



HAL
open science

Silcretes: insights into the occurrences and formation of materials sourced for stone tool making.

Médard Thiry, Anthony Milnes

► To cite this version:

Médard Thiry, Anthony Milnes. Silcretes: insights into the occurrences and formation of materials sourced for stone tool making.. *Journal of Archaeological Science: Reports*, 2016, Special issue, 10.1016/j.jasrep.2016.08.015 . hal-01408425

HAL Id: hal-01408425

<https://minesparis-psl.hal.science/hal-01408425>

Submitted on 4 Dec 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Silcretes: insights into the occurrences and formation of materials sourced for stone tool making

Médard Thiry(1) and Anthony Milnes(2)

(1) MINES ParisTech, PSL Research University, Centre de Géosciences, 35 rue St Honoré 77300 Fontainebleau, France.

(2) Department of Earth Sciences, The University of Adelaide, South Australia 5005.

Corresponding author: Médard Thiry

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35

Abstract

Silcretes are clearly observed and abundant as components of paleolandscapes on several continents. Mechanisms for the formation of several varieties of silcrete, with specific relationships to paleolandscapes, are described. Each type of silcrete displays particular morphological features in its profile in the paleo-regolith, and these features provide pointers to its origin via mechanisms of *absolute* or *relative* accumulation of silica in specific environments relating to groundwater or soil-water hydrology. The characters of silcrete varieties that may have triggered the interest of prehistoric peoples to exploit them for manufacturing stone tools, and which control knappability, include granulometry and the specific nature of silica cements. The successions of silica precipitation and recrystallisation events are clearly evident as a complex of micromorphological features that provide clues to the hydrological environment and its geochemistry at the time or times of silicification. Examples are given of the distribution of different silcrete facies, which could have had differing values for exploitation for stone tool production, in modern-day landscapes in France and Australia.

Highlights

Silcretes occur widely in paleolandscapes in several continents.
What are they and how did they form?
What made silcretes suitable for prehistoric people to form stone tools?

Keywords

silicification, silcrete, petrography, mineralogy, landscapes, prehistoric tools.

36 1 Introduction

37 There is a wealth of literature on silcretes in both the geological sciences and the
38 archaeological sciences. In geology it ranges from initial compilations of knowledge like that
39 edited by Langford-Smith (1978) to the comprehensive overview of Nash and Ulliyot (2007).
40 In archaeology in Australia the studies described by Holdaway and Fanning (2014) also
41 provide a review of current knowledge and a foundation for future research. The science
42 pertaining to silcretes has actually advanced in parallel in both scientific fields with only
43 limited cross-reference, except perhaps for the work of Webb and his colleagues (Webb and
44 Domanski, 2008). In geology the early work focussed on field observations and relationships,
45 and progressed to petrographic and mineralogical studies, from which hypotheses were
46 generated about origin and palaeoenvironmental conditions. From our geological perspective,
47 some studies of stone tools in archaeological science had a ‘primitive’ view of silcrete, such
48 as that expressed in Mulvaney & Kamminga (1999, p 213), but others developed a
49 sophisticated understanding of the rock mechanical properties of silcrete and other siliceous
50 materials (Domanski *et al.*, 1994), and some also used petrographic/micromorphological
51 fabrics and textures (e.g. Summerfield, 1983) to characterise silcrete artefacts and proffer
52 ideas about their provenance. But the connection with step-by-step advances in our
53 understanding of the complex of processes and environmental conditions that have led to the
54 formation of silcretes has not been maintained and the aim of this paper is to at least partly
55 address this situation.

56 In the first instance, we should be clear about terminology. There are several
57 definitions of the term ‘silcrete’ but we prefer something along the lines of that proposed by
58 Eggleton (2001), namely;

59 *‘Strongly silicified, indurated regolith, generally of low permeability, commonly*
60 *having a conchoidal fracture with a vitreous lustre. Represents the complete or near-*
61 *complete silicification of regolith by the transformation of precursor silica or silicates*
62 *and/or the infilling of available voids, including fractures. On a macroscopic scale,*
63 *some silcretes are dense and massive, but others may be nodular, columnar, blocky,*
64 *or cellular with boxwork structure. On a microscopic scale, the fabric, mineralogy*

65 *and composition of silcretes may reflect those of the parent material, but also indicate*
66 *the changes experienced by, as well as the general environments of, silicification.*

67 The key component of the definition, from our perspective, is the phrase ‘*strongly*
68 *indurated, silicified regolith*’. Thus, silica-rich secondary materials including flint, chert,
69 agate, chalcedony, and precious and common opal are not silcretes, though there may be a
70 spatial and temporal association with some forms of silcrete. Sandstone, quartzite and some
71 forms of porcellanite and jasper (as defined, for example, in Gary *et al.*, 1973) that have
72 formed specifically as a result of secondary silicification of the regolith are silcretes, but those
73 resulting from diagenetic alteration or metamorphism are not. Red-brown hardpans (Chartres,
74 1985; Wright, 1983) are not silcretes because they are generally not ‘*strongly indurated*’ by
75 silica.

76 It is also important to note that the term ‘*silcrete*’ is an English word and concept that
77 has no equivalent in the geosciences literature in Latin languages where such material is
78 generally called ‘*sandstone*’, ‘*silicified limestone*’, ‘*silicified claystone*’, and so on. In France,
79 the word ‘*silcrete*’ was used for the first time by Parron *et al.* (1976). As well, ‘*flint tool*’ is
80 often used as a generic term in the French literature and could have been formed from
81 silicified limestone or pedogenic silcrete.

