geological context, its
100 mineralogical nature, and its physico-chemical and thermal properties.
101 Furthermore, the various properties necessary to consider the valuation of
102 halloysite in the field of ceramics were investigated.

103

104 **MATERIAL AND METHODS**

105 *Material*

106 The halloysite deposit is located in the southern part of the Neogene basin of
107 Melilla (NE Morocco), at the foot of the Gourougou volcano, in the Maaza
108 valley (N: 35°16'43.751'' W: 3°01'20.865'') (Fig. 1). The Melilla Basin
109 genesis is related to the main orogenic movements of the Rif domain during
110 the Middle Miocene (Choubert et al., 1968, Guillemin & Houzay, 1982).
111 The opening of this basin is in relation with strike-slip faulting which marks
112 the eastern limit of Alboran basin, following the tectonic directions
113 established during the collision of internal zones of the Rif domain (García-
114 Dueñas et al., 1992). The Melilla Basin is generally characterized by three
115 major sedimentary cycles: (1) upper Tortonian marls, associated with
116 volcanic events; (2) Messinian unconformably overlies the Tortonian
117 deposits, reflecting an open sea environment with normal salinity; (3) early
118 Pliocene corresponds to a shallow marine incursion during the late
119 Messinian seawater evaporation.

120 The halloysite deposit belongs to the Neogene basin, located at the base of
121 the Messinian series between marl which takes a reef-like appearance here,
122 cinerite and red volcanic rounded gravel of millimetric-sized fragments
123 from the Gourougou volcano (Guillemin & Houzay 1982). The halloysite is
124 in the form of clusters or irregular lenses in contact with travertine situated
125 at the base of the reef series, associated with a gray-colored alunite (Hilali &
126 Jeannette, 1981). Halloysite lenses can reach one or two decimeters,
127 intersecting the reef limestone at the base of the series (Figs. 2 and 3).

128 Cross-section involving all the facies described above was performed in the
129 region (Fig. 3). Due the homogeneity of the halloysite deposit, a
130 representative sample of 2 kg was sampled. Red clay, in contact with
131 volcanic sandstone and reef formation, was also sampled.

132

133 *Experimental procedures*

134 *Mineralogical and chemical analysis*

135 The bulk sample was dried in an oven at 40 °C and then ground to < 250 µm
136 size fraction. The mineralogical phases present in the shards were identified
137 by X-ray diffraction using a powder Brucker D8-Advance diffractometer,
138 with copper anticathode (University of Liege, Belgium). The angular range
139 explored is located between 5° and 60° 2θ. The X-ray patterns were treated
140 by the DIFFRACplus EVA software to remove the background noise and to
141 calculate profile parameters such as line positions and intensity peaks.
142 Minerals phases were determined semi-quantitatively (± 5%). Additional
143 measurements were performed on oriented aggregates (Moore & Reynolds,
144 1989) prepared from the < 2 mm fraction obtained by suspension in distilled
145 water of 1g of the bulk sample. The suspension was first sieved at 63 µm to
146 limit particle settling during decantation and to reduce the amount of
147 impurities within the clay aggregates. The < 2 µm fraction was taken from
148 the suspension according to Stoke's law, placed on a glass slide and the

149 XRD patterns recorded between 2° and 30° 2theta using the same step size
150 and time per step parameters mentioned before. These oriented aggregates
151 were subjected to three successive treatments, air drying, glycolation and
152 heating to 500°C for 4 h, to identify the minerals of the clay-size fraction.

153 Chemical composition of major elements was carried out by X-Ray
154 Fluorescence spectroscopy (XRF) using a Panalytical Axios spectrometer
155 equipped with Rh-tube. The gas used is argon-methane and the data
156 program of treatment is IQ+ (University of Liege, Belgium).

157 Fourier transform infra-red (FTIR) were performed on the < 150 mm
158 fraction with a Fourier Transform Spectrometer Nicolet NEXUS type
159 (University of Liege, Belgium). The spectra were acquired on a mixture
160 containing 15% of the clay powder with oven-dried KBr. The spectra,
161 recorded from 4000 cm⁻¹ to 600 cm⁻¹ with a resolution of 4 cm⁻¹, were
162 obtained by accumulating 200 scans.

163 Thermal analysis ATG/DSC was carried out using an STA PT1600 (STA
164 Simultaneous Thermal Analysis - ATG/DSC) type under atmosphere
165 conditions (Mohammed V University of Rabat, Morocco). The sample was
166 heated from room temperature to 1000 °C with a rate of 10 °C/min.

