

1 **ROOT CALCRETES AND URANIUM-BEARING SILCRETES**

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3 **ROOT CALCRETES AND URANIUM-BEARING SILCRETES AT**

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4 **SEDIMENTARY DISCONTINUITIES IN THE MIOCENE OF THE MADRID**

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5 **BASIN (TOLEDO, SPAIN)**

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16 **ABSTRACT**

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17 This paper reports a detailed study of the calcrete and silcrete profiles in the Miocene
18 detrital deposits in the western area of Madrid, at the boundary of two main sedimentary
19 units. The aims of this work were to better understand the pedogenic and diagenetic
20 environments in which these profiles formed and to determine the cause(s) of their
21 enrichment in uranium. Calcrete and silcrete duricrusts are characteristic features of
22 closed continental basins in semiarid climates; this paper discusses the significance of
23 duricrusts as indicators of important change in such basins.

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24 The detailed macromorphological, micromorphological, and geochemical study of
25 three duricrust profiles revealed the sequence of pedogenic, vadose, and groundwater
26 processes responsible for their formation. During the first stage of their development,
27 carbonate laminae formed a white “grill-like” structure within the detrital parent
28 materials. The microstructure and macrostructure of the carbonate, which includes
29 alveolar septal structures and needle-fiber calcite, indicates the important role of roots
30 and their associated microorganisms in calcrete formation. Early silicification occurred
31 in the pedogenic-vadose environment affecting the detrital parent material, roots, and
32 calcretes, forming an early silcrete defined by opaline glaeboles and silica rhizoliths.
33 The detailed preservation of the cells in the silicified roots denotes the early
34 replacement of root organic matter. The green or green-yellowish fluorescence of the
35 silicified root structures under short-wavelength UV shows their preferential enrichment
36 in uranium. Calcitization and silicification coexisted in the pedogenic vadose
37 environment, leading to several reversible replacements of calcite and silica. Later, the
38 rise of the water table promoted silicification under phreatic conditions, as indicated by
39 the good preservation of the texture of the detrital host rocks and calcretes. Other
40 silcrete textures, such as ovoidal opaline accumulations, intraclasts produced by
41 autobreccification, and vadose silica cements, indicate later vadose environments, and
42 consequently variations in the water table.

43 The geochemical features of the calcretes and silcretes (major, minor, and rare
44 earth elements) were inherited from their parent materials. The rare-earth-element
45 patterns of some silcretes show them to have a positive Ce anomaly, suggesting that
46 oxidizing conditions reigned during their formation. The good correlation between silica
47 and uranium suggests that the silica phases acquired uranium through the direct
48 silicification of roots that had fixed uranium from organic matter.

49 This study shows that calcrete-silcrete duricrusts provide detailed information
50 regarding the processes occurring in semiarid continental basins. In the studied basin,
51 roots played a key role in both the development of the duricrust profiles and their
52 enrichment in uranium. These duricrusts provide important information for
53 understanding the overall stratigraphy of the studied basin and its large-scale sequential
54 evolution.

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56 Key words: silcretes, calcretes, roots, geochemistry, continental basins.

57

58 INTRODUCTION

59 Calcretes are calcium carbonate accumulations produced in a variety of soils (and
60 paleosols) via pedogenic processes. They also appear as surface sediments where
61 carbonate precipitation takes place in shallow vadose and phreatic meteoric water
62 (Alonso-Zarza and Wright 2010). Aridisols, Vertisols, Mollisols, and Alfisols (Soil
63 Survey Staff 1975) are the most usual soils to contain calcretes (Wright and Tucker
64 1991), in which they commonly develop in the B or C horizon as illuvial
65 concentrations. In paleosol classifications, calcrete-bearing paleosols are termed
66 Aridisols (Retallack 1993), Calcisols (Mack et al. 1993), or Paleoaridisols (Nettleton et
67 al. 2000).

68 Silcretes are silica accumulations formed by chemical precipitation as part of
69 pedogenic or nonpedogenic processes at or near the Earth's surface. Pedogenic silcretes
70 may form in a vadose environment through intermittent phases of leaching, infiltration,
71 and illuviation alternating with evaporation (Thiry and Milnes 1991). In contrast, the
72 formation of groundwater silcretes is related to silica transport driven by fluctuating
73 water tables or lateral groundwater flows (Thiry et al. 1988; Thiry 1997). Far fewer

74 studies have been published on silcretes than on calcretes, and even fewer on duricrusts,
75 in which calcrete and silcrete interfinger. Silica-carbonate associations form three main
76 types of silcrete-calcrete intergrade duricrust (Nash and Shaw 1998): 1) those with
77 secondary silica occurring within the primary calcareous accumulations, 2) those with
78 secondary carbonate occurring within the primary silica accumulations, and 3) crusts
79 where the precipitation of carbonate and silica appears to have been contemporaneous.
80 The study of the relationships between the textures and structures of calcite and silica
81 minerals (opaline phases, moganite, and quartz) throws light on the various processes of
82 silicification and calcification involved in formation of intergrade duricrusts (Bustillo
83 2010). Interpretations can be complex, since later diagenetic processes mask the
84 primary pedogenic features and because the opaline phases may undergo aging (Thiry
85 and Millot 1987; Lynne et al., 2005), i.e., successive dissolution- precipitation-
86 recrystallization stages that turn opal into moganite and/or quartz, altering the primary
87 textures and mineralogy of these phases.

88 Calcrete and silcrete duricrusts associate in semiarid, closed, continental basins
89 (Watts 1980; Armenteros et al. 1995; Ringrose et al. 2009; Pérez-Jiménez 2010). Such
90 associations are indicators of the prevailing sedimentary regimes, vegetation, and
91 climate, but they also reveal major changes in the position and chemistry of the water
92 table (Watts 1980; Bustillo and Alonso-Zarza 2007). Most studies on calcretes and
93 silcretes have been petrological or have examined their stable isotopes (carbon and
94 oxygen); few have determined their major-element, minor-element, rare-earth-element
95 (REE) and uranium concentrations (Ramakrishnan and Tiwari 1998; Ringrose et al.
96 2009) despite their possible hosting of uranium and gold deposits (McQueen 2006; Liu
97 and Jaireth 2011). Differences in the concentrations of certain elements in the parent
98 material, calcretes, and silcretes can provide clues to the mechanisms and environments

99 of formation of these duricrusts (Kampunzu et al. 2007). Of special importance is the
100 concentration of uranium in siliceous rhizcretions, which suggests a role for vegetation
101 (especially its roots; Dusenkov et al. 1997; Ebbs et al. 1998; Laroche et al. 2005) in the
102 uptake and accumulation of this element (Kabata-Pendias and Pendias 2001).

103 The present paper reports a detailed petrographic and geochemical study of three
104 calcrete-silcrete duricrusts in the western part of the Madrid Basin. The aims of the
105 study were: 1) to characterize the main petrographic and geochemical signatures of
106 these duricrusts, and to determine whether their geochemical compositions help in their
107 interpretation, 2) to determine the environments and conditions of formation of these
108 terrestrial deposits, and 3) to determine the main processes that contributed to the
109 accumulation of uranium in these duricrusts. The results may help us better understand
110 the sequence of pedogenic-diagenetic (vadose and groundwater) processes that acts in
111 distal alluvial-fan areas in semiarid, closed basins. They also indicate the processes that
112 operated in these basins during stages of low sedimentation rates that preceded the
113 major progradations of the alluvial-fan deposits, such as those observed at the boundary
114 between the Lower and Intermediate Units.

