1 Palaeoweathering events recorded on siliciclastic continental deposits (Albian, Lower Cretaceous)

2 in NE Spain.

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8 **ABSTRACT**

9 A set of materials from Teruel (NE Spain), which includes a karst bauxite deposit overlain by an

10 Albian (Lower Cretaceous) kaolin-rich clay succession, has been characterized from a

11 mineralogical, textural and geochemical point of view. The materials under study were examined by

12 X-ray diffraction, optical and electron microscopy and by inductively coupled plasma (ICP) optical

13 emission spectroscopy (OES) and mass spectroscopy (MS). The bauxite is pisolitic and

14 predominantly red and the overlying clay succession is mainly made up of grey claystones. Upper-

15 section of the clay succession is a layer with carbonate nodules and scarce pisolith-like particles that

16 can be distinguished. The studied materials are mainly composed of kaolinite, coupled with gibbsite

17 and accessory boehmite in the bauxite. Gibbsite is also identified in the layer with carbonate

18 nodules. Mineralogical data, kaolinite crystallinity and the Chemical Index of Alteration indicate

19 that the layer with carbonate nodules has recorded a weathering event that was not as intense as the

20 one that led to the in-situ formation of the bauxite deposit. The geochemical behaviour of the

21 analysed elements, especially the REEs, also supports the existence of a weathering event recorded

22 in the layer with carbonate nodules, given the similar trends observed in this layer and in the

23 bauxite. The weathering led to REE+Y leaching, with the HREEs being less mobile than the

24 LREEs, and thus the Albian clay succession, except the layer with carbonate nodules, shows a

25 greater potential as source of these strategic elements. The research has revealed that redox

26 fluctuation made a significant contribution to the distribution of Fe and Ce during bauxitization

27 concerning the precipitation of Fe oxides and accessory minerals such as those of the goyazite-

28 crandallite series.

29 Keywords: karst bauxite; weathering; kaolinite; Lower Cretaceous; SEM; geochemistry

1 INTRODUCTION

31 The present paper deals with the mineralogical, textural and geochemical characterization of a set of

32 Lower Cretaceous materials from NE Spain, which include a karst bauxite deposit overlain by a

33 kaolin-rich clay succession in which another weathering event and pedogenic processes can be

34 recognized.

35 Model simulations of the Late Jurassic palaeoclimate have shown that the Earth was generally

36 warmer and more humid than at present (Sellwood et al., 2000). For the Early Cretaceous, a

37 seasonal warm, semi-arid subtropical climate has been assumed in the Iberian Plate (Ziegler et al.,

38 1987; Buscalioni and Fregenal-Martínez, 2010). During the Barremian (Lower Cretaceous), a

39 warm, humid regime has been well documented throughout northwestern Europe (Wright et al.,

40 2000) in agreement with the occurrence of facies usually considered to be climate proxies, such as

41 bauxite deposits and iron-rich palaeosols (Bardossy, 1982). On the other hand, a strong biannual

42 seasonality of temperature has been pointed out by Haywoord et al. (2004) for the Barremian

43 climates of Western Europe. Subsequently, a phase of increased aridity during the Late Barremian

44 to Early Aptian has been argued to take place in Western Europe (Ruffell and Batten, 1990).

45 In the Iberian Range (NE Spain), the well represented Barremian Weald facies, with abundant

46 kaolinite-rich clay deposits, are in accordance with relatively warm and humid conditions (Bauluz

47 et al., 2014). Important Barremian karst bauxite deposits as well as lateritic clays, consistent with

48 those conditions, have also been documented (Molina and Salas, 1993; Yuste et al., 2015, 2017).

49 Later, extensive kaolin-rich and coal-bearing siliciclastic materials were deposited in the Iberian

50 Range during the Aptian-Albian. These materials constitute the Escucha and Utrillas Formations

51 (Aguilar et al., 1971) and have been the object of numerous studies dating back to the 19th century

52 (Rodríguez-López et al., 2009, and references therein). Mineralogical and geochemical studies

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carried out on these materials have revealed intense weathering processes in their source area, associated to the warm period of the Early Cretaceous (González López et al., 2005a; Bauluz et al., 2008). Additionally, Rodríguez-López et al. (2009) have postulated the development of a Cretaceous sandy desert system in the upper part of the Escucha Fm and the whole of the Utrillas Fm.

The Mediterranean-type karst bauxite deposit under study is located in the Maestrazgo, one of the three main zones of karst bauxite deposits of NE Spain. Karst bauxites are those bauxite deposits overlying carbonate rocks, regardless of whether the bedrock surface is karstified or not (Bardossy, 1982). Bauxite deposits are among the best climate proxies and are formed as a result of intense chemical weathering under tropical, wet climatic conditions (Bardossy and Combes, 1999). The chemical differentiation of elements during weathering is related to the intensity of the process, and thus the distribution of mobile and immobile elements provides important information about palaeoweathering events recorded in weathered rocks. Moreover, significant attention has recently been paid to the processes that control the distribution of several minor elements in these deposits, and to possible extraction techniques (Mongelli et al., 2017). For example, Deady et al. (2016) have recognized karst bauxite deposits as the ideal source material for REE-enriched red mud. Accordingly, research interest in the mineral phases controlling the distribution of these elements is growing (e.g. Liu et al., 2016; Mongelli et al., 2017; Torró et al., 2017). Taking this into account, a precise mineralogical and microtextural analysis is essential to characterize these rocks, given the fine size of the mineral phases and the usually complex relationships between them as a result of the variety of mineralogical transformations (Bardossy, 1982).

The aim of this work is to determine the physico-chemical and climatic conditions under which a weathering event took place, during the Albian, on a succession of claystones that overlie a bauxite deposit and compare the mineralogical and geochemical characteristics of both materials in order to determine its potential as a source of strategic elements. The studied materials have been described

78 as forming part of the Escucha Fm (Galán et al., 1976) and would thus represent important evidence

79 of warm, wet, climate-driven processes during the Lower Cretaceous in the Spanish Iberian Range.

80 **2 GEOLOGICAL FRAMEWORK**

81 The study site constitutes a small outcrop of a ~6 m-thick succession of Albian materials forming

82 part of the Escucha Fm and overlying a karst bauxite deposit (La Ginebrosa deposit, Galán et al.,

83 1976). It is located in the Maestrazgo Basin (Teruel, NE Spain) (Fig. 1). The Maestrazgo Basin is

84 situated in the linking zone between the Iberian Range and the Catalonian Coastal Range. It is an

85 intracratonic basin generated during one of the most active rifting stages that took place during the

86 Late Jurassic-Early Cretaceous, associated with the spread of the Tethys westward and the opening

87 of the Atlantic Ocean (Salas and Casas, 1993; Mas and Salas, 2002). During this stage a system of

88 extensional faults was generated, which triggered the progressive destruction of the Late Jurassic

89 carbonate platforms along with the development of high subsidence sedimentary basins, such as the

90 Maestrazgo Basin (Salas et al., 2001; Mas and Salas, 2002), where continental and coastal deposits

91 are particularly significant.