167 Scanning electron microscopy (SEM) images were performed on clay
168 fraction and sintered clay by using a Philips microscope model XL30
169 (University of Liege, Belgium). Phase identification of the clay was also

170 determined by energy-dispersive X-ray spectroscopy (EDX). The images
171 were obtained with a secondary electron detector at a voltage of 10 kV. The
172 < 250 mm fraction was dispersed over a sample holder and gold-sputtered
173 for (EDX) analysis.

174

175 *Physical and textural analyses*

176 The grain-size distribution is carried out on bulk sample using a particle
177 analyzer by laser diffraction (Malvern Mastersizer 2000). The evaluation of
178 the plasticity and the limits of Atterberg determination were carried out by
179 the of Casagrande method (University of Liege, Belgium).

180 The blue methylene value (VBS) was determined in order to evaluate the
181 capacity of clay to absorb cations from a solution, and thereby predict how
182 the clay will react, based on the property of clays known as cation-exchange
183 capacity. The number of ions available for this exchange values depends on
184 the amount and characteristics of clays minerals, cation exchange capacity
185 and specific surface area. (Mohamed 1^{er} University of Oujda, Morocco)

186

187 *Ceramic proprieties*

188 Ceramic tests require the preparation of specimens (100 × 50 × 10 mm)
189 using a 100 MP press. The drying shrinkage (up to 110°C) and firing
190 shrinkage were obtained according to the relative variation in the length of

191 the specimen. They were thus defined: drying shrinkage = $100(L_p - L_d)/L_p$
192 and firing shrinkage = $100(L_m - L_f)/L_m$, where L_m is the length of the mould
193 and L_p , L_d and L_f are the length of the pressed, dried and fired specimens
194 respectively. The firing shrinkage and bending strength were determined
195 using ASTM norm C326-03 and C674-88 respectively.

196

197 **RESULTS**

198 *Lithological description*

199 The Maaza Valley belongs to the Messinian sedimentary basin (Fig. 1).
200 From lithological point of view, the cross-section performed in the region
201 consists of reef limestone with gorgonians, Gastropods and Lamellibranchs.
202 The later are surmounted by red clays with whitish horizons covered by
203 coarse volcanic sands. Pyroclasts and clays with intercalations of gravel
204 layers with rounded pebbles were then deposited (Fig. 2). At the top, a
205 basaltic flow ends the series. The recorded observations (Figs. 2 and 3),
206 display that the layer of halloysite thick from 25 cm to 130 cm, is not
207 strictly interstratified between limestone reef and volcanic sand, but is
208 wedge-shaped in contact with reef limestone and travertine.

209 *Halloysite characteristics*

210 The XRD results obtained on halloysite sample reveal that it is dominated
211 by clay fraction (total clay, 74%) (Table 1). The raw clay also contains

212 gibbsite, k-feldspar (sanidine), alunite and some small amount of tridymite,
213 fluorite and halite. The red clay sample is mainly composed of total clay
214 fraction (60%), K-feldspar (18%), goethite (10%) and traces of quartz and
215 hematite.

216 Regarding the clay fraction ($< 2\mu\text{m}$), the results (Table 1, Fig. 4) indicate
217 that the clay minerals are essentially represented by dehydrated halloysite. It
218 is characterized by a peak around 7.15\AA under air dried (N) and ethylene
219 glycol saturation conditions (EG) and disappears after heating to $500\text{ }^{\circ}\text{C}$.
220 The (001) halloysite peak is sharp and symmetric suggesting its neoformed
221 origin. The patterns reveal the presence in very small proportion of smectite
222 and illite. Contrary to halloysite sample, illite and smectite are detrital due
223 to the broad peaks at 14\AA and 10\AA , respectively. The red clay sample is
224 mostly made by 60% of clay fraction, including smectite (96%) with traces
225 of illite and kaolinite/halloysite. The sharp (001) peak at $\sim 14\text{ \AA}$ indicates the
226 neoformed origin of smectite (Fig. 4).