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116

GEOLOGICAL SETTING

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118 The Madrid Basin (Fig 1), which is bounded by reverse and normal faults, is
119 infilled by Cenozoic continental deposits ranging from Paleogene to Pliocene in age.
120 Among these, its Miocene sediments (300 m thick) have been divided into three
121 stratigraphic units, formally defined as the Lower, Intermediate, and Upper Units (Junco
122 and Calvo 1983; Alonso-Zarza et al. 2004; and many others) (Fig. 2). The distribution
123 of sedimentary environments and facies shows an irregular concentric pattern,

124 especially in the Lower and Intermediate Units. Coarse alluvial detrital deposits are
125 found close to the margins of the basin, gradually passing into finer clastic sediments
126 (sands and mudstones). In the more central areas of the basin, lacustrine sediments (both
127 carbonates and evaporites) were deposited. Vertical changes can be seen within each
128 Miocene Unit, with clastic deposits situated preferentially at the base and carbonates
129 and evaporites at the top. The distinction of the Miocene units from one another is based
130 upon observable lithological differences in vertical sections and the recognition of
131 sedimentary discontinuities (paleokarstic surfaces, thick calcretes, silcretes, erosional
132 and/or minor angular disconformities) (Cañaveras et al. 1996; Rodríguez-Aranda et al.
133 2002; Pérez-Jiménez 2010). The sedimentary discontinuities are overlain by (usually)
134 clastic deposits of the following unit, a consequence of the progradation of the alluvial
135 deposits coming from the basin margins.

136 The present study area is located in the western part of the basin (Fig. 1), in the
137 Province of Toledo, near the village of Torrijos. The deposits studied correspond to the
138 top of the Lower Miocene Unit (Fig. 2). These deposits are Middle Aragonian in age
139 (López Olmedo et al. 2004); this is corroborated by fossils at the paleontological sites of
140 Torrijos (Aguirre et al. 1982). The Miocene Lower Unit, in the central part of the basin,
141 is composed predominantly of evaporite facies, which grade laterally into reddish-green
142 mudstones containing anhydrite and/or gypsum nodules, and then into coarser clastic
143 materials that were deposited in alluvial environments (Ordóñez et al. 1991). In the
144 western part of the basin, however, the deposits of the Lower Unit consist mainly of
145 arkoses and associated sandy clays supplied by the granitic and high-grade metamorphic
146 rocks of the Central System and the Toledo Mountains. The proximal alluvial fan facies
147 consist of coarse conglomerates with an arkosic matrix; paleosols are very rare. The
148 alluvial facies coalesce distally in this western part of the basin and consist of

149 mudstones with associated calcretes and/or carbonate pond deposits (Alonso-Zarza et al.
150 2002; López Olmedo et al. 2004). These carbonates are commonly silicified and occur
151 mostly at the top of the Lower Unit, and are the focus of the present work. They are
152 overlain by the detrital alluvial deposits of the Intermediate Miocene Unit.

153

154

MATERIALS AND METHODS

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156 Samples of silcretes, calcretes, and parent materials were studied using
157 conventional mineralogical, petrographic, and geochemical techniques. The basic
158 mineralogical and petrographic study involved transmitted-light-microscopy inspection
159 of thin sections under polarized light. Powder X-ray diffraction (XRD) patterns were
160 obtained from pressed powder mounts using a Philips semiautomatic PW 1710
161 diffractometer with monochromatized $\text{CuK}\alpha$ radiation. Clay mineralogy was determined
162 in oriented, glycol-solvated aggregates heated to 550°C . Uranium-bearing silica zones
163 were identified under short-wave UV light.

164

165 Appropriate areas for analysis by Micro-Raman spectroscopy were selected by
166 optical microscopy. A Thermo Fisher Raman microscope, which has a point-and-shoot
167 Raman capability of $1\ \mu\text{m}$ spatial resolution, was used with a 532 nm laser source.
168 Variations in the moganite/quartz ratio were obtained from the intensity ratios of the
169 main symmetric stretching-bending vibrations of moganite ($502\ \text{cm}^{-1}$) and alpha-quartz
($465\ \text{cm}^{-1}$), multiplied by 100 ($R_{M/Q}$). This method provides a relative measure of the
170 moganite content in relation to quartz (Bustillo et al. 2012)

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172 Scanning electron microscopy (SEM) observations were made using a FEI
173 INSPECT microscope, working at 30 kv and a distance of 10 mm, operating in high-
vacuum mode and using secondary electrons and backscatter detectors. The instrument

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The Goya Profile

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202 **Macromorphology.** This profile is about 2.5 m thick and is composed of three
203 parts: detrital parent material, calcrete duricrust and silcrete duricrusts. The 80-cm-thick
204 parent -material outcrop is a reddish-brown, loose, sandy mudstone, interbedded with
205 sand lenses. The number of these lenses increases toward the top. Carbonates are
206 absent at the base, but they become increasingly common towards the upper part as fine
207 carbonate laminae, giving rise to a gradual transition from the detrital parent material to
208 the calcrete horizon.

209 The calcrete is composed of three horizons. The lower horizon includes scarce
210 white powdery carbonate nodules and very thin carbonate laminae, slightly inclined
211 with respect to the stratification of the detrital sediments. The intermediate level forms a
212 grill-like horizon about 50 cm thick. It includes horizontal laminae, 2-4 cm thick,
213 connected by vertical veins of the same dimensions. The laminae are composed of
214 powdery, soft, whitish carbonate. In the upper horizon, the carbonate laminae are
215 numerous and coalescent.

216 The top of the profile is harder and shows intense silicification. The mean thickness
217 is 60 cm, varying laterally. This silicified horizon is beige to brown in color with a
218 vitreous luster. At its base it is composed of laminae that correspond to the silicification
219 of the laminar calcrete. Above, the silicification preserves many features of argillaceous
220 sands with partly silicified carbonate laminae. Some spherical, ellipsoidal or irregular
221 small silica accumulations (< 1 cm) are visible in the general mass.

222

223 **Mineralogy and Petrology.** The parent material is composed mainly of detrital
224 grains (quartz 40%, feldspar 30%, and mica 5 to 10%), dioctahedral smectite (around
225 20%), and minor amounts of iron oxides. When observed in thin section, samples show
226 irregular, subparallel, flattened patterns of variable orientation corresponding to the
227 smectite.

228 The carbonate horizons are composed of calcite (around 90%), minor amounts of
229 quartz (< 10%), and traces of feldspar, mica, and smectites. The carbonate laminae of
230 the grill-like structures and of the laminar level are composed of a carbonate
231 groundmass and relicts of sandy mudstones. The carbonate groundmass is composed of
232 micritic nodules of differing size (0.20-2 mm), plus small quartz, feldspars, and mica
233 detrital grains, with the porosity filled by calcite spar cement. The detrital grains have
234 rounded or angular shapes, in some cases corroded by micrite. These grains are 1 mm
235 wide and up to 0.8 mm across. Isolated opaline roots, with the cellular structure
236 preserved, can be seen in the relicts of the detrital parent material and in the carbonate
237 groundmass (Fig. 4A). In addition, local gray patches (up to 0.5 mm long) composed of
238 needle-fiber calcite crystals (NFC) can be seen (Fig. 4B). According to Verrecchia and
239 Verrecchia (1994), two types of NFC exist: 1) straight needles with a central cavity,
240 known as MA1 rods, and 2) undulating needles, known as MB rods. Both types were
241 seen in the present work. The surface of the needles is coated by microrods (about 100
242 nm across and 1 μ m long) and sparse coccoids (Fig. 4C). The microrods are organized
243 into ovoid masses with a central spherical hole 1-5 μ m in diameter. Locally, some
244 fungal filaments are visible (100 μ m long), their surfaces also covered in microrods.
245 EDS analyses of the NFC suggests proportions of carbon attributable to organic matter.
246 The C/Ca ratio of an analyzed standard inorganic calcite was around 0.09, whereas for
247 the studied NFC it was about 2.55.