82 The environments of formation and ages of silcretes have been the subject of many
83 investigations over many years, but definitive answers still elude us. Recent work in
84 Australia on the formation and age of precious opal in Great Australian Basin landscapes
85 (Dutkiewicz *et al.*, 2015; Rey, 2013; see also critique by Dickson, 2014 and response by Rey,
86 2014) did not unravel the genetic and temporal relationship between the widespread formation
87 of opal in voids and fractures in the regolith (within and outside the margins of the Great
88 Australian Basin) and the complex suite of silcrete facies in these regions. Some work on
89 O/H isotope composition and trace element chemistry of opal and the siliceous matrix in
90 silcretes (Alexandre *et al.*, 2004; Dutkiewicz *et al.*, 2015; Harwood *et al.*, 2013; Webb and
91 Golding, 1998), may provide a future basis for interpreting conditions of formation, though
92 not age.

93 In this paper we summarise our current thinking on the characteristics, landscape
94 associations, origin and age of silcretes. We also attempt to link petrological and

95 mineralogical features (which are of specific importance to geologists in generating
96 hypotheses to explain the origin of silcretes) to the potential value of silcretes to prehistoric
97 peoples for the production of stone tools,. However, we recognise that there are substantial
98 fields of knowledge in geoarchaeology and lithic technology that rightly lay claim to the
99 development of an understanding of the associations between prehistoric peoples and the
100 source materials for stone tools.

101 Numerous siliceous materials used for tool making (flint, chert, quartzite, quartz) are
102 bound to geological formations which were buried, then exhumed and exposed fortuitously at
103 the surface in landscapes where they could be accessed, tested and exploited if suitable. On
104 the other hand, silcretes are directly linked to the landscapes in which prehistoric people lived.
105 Those silcretes that frame and armour landsurfaces as duricrusts and lags were highly visible
106 and available for testing and exploitation over wide areas of continents.

107 The most widely known silcrete duricrusts occur now in the desertic landscapes of
108 inland Australia, South Africa, Saharan Africa and the northeast of Brazil. They armour
109 plateaux and mesas dissected by erosion, thus maintaining steep scarps or ‘breakaways’ cut in
110 vari-coloured soft substrate formations that confer a spectacular aspect to the lands that
111 fascinated prehistoric people and still fascinate tourists. Silcretes are also important regolith
112 features and frame a number of landscapes in temperate regions (for example the
113 superimposed plateaux in the Paris Basin), but are less spectacular because they tend to be
114 covered and hidden by vegetation. During the glacial periods in the Late Cenozoic these
115 northern countries were somewhat bare of vegetation, with contrasting relief.

116 Although there are several forms of silcrete that can be found and recognised on many
117 continents, only some appear to have been suitable for stone tool making. The sites that have
118 generated starting materials for appropriate tools can be readily recognised in the field from
119 the litter of flakes and chips discarded during tool production. Mineralogical and
120 micromorphological properties can explain physical appearance, hardness, lustre and potential
121 durability of silcrete tools and, in some cases, in some regions, point to their provenance.
122 However, archaeologists may not be particularly focussed on sources of silcrete (or other
123 forms of siliceous rocks) that have been opportunistically exploited for the production of

124 stone tools, but rather seek to recognise specific source materials that have been valued from a
125 technological, aesthetic or symbolic viewpoint and which potentially have been transported
126 long distances. Identifying provenance from this perspective permits them to potentially trace
127 out migration patterns, exchanges, and possibly social behaviour.

128 **2 Behaviour of silica in regolith environments**

129 In order to explain the internal structures of silcretes, as well as their distribution and
130 location in specific landscape settings, it is important to understand some concepts of silica
131 behaviour in surficial environments.

132 *2.1 Silica solubility*

133 The solubility of amorphous silica in water under earth-surface conditions is about 120
134 mg/L SiO₂ while the solubility of all other silica phases is significantly lower than this (Fig.
135 1). The most soluble phases in a geochemical system control the precipitation of the less
136 soluble ones and, in this way, amorphous silica in equilibrium with a solution is able to
137 sustain the crystallisation of every other crystalline silica phase. In turn, cristobalite,
138 tridymite, chalcedony and opal in equilibrium with a solution are able to sustain the
139 crystallisation of quartz (Fig. 1; Garcia-Hernandez, 1981; Gislason *et al.*, 1993; Iler, 1979;
140 Siffert, 1967).

141 Detailed mineralogical and petrographic studies of silcretes show a consistent and
142 specific sequence of transformation/recrystallisation from more to less soluble phases,
143 namely:

144 opal → microcrystalline quartz → euhedral quartz

145

146 These transformations are the mainspring of the evolution of silcrete profiles and
147 especially account for the development of complex nodular structures in some forms. The
148 succession of recrystallization is irreversible and ultimately favours the formation of quartz
149 (Thiry and Millot, 1987).

150 It should be noted that most natural groundwaters around the world have a silica
151 content between 12 -18 ppm SiO₂ (Garrels and Christ, 1965, Swanberg and Morgan, 1978;
152 White *et al.*, 1963) that is roughly in equilibrium with clay minerals. This means that most
153 groundwaters are oversaturated with respect to quartz (solubility 4 - 7 mg/L) and are thus
154 potentially able to precipitate quartz when favourable physico-chemical conditions occur. As
155 pointed out by Thiry *et al.* (2014), solutions with a high silica content favour the formation of
156 crystal nuclei and crystal defects that restrict the growth of crystals and consequently the
157 precipitation of amorphous or low crystallinity silica varieties. However, in dilute solutions,
158 the number of nuclei and impurities remains limited. As a consequence, pure silica crystallites
159 generally form and large quartz crystals can develop or, under less favourable conditions,
160 microcrystalline or fibrous silica varieties are formed.