227 Chemical composition of halloysite sample is dominated by SiO_2 (37.1%)
228 and Al_2O_3 (37.4%), while red clay sample is enriched in SiO_2 (54.1%) with
229 16.6% of Al_2O_3 (Table 1). In addition, Fe_2O_3 content is higher for red clay
230 (4.0%) than in halloysite sample (0.5%), which explains the white color of
231 halloysite. K_2O , MgO , CaO , TiO_2 and SO_3 are also present in both samples
232 but as small amount. It is noted that these elements are slightly higher in red
233 clay than halloysite sample, except for SO_3 (1.6%) which is higher for

234 halloysite sample. The loss on ignition at 1000°C is relatively high (18%) in
235 the halloysite sample, related to the high amount of halloysite
236 (dehydroxylation) and the presence of aluminum hydroxide as gibbsite
237 which loss its mass during heating.

238 The infrared analyzes (FTIR) of halloysite sample display several
239 absorption bands which are reported in table 3. In the interval (between 400
240 and 4000 cm^{-1}), two types of characteristic vibrations are mainly observed:
241 elongation vibrations and vibrations deformation. The obtained bands are
242 slightly shifted compared to kaolinite ones, in addition to two others bands
243 are recorded in the sample at 3695 and 3618 cm^{-1} . The characteristic peaks
244 of halloysite were observed at 1033 cm^{-1} for Si-O-Si vibration and at 3695
245 cm^{-1} for Al-OH vibration (Abdullah et al., 2015, Muthu et al., 2016). In
246 good agreement with the dehydrated halloysite spectra published by Anton
247 & Rouxhet (1977), studied halloysite presents two bands of vibration with
248 almost equal intensities, located respectively at 3695 cm^{-1} (external
249 hydroxyls) and 3618 cm^{-1} (internal hydroxyls).

250 The SEM images (Fig. 5) indicate that the white clay sample consists of
251 tubular-facies, sometimes agglomerated, typical of halloysite having a
252 diameter of 0.15 μm and a length of 600 μm in average. This result is in
253 agreement with halloysite dimensions established by Bordeepong et al.,
254 (2011) but higher than those found by Lvov & Abdullayev (2013). EDX

255 analysis displays that the sample contains in addition to silicon and
256 aluminum, other elements as iron, sodium, potassium, chlorine and fluoride.

257 The physical properties of halloysite sample are reported in the Table 1.
258 Halloysite sample is made by clayey silt with 62% and 38% of clay and silt
259 fraction, respectively. The Atterberg limits indicate a high liquid limit
260 (70%), plastic limit (38.5%) and plastic index (31.5%). According to
261 Casagrande (1947), this sample has a plastic behavior indicated by a fairly
262 high plasticity index. The halloysite sample has a fairly large specific
263 surface area (55.48 m²/g) compared to that for kaolin clay (10-30 m²/g).
264 This great value is explained by the dominance of the clay fraction and by
265 the minority content of non-clay minerals. Halloysite has higher plastic
266 limits (60-70) compared with those of kaolinite (40-60), due to the special
267 tubular form and trough-like form of the clay mineral constitutes the main
268 cause of the water retention properties of halloysite (Bain, 1971).

269 Differential thermogravimetric and thermal (ATD/TG) analysis indicate
270 three endothermic and exothermic peaks (Table 3), which is typical of those
271 of kaolinitic clays (Rollet & Bouaziz, 1972, Aliprandi, 1996, Jouenne,
272 1990). The endothermic peak at ~100 °C is due to the loss of water. For the
273 endothermic peak that appears at ~304 °C, it was highlighted by Martin
274 Vivaldi & Girela Vilchez (1958) on samples rich in gibbsite. The
275 endothermic peak at 534 °C is characteristic of the kaolin group, and is
276 attributed to the transformation of halloysite to metakaolinite (e.g, Minato &

277 Aoki, 1979; Caillere, 1982, Johnson, 1990, Prodanovic et al., 1997). The
278 exothermic peak at 975 °C is due to the formation of mullite, pseudo-
279 mullite, spinel, amorphous silica and $\gamma\text{Al}_2\text{O}_3$ (Földvári, 2011).

280

281 *Ceramic properties*

282 The drying shrinkage is relatively low having about 0.5% of initial length of
283 the halloysite bodies (Table 1). While, a high shrinkage of about 7.5% is
284 recorded for specimen fired at 1100°C, that can be attributed to the loss of
285 water and other volatile as well as to the sample melting. Linear shrinkage is
286 a parameter which influences the reactivity of a material during firing.
287 Generally, linear shrinkage increases as firing temperature increases. The
288 increase in linear shrinkage means that a chemical transformation has taken
289 place in the material. This change is associated with a flexural strength of
290 16.3 MPa. SEM analysis allows us to examine microstructure of the sintered
291 bodies. Micrographs of heated halloysite bodies at 1100 °C do not evidence
292 any tubular structure of halloysite (Fig. 8). The structure becomes more
293 complex, with two forms of mullite: a cuboidal aspect, also called "primary
294 mullite", and a needle-shaped mullite crystals or "secondary mullite". A
295 heterogeneous microstructure is observed at 1100°C that arises from mixing
296 and agglomeration of the original materials with more elongated tabular
297 mullite in a glassy matrix than cuboidal form.