248 The silcretes reproduce, in part, the fabric of the parent material, and include
249 relicts of argillaceous sands, sandy mudstones, and some carbonate laminae. The XRD
250 results show the main silica phases to be opal CT (45 to 60%) and quartz (35%), with
251 small amounts (up to 15%) of clays and feldspars. Some opal A may be masked within
252 the opal CT peak. Moganite associated with quartz was identified by micro-Raman
253 analysis revealing a ratio of a moganite (502 cm^{-1}) to alphaquartz (465 cm^{-1}) ($R_{M/Q}$) of
254 between 28 and 44. (Fig 5)

255 Silicification of the detrital parent materials generated a groundmass containing
256 spherical and ellipsoid opaline accumulations, parent material relicts (Fig. 4D), and
257 silica rhizoliths (Fig. 4E). Locally, the disorganized striated texture of the smectites and
258 many features of the detrital parent materials are preserved. Some siliceous pendant
259 cements are also present (Fig. 4F). Horizontal and vertical rhizoliths appear as fine
260 white silica tubes in the brown opal. Locally they show numerous remains of root cells.
261 In longitudinal section these often appear elongated (about $50\text{ }\mu\text{m}$ long by $10\text{ }\mu\text{m}$
262 across) in the direction of the rhizoliths. Some rhizocretions show a structure with: 1) an
263 interior composed of grayish opaline root cells along with cryptocrystalline-to-
264 microcrystalline quartz mosaics and, locally, length-slow chalcedony (generally the
265 cellular structure is better preserved in the opaline part), and 2) a fine outer layer of
266 clear opal with no visible cellular structure or detrital grains.

267 SEM images show root cells in some cases associated with short NFC crystals
268 (about $6\text{-}10\text{ }\mu\text{m}$ long). The small size of the latter may be due to preferential dissolution
269 of their ends. EDS analyses of the silicified roots revealed the presence of organic
270 matter (atomic Si/C ratio = 1.03).

271

272

273 **Macromorphology.** The profile is composed of detrital parent material, calcrete
274 duricrust, and silcrete duricrust. The parent material is composed of reddish-brown
275 sands with very little pedogenic modification; it contains some centimeter-size
276 carbonate nodules. The calcrete (80 cm thick) is composed of sparse carbonate laminae
277 with nodules at its base, but its top is composed entirely of amalgamated carbonate
278 laminae. The silcrete has two parts: 1) a lower laminar part (up to 30 cm thick) showing
279 an alternation of whitish opal and darker, harder crystalline quartz zones about 10 cm
280 thick, and 2) an upper part (up to 90 cm thick) composed of a whitish-beige silica
281 groundmass showing nodular shapes.

282

283 **Mineralogy and Petrology.** The parent material is composed mainly of detrital
284 grains (quartz 70% and feldspar 20%), traces of hematite, and smectites.

285 In the calcrete, the carbonate laminae are composed of up to 95% calcite, with
286 minor amounts of quartz and feldspar. Under the optical microscope they show a
287 micritic groundmass with sparite cements in cracks (Fig. 6A), and in some places quartz
288 cements filling voids. The scarce detrital grains are highly corroded. The micritic
289 groundmass and the cracks contain many alveolar septal structures (Fig. 6A) and some
290 calcified root cells. Locally there are opal and cryptocrystalline-to-microcrystalline
291 quartz root structures (Fig. 6B). In general, root cells are better preserved in opal. Some
292 silica rhizoliths appear cracked and fragmented, probably due to dehydration. The
293 cracks are filled with calcite, indicating that calcretization took place. Later, the opaline
294 root structure was transformed into microquartz in the central part of the rhizolith
295 fragments (Fig. 6C). Remains of plant tissue, preserved as opal, can be seen in the outer
296 part.

297 The silcrete level shows variable degrees of silicification. The lower part is the
298 richest in silica, with 15% opal and up to 85% quartz. The moganite, identified by
299 micro-Raman analysis, has $R_{M/Q}$ values of between 30 and 50. Quartz zones show some
300 areas of homogeneous cryptocrystalline-to-microcrystalline quartz mosaics, and others
301 with mosaics of varied crystal size and length-fast chalcedony. Ovoids and laminations
302 can be observed under crossed-polarized light. The presence of cracks in the
303 cryptocrystalline-to-microcrystalline zones, and the close association between the opal
304 and quartz areas, suggest that the quartz is the result of opal recrystallization. Some
305 carbonate micrite remains and partially silicified pendant carbonate cements can be
306 recognized (Fig. 6D). Detrital grains are absent in this level. The upper level of the
307 profile is a partially silicified calcrete (calcite 65%, silica 35%) with micrite ellipsoid
308 accumulations (average 1 mm in diameter) and root structures. Cryptocrystalline-to-
309 microcrystalline quartz mosaics and length-fast chalcedony are the main products of
310 silicification. Opaline patches with detrital grains can be seen in the micrite; these are
311 ellipsoidal, irregular, or angular in shape, and are cut by many micritic veins. Many of
312 these patches show external parts corroded by micrite. In these areas, transformation of
313 the opal into quartz can be seen.

314 Some silicified roots with preserved cellular structures are composed of
315 cryptocrystalline-to-microcrystalline quartz mosaics and, locally, length-slow
316 chalcedony. The SEM images show the cellular structure to be preserved in calcite with
317 various degrees of silicification (Fig. 6E) and short NFC crystals in the root trace, as in
318 the Goya profile (Fig. 6F).

319

320

The Castillo Profile

321

322 **Macromorphology.** This profile is 1.40 m thick and has three levels. The lower
323 level (30 cm thick) is composed of either soft whitish or partially silicified carbonate
324 horizons, and contains relicts of clays and calcified root hairs. The middle level (1 m
325 thick) is massive and intensely silicified (Fig. 3), and of variable color (white, cream,
326 brown, or even bluish). Spherical, ellipsoidal, and irregular small silica accumulations,
327 intraclasts, and cemented horizontal cracks are common. In some places, this level
328 shows silicified nodular structures. The upper level (30 cm thick) is a laminar calcrete
329 composed of 2-cm-thick carbonate laminae with sparse silica nodules.