92 During the sedimentation of the Escucha Fm, the Maestrazgo Basin was subdivided into four sub-

93 basins delimited by thresholds, including the Calanda sub-basin (Querol, 1988), where the study

94 site is located. The Escucha Fm unconformably overlies different Cretaceous, Jurassic and Triassic

95 units, and is characterized by the occurrence of mineable coal deposits (Querol, 1990). It constitutes

96 a heterolithic unit that includes claystones, siltstones, sandstones and limestones. Traditionally, the

97 Escucha Fm has been divided into three members (lower, middle and upper) (Cervera et al., 1976),

98 with the coal deposits forming part of the lower and middle members. Pardo et al. (1991) described

99 iron and carbonate nodules in grey claystones in the lower member. The different facies of the

100 Escucha Fm have been interpreted in terms of sedimentation in a deltaic-estuarine environment

101 dominated by tidal processes (Pardo, 1979; Querol, 1990; Querol et al., 1992). In the Calanda sub-

102 basin, in a site very close to the one studied in this work, the Escucha Fm overlies ferruginized and

103 karstified Kimmeridgian limestones, and an upper delta plain facies association in turn composed of

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104   a fluvial delta plain and a flood plain, has predominantly been recorded (Querol and Solé de Porta,

105   1989). More recently, Rodríguez-López et al. (2009) indicated that the lower and middle part of the

106   formation is the response to different marine and coastal sedimentary environments, which started

107   in the upper Aptian with the development of a shallow carbonate platform. The system evolved into

108   a siliciclastic setting where coal-forming environments were associated with back-barrier swamps

109   and swamps that developed in a coastal siliciclastic system. The evolution of the organic matter

110   reached the grade of subbituminous coal (lignite), suggesting that the diagenetic grade was low

111   (eogenesis), with burial temperatures <50-60 ºC, and therefore that no significant diagenetic

112   modifications occurred in the sediments (González López et al., 2005b; Bauluz et al., 2008).

113   The materials studied in this work outcrop very close to the Val de la Piedra ravine, SW Calanda

114   (Fig. 1, UTM: 30T 734578.35E, 4530336.41N, datum WGS84), where coal deposits were mined

115   until last century. The Val de la Piedra site constitutes the depocentre of the Calanda sub-basin (255

116   m) (Querol and Solé de Porta, 1989). The outcrop comprises an approximately 15m-thick

117   succession including a pisolitic bauxite underlying grey claystones (Fig. 2). The bauxite overlies

118   Kimmeridgian limestones and marls (Galán et al., 1976), and, according to these authors it is

119   approximately 7.5 m thick, although at present the total thickness cannot be ascertained due to the

120   mining of the bauxite that took place last century.

121   **3 METHODS**

122   Sampling of both the bauxite and the overlying claystone was carried out taking into account field

123   observations as described in the Results section. Location of samples is shown in Figure 2.

124   Approximately 3 kg of material was taken from every sampling point and aliquots of these material

125   were used for X-ray diffraction and chemical analyses. The whole rock and <2μm-fraction

126   mineralogical composition was determined by X-ray diffraction (XRD) using a Philips PW 1710

127   diffractometer, with Cu-Kα radiation, an automatic divergence slit, and a graphite monochromator.

128   The <2 μm fraction was concentrated by centrifuge and analysed in air-dried and ethylene-glycol-

129   treated (at 60 °C for 48 h) oriented aggregates. The XPOWDER software by Martín (2004) was

130   used to store the XRD data. Abundances of whole-rock mineral phases were semi-quantitatively

131   determined using the reference intensity ratios (RIRs) given by Smith and Johnson (2000), which

132   have yielded successful results in the characterization of nearby karst bauxites (Yuste et al., 2015).

133   Nevertheless, the semi-quantification was carried out with the only purpose of comparing relative

134   abundances of mineral phases among the study samples. The semi-quantification of phyllosilicate

135   abundances in the < 2 μm fraction was carried out using the RIR values of Biscaye (1965).

136   Kaolinite crystallinity (KC) was calculated measuring the full width at half maximum (FWHM) of

137   the 001 and 002 reflections, in both air-dried and ethylene glycol-treated oriented aggregates.

138   Samples were examined by optical microscopy, under transmitted light, and the pisolitic bauxite

139   was described following the terms given by Bardossy (1982). To obtain more precise textural

140   information as well as chemical information, selected samples were analysed by field emission

141   scanning electron microscopy (FESEM) using secondary electron (SE), backscattered electron

142   (BSE), and energy-dispersive X-ray (EDS) analysis. The observations were performed using a Carl

143   Zeiss MERLIN FESEM equipped with an Oxford instrument detector (EDS). SE images were

144   acquired with an accelerating voltage of 15 kV and a beam current of 600 pA. BSE images were

145   obtained using two types of detectors: angular-selective (AsB) and energy-selective (EsB). Semi-

146   quantitative analyses were acquired by an energy-dispersive X-ray (EDS) detector, with a detection

147   limit of 0.1%. The accelerating voltage for AsB and EDS was 15 kV with a beam current of 600 pA

148   with a counting time of 50 s for analysis; for EsB, the accelerating voltage was 4 kV with a beam

149   current of 1 nA. Samples were carbon coated.

150   Chemical analyses of the major and trace elements in bulk samples were performed at Actlabs

151   Laboratories (Canada) using the following techniques (detection limits in brackets): the major

152   elements (0.01%, except MnO and TiO_2 with detection limits of 0.001%) and the trace elements V

153   (5 ppm), Sr (2), Ba (3), Sc (1), and Be (1) by inductively coupled plasma/optical emission

154   spectroscopy (ICP/ OES). The other trace elements, such as Cr (20 ppm), Co (1), Ni (20), Rb (1),

155   Cs (0.1), Th (0.05), U (0.01), Y (0.5), Zr (1), Nb (0.2), Hf (0.1), La (0.05), Ce (0.05), Pr (0.01), Nd

156   (0.05), Sm (0.01), Eu (0.005), Gd (0.01), Tb (0.01), Dy (0.01), Ho (0.01), Er (0.01), Tm (0.005), Yb

157   (0.01), and Lu (0.002) were determined by inductively coupled plasma/mass spectroscopy

158   (ICP/MS). Fused samples (lithium metaborate/tetraborate fusion) were run for major oxides and V,

159   Sr, Ba, Sc, and Be on a combination simultaneous/sequential Thermo Jarrell-Ash ENVIRO II ICP

160   or a Varian Vista 735 ICP. Seven prepared USGS and CANMET certified reference materials were

161   used for calibration. One of the seven standards was used during the analysis for each group of ten

162   samples. For the analysis of the other trace elements, fused samples were diluted and analysed by

163   Perkin Elmer Sciex ELAN 6000, 6100 or 9000 ICP/MS. Three blanks and five controls were

164   analysed per group of samples. Duplicates were fused and analysed every 15 samples. The

165   molecular proportions of some major oxides were used to calculate the Chemical Index of

166   Alteration (CIA; Nesbitt and Young, 1982) as follows: CIA = $(Al_2O_3/Al_2O_3 + CaO/ + Na_2O + K_2O)$

167   * 100, where CaO represents the amount of CaO associated with the silicate fraction of the rock.

168   Further, to estimate element mobility, an absolute weathering index (Nesbitt, 1979) was calculated.

169   According to this author and assuming Ti as an immobile element and the Upper Continental Crust

170   (UCC; Taylor and McLennan, 1985) as the parent material, the increase or decrease (change %) in

171   any element (X) compared to the parent material is given by the following formula:

172   $[(X_{sample}/Ti_{sample})/(X_{UCC}/Ti_{UCC}) \_ 1] * 100$.

173   **4 RESULTS**

174   **4.1 Field description**

175   The bauxite is predominantly red although more whitish and grey colours can be observed in the

176   upper part. In the red and whitish bauxite, mainly white pisoliths, up to 2 cm in diameter, are very

177   abundant, whereas red or pinkish pisoliths are scarce (Fig. 2a, b). The grey bauxite shows the

178   appearance of a very compact claystone where only scarce white pisoliths are present (Fig. 2c).