298

299 **DISCUSSION**

300 *Genesis of halloysite*

301 Fieldwork investigations indicate that fine white clay develops in contact
302 with carbonate formations (reef limestone and travertine) and sandy layers
303 (Figs. 2 and 3). This results from the gradual dissolution of calcite by acidic
304 fluids rich in CO₂. The CO₂ comes from the atmosphere as well as derived
305 from the leaching of the overlying sedimentary cover (karstification). The
306 gradual dissolution of calcite generates a significant porosity in the reef
307 limestone, improving the drainage and circulation of the weathering solution
308 through the karst filling. The occurrence of lenticular shaped halloysite
309 suggests its neoformed origin involving a transfer of silica and aluminum
310 from volcanic ash from the Gourougou volcano. Mineralogical results
311 obtained from red clay indicated the neoformed origin of smectite due to its
312 (001) sharp peak. Likewise, the XRD spectra confirm that the halloysite is
313 neoformed (Fig. 4). However, the occurrence of illite and smectite in white
314 sample, and illite and kaolinite in red sample, suggest their inherited origin
315 from parent rock, namely reef limestone and volcanic sandstone (Fig. 2). It
316 is known that hydrothermal alteration of volcanic host rocks involves the
317 replacement of primary igneous minerals and glass (e.g. plagioclase,
318 orthoclase, quartz, biotite, muscovite, amphibole and pyroxene), other forms
319 of silica (e.g. illite, smectite, chlorite, serpentine, albite, carbonates, talc,

320 kaolinite), sulfates (anhydrite, barite, alunite, jarosite) and oxides
321 (magnetite, hematite, goethite) (Shanks et al., 2012). Consequently the
322 presence of inherited illite, smectite and kaolinite as well as gibbsite and
323 alunite allows us to confirm the volcanic origin of the halloysite through the
324 hydrothermal circulation of fluid rich in sulphur. Ishikawa Alteration Index
325 (AI) is 37 for red clay and 72 for halloysite sample indicates that both
326 samples have experienced hydrothermal alteration (Ishikawa et al., 1976).
327 Vivaldi & Vilchez (1958) have demonstrated the evolution of silico-
328 aluminous amorphous phases (allophane) to well-crystallized minerals by
329 release of silica and alumina, mainly (halloysite, gibbsite and alunite) as the
330 following reaction: volcanic ash \rightarrow silico-aluminous amorphous minerals
331 (allophane) \rightarrow halloysite, gibbsite and alunite.

332 Massive kaolin deposits are rare in North Africa, especially halloysite
333 (Bechtel et al., 1999). In Algeria (Djebel Debbagh, north-eastern), western
334 (Ain Khemouda) and northern (Tamra) Tunisia, halloysite is detrital
335 occurred after the karst windows formed during Oligocene to Eocene times
336 (Renac & Assassi, 2009, Mellouk et al., 2009; Moussi et al., 2011; Jemaï et
337 al, 2015).

338 In Algeria, halloysite occur associated with minor alunite, absence of quartz,
339 dominant kaolinite and illite. Halloysite occurrence has been interpreted as
340 either hypogene, supergene or hydrothermal related to fluid circulation
341 (Renac & Assassi 2009). In northern Tunisia, halloysite occurs in

342 association with kaolinite and Zn-aluminous hydrated halloysite (10 Å), its
343 genesis is driven by pedogenesis and hydrothermal alteration (Moussi et al.,
344 2011).

345 Algerian halloysite showed a tubular morphology with tube lengths of 2.5
346 µm and an outer diameter of 0.15 µm, while Moroccan halloysite displays
347 tube lengths of 600 µm in average with similar diameter. Tunisian halloysite
348 has tubular morphology of variable size in length and thickness and
349 sometimes spheroidal (Chaari et al., 2015). Relatively low cation exchange
350 capacity value (18 meq/100 g) is showed for Tunisian halloysite, as
351 Algerian value (19 meq/100 g) indicating insufficient edge valences (Jemai
352 et al., 2015). Specific surface area of Algerian halloysite is 64 m²/g greater
353 than Moroccan value (56 m²/g). Similar value of ~57 m²/g was obtained for
354 halloysite from New Zealand (Levis and Deasy, 2002).