330

331 **Mineralogy and Petrology.** The lower horizon is composed mostly of calcite (>
332 90%) with scarce detrital grains (quartz and feldspar) and traces of clays. Under optical
333 microscopy its micritic groundmass appears highly porous (largely the porosity left by
334 root networks). Sparite is the most common cement. Locally, argillaceous glaeboles
335 with detrital grains are crossed by micrite-filled cracks. The upper part of this lower
336 horizon is silicified (up to 75%) and consists of quartz (up to 55%) and opal CT (up to
337 20%). Opal is found in discontinuous levels with quartz. The quartz occurs in voids
338 (mosaic quartz and length-fast chalcedony cements), but it is sometimes intermixed
339 with the opal in the groundmass as recrystallization textures (aging). Some horizontal
340 levels of opal and cryptocrystalline-to-microcrystalline quartz mosaics contain root
341 structures silicified as length-slow chalcedony; no carbonate precursor is visible.
342 Locally, calcified roots can be seen, but their cells are more poorly preserved than in
343 silicified roots. Some of the silica accumulations are broken by cracks filled by micrite,
344 which also etch the opal (Fig. 7A), indicative of a later calcretization stage.

345 The middle massive level is composed mainly of opal CT (25 to 50%), quartz (30
346 to 70%), and relicts of calcite and feldspar. Micro-Raman spectrometry showed

347 moganite to also be abundant ($R_{M/Q}$ 20-90 depending on the area). The
348 cryptocrystalline-to-microcrystalline quartz zones show the highest $R_{M/Q}$ values.

349 Thin sections showed this middle level to be composed of an opaline groundmass,
350 either very light in color and poor in detrital grains, or darker (brown or grayish) with
351 more grains. Some areas are richer in micrite containing many rounded or angular
352 detrital grains, in some instances corroded at their edges. Root structures appear as gray-
353 brown opal with some preserved cell walls. The uppermost part of this massive silica
354 level contains no carbonates, but it does contain floating detrital grains. It also includes
355 silicified intraformational sandy mudstone clasts (Fig. 7B). The number of detrital
356 grains in these clasts is larger than in the opaline groundmass.

357 Quartz cementation varies from microcrystalline mosaics to length-fast chalcedony
358 (a normal systematic organization for silica cements between the walls and centers of
359 voids), the result of decreasing amounts of dissolved silica in the pore water. Locally,
360 the infills of some voids are complex and show a base of silicified laminated micrite
361 overlain by length-fast chalcedony cements. These infillings are texturally similar to
362 those of carbonate pseudomicrokarst (Fig. 7C, D).

363 SEM images show some cavities to contain thin opaline cements (2-3 μm thick)
364 that are very different from the groundmass. These cements are composed of silica
365 microspheres (up to 200 nm size) and lack carbon (as determined by EDS). The opaline
366 cements are made up of lepispheres with a carbon chemical signal (atomic Si/C ratio =
367 4.9). Some lepispheres, seen individually and under higher magnification, appear to be
368 composed of an assemblage of nanospheres (which might be an association of more
369 elongated shapes). Larger and more homogeneous branching filaments are coated and
370 trapped by these lepispheres (Fig. 7E, F).

371 The upper level is composed mainly of calcite (> 85%) with small amounts of
372 quartz (10%) and opal (< 5%). The groundmass is composed of micrite, with cracks
373 filled by sparite but in some cases also by length-fast chalcedony. Opaline glaeboles are
374 interspersed among the micrite. These angular or rounded glaeboles are crossed and
375 etched by many micrite veins. While some root networks are observed locally, cell
376 structures are very rare or absent. Some silica vadose cements are also found.

377

378

GEOCHEMISTRY

379 The geochemical compositions of 23 bulk samples representing all material types
380 were analyzed (Tables 1, 2, and 3 in supplementary material online).

381

382

Major Elements

383

384 The considerable parent-material variation in SiO₂ (49% to 74 %), Al₂O₃ (9.3% to
385 16.1%), Fe₂O₃ (2.7% to 5.2%) and CaO (1.32% to 10.97%) depends on the amount and
386 composition of the detrital sediment, and on the presence of minor amounts of calcite.

387 The calcrete CaO content varies from 35.26% to 42.74%. The SiO₂ content (15.42
388 to 27.98%) correlates with that of Al₂O₃ (1.69 to 3.78%), indicating that both are
389 sourced from detrital parent-material components, with minor contributions from silica
390 accumulations. In the silcretes, SiO₂ varies between 80.83% and 97.07%, whereas sil-
391 calcrete intergrades have less SiO₂ (42.20 to 77.56%) and more CaO (9.89 to 29.61%).

392 In the silcrete and sil-calcrete intergrades, the coefficient of correlation for silica
393 with other major elements is negative ($r < -0.98$), since SiO₂ is the product of a
394 silicification process; it therefore replaces other components. The correlation of Al₂O₃

395 with other major elements (Fig. 8A, e.g., see Fe_2O_3 and Al_2O_3) is overall strong and
396 positive, reflecting the composition of the initial detrital components.

397

398 *Minor elements*

399

400 With the exception of U and Sr, the minor-element contents of the detrital parent
401 material (Ba, Be, Co, Cs, Ga, Hf, Nb, Rb, Sn, Ta, Th, V, W, and Zr) are higher than
402 those of the duricrust. The correlation matrix indicates a good positive correlation of
403 Al_2O_3 (generally $r > 0.80$) with most minor elements, indicating that the minor elements
404 (except for U and Sr) come from detrital minerals of the parent material.

405 In the duricrusts, the correlation between U and SiO_2 is good ($0.84 < r < 0.96$) (Fig
406 8B). The U shows a negative correlation with Al_2O_3 (up to -0.82) and with CaO (up to -
407 0.95), suggesting that it is associated with the opal and quartz. The good positive
408 correlation of Sr with CaO ($0.80 < r < 0.97$) (Fig. 8C) is due to the substitution of Ca by
409 Sr in the carbonate horizons. In the calcretes, the amount of Sr varies between 320 and
410 461 ppm.

411 The content of metals depends on the nature of the rock. While detrital parent
412 material is relatively rich in all metals, these are less common in the silcretes, with the
413 exception of Au (< 0.5 to 87.3 ppm). The good correlation ($0.93 < r < 1$) of the metal
414 values (with the exception of Au and Hf) with Al_2O_3 and Fe_2O_3 indicates that they are
415 present in detrital grains and clays within the duricrust. Au does not correlate well with
416 any element, indicating its sporadic detrital origin.

417

418 *Rare Earth Elements*

419

420 The results of REE analyses were normalized using the composition of North
421 American shales (NASC index) (Gromet et al. 1984).

422 REE contents vary widely, with greater anomalies recorded for the detrital parent -
423 material than for the duricrusts (Fig. 9). In the duricrusts, only weak, negative
424 correlations between REE and SiO₂ and CaO exist. However, total REE correlates well
425 with Al₂O₃ (Fig. 8D), and with Fe₂O₃ ($0.80 < r < 1$), indicating that the REE are located
426 in relicts of detrital parent materials. In the Castillo profile, the values are lower ($r =$
427 0.73), possibly because the samples include silcrete lithoclasts of different chemical
428 composition.

429 In the Goya profile (Fig. 9A), the Eu anomaly of the silcretes is negative, but
430 smaller ($\text{Eu}/\text{Eu}^* = 0.57$) than in the detrital parent material (Eu/Eu^* around 0.64). A
431 weak positive anomaly for Ce is seen in these silcretes, something not seen for the
432 detrital parent material or the silicified roots (see Goya sample 8-clear), which show a
433 flat pattern.

434 In the Golf profile (Fig. 9B), the calcrete Ce and Eu anomalies are negative.
435 Silcrete REE concentrations are low and their patterns nearly flat, with a weak, negative
436 anomaly for Eu and a weak positive anomaly for Ce.