161 If silica is present in solution it has to be precipitated in order to generate silicification
162 and ultimately produce a silcrete. Several tracks are possible. It has long been thought that
163 increasing the concentration of the solution by evaporation was the principal triggering factor
164 for silica precipitation in relation to silcrete formation (Auzel and Cailleux, 1949; Millot
165 1970; Smale, 1973; Storz, 1928). This hypothesis resulted mainly from studies of the
166 widespread silcrete duricrusts in current desertic environments, for example in Australia,
167 South Africa and North Africa. It has now been established that these silcretes do not relate
168 to present day landscapes and climates and are in fact much older. Moreover, it is unlikely
169 that evaporation could be effective in developing meter-thick silicified horizons because it
170 would be much reduced, or cease, as soon as silica cementation commenced. Nevertheless,
171 evaporative processes may assist in concentrating silica in solution in near-surface
172 environments.

173 In contrast to evaporation, silica solubility decreases exponentially with decreasing
174 temperature. Between 12.5 and 0°C, the solubility of quartz decreases to half its initial value
175 (Fig. 2). This appears to be a very effective factor in precipitating silica from solution: it had
176 never been envisaged as a mechanism for precipitating silica in the supergene realm until
177 proposed by Thiry *et al.* (2013, 2015b) but was commonly advocated in hydrothermal
178 environments.

179 Increasing the concentrations of salts in solution is another efficient way to decrease
180 silica solubility: the solubility of amorphous silica decreases with increasing salt
181 concentration to saturation (Fig. 3), up to 96% in the case of CaCl₂ and up to 30% in the case
182 of a NaCl saturated solution (Marshall, 1980). The mixing of a silica solution with chlorite-
183 and/or sulphate-rich brine is certainly a very effective mechanism for inducing the
184 precipitation of silica. The often advocated relation between silicification and warm and dry
185 climates most probably results from the negative relationship between increasing
186 concentrations of evaporite brines and silica solubility.

187 2.2 Key geochemical processes in regolith solutions

188 As silica in regolith solutions mainly originates from the weathering or alteration of
189 alumino-silicates (such as feldspars and clay minerals) in rocks and sediments, the relative
190 solubilities of Si and Al must be taken into account. Si and Al have different domains of
191 stability (Fig. 4).

192 (1) In acidic environments, Al and Si have contradictory behaviours. Al is more
193 soluble than Si, and so alumino-silicates (clays and feldspars) are destroyed and leached of Al
194 whereas Si in the silicate frameworks, and silica minerals, remain essentially *in situ*, most
195 often in the form of opal;

196 (2) At neutral pH, Al and Si behave similarly. Al and Si both have a low
197 solubility. Both silicates and silica are relatively stable in this domain;

198 (3) In alkaline environments Al and Si are both highly soluble. Silicates and silica
199 may be altered, but such environments are rare and restricted in continental landscapes (for
200 example alkaline lakes in the east African graben).

201 Highly acidic conditions appear to be especially favourable for the degradation of
202 silicates and clay minerals via dissolution and leaching of Al and other cations to concentrate
203 silica. However, such acidic environments are not common in regolith environments and
204 require specific conditions to develop.

230 in solution to infiltrate, and initiate silicification of, specific zones or horizons in the regolith
231 (*absolute* accumulation of silica).

232 2.3 *Silicification in the regolith*

233 In general, silcretes have formed as a result of either *absolute* or *relative* accumulation
234 of silica.

235 *Relative* accumulation of silica occurs primarily as the result of the dissolution and
236 leaching of alumino-silicate minerals, specifically silicates such as feldspars and clays (Rayot
237 *et al.*, 1992; Thiry *et al.*, 2006). The process requires an acidic environment that is aggressive
238 towards these minerals and generates the loss of non-Si elements, resulting in an *in situ*
239 concentration of silica. There appears to be no significant transport of Si within the system
240 but only limited local reorganization and adjustment. However, leaching of cations other than
241 silica generates a significant loss of material leading to the disruption and collapse of primary
242 fabrics and structures.

243 *Absolute* accumulation occurs through importation of silica to the system. The silica
244 may replace pre-existing minerals or simply fill voids, fractures and intergranular pores. The
245 silica has to originate from somewhere else and has to be brought into the horizon that
246 undergoes silicification. With regard to the relatively low solubility of silica in surficial
247 waters and the relatively large volume of silica needed to infill pore spaces to effect
248 silicification, this kind of silica accumulation requires large volumes of water to flow through
249 the horizon. This is only conceivable in groundwater outflow zones (springs, seeps) and
250 implies landscape incision in order to intersect groundwater tables. Primary geological
251 structures in the host horizon are characteristically preserved.

252 **3 Varieties of silcrete**

253 Silcretes take a wide variety of forms and detailed investigations of these forms from
254 the field scale to that available via scanning microscopy provide clues to their origin. Aspects
255 such as field distribution, geomorphological patterns and relationships to current and former
256 landscapes, petrology and mineralogical-geochemical characteristics have all to be

257 considered. We group silcretes into two classes: groundwater silcretes that form mainly as a
258 result of the absolute silica accumulation of silica in regolith environments; and pedogenic
259 silcretes that reflect the relative accumulation of silica, as well as a complex of dissolution,
260 eluviation and illuviation processes typical of soil environments. Nash and Ulllyott (2007)
261 have suggested a sub-classification of ‘*non-pedogenic*’ silcretes into ‘*drainage-line*’ and
262 ‘*pan/lacustrine*’ types’, but these forms can be encompassed satisfactorily within groundwater
263 silcretes from our perspective. Of particular interest in the landscape context is that volume is
264 mostly conserved during the formation of groundwater silcretes, whereas volume is
265 substantially lost during the formation of pedogenic silcretes, some of which can be metres
266 thick in profile.