355

356 *Characterization of halloysite*

357 Al₂O₃ (37.4%) and SiO₂ (37%) are the main oxides in the sample, with a
358 SiO₂/Al₂O₃ ratio of 0.98, is close to 1 that is characteristic of the kaolin
359 group (Table 1). The absence of quartz and the presence of gibbsite Al(OH)₃
360 and alunite KAl₃(SO₄)₂(OH)₆ may explain the high concentration of
361 aluminum. The occurrence of small amount of TiO₂ and Fe₂O₃ (< 1.5%)
362 could not influence the color of the kilned product. The SO₃ (1.6%) and F₂O

363 (0.9%) contribution confirms the presence of alunite and fluorite,
364 respectively as observed on XRD results. The low amount of alkali
365 (K_2O+Na_2O) indicates the high degree of kaolinization, since halloysite is
366 formed from the alteration of volcanic rocks.

367 Halloysite sample has higher clay fraction (74%) with greater plasticity and
368 higher specific surface area than kaolinite clay. The high plasticity is
369 confirmed by the high absorption of the methylene blue by the sample (VBS
370 > 2). Methylene blue is absorbed preferentially by clay due to the fact that
371 their sheet can easily be affixed water molecules. Furthermore, the
372 measured specific surface area value is close to that determined for
373 halloysite by Hofmann et al., (1966) ($61 \text{ m}^2 / \text{g}$). It noted that the studied
374 halloysite from Morocco trends to exchange calcium and magnesium
375 cations, which may explain the elevated amounts of these elements given by
376 chemical results (Table 1). This fact also confirms the presence of tubular
377 clay such as halloysite.

378 The halloysite displays a great plasticity that can be explained by the XRD
379 results, indicating the predominance of phyllosilicate and the absence of a
380 degreasing agent, especially quartz. The grain-size plays an important role
381 for ceramic manufacturing, especially clay fraction which influences its
382 plastic behaviour (El Ouahabi et al., 2014). Plasticity is one of the most
383 important parameters for making clay products, which depends on the
384 nature of their clay minerals (Allaoui et al., 2005, Guerraoui et al., 2008),

385 the presence of impurities (non-clay minerals) (Bergaya et al., 2006), and it
386 is inversely proportional to grain size (ASTM C 326-03).

387 *Suitability for ceramics*

388 Halloysite has high plastic behaviour that has to be corrected by the addition
389 of quartz to avoid any cracks development during drying. Furthermore,
390 quartz plays the role of a filler to control deformation and shrinkage of the
391 fired bodies, whereas K-feldspar, acting as a flux, is the main responsible
392 for the formation of quasi-liquid phase during firing that affects the
393 densification process (Toprak & Arslanbaba 2016). Moreover, flux interacts
394 with halloysite, which confers to the plasticity for the bodies shaping and
395 gives mullite and glass during firing (Carty et al., 1998; Iqbal & Lee 2000;
396 Martín-Márquez et al., 2010). Therefore this influences the micro-structural
397 features and physical properties of the fired bodies (Pagani et al., 2010).

398 Mineralogical evolution of fired bodies from 500 to 1100°C allows us to
399 follow vitreous phase transformation and disappearance of initially existing
400 phases (Fig. 6). Based on XRD results of fired bodies, disappearance of
401 halloysite, gibbsite and tridymite occurred from 550°C, which therefore lead
402 to neoformation of other stable silica–alumina phases. Crystalline phases
403 (cristobalite, spinel, mullite, corundum and hematite) are neoformed from
404 900°C, which is also highlighted by thermal analysis (Table 3). Fluorite
405 abundance decreases with intensity as increasing firing temperature until

406 1100°C. Fluoride improves the nucleation and growth of glass ceramics and
407 decrease the aggregation extent of the glass network (Duan et al., 1999).