179   Overlying the bauxite, a ~6 m-thick claystone succession outcrops in the study site (Fig. 2). This

180   consists of mainly grey claystone with common ochre zones and Fe- oxide/oxyhydroxide patinas.

181   Larger amounts of Fe oxides in the form of irregular accumulations and patinas result in a more

competent level in the middle part of the succession. The up-section can be distinguished by a thin

level (~10 cm-thick) with centimetric carbonate nodules and scarce white pisolith-like particles.

Above this level, there is a 10-30 cm-thick layer of dark grey to black compact claystone with

abundant coal remains and millimetric soft-sediment clasts.

4.2 X-ray diffraction (XRD)

XRD data indicate that samples are mainly composed of kaolinite (Table 1). Representative whole

rock XRD patterns of the study materials are shown in Figure 3a and b. The kaolinite contents are

higher in the pisolitic bauxite than in the clays except for the black clay from the uppermost part of

the study section, which shows the highest kaolinite content. In the pisolitic bauxite, gibbsite along

with accessory boehmite appears in addition to kaolinite. Gibbsite is also identified in the level with

carbonate nodules. On the other hand, illite or muscovite is detected in the middle part of the

claystone succession, coinciding with evidence of the presence of diaspore. Accessory Ti oxides

(rutile and anatase) are present in all the samples, and Fe oxides (goethite and hematite) are

frequent. With regard to the latter, hematite is more abundant in the red pisolitic bauxite whereas

goethite predominates in the middle part of the claystone succession, especially in the more

competent level described above. Finally, calcite together with evidence of quartz and gypsum are

identified only in the level containing carbonate nodules.

As regards the <2 μm fraction (Table 2), kaolinite is almost the only phyllosilicate, accompanied by

illite mainly in those levels where it is already detected in the whole sample. Representative XRD

patterns of the clay fraction can be observed in Figure 3c and d. In the red pisolitic bauxite,

accessory smectite is identified. Kaolinite crystallinity (KC) values (Table 2) show no significant

differences between the two measured reflections in both air-dried and ethylene-glycol-treated

oriented aggregates, allowing the presence of expandable components, such as smectite, to be ruled

out. The lowest KC values were obtained from the pisolitic bauxite, and it is worth mentioning that

the kaolinite from the level with carbonate nodules shows very similar crystallinity to the kaolinite

from the bauxite.

4.3 Light microscopy

Bauxite samples contain (homogeneously represented in terms of abundance) macropisoids (>5 mm), pisoids (1 to 5 mm), ooids (100 to 1000 μm), and less commonly micro-ooids (<100 μm), following the terms proposed by Bardossy (1982). All these particles are embedded in a clay-rich matrix, which is more abundant in the grey bauxite. Morphologies are most frequently spheroidal, but elongated or flattened, bean-like, and even more irregular shapes are also common. Some of the larger ones are fractured and deformed. The matrix comprises very fine particles, with sizes generally below optical microscope resolution and, in the case of the red bauxite, too dark and opaque to allow any observation.

Ooids and micro-ooids are composed of fine particles similar to the matrix (Fig. 4a). Generally, they are slightly darker than the matrix and do not show any structure, except for the grey bauxite, where occasionally a darker core and a darker outer part can be distinguished (Fig. 4a). In the red bauxite, some ooids and micro-ooids seem to have a thin dark-red hematite-rich coating but this feature is frequently unclear due to the high amounts of this phase in the sample.

Pisoids and macropisoids are very often complex and show a variable internal structure although some of the smaller ones are massive. They usually have a core and an outer cortex, following the terms given by Taylor et al. (2008). The core is frequently light-coloured and massive, composed of particles similar to those of the matrix, and occasionally contains ooids (Fig. 4b). In the innermost part of the core an irregular or sharp Fe-oxide-rich zone, sometimes fractured (Fig. 4c) and occasionally occupying the whole core, can be observed in some pisoids and macropisoids. In the red bauxite the cores are often very dark and opaque. The cortex thickness varies from 50 μm up to 2 mm, and it is composed of Fe oxides or made up of several thin concentric layers, sometimes irregular and discontinuous (Fig. 4d), which are occasionally indiscernible owing to the high amount of opaque phases. In some macropisoids, the innermost layer of the cortex can reach more than 1 mm in thickness and show radial fractures filled with Fe oxides (Fig. 4e). On the other hand,

233 a Fe-oxide-rich crust, sometimes showing radial, tangential and sinusoidal fissures, is frequently

234 observed between the massive core and the layered cortex (Fig. 4d, f).

235 Claystones are mainly composed of clay phyllosilicates, as evidenced by XRD data, and thus are

236 generally below optical microscope resolution. However, in the goethite-rich sample, despite the

237 brownish-reddish colour that prevents a precise observation from being made, occasional kaolinite

238 "booklets" are observed (on the basis of birefringence) (Fig. 5a). In the level where carbonate

239 nodules are identified, these are composed of micritic calcite with scarce fossil remains and fissures

240 filled with coarser calcite. In the sample from the uppermost part of the succession, soft-sediment

241 clasts are frequent. These are generally rounded or elongated, with sizes from 200 μm up to >2 mm,

242 and constituted by phases with sizes below optical microscope resolution (Fig. 5b). Also in this

243 sample, carbonaceous organic matter remains are frequent, responsible for the dark grey to black

244 colour (Fig. 5b).

245 **4.4 Scanning electron microscopy**

246 Secondary electron (SE) images of the bauxite show mainly euhedral to subhedral nanometric

247 kaolinite (Fig. 6a). Also, kaolinite occurs as >1 μm plates forming "booklets" (Fig. 6b). Occasional

248 nanometric prismatic crystals of probable Al hydroxides or oxyhydroxides are also observed, on the

249 basis of the Al-rich results of the EDS analysis obtained from those areas (Fig. 6c). The Fe oxides

250 (identified by EDS analyses) show planar habits, sometimes forming rose aggregates, or appear as

251 anhedral nanometric crystals (Fig. 6d). Subhedral Ti oxide crystals (identified by EDS analyses

252 obtained from those crystals) with sizes larger than 1 μm and a detrital appearance are occasionally

253 observed, partially coated by nanometric kaolinite.

254 Individual pisoids and macropisoids, mainly white ones, were separated and investigated under the

255 FESEM. The SE images of these particles revealed that they are composed of euhedral-subhedral

256 nanometric kaolinite, randomly arranged with regard to the pisoid/macropisoid morphology.

257 Vermicular kaolinite aggregates and "booklets" are also observed. These aggregates are randomly

258 arranged too, can reach up to >10 μm long, and are composed of plates with diameters >1 μm (Fig.

259   6e). Al hydroxides or oxyhydroxides are observed in these particles, showing different

260   morphologies. On the one hand, they appear as accumulations of elongated nanometric crystals,

261   which seem to be coated by vermicular kaolinite aggregates (Fig. 6e). On the other hand, they occur

262   as subhedral tabular crystals with sizes >1 μm (Fig. 6f). Finally, according to Fe- and Ti-rich

263   results of EDS analyses, accumulations of anhedral nanometric Fe and Ti oxides are also frequent.