267 3.1 Groundwater silcretes

268 The main characteristics of groundwater silcretes are their disposition as a series of
269 superposed silicified lenses in the regolith and the preservation of primary host-rock
270 structures (stratification, bioturbation, fossils). There are two main varieties: those that occur
271 in sands and develop into massive quartzitic facies by infilling and cementation of pore spaces
272 between detrital quartz grains; and those that are created by epigenetic replacement of
273 limestones, claystones and even gypsum horizons, and therefore have more irregular and
274 discontinuous shapes.

275 3.1.1 Quartzitic types

276 These are typically formed in sands by cementation of the detrital quartz grains via
277 syntaxial quartz overgrowths, or other forms of silica, precipitated in pore spaces. The initial
278 condition is always a porous sediment. Quartzitic silcretes generally form well-confined flat-
279 lying pans within unconsolidated or poorly cemented sands. Those in the Fontainebleau Sand
280 have been studied in detail and are good examples.

281 In the Paris Basin, flat-lying quartzitic silcrete lenses (1-8m thick) occur at different
282 levels within the Fontainebleau Sand formation (Thiry *et al.*, 1988; Thiry *et al.*, 2013; Thiry *et*
283 *al.*, 2015a). The silcrete lenses typically crop out on the edges of plateaux or in valley
284 margins but pinch out rapidly under the limestone-capped plateaux, as shown by drill holes

285 and observations in sand quarries (Fig. 6). This strong link between silcrete distribution and
286 present-day geomorphology suggest that these silcretes developed relatively recently in and
287 near outcrop zones of the Fontainebleau Sand. Sand calcite contained in the silcretes date the
288 silicification to Pleistocene glacial periods (Thiry *et al.*, 2013).

289 Geomorphological and geological constraints suggest that silicification occurred in
290 groundwater outflow zones (springs, seeps) during landscape incision (Thiry *et al.*, 1988;
291 Fig. 7). The key process sequence is:

- 292 • precipitation of silica in horizons of the Fontainebleau Sand in a zone of groundwater
293 outflow; and
- 294 • resumption of erosion leading to lowering of the groundwater table and the formation of
295 a new silcrete pan via groundwater outflow during a subsequent period of landscape
296 stability;

297 The superposition of separate silcrete pans rather than the formation of a continuous zone of
298 silicification reflects periodicity in valley down-cutting and landscape stability.

299 The silica necessary for cementation of the Fontainebleau Sand to form quartzitic
300 silcrete has come from groundwater contained within the formation. Its silica content ranges
301 from 10 - 15 ppm, which is about three times the saturation value of quartz (4 - 6 ppm) at
302 surface temperatures and pressures.

303 The correlation of silica cementation with glacial periods, as determined by age dating
304 of contained calcite crystals, suggests that silica precipitation occurred by cooling of
305 groundwaters along discharge pathways towards outflow zones in frozen soils in the valleys.
306 Hydraulic and geochemical mass balance calculations, based on the silica content of water in
307 an average current-day spring, indicate that cementation could potentially take place over
308 about 2 000 years. This is a short geological time span and totally changes previous
309 interpretations of the time-scale for the formation of some silcretes.

310 Similar quartzitic silcretes appear to have formed under cold environments during the
311 Pleistocene in North America (Ludwig and Paces, 2002; McCoy, 2011), and such an origin
312 may apply to other occurrences, like those within white sandstone formations in Germany

313 (Götze and Walther, 1995) and in the Czech Republic (Mikulas, 2002), Greece (Skarpelis,
314 2006), southern France (Parron *et al.*, 1976) and Spain (Bustillo and Bustillo, 2000; Parcerisa
315 *et al.*, 2001), for which the origins have not yet been considered in detail. Quartzitic silcrete
316 pans may also develop in very different environments, including those that have not
317 apparently experienced cold climates. For example, in Australia (Thiry and Milnes, 1991)
318 and southern Africa (Summerfield, 1983; Nash *et al.*, 1998), quartzitic silcretes may have
319 formed in groundwater environments in dry paleoclimates where silica precipitation could be
320 attributed to a mixing of fresh and saline waters. Nevertheless, all examples relate to
321 groundwater outflows in incised landscapes and for which silica has been imported in order to
322 provision precipitation and cementation.

323 **3.1.2 Silicified limestone/calcrete types**

324 Many lacustrine limestone formations contain irregular silicified masses and have long
325 been described from dry regions such as the Kalahari Desert, North Africa and Australia, as
326 well as in more humid countries like France, Spain and the USA (Alimen and Deicha, 1959;
327 Banks, 1970; Daley, 1989; Kaiser, 1928; Nash *et al.*, 2004; Thiry and Ben Brahim, 1997).
328 The silica was generally thought to have precipitated during dry periods at the time of
329 limestone deposition in confined environments. However, petrographic observations and
330 geochemical data have generated new ideas about the formation of these silcretes.