437 In the Castillo profile (Fig. 9C), the correlations are not as strong as in the other
438 profiles. Only Sm and Eu correlate well with Al₂O₃ and Fe₂O₃ ($0.80 < r < 0.89$),
439 possibly because they are located solely in feldspars. The highest REE values were
440 recorded in the duricrust samples (calcretes and some silcretes) with the largest numbers
441 of detrital grains. The Eu negative anomaly of the Castillo profile is very clear, while
442 its Ce anomaly is weak and variable. The REE content of the intermediate massive
443 silica level is uniformly very small (the curves are nearly flat), with the exception of the
444 Eu negative anomaly (Fig. 8C).

445

446

Uranium: Localization and Study

447

448 Under short-wavelength UV, many of the samples show green or green-yellowish
449 fluorescence, indicating the possible presence of uranium. Many areas of fluorescence
450 are associated with vertical or horizontal silicified root structures (Fig. 10A, B). Indeed,
451 in some cases more intense fluorescence is seen at the center of the root structure. In
452 other cases, however, the fluorescence is restricted to fine silicified levels, which in
453 hand samples appear more crystalline (Fig. 10C, D). Geochemical analyses of bulk
454 silcretes and calcrete-silcrete intergrades showed the uranium content to vary from 6.2
455 ppm to 97.5 ppm (Table 2). The coefficient of correlation of SiO₂ with uranium is high
456 (> 0.9) suggesting the latter to be located in the silica phases and not in the carbonates.
457 The coefficient of correlation of CaO with uranium is $-0.84 < r < -0.94$. The optical-
458 microscopy observations made indicate the fluorescent areas to be concentrated in zones
459 of cryptocrystalline-to-microcrystalline quartz mosaics. In root structures, the
460 cryptocrystalline-to-microcrystalline quartz displays features corresponding to
461 recrystallization (aging) and to the remains of opal with well-preserved root cell
462 structures. Other fluorescent zones correspond to areas of aging; here the quartz shows
463 striated birefringence, and Micro-Raman analysis indicates relatively large amounts of
464 moganite.

465 The main Micro-Raman spectroscopy uranium peaks defined by Pointurier and
466 Marie (2010) were not seen in the phases studied. Only a small number of opaline rims
467 showed low-intensity peaks, at 228-237 cm⁻¹, 334-350 cm⁻¹ (broad band), 412-414 cm⁻¹,
468 and 781-784 cm⁻¹. Peaks around 237 cm⁻¹ and around 335 cm⁻¹ have been recorded in
469 some UO₂ samples (Manara and Renker 2003). The 412 cm⁻¹ (Piltch et al. 2009;

470 Pointurier and Marie 2010) and the 780 cm^{-1} peaks have been found in some uranyl
471 chemical compounds (Sarsfield and Helliwell 2004; Frost and Cejka 2009), but for the
472 present samples these peaks appear only weakly, making uranium identification
473 difficult. The CL-SEM studies for uranium yielded more conclusive results. Analyses
474 of the nonfluorescent zones showed spectra with various broad emission bands around
475 320, 380, 440, 460, and 650 nm (Fig. 11A) corresponding to opal and quartz (Stevens-
476 Kalceff et al. 1997; Gotze et al. 2001). Other silica zones have two major peaks around
477 505 nm and 525 nm, and two minor peaks at 545 and 570 that overlap the silica
478 emission bands (Fig. 11B). These four peaks are attributed to the presence of uranyl
479 ions (Billard and Geipel 2008) in silica minerals. The general shape of the spectra (Fig.
480 11B) coincides with those of silica gel containing uranium (Cheng 2010). In some
481 cases, silica bands are dominant and can mask the main potential uranium peaks; in
482 other instances the main uranium peaks are so intense that the silica signal is masked
483 (Fig. 10C). CL fluorescence intensity can vary due to the number of uranyl ions, but
484 also because of factors such as particle and pore size or water content in the silica
485 phases (Cheng 2010). In general, spectral analyses show a greater intensity of the major
486 uranium peaks in cryptocrystalline-to-microquartz areas than in opal areas. The CL
487 panchromatic images showed differences of luminescence associated with rock textural
488 features such as ovoid morphologies or groundmass. The SEM with WDS analyses
489 detected very small quantities of uranium (between 0.004 and 0.017 in atomic weight
490 %) in some areas of the silicified roots. It is therefore very probable that uranium is
491 dispersed in the opal and quartz, and does not form independent minerals.

492

493

DISCUSSION

494

Calcretes

495

496

497 The three profiles studied differ from classic calcrete profiles (Esteban and Klappa
498 1983). The main difference is the lack of well developed nodular horizons below the
499 laminar ones; such nodular horizons are commonly described in thick calcrete profiles
500 (Meléndez et al. 2011). Following the classification of Retallack (1988), the soil
501 profiles can be said to be only weakly developed, and it is difficult to classify them
502 according to the morphological classifications of calcic soils (Gile et al. 1965; Machette
503 1985) or Calcisols (Mack et al. 1993). It is also difficult to determine whether they are
504 part of an A or B horizon of a soil since they occur in different positions within the soil
505 profiles. Mack and James (1992) refer to them as Ak horizons since they occur in the
506 uppermost horizon of a soil and contain carbonate, while Wright et al. (1995) refer to
507 Krh horizons. In two of the profiles studied (Golf and Goya), the horizon below the
508 laminar zone is made up of a framework of horizontal and/or vertical carbonate laminae
509 intercalated within the parent material (Fig. 3). In the Castillo profile the initial calcrete
510 structure has disappeared due to silicification. The organization of the macrofabric and
511 microfabric of the carbonates is characteristic of incipient calcrete profiles the formation
512 of which is mostly driven by root activity (Alonso-Zarza 1999). Very commonly,
513 calcification of horizontal root mats results in the formation of isolated, thick laminar
514 calcretes, but in other cases thin laminar calcretes are isolated within the parent material
515 (Alonso-Zarza and Wright 2010). The calcification of vertical root systems has also
516 been described (Rossinsky et al. 1992; Alonso Zarza and Jones 2007). In both the Golf
517 and the Goya profiles, the mostly horizontal root systems were connected vertically to
518 form a grill-like framework. All these calcretes can be understood as rootcretes (Jones
519 1992) or rhizogenic calcretes (Wright et al. 1995).

520 Evidence of root and associated microorganism activity can be seen in the
521 carbonate laminae. Alveolar septal structures attributed to the calcification of root
522 structures, in association with fungi (Wright 1986), are very common, along with
523 calcified root cells, such as those described by Jaillard et al. (1991) and Kosir (2004).
524 NFC coated with microrods is commonly found in modern and recent carbonate soils
525 (Verrecchia and Verrecchia 1994), which is indicative of either direct fungal
526 biomineralization (MA rods) or of physicochemical mineralization of decayed fungal-
527 sheath organic matter (Verrecchia and Verrecchia 1994; Bajnóczi and Kovács-Kis
528 2006).