264   BSE images of the bauxite matrix show that it is mainly composed of kaolinite along with an Al

265   phase, probably gibbsite given the XRD data, and scattered Ti and Fe oxides. Kaolinite occurs as

266   nanometric crystals and vermicular aggregates and "booklets", whereas the Al phase appears as

267   anhedral crystals, which sometimes cement kaolinite aggregates (Fig. 7a). Ooids and micro-ooids

268   (Fig. 7b) show mineralogical and textural features similar to the matrix. The core of pisoids and

269   macropisoids is composed of phases of detrital appearance, such as anhedral, sharp-edged clasts of

270   quartz and commonly fractured and bent mica-type phyllosilicates, together with frequent

271   vermicular kaolinite aggregates and "booklets", and Fe and Ti oxides (Fig. 7c), identified on the

272   basis of EDS analyses. Kaolinite also appears between opened cleavage sheets of pre-existing mica-

273   type phyllosilicates (Fig. 7c). In the grey bauxite, the cores are frequently richer in kaolinite than in

274   the other bauxite samples. By contrast, in the core of a Fe-rich pisolith from the red bauxite, an Al-

275   and Sr-rich phosphate phase is identified. The average structural formula calculated after EDS

276   analyses is $(Ca_{0.4}, Sr_{0.6})$ $(Al_{2.8}, Fe_{0.1})$ $(PO_4)_2$ $(OH)_5 \cdot H_2O$, indicating that it belongs to the goyazite-

277   crandallite series. Ce is detected in some EDS analyses of this mineral. The goyazite-crandallite

278   series mineral appears cementing quartz grains with evident signs of dissolution and is associated

279   with Fe oxides (Fig. 7d). With regard to the cortex of pisoids and macropisoids, the BSE images

280   show the different mineralogical composition of the concentric layers, with Al phases (hydroxide

281   and oxyhydroxide)-rich layers and other layers where kaolinite "booklets", embedded in nanometric

282   Al-rich phases, predominate (Fig. 7c, e).

283   SE images of the claystone reveal, in agreement with the XRD data, the predominance of kaolinite

284   as the main component. Kaolinite is observed as subhedral nanometric plates or as vermicular

285   aggregates and "booklets" up to >10 μm long and composed of >1 μm euhedral-subhedral plates

286   (Fig. 8a). Also, mica-type phyllosilicates of detrital appearance are observed. It is worth mentioning

287   that nanometric kaolinite crystals from the level with carbonate nodules show a more euhedral

288   character than those from the rest of the claystone succession. From this level, individual rounded

289   white particles were investigated under the FESEM. The SE images of these particles show

290   accumulations of Al-rich phases (hydroxides or oxyhydroxides) occurring as nanometre-sized,

291   slightly wavy, laminar crystals (Fig. 8b), sometimes partially included in gypsum (Fig. 8c).

292   BSE images show that the claystones are composed of <2 μm phyllosilicates, mainly kaolinite and

293   less abundant illite, as well as aggregates of larger phyllosilicates (Fig. 8d). Some of them constitute

294   kaolinite "booklets", among which occasional mica sheets can be observed (Fig. 8e). Occasionally,

295   kaolinite is also observed between opened cleavage sheets of mica (Fig. 8d, e). On the other hand,

296   kaolinite "booklets" with scarce mica sheets, and cemented by micritic calcite, are also observed in

297   the carbonate nodules described above (Fig. 8f). Finally, abundant C- and O- rich matter, according

298   to EDS analyses, and interpreted as organic matter remains, are seen in the uppermost part of the

299   succession (Fig. 8g), together with nodular accumulations of pyrite cubes along with illite and

300   kaolinite (Fig. 8h).

301   **4.5 Geochemistry**

302   In general, the major element concentrations (Table 3) support the mineralogical data. Si, Al, Fe

303   and Ti account for more than 97% of the total amount of major elements, except for the level with

304   carbonate nodules, which shows ~15% CaO. In general, claystones exhibit higher Si contents than

305   bauxite, which shows higher amounts of Al. Among the claystones, the highest goethite content

306   revealed by XRD results in lower Si amounts, compared to the other claystones, and the highest Fe

307   contents (above 36%). In the bauxite, Fe amounts are related to the presence of hematite. On the

308   other hand, the Mg content (higher in claystone) may be related to illite along with other

309   phyllosilicates not detected by XRD, such as chlorite. Finally, the highest K contents are clearly

310   related to the presence of illite. Of the major elements, Ti and Al show the only significant

311 correlation (r = 0.87) (Fig. 9a). CIA (Chemical Index of Alteration) values (Table 3) are always

312 over 95, the highest values being shown by the bauxite (> 99). Claystones exhibit more

313 heterogeneous values, with higher values in the uppermost part of the succession, especially in the

314 level with carbonate nodules, where the CIA is very similar (> 99) to that of the bauxite.

315 Major element concentrations normalized to the Upper Continental Crust (UCC) average values

316 (Fig. 9b) show that although both bauxite and claystone are Al- and mainly Ti-enriched and Si-

317 depleted, the bauxite, especially the red bauxite, is more Al- and Ti-enriched than the claystone.

318 With regard to Fe, claystones are generally depleted or slightly enriched, except for the level with

319 high amounts of goethite, which shows the highest Fe enrichment. Of the bauxite, the red bauxite is

320 more Fe-enriched, whereas the grey bauxite is the most Fe-depleted of all the studied materials. As

321 regards the other elements, all the materials are generally depleted except for the level with

322 carbonate nodules, which is Ca-enriched. The change % values in Figure 9c evidence that the

323 studied materials have undergone greater decreases in Si than Al relative to Ti, especially the

324 bauxite followed by the samples from the uppermost part of the claystone succession. With regard

325 to Fe, it is worth mentioning that the bauxite shows lower Fe decreases than the claystone, except

326 for the grey bauxite, which shows the highest decrease among the studied materials. On the other

327 hand, high goethite content is related to an increase in Fe, and the presence of carbonate nodules to

328 the lowest decrease in Ca.

329 Figure 10a shows some important trace element concentrations normalized to the UCC. The studied

330 materials are clearly Sc-, V-, Cr-, Ga-, Zr-, Nb-, Ni, Hf-, Th-, and U- enriched and Rb- depleted.

331 The bauxite is Co-, Ge-, Sr-, Cs-, Ba, and Cu-depleted. U and Cu show heterogeneous behaviour.

332 The change % values (Fig. 10b) indicate a general decrease in the trace elements, in particular Rb,

333 with lower decreases undergone by Cr, Ga, Zr, Th and especially Nb.

334 Y was considered together with the REEs since there is a high positive correlation between them (r

335 = 0.95), indicating similar behaviour. The REE+Y contents (Table 3) of the claystone are higher

336 and more heterogeneous than those of the bauxite, except for the level with carbonate nodules,

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337 which shows similar values to the bauxite. The REE+Y contents normalized to the UCC (Fig. 11a)

338 show similar trends for the bauxite and the claystone with carbonate nodules, exhibiting LREE

339 depletion (except for Sm in some cases) and clear Y and HREE enrichment. The rest of the

340 claystone is enriched in REE+Y. The change % values (Fig. 11b) are also similar in the bauxite and

341 the claystone with carbonate nodules, showing the highest decreases in REE. The chondrite-

342 normalized REE+Y patterns (Fig. 11c) also differ depending on the samples considered. REE

343 fractionalda in the bauxite and, again, the claystone with carbonate nodules is lower than in the rest

344 of the claystone. Furthermore, these materials also show significantly lower LREE fractionation

345 than what is exhibited by the rest of the claystone. On the other hand, LREE fractionation is higher

346 than HREE fractionation in all the materials, with the HREE showing an almost horizontal slope.