331 The extensive Tertiary lacustrine limestones of the Paris Basin form superimposed
332 plateaux that constitute the dominant geomorphologic features. Typical examples are the Brie
333 and Beauce plateaux. Almost all of these limestones contain zones of silicification (Cayeux,
334 1929). Their size varies from millimetre-sized dots to siliceous bodies several tens of meters
335 long. The silicified facies have an irregular distribution (Fig. 8): locally, they can form over
336 10% of a quarry cliff-face, but are absent a short distance away. On the regional scale they
337 average about 5% of the volume of the lacustrine limestone in the southern Paris Basin.

338 Two types of silicification coexist: deposits of quartz and chalcedony in voids; and
339 epigenetic replacement of the limestone matrix by microcrystalline quartz, with preservation
340 of the primary sedimentary structures. Thin sections show a systematic link between

341 silicification and zones of high porosity, either preserved or partly infilled by silica deposits
342 (Thiry and Ribet, 1999).

343 Because the silicified limestones are pure, without any sandy or clayey layers, silica
344 had to be imported from elsewhere. And as the limestones have never been deeply buried, the
345 importation of silica can only have been via substantial near-surface groundwater flows,
346 which could explain the relationship between porosity and the intensity and extent of the
347 silicification. This is a very different mechanism of silica accumulation from that represented
348 by flints and cherts. In this case, silicification occurs during burial diagenesis whereby there
349 is epigenetic replacement of limestone by silica originating in microfossils in specific
350 sedimentary layers, without the formation of any voids.

351 Substantial groundwater outflows are only possible after uplift and incision of the
352 limestone formation. In the Paris Basin, such conditions were only fulfilled during the
353 Pliocene and the Quaternary periods and, therefore, the silicification had to occur relatively
354 quickly (Thiry and Ribet, 1999). Similar groundwater silicification of limestone has already
355 been described in present day hydrologic systems in inland Australia (Arakel *et al.*, 1989;
356 Benbow, 1993), southern Africa (Nash *et al.*, 2004) and Spain (Armenteros *et al.*, 1995). As
357 for quartzitic silcretes, silica precipitation was probably triggered by different geochemical
358 mechanisms (water cooling or water mixing, or others), under very different climatic and
359 environmental conditions. However, the resulting petrographic fabrics are similar: dissolution
360 of calcite making space for precipitation of silica, which may lead to very contrasted fabrics.

361 Weathering of Paris Basin silicified lacustrine limestone during Pliocene-Quaternary
362 times produced cavernous silicifications called "meulières" which delineate plateau surfaces
363 in the southern Paris Basin (Beauce Plateaux; Thiry, 1999). The meulières show a large
364 variety of facies from massive to highly porous 'cellular' facies and can be weathered and
365 desilicified into friable blocks, even breaking down into a rough sand-like material.

366 **3.1.3 Porcellanite/jasper types**

367 Fine grained silcretes, obviously resulting from silicification of primary clay-rich
368 materials, form specific facies, generally of glassy appearance, and often resembling flint or
369 chert except for their colour which is generally due to iron-oxide inclusions. Such materials

370 have been described in several geological contexts (Boule, 1888; Millot *et al.*, 1959, Valleron,
371 1981).

372 Such silicifications are widespread in inland Australia and are commonly associated
373 with bleached and weathered profiles in rocks and sediments ranging in age from Precambrian
374 to Quaternary (Simon-Coinçon *et al.*, 1996). The profiles are up to 60m deep. Their main
375 characteristics are white or pastel colour and low bulk density, together with the occurrence of
376 alunite, iron oxide mottling, extensive bioturbation by termite burrows that penetrate to great
377 depth, and ubiquitous gypsum that has crystallised in fractures and voids (Thiry *et al.*, 1995;
378 Thiry *et al.*, 2006). The bleached material is mainly formed of quartz, large booklet-like
379 kaolinite and opal A, with alunite and gypsum in pods and veins (Fig. 9). In some localities
380 the burrows and their fillings, as well as the enclosing saprolite, have been silicified. K/Ar
381 dating of alunite in these profiles indicates a Miocene age for the bleaching and weathering,
382 varying from about 16 - 18 Ma in the Coober Pedy opal field to about 8 - 12 Ma in the
383 Andamooka opal field (Bird *et al.*, 1990).

384 These profiles have resulted from alteration under acidic conditions in a saline
385 groundwater environment nearly saturated in gypsum (Thiry *et al.*, 1995). The bleaching was
386 related to the lowering of the groundwater table. Arid conditions at the time restricted water
387 flow and allowed an acidic environment to develop to leach original alumino-silicates, retain
388 Si (as amorphous silica and quartz), but not completely lose some of the most soluble
389 elements like K, Ca, SO₄ and Al from the system that form nodules and veins of alunite and
390 gypsum in places. Elevated concentrations of anatase (Fig. 9) could indicate that Ti released
391 from primary alumino-silicates has also been retained.

392 Horizontally disposed lenses or pods of porcellanite or jasper subsequently developed
393 in the bleached saprolite (Fig. 9). Primary sedimentary structures and fabrics, as well as some
394 fabrics relating to weathering and bleaching, in particular iron-mottling, have been retained
395 within these silica-indurated horizons. The superposition of several silica-indurated layers
396 relates to still-stand positions of paleo-water tables which rose significantly after the
397 widespread bleaching, thus reflecting a return to more humid climatic conditions.