529 The REE and minor-element contents of the calcretes reflect mainly the
530 composition of the parent material, with the exception of Sr, which is associated with
531 previous carbonate phases. Calcrete enrichment in Sr is possibly due to the replacement
532 of Ca by Sr in carbonates, a consequence of the strong affinity of Sr for Ca (both have
533 similar chemical properties) (Morse and Mackenzie 1990; Capo and Chadwick 1999;
534 Dart et al. 2007). This explains the strong correlation between Sr and Ca in the studied
535 profiles. Ringrose et al. (2009) suggest that such enrichments may be the product of Sr-
536 enriched plant uptake within the calcrete level. The shape of calcrete REE patterns does
537 not differ greatly from those of the siliciclastic parent material, but the concentration of
538 REE elements is different, indicating a common source for the REE. Relicts of detrital
539 components included in the calcretes are the likely cause of the negative Eu anomaly.

540

541

Silcretes

542

543 The silcretes formed by the extensive replacement of detrital parent materials and
544 calcretes. The main characteristics of the observed silcretes are the partial preservation

545 of: 1) the textures, structures, and components of the detrital parent materials, 2) the
546 macrostructure and microstructure and some components of the calcrete (some detrital
547 grains, relicts of clays, laminar and root structures, glaeboles, vadose cements,
548 microkarts cements, etc.), and 3) the presence of silicified root structures.

549 The silicification of detrital parent material and the calcretes initially yielded opal.
550 The replacement of calcite by silica (which is very common) is driven mainly by
551 variations in pH. Maliva and Siever (1989) reported three mechanisms for the
552 replacement of carbonates by silica: (1) the production of CO₂ by the decomposition of
553 organic matter, or the introduction of CO₂ into the water present by biological activity,
554 resulting in a local lowering of the pH and thus affecting calcite solubility and inducing
555 silica precipitation (Siever 1962; Knoll 1985; among others) (pH values of < 9 favor the
556 dissolution of calcite and the precipitation of silica whereas higher values induce the
557 opposite, promoting the calcification of silcretes; Nash and Shaw 1998), (2) oxidation of
558 hydrogen sulfide, reducing the pH at oxic-anoxic boundaries (Clayton 1986), and (3) the
559 dissolution of calcite and the precipitation of silica via the mixing of marine and
560 continental waters (Knauth 1979). Part of the groundwater in the mixing zone can be
561 simultaneously supersaturated in quartz and opal, and undersaturated in calcite. In
562 continental semiarid environments, the same mechanism can occur at the top of the
563 groundwater, where more saline percolating waters mix with less salty groundwater. In
564 the studied duricrusts, mechanisms 1 and 3 may have caused the silicification seen.

565 The mechanism of silicification of detrital parent material has been studied less
566 extensively than that affecting limestone. However, it involves a progressive loss of Al
567 in the clay-mineral structures and other aluminum silicates. Any structure remaining
568 after the destruction of the octahedral sheets of the clay minerals must become totally
569 disorganized before any new recrystallization into silica, and this transition could occur

570 only through a local dissolution-recrystallization process (Elssas et al. 2000). The
571 problem is to explain the evacuation of Al after the replacement of clay minerals and
572 other aluminosilicates. Summerfield (1983) proposes the gradual replacement of clay
573 minerals by silica through the removal of Al where the pH is below 4, implying a high
574 rate of organic activity with abundant production of humic acids. However, it would be
575 difficult for such pH values to exist in the studied environments, except in areas of root
576 decomposition.

577 The source of silica in groundwater silcretes is sometimes difficult to find. During
578 the Miocene, the Madrid Basin was closed and had an arid or semiarid climate. In
579 semiarid closed basins and near-surface environments, variations in the water table
580 might give rise to complex replacements. Some silica might come from the alteration of
581 siliclastic grains, but much more may come from the formation of calcretes. During
582 calcrete formation, siliclastic grains are replaced by calcite, and the groundwater,
583 enriched in silica, will migrate across the corresponding alluvial fan towards the lake
584 margins. This source of silica has been recognized for several types of silcrete formed in
585 arid environments (Summerfield 1982; Khalaf 1988; Armenteros et al. 1995). A great
586 deal of silica concentration and precipitation may also occur when water evaporates
587 from plants (Sommer et al. 2006). McCarthy and Ellery (1995) showed the
588 accumulation of silica in the distal reaches of the Okavango Fan (Botswana) to be due to
589 (1) phytoliths mixed with the substrate by illuviation and bioturbation, and (2) the
590 precipitation of fine-grained amorphous silica from the groundwater induced by the
591 transpiration of rooted plants, plus increases in salinity.

592 The aging process promotes the transition opal→moganite→quartz. Consequently,
593 part of the opal aged to cryptocrystalline-to-microcrystalline quartz mosaics, moganite
594 and small-sized (up to 40 μ) length-fast chalcedony. Due to the inhibition of aging

595 caused by clay minerals (Bustillo 1982), silcretes that form directly on argillaceous
596 sands contain more opal than quartz; this is not the case for silcretes that replace
597 calcretes. The aging of opal, which is common in surface silcretes (Thiry and Millot
598 1987), erases part of the original opal textures.

599 Root cellular structures are better preserved in silica (opal and cryptocrystalline-
600 to-microcrystalline quartz) than in calcite, indicating that some roots were directly
601 silicified without first passing through a carbonate phase. Length-slow chalcedony
602 occurs only in roots, whereas chalcedony is length-fast in the silicified calcrete
603 groundmass. Length-slow chalcedony, which indicates a basic pH or evaporitic settling
604 (Folk and Pittman 1971), can be taken as evidence that silicification of root tissue
605 occurred in a microenvironment different from that of calcrete silicification.

606 Premortem or postmortem silicification of roots is possible. Owen et al. (2008)
607 suggest that the close association of opal with roots indicates that plants contribute to
608 their own silicification through evapotranspiration, which would locally increase the
609 silica concentration. Silica provides mechanical strength, resistance to toxicity, and fluid
610 loss (Epstein 2001). Silica is taken up through the roots as monosilicic acid (H_4SiO_4)
611 and is commonly precipitated as opal-A. The absorption of silica is likely to continue as
612 long as the silica concentration does not inhibit growth. If concentrations of dissolved
613 silica become very high, the silica and associated salts might have a potentially lethal
614 effect on plant metabolism.

615 In addition, in pedogenic environments permeated by root networks, pervasive but
616 incomplete decomposition of plant tissue may lead to the post-mortem silicification of
617 root cells (Knoll 1985). Such decomposition impacts the microenvironment, leading to a
618 local increase in CO_2 coupled with a reduction in pH.

619 The studied silcretes are made up of parent material, calcrete relicts, a massive
620 groundmass with spherical, ellipsoidal, or irregular opaline accumulations, and
621 intraclasts. All of these features are common in silicification occurring in surface
622 environments with interplay between phreatic and vadose environments (Bustillo and
623 Alonso-Zarza 2007). Some of the opaline accumulations and intraclasts are replaced by
624 micrite in cracks and/or at the outer edge. Such replacement by calcite indicates that
625 some opal accumulated before or during calcrete development.