347 Finally, all the study materials show negative Eu and Ce anomalies, except for the grey bauxite,

348 which displays a positive Ce anomaly.

349 **5 DISCUSSION**

350 **5.1 The karst bauxite deposit**

351 The karst bauxite deposit under study (La Ginebrosa deposit) has been described as an Albian

352 argillaceous series on Jurassic limestone, where only the first few metres of clay in contact with the

353 limestone were bauxitized (Galán et al., 1976). Intense chemical weathering processes, which took

354 place during the Barremian (Lower Cretaceous), have been well documented in NE Iberia (e.g.

355 Molina and Salas, 1993; Bauluz et al., 2014). Thus, the occurrence of bauxite deposits in the Albian

356 Escucha Fm would suggest several warm, humid intervals during the Early Cretaceous in the

357 Iberian Range. On the other hand, La Ginebrosa deposit is quite similar to the nearby Barremian

358 Fuentespalda deposit (Yuste et al., 2015, 2017), which occupies karst cavities in Jurassic rocks

359 overlain by Albian materials. Taking into account that the Escucha Fm overlies different

360 Cretaceous, Jurassic and Triassic units, it cannot be ruled out that the genesis of La Ginebrosa

361 bauxite is related to intense weathering processes during the Barremian and is overlain by a

362 claystone succession that forms part of the Albian Escucha Fm. In any case, mineralogical data

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363   from the claystone succession overlying the studied bauxite, where the Al-phases gibbsite and

364   diaspore are identified by XRD, could indicate weathering events during the Albian, although not as

365   intense as those that led to the formation of the underlying bauxite.

366   In accordance with the above paragraph, the higher crystallinity of the kaolinite from the bauxite

367   than from the claystone may be related to the more intense chemical weathering undergone by the

368   bauxite, which generated, therefore, more favorable conditions for kaolinite crystallization. The KC

369   values from the claystone level with carbonate nodules and gibbsite-bearing pisolith-like particles

370   are comparable to those from the bauxite, which could likewise indicate more intense chemical

371   weathering for this level compared to the rest of the claystone.

372   A pisolitic texture is a common feature in bauxite deposits (Bardossy, 1982). Textural similarities

373   between the matrix and ooids and micro-ooids can be interpreted in terms of the autochthonous

374   nature of the studied bauxite, as suggested by Yuste et al. (2015) for nearby karst bauxite deposits.

375   The presence of sinusoidal ducts affecting the Fe-oxide-rich crust of some pisoids and macropisoids

376   (Fig. 5f) is very probably related to bioturbation, and also points to an autochthonous origin for the

377   bauxite. Nevertheless, it can be stated that the bauxitization is a complex process, as can be

378   gathered, for instance, from the homogeneous distribution of the different spheroidal particles and

379   the variety of their internal arrangements, including the presence of ooids and micro-ooids forming

380   part of larger particles (Fig. 5b). Indeed, the growth of the concentric layers making up the cortex of

381   the pisoids and macropisoids along with Fe-oxide-rich crusts and fillings implies changes in the

382   physical-chemical environmental conditions, which would favour the precipitation of different

383   mineral phases (kaolinite, Al hydroxides/oxyhydroxides, Fe-oxides) in different proportions.

384   Furthermore, sharp Fe-oxide accumulations, sometimes fractured, in the core of some particles,

385   points to previously weathered material acting as aggregation nuclei. The elongated, flattened,

386   bean-shaped and more irregular morphologies of some spheroidal particles indicate semi-plastic

387   deformation in waterlogged conditions during bauxitization (Bardossy, 1982). Even so, the radial

388   fractures (Fig. 5e) affecting some layers of the cortex of some pisoids and macropisoids, interpreted

389 as mud cracks, indicate variations in the water saturation conditions. All these textural features

390 evidence that bauxitization, although considered as a whole single process, took place through

391 changing physico-chemical conditions within the context of intense chemical weathering.

392 **5.2 Mineralogical keys to weathering**

393 From a mineralogical perspective, the euhedral to subhedral character of the nanometric kaolinite in

394 the bauxite (Fig. 6a) is consistent with an authigenic origin during weathering. The nanometric

395 kaolinite in the claystone shows frequent subhedral morphologies, possibly in relation to less

396 intense weathering or, at least in part, to a detrital origin, as is the case in nearby Albian outcrops

397 (Bauluz et al., 2008). However, the kaolinite in the level with carbonate nodules is euhedral, as in

398 the bauxite, in accordance with the KC values and supporting the idea of more intense chemical

399 weathering than in the rest of the claystone, albeit not as intense as that recorded in the bauxite. The

400 vermicular kaolinite aggregates and "booklets" in both the bauxite and claystone (Figs. 6e, 8a)

401 should be considered authigenic as well, since they are too delicate to resist transport processes.

402 Also, the kaolinite between cleavage sheets of mica-type phyllosilicates (Fig. 8d) has been related

403 to chemical weathering processes in Lower Cretaceous siliciclastic materials (Bauluz et al., 2014)

404 and karst bauxite deposits (Yuste et al., 2015) from nearby areas. Furthermore, in the core of pisoids

405 and macropisoids in the bauxite as well as in the claystone, illite- or mica-type phyllosilicates of

406 detrital appearance are also observed (Figs. 7c, 8d, e), indicating that the bauxite originated through

407 the weathering of a parent material similar to the overlying claystone.

408 The different Al minerals identified by XRD (gibbsite, boehmite and diaspore) cannot be

409 differentiated by means of FESEM. These appear in the bauxite with various morphologies,

410 sometimes constituting some of the layers of the cortex of pisoids and macropisoids. They also

411 cement kaolinite "booklets" (Fig. 7a, b) in both the matrix and pisoliths or are covered by kaolinite

412 vermicular aggregates (Fig. 6e). As regards the latter textural feature, Yuste et al. (2017) have

413 documented kaolinization processes subsequent to gibbsite formation in nearby Barremian karst

414 bauxite deposits, possibly related to acid solutions favoured by the presence of organic and coal-

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415   rich materials. In the present context it is worth mentioning the occurrence of abundant organic

416   matter remains and pyrite nodules in the upper section of the study site, as well as abundant

417   mineable coal deposits throughout the Escucha Fm (Querol, 1990).

418   In such a context of intense weathering as to produce bauxite, related intense dissolution processes

419   affecting previous silicates would enhance the crystallization of authigenic phases rich in relative

420   immobile cations and the lixiviation of mobile elements. That is to say, the dissolution-

421   crystallization process led to the crystallization of kaolinite, Al hydroxides, and Fe oxides and

422   oxyhydroxides, along with the relative concentration of Ti oxides. In less weathered nearby

423   Barremian materials, replacement of detrital silicates (quartz and feldspars) by kaolinite with no

424   intermediate phases between them, has been interpreted as a consequence of

425   dissolution/crystallization processes at the micron scale, indicating a high fluid/rock ratio in the

426   alteration process (Bauluz et al., 2014). In the study bauxite, only scarce quartz with signs of

427   dissolution has been noticed, and no evidences of replacement by authigenic phases have been

428   observed. The more intense weathering that led to bauxite formation would have enhanced the

429   almost complete dissolution of detrital silicates such as quartz and especially feldspars, probably in

430   relation to even higher fluid/rock ratio, provided the above-mentioned waterlogged conditions

431   during bauxitization.