398 Low concentrations of clays in the porcellanite and jasper horizons compared with the
399 host regolith (Fig. 9) points to acidic environments that probably developed via ferrolysis and
400 generated silica via relative accumulation. However, micromorphological examination shows
401 that the silicified horizons are cemented by various silica phases. The silica cements were
402 precipitated from water inflow, either by infiltration through the upper part of the profile, or
403 by lateral flow of groundwater containing silica through the profile. The silica was probably
404 derived from dissolution of silica (opal-A, quartz) and silicates (clays) in the bleached profile.
405 The formation of these groundwater silcretes required a consistent hydraulic flow regime that
406 was probably related to down cutting of the landscape (Simon-Coinçon *et al.*, 1996). Silica
407 precipitation points to mixing of fresh silica-charged water with sulphate-rich groundwater,
408 thus lowering silica solubility.

409 3.2 Pedogenic silcretes

410 Pedogenic silcretes developed near the landsurface, within soil environments, and
411 display typical soil structures (geopetal features) related to infiltration of downward
412 percolating water (such as differentiated horizons, eluviation and illuviation structures).
413 Details of this silcrete type come mainly from Eocene occurrences in the Paris Basin (Thiry,
414 1981). Specific characteristics and mechanisms of formation are also derived from
415 observations of similar materials in Australia (Milnes and Thiry, 1992; Simon-Coinçon *et al.*,
416 1996; Thiry and Milnes, 1991) and Central America (Elsass *et al.*, 2000).

417 In the southern part of the Paris Basin, silicified pans and lenses cap Eocene detrital
418 kaolinitic deposits. These are very hard, tightly cemented quartzitic silcretes that break up into
419 variably sized blocks, with puffy, tear-like shapes, coated with deposits ('cappings') of
420 yellow-white opaline silica that mask the internal structures. Typically, the silcretes have a
421 columnar structure with characteristic laminated cappings on the columns (Fig 10). They are
422 about 2 m thick and display several distinct horizons with systematic micromorphological and
423 mineralogical structures (Thiry, 1981).

424 A lower granular horizon consists of a sandy claystone with millimetric- to
425 centimetric-sized granules of microcrystalline quartz and opal. TEM and electron diffraction

426 studies of the clay matrix show that hexagonal-shaped kaolinites have corrosion embayments
427 and are coated and welded together by a silica gel.

428 An overlying columnar horizon has a matrix composed of detrital quartz grains with
429 irregular overgrowth apophyses which grade into titania-enriched microcrystalline quartz.
430 Ghosts of granules are easily recognizable within the matrix. Illuviation cutans of opal have
431 developed in fractures. The youngest laminae, at the top of the illuviation structures, always
432 consist of opal with a low titania content. The initial laminae, at the base of the illuviation
433 structures, commonly have a nodular structure and are formed of microcrystalline quartz with
434 a higher titania content. This sequence indicates a progressive recrystallisation of the opal.
435 Recrystallisation is accompanied by loss of silica, which induces the destruction of the
436 primary structures and relative accumulation of titania.

437 A more massive horizon, with complex nodular and pseudo-breccia fabric, is found at
438 the top of the profile. It is devoid of opal and the microcrystalline quartz matrix has partly
439 dissolved. Titania has accumulated in rims around the nodules. Euhedral quartz has developed
440 in the voids and some quartz grains show overgrowths.

441 Pedogenic silcretes occur widely in central and southern Australia and have been
442 described in detail from the opal fields (for example Fig. 9, near-surface horizon) and the
443 region around Alice Springs (Milnes and Thiry, 1992; Milnes and Twidale, 1983; Simon-
444 Coinçon *et al.*, 1996; Thiry and Milnes, 1991). Their morphology is typically that described
445 by Thiry and colleagues from around the Paris Basin (Barrois, 1878; Thiry, 1981), with wide
446 variations in the appearance of the columnar facies being evident in different localities. As
447 well, pedogenic silcretes occur widely in north-western Europe, in Belgium on the Ardennes
448 (Gosselet, 1888), in Germany on the Slate Mountains massifs (Lange; 1912; Teichmüller,
449 1958) and in the London Basin (Kerr, 1955, Summerfield, 1980). They occur in South African
450 and Botswanan landscapes where Summerfield (1983) described highly variable textures and
451 fabrics classifying the main petrographic characteristics as '*grain-supported fabric*' (quartzitic
452 silcrete with quartz overgrowths), '*floating fabric*' (silicified clayey matrix with coarse
453 detrital grains), and '*glaebular fabric*' (containing illuviation structures typical of soils).

454 In terms of the origin of pedogenic silcretes, opal initially formed in the granular
455 horizon and at the base of joints in the columnar horizon where water circulation was slow
456 and stagnation had occurred. Higher in the profile, the microcrystalline matrix dissolved.
457 Well-crystallised quartz crystals formed at the top of the profile. Profiles clearly show a
458 migration of silica from top to bottom and the inheritance, in the uppermost horizons, of
459 micromorphological features which initially developed in the lowermost horizons. This
460 inheritance demonstrates that silicification progressively ‘eats’ into the landscape like a
461 weathering front. The greatest amount of silica comes from dissolution at the top of the
462 profile followed, from top to bottom, by a sequence of precipitation and re-dissolution events.

463 The close link between leached and confined environments does not imply a strict
464 synchronism of degradation and construction. The two systems work in an alternating fashion,
465 whereas periods of loss (leaching) and accumulation (precipitation) follow one another more
466 or less sequentially.

467 Initially silica originated from the degradation of clay minerals at the base of the
468 profile, possibly in a highly acidic environment triggered by ferrollysis. The mineral sequence,
469 from top to base of the profile, results from a progressive concentration of silica and other
470 cations in infiltrating and downward-moving solutions. The silica content of the solution
471 could be concentrated by 2 to 4 times through evaporation during dry periods and silica
472 precipitation favoured by increasing cation concentration.