626 With the exception of uranium, these silcretes are deficient in elements found in the
627 relicts of parent materials and calcretes. The REE patterns of the silcretes are nearly flat,
628 but in some cases negative Eu anomalies are related to detrital parent material and
629 calcrete relicts. Ce anomalies are more variable. A positive Ce anomaly is present in the
630 Goya profile but not in the detrital deposits of the section (Fig. 9). In the Golf profile,
631 small Ce-negative anomalies occur in the REE patterns of some calcretes, while small
632 Ce-positive anomalies occur in those of some silcretes (Fig. 9). Ce-positive anomalies
633 are due to a change in valency, from Ce^{+3} to Ce^{+4} (immobile form) under oxidizing
634 conditions, and the oxidized Ce occurring in cerianite (CeO_2) is accumulated in higher
635 concentrations than other REEs. Positive Ce anomalies tend to form at the tops of
636 weathering profiles in lateritic soils (Braun et al. 1990). Kampunzu et al. (2007) reported
637 duricrusts in the Moshawengh dry valleys of the Kalahari in which calcretes had
638 negative Ce anomalies, while in the cal-silcretes the Ce anomaly was positive, possibly
639 indicating that the silcretes formed from residual solutions after the calcrete precipitated.

640

641 *Sequences of Processes and Environments*

642 The processes in the alluvial fans responsible for the formation of the studied
643 profiles include pedogenic, vadose and groundwater processes (Fig. 12)

644

645 **Pedogenic-Vadose Environment.** Features such as glaebules, nodules,
646 rhizcretions, NFC, and laminar structures indicate that calcrete formed in a pedogenic
647 vadose environment. This is also indicated by the pendant vadose cements.

648 In the initial stage (stage 1, Fig. 12,) the mineralization of roots by silica and
649 calcite occurred. Later on (stage 2, Fig. 12), the formation of calcite nodules and the
650 progressive calcification of roots accounted for the formation of the thin laminar
651 calcretes. Isolated silica glaebules formed by replacement of the carbonate nodules and
652 laminae, and of the detrital parent material. New silica rhizoliths may also have formed
653 at this stage. Both types of silica accumulation (rhizoliths and glaebules) would lead to
654 the formation of a pedogenic silcrete (Dixon and McLaren 2009). The micrite corrosion
655 of opaline glaebules and the pendant vadose cements indicate a new stage of
656 calcretization (stage 3, Fig. 12).

657 **Phreatic Environment.** The calcretes and incipient silcretes underwent intense
658 silicification to generate the laterally continuous thick layers and lenticular silica levels.
659 This groundwater silicification affected the detrital rocks of the alluvial fans, the
660 calcretes forming therein (stage 4, Fig. 12), and also the incipient pedogenic silcrete
661 (silicified roots and sparse silica glaebules), reproducing the features of the host rocks,
662 as seen in many groundwater silcretes (Thiry and Ribet 1999; Nash et al. 2004). The
663 groundwater must have contained and transported large amounts of dissolved silica.
664 According to Nash and Ulliyott (2007), silicification occurs at the water table, or near
665 groundwater outflow zones, with water-table fluctuations exerting a strong control over
666 silicification. Within the groundwater fluctuation zone, variations in pH due to recharge
667 caused by meteoric water percolating through the soil capillary zone, plus surface
668 evaporation, would have favored opal precipitation (Arakel et al. 1989). During dry

669 periods a lowering of the water table would have led to the localization of silicified
670 layers and lenticular levels in a vadose environment. New silica textures (spherical or
671 ellipsoidal opaline accumulations, intraclasts produced by autobreccification, etc.), and
672 vadose silica cements formed, highlighting the interplay between phreatic and vadose
673 environments (stage 5, Fig. 12).

674 The studied calcrete-silcrete intergrades were favored by a period of very
675 reduced or absent sedimentation in the basin that allowed pedogenic and diagenetic
676 (vadose and phreatic) modification of the primary detrital sediments. It is not easy to say
677 how long this period lasted, but it was probably some hundreds of thousand of years
678 (Bustillo 2010). The landscape was probably very stable over this period.

679 All the features and processes described herein are linked to a sedimentary
680 discontinuity recognized in most of the Madrid Basin. This discontinuity is the boundary
681 between the Lower and Intermediate Miocene Units (Fig. 2). In the eastern and southern
682 areas of the basin, a large paleokarst developed on evaporite deposits, whereas in the
683 northeastern and western areas, thick palustrine deposits, calcretes, and silcretes record
684 the discontinuity. In short, these duricrusts and their intergrades can also be used as
685 indicators of significant sedimentary discontinuities in continental basins.

686

687 **The Concentration of Uranium.** The detrital siliciclastic strata of alluvial fans are
688 permeable. In the present basin, groundwater circulating through the sediments
689 dissolved uranium sourced from the oxidation of detrital uraninite and thorite from
690 cracks in dikes of the Berrocal granitic system (Central Spain) (Gómez et al. 1996). In
691 the initial stages, dissolved uranyl ions possibly accumulated in the roots of living
692 plants, as is seen in some plant species that inhabit arid regions (Kabata-Pendias and
693 Pendias 2001; Luna Porres et al. 2011). The absorption of uranium by roots - probably

694 the result of positively charged uranium ions being attracted to the negatively charged
695 root surface - depends on the initial concentration of the element, the pH, and the
696 duration of contact (Shawky et al. 2005). When available in a solution of oxidizing
697 water, uranium is fixed by local redox reactions in roots.

698 During early silicification, roots are efficient silica traps due to the presence of
699 organic matter. Uranium taken up by the root would have been incorporated into the
700 opal that formed during the replacement of the root structures. The ability of opal to
701 concentrate uranium is widely referred to in the literature. In colloidal silica, the Si-O-
702 surface termination is a strong Lewis base that forms a stable bond with strong Lewis
703 acids such as $(\text{UO}_2)^{2+}$. This allows $(\text{UO}_2)^{2+}$ to form a strong complex with Si-O
704 polymers (Schindler et al. 2010). An increase in evaporation during the precipitation of
705 opal would favor the incorporation of uranium into the opal structure (Cheng 2010). The
706 recrystallization of opal to quartz (aging) liberates uranium, which would have
707 accumulated on the surface of cryptocrystalline-microcrystalline quartz. The aging and
708 renewed mobilization of silica would have promoted minor uranium redistribution and
709 its accumulation in some fine silica layers outside of the silica rhizoliths.

710

711 CONCLUSIONS

712

713 This paper describes and discusses three calcrete-silcrete profiles occurring in
714 distal areas of alluvial-fan systems within the Madrid Basin. The following conclusions
715 can be drawn.

716

717 1. The studied calcretes do not show “classic” profiles since they lack nodular,
718 massive, powdery, or hardpan horizons. On the contrary, they consist mostly of calcified

719 root systems developed in the detrital parent material. The mechanisms of carbonate
720 precipitation were mostly driven by the activity of roots and their associated
721 microorganisms, forming thin laminar calcretes.

722 2. Silcretes formed by replacement in several stages. Early silicification occurred in
723 a pedogenic-vadose environment affecting the detrital parent material, roots, and
724 calcretes, forming an early silcrete (pedogenic silcrete) defined by opaline glaeboles and
725 silica rhizoliths. The initial silica accumulations were, in some cases, disrupted by a
726 phase of calcrete development, indicating that some silicification processes were very
727 early indeed. Later on, more general silica replacement of the detrital parent material
728 and calcretes occurred in both phreatic and vadose environments, as respectively
729 indicated by the preservation of the texture of the host rocks (typical of groundwater
730 silcretes) and by the characteristic textures of the vadose silcretes seen, e.g., ovoidal
731 opaline accumulations, intraclasts produced by autobrecchification, and vadose silica
732 cements. Calcrete-silcrete intergrades therefore formed under pedogenic-vadose and
733 phreatic conditions.