432   On the other hand, with regard to the observed mica/kaolinite intergrowths, displacements of mica

433   sheets would be related to kaolinite growth, indicating that the mica is an earlier phase. No

434   evidences of alteration characteristics in the mica have been noticed, which would indicate that

435   micas acted as a substrate for the kaolinite growth, as pointed out by Bauluz et al. (2014). The

436   observed KC values indicating higher degree of ordering in relation to more intense weathering, and

437   the absence of expandable interlayered components are consistent with kaolinite originated by

438   dissolution-crystallization processes, such as those reported from lateritic paleosols by Fernández-

439   Caliani and Cantano (2010).

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440   The presence of authigenic gibbsite (as indicated by XRD data) in pisolith-like particles in the level

441   with carbonate nodules supports the idea of a weathering event recorded on that level, leading to

442   incipient bauxitization. This event would reflect conditions that did not favour such intense long-

443   term chemical weathering as to generate true bauxite, possibly as a result of different climatic

444   conditions. The mineralogical and textural features of the carbonate nodules observed in this level

445   could indicate that they are pedogenic carbonates (Zamanian et al., 2016) formed in situ by the

446   impregnation of the soil matrix with $CaCO_3$ at specific locations (Durand et al., 2010). Slightly

447   acidic conditions favouring kaolinite genesis would promote $CaCO_3$ dissolution from fossil

448   remains. Further supersaturation of the bicarbonate ion in the soil solution and a change to more

449   alkaline conditions could favour a high nucleation rate and the fast precipitation of small calcite

450   crystals (Ma et al., 2010), such as those constituting the observed carbonate nodules. The $CaCO_3$

451   accumulation probably initially began around a nucleus (Zamanian et al., 2016), such as non-

452   dissolved fossil remains or kaolinite "booklets", thus remaining included in the carbonate nodules

453   (Fig. 8f). Climate has been pointed out as the main controlling factor for pedogenic carbonate

454   formation and localization (Borchardt and Lienkaemper, 1999; Eswaran et al., 2000). Accordingly,

455   low precipitation and high potential evapotranspiration strongly limit the dissolution and leaching

456   of carbonates from soil (Eswaran et al., 2000; Royer, 1999, Zamanian et al., 2016). Zamanian et al.

457   (2016) indicate that the soil inorganic carbon (SIC) content decreases as mean annual precipitation

458   (MAP) increases, the highest SIC content being accumulated in soils in arid regions. Therefore, the

459   specific conditions that did not favour such intense chemical weathering in the level with carbonate

460   nodules as in the underlying bauxite could be related to lower mean annual precipitation and to

461   evapotranspiration that is high enough to promote the formation of pedogenic carbonate nodules.

462   **5.3 Geochemical keys to weathering**

463   The high correlation (r=0.87) between Ti and Al is interpreted as an indicator of the immobile

464   nature of these elements during weathering related to the concentration of Al-rich minerals and Ti

465   oxides (Nesbitt, 1979; Valeton et al., 1987; Gow and Lozej, 1993). Therefore, the Al- and Ti-

466   enrichment, and the Si-depletion observed in the UCC-normalized concentrations are correlated

467   with the more intense chemical weathering recorded by the bauxite. This is in agreement with the

468   CIA values, which are higher in the bauxite than in the overlying claystone succession. However,

469   the uppermost part of the claystone succession also shows high CIA values, especially the level

470   with carbonate nodules and gibbsite-bearing pisolith-like particles, thus pointing to a further

471   weathering event, as previously indicated. More intense weathering would also imply higher Si- and

472   lower Fe-losses as shown by the change % values, with the exception of the grey bauxite sample,

473   which shows the highest Fe decrease among the studed materials. Yuste et al. (2017) related Fe

474   losses to late kaolinization processes leading to the formation of white, kaolinite-rich zones in

475   nearby karst bauxite deposits. Nevertheless, in the present study the grey bauxite does not show the

476   highest kaolinite contents (Table 1) and so the Fe decrease cannot be related to kaolinization of the

477   bauxite. It should be pointed out that Fe is known to change the oxidation state in the weathering

478   environment (Chapela Lara et al., 2018), and therefore its behaviour could have been related to

479   variations in redox conditions during bauxitization.

480   UCC-normalized trace element concentrations show that the bauxite and some clay samples are Ge-

481   , Sr-, Cs- and Rb- depleted and Nb-enriched, the latter showing higher enrichment in the bauxite

482   than in the claystone succession. Nb is regarded as less mobile than Zr or Ti in tropical settings

483   (Kurtz et al., 2001; Ma et al., 2007). However, the Nb change % values in the present study are

484   similar among all the samples, and thus its behaviour cannot be used to trace more or less intense

485   weathering records in the studied materials. According to the UCC-normalized and change %

486   values for Rb and Cs, which are very similar in the bauxite and the level with carbonate nodules

487   (Fig. 10a, b), these elements behaved as the most mobile elements during the weathering processes.

488   With regard to the REE+Y, the most striking feature is again the similar trends observed in the

489   bauxite and the claystone level with carbonate nodules (Table 3, Fig. 11). The more heterogeneous

490   character of the other claystones as regards these elements could be related to their detrital

491   signature, as has been reported in nearby karst bauxite deposits and associated materials (Yuste et

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al., 2017). The higher REE+Y contents in the claystone could thus be associated with a variety of

inherited minerals. On the other hand, the observed trend in the bauxite and the claystone level with

carbonate nodules may be related to the weathering events recorded by these materials, and it can

thus be deduced that weathering led to REE+Y leaching. Several authors have pointed out that

HREEs are more easily leached during weathering than LREEs (e.g. Ma et al., 2007; Laveuf and

Cornu, 2009, and references therein). In the present study, however, the materials recording

weathering events show the highest LREE depletion and the lowest (La/Yb)c, as occurs in other

karst bauxite deposits (eg. Maksimovic and Pantó, 1991; Yuste et al., 2017). In addition, they show

higher LREE than HREE fractionation (Table 3), indicating that the HREEs were less mobile than

the LREEs. As weathering takes place, chemical elements are removed from primary minerals and

leached or retained in the solid phase (Chapela Lara et al., 2018). Several authors have pointed out

the important role played by certain accessory minerals in the distribution and behaviour of REE in

karst bauxite deposits. For example, Karadag et al. (2009) pointed to the concentration of rutile and

anatase as scavengers for HREE, whereas Nyakairu et al. (2001), Kanazawa and Kamitani (2006)

and Roy and Smykatz-Kloss (2007) reported the importance of P-bearing phases as LREE carriers.

On the other hand, Bardossy and Panto (1973), Maksimovic and Pantó (1991), Mongelli (1997) and

Mameli et al. (2007) indicated fluorocarbonate minerals of the bastnäsite group as the most frequent

REE minerals in Mediterranean karst bauxite deposits.

Furthermore, REEs that have more than one valence state can also fractionate due to variations in

redox conditions. Particularly, Ce(III) is oxidized to less mobile Ce(IV) at Eh values of ˗0.3 V (De

Carlo et al., 1998), which can result in solids exhibiting a positive Ce anomaly (Chapela Lara et al.,

2018). Therefore, the variation in the Ce anomaly observed in the bauxite may be related to redox

fluctuations, probably as a consequence of variations in water saturation. Evidence of variations in

redox conditions during bauxitization has been suggested above in relation to the observed Fe

behaviour. These redox fluctuations could favour the reductive dissolution of Fe oxides resulting in

Fe loss, as observed in the grey bauxite. The consequent release of Ce(IV) into the solution would

promote its redistribution through its incorporation into secondary solid phases, resulting in a

positive Ce anomaly, or its incorporation as Ce(III) in nearby oxidizing areas, such as the observed

goyazite-crandallite series mineral, whose textural features indicate its authigenic character and

which appears closely associated with Fe oxides in the red bauxite.