473 **4 Characteristics of silcretes of relevance to tool making**

474 Silcretes show numerous variations in their morphology and their spatial arrangement
475 but also vary in their composition and internal texture. A classification of silcretes based on
476 micromorphological fabrics by Summerfield (1983) has been used widely in archaeological
477 studies to identify different types of silcrete artefacts. Indeed, each silcrete type may display
478 various types of cement and porosity, with sometimes decimetric scale variation, but this does
479 not relate to their convenience or value for tool making. Particular facies, with interesting
480 mechanical properties or appearance could exist within larger masses and may have been
481 specifically sought and used.

482 Various crystallization fabrics have developed according to the nature of the host
483 formation and/or the chemistry of the silica-bearing solutions. The nature of silica cements
484 and the geometrical relations between crystals are the predominant determinants of the
485 mechanical properties of silcretes. Substantial research in this field has been undertaken in
486 Australia from an archaeological perspective (e.g. Domanski *et al.*, 1994; Webb and
487 Domanski, 2008). These investigations have determined that tool-making depends on two
488 main characteristics: the hardness of the material to form cutting and wear-resistant tools, and
489 the capacity to produce a regularly curved conchoidal fracture that permits the detachment of
490 long and thin knappings.

491 It is not within our capability to examine the knappability of silcrete types, nor to
492 make reference to the variety of silcrete facies used by prehistoric peoples to make stone
493 tools. Much of the formal understanding of the mechanical properties of silcretes and other
494 rocks from which stone tools were made, and the influence on these properties by heat
495 treatment, which is believed to have been commonly practiced, has been comprehensively
496 detailed (e.g. Domanski *et al.*, 1994; Domanski and Webb, 1992; Domanski and Webb, 2007;
497 Webb and Domanski, 2008). Our objective is to illustrate how some petrographic fabrics of
498 silcretes, which we use to help unravel their origin and environment of formation, may effect
499 knappability.

500 Broadly speaking, silcretes that have the finest grain size and the least porosity display
501 the best developed conchoidal, vitreous fracture surfaces. From a petrological and
502 mineralogical perspective, the finest grain size will occur in those silcretes formed
503 predominantly of opal, which can be a complex of hydrated, poorly crystallised silica phases
504 (opal-A, opal-CT) and is consequently comparatively soft (Mohs hardness ~5-6). In those
505 silcretes in which the matrix is dominantly microcrystalline quartz, of which there are several
506 types ranging from granular to fibrous varieties, the Mohs hardness is that of quartz (7) and,
507 depending on the microporosity, fracture surfaces can be glassy in appearance. As the
508 abundance of detrital framework quartz grains increases, for example in pedogenic silcretes
509 and some quartzitic groundwater silcretes, the smoothness and lustre of fracture surfaces is

510 controlled essentially by the bonding between framework grains and matrix silica, and can be
511 influenced by the abundance of other constituents including micro-cryptocrystalline anatase.

512 4.1 *'Sandstone' cementation*

513 In clean sands, without a clay matrix, such as the Fontainebleau Sand, precipitated
514 silica builds on the crystal structure of each detrital quartz grain, leading to the development
515 of euhedral crystal faces. On continued precipitation, crystal faces come into contact, and
516 finally form triple point junctions at the site where the pore space has closed (Fig. 11). The
517 overgrown and expanded quartz grains are not welded together, but only meshed in a compact
518 way. This provides cohesion and hardness to a quartzitic silcrete formed in this manner.
519 When broken by hammering or knapping, the fractures can cross cut quartz grains but tends to
520 follow the euhedral crystal faces of the overgrowth quartz that make contact between the
521 grains. This results in a rough fracture surface of sugary appearance. Such fractures are not
522 suitable for making thin blades or sharp cutting edges.

523 Cementation of quartz grains may also be achieved as the result of precipitation of
524 silica in pore spaces between the grains (Fig. 11), either in the form of opal (quasi-amorphous
525 silica) which may have later re-crystallized into chalcedonite, or direct precipitation of
526 chalcedonite sheaves. These silica deposits give rise to stronger cementation than quartz
527 overgrowths and this is linked to the bonding between the detrital quartz grains and the silica
528 precipitates and the complex intercrystallite connections in the pore spaces. Accordingly, the
529 fracture in these silcretes tends to be 'clean' and cuts across the detrital quartz grains. When
530 the detrital quartz grains are relatively small and the silica deposits occupy the main part of
531 the porosity, the fractures may even be conchoidal and lustrous. This is most likely when the
532 pore fillings are of microcrystalline quartz.

533 4.2 *Silicified limestones*

534 In silicified limestones the carbonate matrix has been replaced by silica. The
535 substitution is mainly epigenetic, which means that primary limestone structures such as
536 nodules and fossils are replaced by silica and conserved. For this to occur, there can be no

537 dissolution of the carbonate before replacement: substitution occurs step by step along a clear
538 'alteration front' between existing limestone and incoming silica. This replacement implies
539 concomitant leaching of the carbonate and precipitation of silica. Voids are necessary for
540 water circulation and their shape and size determines the density and 'quality' of the
541 silicification.

542 If the voids have the form of micro-karst, which develops as the silica precipitates
543 (Fig. 12), the resulting silcrete could be very dense, as translucent as flint and with a lustrous
544 conchoidal fracture. On the other hand, when the dissolution features are larger, or when
545 carbonate residues remain as impurities in the silicified zones, then the resulting silcrete has a
546 dull aspect and a rough surface and is much less convenient for tool making.