408 The behaviour of halloysite fired at 1100°C displays a high flexural strength
409 (16.3 MPa) associated with shrinkage of 7.5% indicating some melting and
410 development of vitreous phases. However, this change involved cracks
411 development (Fig. 7) due to the absence of filler as quartz (Souza et al.,
412 2006). Flexural strength is mainly influenced by the mullite development
413 and the formation of a vitreous phase which likely improves the mechanical
414 strength. Regarding the microstructure from 1100°C based on SEM
415 observations, the occurrence of two mullite crystals forms is related to
416 feldspar and its interaction with halloysite. In general, mullite crystals grow
417 in a viscous aluminosilicate liquid, as primary mullite in pure clays and
418 secondary mullite in the presence of alkali fluxes ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) (Lee et al.,
419 2008), which is in agreement with chemical and mineralogical results
420 obtained from halloysite sample. It should be noted, however, that other
421 variables influence mullite formation by affecting the composition and
422 viscosity of the liquid in which it grows. Since is difficult of determine the
423 stoichiometry of mullite formed in vitreous systems due to the heterogeneity
424 of the microstructure.

425 In the light of the obtained results, studied halloysite is suitable for light
426 vitrified raw materials for ceramic from 900°C, but appropriate formulations
427 need to be done in order to prevent manufacturing defaults.

428 **CONCLUSION**

429 In this work, halloysite deposit from the Neogene basin (Nador region),
430 located at the foot of the Gourougou volcano in the Maaza Valley have been
431 investigated. White layer of halloysite, of 25 to 130 cm thick, occurred in
432 wedge-shaped form in contact with lower reef limestone and upper volcanic
433 sand. The clayey material consists of fine particles (68%) with a high
434 plasticity (31.5%) and a fairly large specific surface area (55.48 m²/g).

435 XRD results revealed the presence of 7Å non-hydrated halloysite
436 (metahalloysite) and traces of smectite and illite, which is confirmed by
437 SEM observations. The halloysite occurs in association with gibbsite,
438 alunite, K-feldspar and other minor phases (tridymite, fluorite and halite).
439 This halloysite has characteristics infrared bands at 3695 and 3618 cm⁻¹.
440 Thermal and thermogravimetric analysis revealed halloysite
441 dehydroxylation in metakaolinite followed by the rearrangement of
442 metakaolinite to form mullite and spinel from 900°C. The chemical analysis
443 revealed a high aluminum content (Al₂O₃ = 37.4%) linked to the presence of
444 some aluminous phases (gibbsite and alunite), which reduces slightly the
445 SiO₂/Al₂O₃ ratio.

446 Regarding to ceramic proprieties, specimens were produced and fired from
447 500-1100°C in order to appreciate the processing technique in ceramic
448 products from raw halloysite material. An increase in linear shrinkage with
449 great flexural strength was recognized. Given these results, Moroccan

450 halloysite has good properties for application in the refractory ceramic
451 industry. However, addition of quartz sand fraction is required for avoiding
452 cracks development at firing as well as to reduce the high plastic behaviour
453 of halloysite and minimize its shrinkage during sintering.

454

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700

701 **Figure captions**

702 FIG. 1. Geographical localization (A) and geological map of the study area
703 indicating the prospected area (B).

704 FIG. 2. Geological cross-section (A) performed in the Maaza region based
705 on the stratigraphy and lithological description in the field. Cross-section
706 (B) showing sharp lateral and vertical changes in lithology within the area
707 (modified after Hilali & Jeannette (1981)).

708 FIG. 3. Images illustrate the beveled shape of the various outcrops of
709 studied white clay (halloysite).

710 FIG. 4. X-ray diffractograms of the studied clay fractions (<2 μ m) with the
711 three different treatments (N: air dried run; EG: Saturated with ethylene
712 glycol, H: Heated at 500 °C for 4h). A: white clay sample (halloysite); B:
713 red clay sample.

714 FIG. 5. SEM images of white clay sample showing tubular morphology of
715 halloysite associated with detrital illite. It: illite; Hls: halloysite.

716 FIG. 6. XRD patterns of white sample in terms of heating temperature
717 evolution up to 1100°C. Ha: halloysite; Aln: alunite; Gbs: gibbsite; Tclay:
718 total clay; Trd: tridymite; Hl; halite; Sa; sanidine; Fl; fluorite; Mul; mullite;
719 Crs; cristobalite; Crn: corundun; Spl: spinel; Hem; hematite. Mineral
720 abbreviations are according to Whitney & Evans (2010).

721 FIG. 7. Aspect of the halloysite fired product at 1100°C showing some deep
722 cracking features.

723 FIG. 8. SEM images of halloysite sample showing primary (Mul1) and
724 secondary (Mul2) mullite microstructural features of fired sample after
725 1100°C.