6 CONCLUSIONS

Mineralogical data, kaolinite crystallinity and the CIA (Chemical Index of Alteration) values of the

studied materials point to a weathering event that occurred during the Albian in the Spanish Iberian

Range and was recorded in one specific level included in the succession under study. This

weathering event was not as intense as the one that led to the formation of true bauxite.

The specific conditions that did not favour such intense chemical weathering may be related to a

less humid climate than the one under which true bauxite formed but a climate warm enough to

allow evapotranspiration and the consequent formation of pedogenic carbonate nodules.

The formation of the studied bauxite took place in situ and under changing physico-chemical

conditions. The intense chemical weathering that led to bauxite formation produced relative Al and

Ti-enrichment and Si-depletion, as is common in bauxites. Of the trace elements, Rb and Cs

behaved as the most mobile elements during bauxitization.

The similar trends observed in the bauxite and the claystone level with carbonate nodules indicate

that the weathering led to REE+Y leaching, with the HREEs being less mobile than the LREEs.

Therefore, with the exception of the claystone level above mentioned, the Albian claystone

succession overlying the bauxite shows a greater potential as source of these strategic elements.

Redox fluctuations would have played an important role in the distribution of Fe and Ce during

bauxitization in relation to the precipitation of Fe oxides and accessory minerals such as those of the

goyazite-crandallite series. Accessory minerals seem to have played a major role in the distribution

and behaviour of, at least, some of the REEs.

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TABLE AND FIGURE CAPTIONS

749 Table 1. Whole-sample mineralogical composition (%). Kln: kaolinite, Gbs: gibbsite, Bhm:

750 boehmite, Dsp: diaspore, Hem: hematite, Gt: goethite, Ant: anatase, Rt: rutile, Ill: illite, Qtz: quartz,

751 Cal: calcite, Gyp: gypsum, tr.: traces.

752 Table 2. The <2 μm fraction mineralogical composition (Kln: kaolinite, Ill: illite, Sm: smectite tr.:

753 traces) and kaolinite crystallinity (KC).

754 Table 3. Chemical composition of the analysed samples. Major elements in weight per cent (wt. %)

755 and trace elements in parts per million. wt. % oxides recalculated to 100 % on a volatile-free basis.

756 Figure 1. Geological setting of the study area located in the Maestrazgo region (NE Spain).

757 Figure 2. Stratigraphic sketch of the studied outcrop, location of the studied samples, and hand

758 specimens of the bauxite.

759 Figure 3. Representative XRD patterns of the study samples. a: Bauxite Gi-2, whole sample. b:

760 Claystone Gi-4, whole sample. c: Bauxite Gi-1, < 2μm fraction, ethylene-glycol-treated (EG)

761 oriented aggregate. d: Claystone Gi-6, air-dried (AO) oriented aggregate. Kln: kaolinite, Gbs:

762 gibbsite, Bhm: boehmite, Dsp: diaspore, Hem: hematite, Gt: goethite, Ant: anatase, Rt: rutile, Ill:

763 illite, Sm: smectite.

764 Figure 4. Optical microscope images of claystone samples under transmitted light. a: occasional

765 observable kaolinite "booklets" (low birefringence). b: carbonaceous organic matter remains (OM)

766 in the uppermost part of the claystone succession.

767 Figure 5. Optical microscope images of the bauxite under transmitted light. a: Spheroidal to

768 elongated ooids composed of fine particles similar to those of the matrix where they are embedded.

769 b: Core of a pisoid composed of particles similar to those of the matrix, and containing ooids. c:

770 Irregular and fractured Fe-oxide-rich zone in the innermost part of a pisoid. d: Pisoid cortex made

771 up of several concentric thin, irregular and discontinuous layers. e: Radial fractures filled with Fe

772 oxides affecting the thick, innermost part of the cortex of a pisoid. f: Fe-oxide-rich crust showing

773   radial, tangential and sinusoidal fissures, between the massive core and the layered cortex of a

774   pisoid.

775   Figure 6. Secondary electron (SE) images of the bauxite. a: Mainly euhedral to subhedral

776   nanometric kaolinite (Kln). b: > 1 µm kaolinite plates forming "booklets". c: Elongated crystals of

777   probable Al hydroxides (Al ph). d: Planar and anhedral Fe oxide (Fe Ox) crystals. e: Accumulations

778   of elongated, nanometric crystals of an Al phase coated by a vermicular kaolinite aggregate in an

779   individual macropisoid. f: Subhedral tabular crystal of an Al phase in an individual macropisoid.

780   Figure 7. Backscattered electron (BSE) images of the bauxite. a: Kaolinite aggregate cemented by

781   an Al phase (Al ph), probably gibbsite, in the bauxite matrix. b: Ooids and micro-ooids show a

782   similar appearance to the matrix, and probable gibbsite (Al ph) can be observed cementing kaolinite

783   (Kln) aggregates too. c: Detrital mica-type phyllosilicates in the core of pisoids and macropisoids,

784   together with vermicular kaolinite aggregates, Fe oxides (Fe OX) and Ti oxides (Ti Ox). d:

785   Goyazite-crandallite series mineral (G-C) cementing quartz (Qtz) grains with signs of dissolution

786   and associated with Fe oxides in the core of a Fe-rich pisolith. e: Al-phase-rich layer and another

787   layer where kaolinite "booklets" embedded in nanometric Al-rich phases predominate, in the cortex

788   of a pisolith.

789   Figure 8. Scanning electron microscopy (SEM) images of the claystone. a: Vermicular aggregate of

790   kaolinite (Kln); secondary electron (SE) image. b: Accumulation of nanometre-sized slightly wavy,

791   laminar crystals of an Al-rich phase in a pisolith-like particle from the claystone with carbonate

792   nodules; SE image. c: Al-rich phases (Al ph) like those shown in b are sometimes partially included

793   in gypsum (Gyp); SE image. d: < 2 µm kaolinite and illite (Ill) together with kaolinite "booklets"

794   and larger mica-type phyllosilicates; sometimes kaolinite occurs between open cleavage sheets of

795   mica; backscattered electron (BSE) image. e: Kaolinite "booklets" with occasional mica sheets and

796   kaolinite between opened cleavage sheets of mica; BSE image. f: Kaolinite "booklets" with scarce

797   mica sheets cemented by micritic calcite (Cal) in a carbonate nodule; BSE image. g: Organic matter

798   remains and nodular accumulations of pyrite (square) in the uppermost part of the claystone

succession, BSE image. h: Higher magnification BSE image of the square in g, showing pyrite

cubes along with nanometre-sized illite and kaolinite particles.

Figure 9. a: Plot of Al_2O_3 vs. TiO_2. b: Average and range values of major element concentrations

normalized to the Upper Continental Crust (UCC) concentrations (Taylor and McLennan, 1985). c:

Average and range of change % values of major elements.

Figure 10. a: Average and range values of some important trace elements normalized to the UCC. b:

Average and range change % values of trace elements.

Figure 11. a: Average and range REE+Y concentrations normalized to the UCC. b: Average and

range change % values of the REE+Y. c: Chondrite-normalized REE+Y patterns.