734 3. Geochemical features of calcretes and silcretes are inherited from relicts of the
735 parent materials. However, the Ce anomalies of some silcretes are different from those
736 of the parent materials. That these Ce anomalies are sometimes positive suggests
737 oxidizing conditions during silcrete formation, possibly due to residual solutions left
738 behind after the main calcretization process.

739 4. The good correlation between silica and uranium suggests that the latter is located
740 in the silica phases and not in the carbonates. Uranium-bearing silcretes initially
741 acquired the element through the direct silicification of roots that fixed it from organic
742 matter. Subsequent uranium mobilization was due mainly to the aging of opal to quartz.

743 U-bearing siliceous rhizoliths indicate the important role of plants in uranium fixation in
744 surface environments.

745 5. The location of these integrades at the boundary between the Lower and
746 Intermediate Miocene Units indicates that similar overlappings of pedogenic and
747 phreatic duricrust profiles can be used as a marker of important sedimentary
748 discontinuities in other continental basins.

749

750

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FIGURE CAPTIONS

1032

1033 Fig. 1.- Location of the study area, shown in a paleogeographic sketch of the Madrid
1034 Basin at the time of the deposition of the topmost Lower Miocene Unit. The black area
1035 is the city of Madrid.

1036

1037 Fig. 2.- Stratigraphy of the study area showing the location of the studied calcrete-
1038 silcrete profiles at the top of the Lower Miocene Unit. Modified from Alonso-Zarza et
1039 al. (2002).

1040

1041 Fig. 3.- Measured sections and field images of the Goya, Golf, and Castillo profiles. All
1042 correspond to the same stratigraphic position (top of the Lower Miocene Unit). The
1043 numbers 1, 2, and 3 correspond to the parts described in the text. The hammer is 33 cm
1044 long.

1045

1046 Fig. 4.- Goya profile. Optical microscopy (plane-parallel light) and SEM photographs.
1047 The optical-microscope images correspond to thin sections taken perpendicular to the
1048 surface of the beds. **A)** Silica rhizoliths (SR) within detrital host sediments. The root
1049 tissues are neatly preserved (red arrow). **B)** SEM image. Mass of needle-fiber calcite
1050 (NFC) crystals within grumelar micrite (GM). **C)** Detailed view of NFC crystals coated
1051 by microrods (red arrow), including some spherical bacterial bodies less than 1 μm in
1052 diameter (blue arrow). **D)** Relicts of the detrital parent material (quartz and feldspar
1053 grains in a clay matrix) within the opaline mass (OP). **E)** Horizontal silica rhizoliths
1054 (SR) within an opaline mass with ovoids (red arrows). **F)** Pendant vadose opaline and
1055 quartz cements (red arrows) within silica rhizoliths.

1056

1057 Fig. 5.- Raman spectra obtained from a cryptocrystalline-microcrystalline quartz area of
1058 the silcrete, where the moganite peak (Mo) appears next to the quartz peak (Qz).

1059

1060 Fig. 6.- Golf profile. Optical microscopy (cross-polarized light) and SEM photographs.
1061 The optical-microscope images correspond to thin sections taken perpendicular to the
1062 surface of the beds. **A)** Micritic groundmass with sparite cements. The cracks contain
1063 calcified alveolar septal structures (arrows). The black zones are pores. **B)** Microquartz
1064 rhizoliths (SR) within a micritic calccrete with desiccation cracks (yellow arrow). **C)** Part
1065 of a large silica rhizolith cut by a network of cracks infilled with calcite. The red arrows
1066 indicate areas where calcite clearly cuts the silica rhizolith. The fragments of the silica
1067 root structure (FR) show an external part of the opal; the internal parts have been
1068 transformed into microquartz by ageing. The high-magnification image shows the
1069 structure of the plant tissue in the external opaline area. **D)** Partially silicified vadose
1070 pendant calcite cements showing residual calcite layers (CA) and quartz (QZ) layers. **E)**
1071 SEM image of silica rhizoliths (SR) within a mass of carbonate crystals (CA). **F)** SEM
1072 image of short NFC within the opaline mass of a rhizolith.

1073

1074 Fig. 7.- Castillo profile. Optical microscopy and SEM photographs. The optical-
1075 microscopy images correspond to thin sections taken perpendicular to the surface of the
1076 beds. **A)** The parent material includes opal angular clasts (OP) that are cut by a dense
1077 network of calcite veins (cross-polarized light). **B)** A silicified intraformational
1078 argillaceous sandy clast (LT) in the opaline mass (plane-parallel light). **C)** The base is a
1079 silicified vadose carbonate silt (VS), the middle part corresponds to a new and erosional
1080 silicified carbonate vadose layer that also includes opaline intraclasts (OI) such as root
1081 tissues (arrow). The upper part it is a quartz cement (QZ) composed mainly of length-

1082 fast chalcedony (plane-parallel light). **D)** Same as Part C (cross-polarized light). **E)**
1083 SEM image of opal lepispheres with organic filaments (red arrow). **F)** Detailed view of
1084 Part E.

1085

1086 Fig. 8.- Binary diagrams of major-elements, minor-elements and total rare-earth-element
1087 concentrations for the Goya, Golf and Castillo profiles. **A)** Fe_2O_3 vs. Al_2O_3 . **B)** U vs.
1088 SiO_2 . **C)** Sr vs. CaO. **D)** Al_2O_3 vs. ΣREE . Major-elements are in % weight; minor-
1089 elements and rare-earth-elements are in ppm.

1090

1091 Fig. 9.- NASC-normalized (Gromet et al. 1984) REE plots for samples from the Goya,
1092 Golf, and Castillo profiles. Detrital parent materials: Goya-1, 2, and 3 and Golf-8
1093 (brown). Calcretes: Golf-7 and Castillo-1 and 7 (blue). Calc-silcretes: Golf-1, 3, 4, and
1094 Castillo-2 (light green). Silcretes: Goya- 5, 6, 7, and 8 dark, Golf-2, 5, 6, and Castillo-3,
1095 4, 5, 6 (intense green). Silica rhizolith: Goya-8 clear.

1096

1097 Fig. 10.- **A)** Hand sample of silcrete from the Goya profile, formed by the silicification
1098 of detrital parent material. The brown parts are the silicified detrital deposits; the white
1099 parts are mainly opaline rhizocretions (red arrows). **B)** Image of Part A under short-
1100 wavelength UV light. The greener fluorescent areas correspond mainly to rhizocretions.
1101 **C)** Hand sample of silcrete from the Golf profile, formed by the silicification of calcrete.
1102 The laminar structure is composed of partially silicified calcrete and cryptocrystalline-
1103 microcrystalline quartz zones (MQ). **D)** Image of PartC under short-wavelength UV
1104 light. Zones with green fluorescence are mainly cryptocrystalline-microcrystalline
1105 quartz.

1106

1107 Fig. 11.- Cathode-luminescence SEM spectra. **A)** Nonfluorescent silica zones with
1108 broad emission bands (Si) around 320, 380, 440, and 460 nm, and a weak signal at 650
1109 nm. **B)** Two major uranium peaks around 505 nm and 525 nm, and two minor uranium
1110 peaks at 545 and 570, overlap the broad emission silica spectra bands (Si). **C)** The major
1111 uranium peaks are so intense that the silica signal (Si) is relatively weak.

1112

1113 Fig. 12.- Successive stages in the formation of the calcrete and silcrete duricrusts.