Table 1

| | | Whole sample | | | | | | | | | | | |
| | | Kln | Gbs | Bhm | Dsp | Hem | Gt | Ant | Rt | Ill | Qtz | Cal | Gyp |
sample description	sample												
Grey-black claystone	Gi-8	92	-	-	-	-	-	5	tr.	-	-	-	-
Grey claystone (carbonate nodules)	Gi-7	66	tr.	-	-	tr.	-	tr.	tr.	-	tr.	18	tr.
Grey claystone	Gi-6	68	-	-	10	tr.	-	5	-	15	-	-	-
Grey-ochre claystone	Gi-5	70	-	-	-	-	26	tr.	-	-	-	-	-
Grey claystone	Gi-4	67	-	-	6	-	9	tr.	tr.	14	-	-	-
Grey pisolitic bauxite	Gi-3	77	19	-	-	-	-	tr.	tr.	-	-	-	-
White pisolitic bauxite	Gi-2	87	5	tr.	-	tr.	-	tr.	tr.	-	-	-	-
Red pisolitic bauxite	Gi-1	71	16	tr.	-	6	-	tr.	tr.	-	-	-	-

826

827 Table 1. Whole-sample mineralogical composition (%). Kln: kaolinite, Gbs: gibbsite, Bhm:

828 boehmite, Dsp: diaspore, Hem: hematite, Gt: goethite, Ant: anatase, Rt: rutile, Ill: illite, Qtz: quartz,

829 Cal: calcite, Gyp: gypsum, tr.: traces.

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Table 2

| | | < 2 μm fraction | | | | | | |
| | | Kln | Ill | Sm | KC | | | |
Sample description	sample				AO (001)	AO (002)	EG (001)	EG (002)
Grey-black claystone	Gi-8	100	-	-	0.3	0.3	0.3	0.3
Grey claystone (carbonate nodules)	Gi-7	100	-	-	0.2	0.2	0.2	0.1
Grey claystone	Gi-6	89	11	-	0.4	0.4	0.5	0.3
Grey-ochre claystone	Gi-5	76	24	-	0.4	0.3	0.3	0.2
Grey claystone	Gi-4	79	21	-	0.3	0.3	0.3	0.3
Grey pisolitic bauxite	Gi-3	100	-	-	0.1	0.2	0.2	0.2
White pisolitic bauxite	Gi-2	100	-	-	0.2	0.1	0.2	0.1
Red pisolitic bauxite	Gi-1	97	-	tr.	0.2	0.2	0.2	0.2

831

832 Table 2. The <2 μm fraction mineralogical composition (Kln: kaolinite, Ill: illite, Sm: smectite tr.:

833 traces) and kaolinite crystallinity (KC).

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Table 3

Sample description	sample	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$(T)	TiO$_2$	MnO	MgO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$	Sc	V	Cr	Co	Ga	Ge	Rb	Sr	Zr	Nb	Cs	Ba	Ni	Cu	Zn	Hf
Grey-black claystone	Gi-8	49.75	42.09	4.12	2.61	0.01	0.38	0.30	0.10	0.53	0.10	23	248	210	11	48	1	32	265	431	39.10	4.90	172	91	46	78	11.80
Grey claystone (carbonate nodules)	Gi-7	42.96	35.48	3.91	2.34	0.02	0.30	14.76	0.05	0.15	0.04	20	234	220	18	36	1.30	7	134	426	32.80	1.10	52	110	28	134	12.10
Grey claystone	Gi-6	53.26	39.25	3.42	2.04	0.01	0.36	0.44	0.10	1.01	0.09	19	204	210	8	44	1.40	53	338	366	33.20	9.10	177	88	32	51	10.70
Grey-ochre claystone	Gi-5	32.99	27.26	36.35	1.38	0.01	0.23	0.75	0.08	0.82	0.13	17	215	160	24	37	1.70	43	387	237	21.50	7.90	261	99	113	44	6.70
Grey claystone	Gi-4	56.64	32.94	5.82	2.36	0.01	0.27	0.45	0.12	1.12	0.27	24	264	190	12	42	2.40	67	774	462	38.20	11	209	80	23	40	13
Grey pisolitic bauxite	Gi-3	43.54	51.75	1.15	3.01	0.02	0.19	0.15	0.06	0.09	0.05	20	291	290	14	49	1.30	3	187	592	42.80	0.70	36	87	15	50	16.20
White pisolitic bauxite	Gi-2	44.29	42.52	10.17	2.64	0.03	0.10	0.11	0.06	0.04	0.05	30	319	250	10	47	1	2	147	550	41.20	0.50	23	75	21	63	15.20
Red pisolitic bauxite	Gi-1	38.86	43.21	14.55	2.90	0.01	0.15	0.21	0.05	0.04	0.04	29	326	240	7	46	1	2	85	609	44.60	0.60	1074	92	16	98	16.20

Sample description	sample	Th	U	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	CIA	∑REE+Y	∑LREE	∑HREE	Eu/Eu*	Ce/Ce*	(La/Sm)c	(Gd/Yb)c	(La/Yb)c
Grey-black claystone	Gi-8	25.40	20.90	47.70	83.40	143	15.30	46.80	6.35	1.21	5.65	1.06	7.28	1.57	4.90	0.78	5.13	0.74	98.27	370.87	294.85	27.11	0.62	0.86	8.27	0.89	10.99
Grey claystone (carbonate nodules)	Gi-7	28	11.30	49.50	18.50	40.20	4.90	19.60	4.68	1.11	5.73	1.05	7.61	1.67	4.66	0.76	5.04	0.77	99.29	165.79	87.88	27.30	0.66	0.98	2.49	0.92	2.48
Grey claystone	Gi-6	21.40	3.87	64.00	150	272	23.80	76.10	15.70	3.45	14.50	2.01	11.80	2.16	6.50	0.99	6.86	1.08	96.88	650.95	537.60	45.90	0.70	0.92	6.01	1.71	14.78
Grey-ochre claystone	Gi-5	22.90	3.29	99.40	327	120	52.10	168	27.10	5.23	20.90	2.59	13.80	2.52	7.61	1	6.17	0.95	96.37	854.37	694.20	55.54	0.67	0.19	7.59	2.75	35.81
Grey claystone	Gi-4	27.10	5.13	343	681	288	113	318	45.70	9.53	43.70	8.20	55	11.30	33.60	5	31.90	4.82	95.91	1991.75	1445.70	193.52	0.65	0.22	9.38	1.11	14.43
Grey pisolitic bauxite	Gi-3	36.90	9.21	55.50	21.20	57	5.41	20.70	3.61	0.83	4.82	1.07	8.19	1.78	5.49	0.85	5.72	0.90	99.62	193.07	107.92	28.82	0.61	1.24	3.70	0.68	2.50
White pisolitic bauxite	Gi-2	35.70	9.68	68	25.10	37.20	5.66	22.60	4.96	1.18	7.01	1.33	9.31	2.03	5.87	0.87	5.86	0.93	99.68	197.91	95.52	33.21	0.61	0.69	3.19	0.97	2.89
Red pisolitic bauxite	Gi-1	34.50	9.18	65.20	23.50	38	5.14	19.40	4.05	1.09	6.43	1.32	9.06	2	5.95	0.90	6.15	0.99	99.72	189.18	90.09	32.80	0.65	0.77	3.65	0.85	2.58

Table 3. Chemical composition of the analysed samples. Major elements in weight per cent (wt. %) and trace elements in parts per million. wt. % oxides recalculated to 100 % on a volatile-free basis.