547 Quartz is generally the main silica mineral and occurs as both epigenetic replacement
548 and also euhedral overgrowths in pores. Some of the fine microcrystalline matrix may result
549 from recrystallization of primary opal. Chalcedonite and laminated opal deposits occur in
550 pores in some sites (Fig. 12). The presence of opal and poorly crystallized forms of silica
551 may be favourable for heating transformation of these silcretes which is sometimes observed
552 naturally in outcrop in Australia.

553 4.3 *Porcellanites and jaspers*

554 These materials are of fine grain size and are formed mainly of various petrographic
555 varieties of opal. The matrix resulting from the alteration of the primary material is generally
556 formed of milky opal made opaque by impurities and microporosity. The most compact
557 samples, with a glossy break, also contain translucent concretionary opal that cements the
558 pores within the matrix (Fig. 13) and this may, in some samples, make up more than 50 % of
559 the silcrete. Concretions generally show successive sequences of silica precipitation in which
560 there are alternations of thin laminae and thicker botryoidal layers of clear and brown opal.
561 The opal has been deposited uniformly around the voids, indicating a saturated groundwater
562 environment.

563 Crystalline varieties of silica occur also in these silcretes. They have formed by
564 recrystallisation of opal, either preferentially in some concretions as part of the sequence of

565 deposition, or as in response to some form of alteration front (Fig. 13). The initial opal
566 deposits have often recrystallized to chalcedonite while the brown opal of the matrix has
567 transformed to microcrystalline quartz.

568 The opal deposits generally strengthen the silcrete and generate lustrous conchoidal
569 fractures when knapped. However, when exposed at the landsurface in Australia,
570 porcellanites can exhibit extensive crazing as a result of volume changes on dehydration of
571 the opal phases.

572 4.4 *Pedogenic silcretes*

573 Pedogenic silcretes are highly variable in form and facies which results from the
574 diversity of the silicified parent materials (colluvium, clayey sand, clay silt, granite, bedrock
575 sandstone) and the position of the sample within the profile (columnar or nodular facies).
576 Adding to the variability is the mineralogical composition which records successive
577 recrystallization stages within the profile.

578 The most abundant and the most typical facies are tightly indurated by a dominantly
579 microcrystalline quartz cement and have a conchoidal and lustrous fracture. Opal is mostly
580 limited to less indurated facies at the base of the profiles and to specific micromorphological
581 features within the profile that are always limited spatially and in volume.

582 The density and homogeneity of the microcrystalline quartz matrix can result in a
583 material that is well-suited for knapping. The amoeboid microcrystals of quartz in net-like
584 arrangement (Fig. 14) confers a structure and texture that mimics the characteristics of some
585 flints. Silicified silty claystones that contain fine-grained detrital quartz and a substantial
586 microcrystalline matrix can be knapped particularly well.

587 A principal criterion for recognising pedogenic silcretes is the omnipresence of
588 illuviation structures, particularly cutans at the base of voids and cappings over quartz grains
589 and granules. These are very clearly distinguished because they are outlined by opaque
590 microcrystalline titania (Fig. 14). As well, the common shard-like remnants of detrital quartz

591 grains point to significant dissolution and concomitant ‘repacking’ of the framework prior to
592 cementation, leading to a net volume loss in the profile as a whole.

593 **5 Silcrete in landscapes**

594 There are two aspects relating to silcretes in a landscape context. In the first case,
595 from the geological perspective, the occurrence and form of silcretes, particularly where
596 profile observations can be made, provides the basis for interpreting the environment of
597 formation of the silcrete. Macroscopic form and structure indicate the relative simplicity or
598 complexity of the processes of formation, point to single stage or overprinting characteristics,
599 and indicate conservation of volume and preservation of fabric and structure (groundwater
600 environments) or dissolution and loss of material with consequent and complex disruption in
601 the profile and, presumably, of the landsurface (pedogenic silcretes).

602 In the second case, within each category of silcrete, and even within a given category
603 in a particular location, the macroscopic and microscopic fabric and structure can vary
604 considerably. This is less so in the case of groundwater silcretes than for pedogenic silcretes.
605 Only particular forms of silcrete appear to have had value for the production of stone tools.
606 Mulvaney and Kamminga (1999), for example, point to the possibility that some forms of
607 silcrete could have been selected for tool production for aesthetic or symbolic reasons,
608 including their colour, which can be variable. Holdaway *et al.* (2008) and others (Doelman *et*
609 *al.*, 2001) make the distinction between ‘outcrop silcrete’ and the extensive lag gravels
610 (‘gibber plains’), the latter (also called ‘stony deserts’) resulting from downwasting of the
611 ancient pedogenic silcrete-capped landsurfaces and associated groundwater silcrete-
612 impregnated regolith over large areas of inland Australia (Fujioka *et al.*, 2005). They point
613 out that artefacts were made from each source, but that outcrops were more difficult for
614 Aboriginal people to exploit for tools than gibber lags because of the greater supply of hand-
615 sized cobbles in the latter.

616 Thus, if we want to explore the use of silcrete as a raw material for stone tools, for
617 example to map the routes of particular source materials and thus delimit territories and
618 exchanges between prehistoric groups of peoples, it is necessary to locate these materials in

619 the landscapes of the studied areas and the territories of the people exploiting them. In this
620 context, inventories of the locations of specific silicified formations, and their petrographic
621 characteristics, would be required for both local and regional areas. This research would
622 utilise an understanding of silcretes and silcrete facies in a landscape context because
623 prehistoric peoples had deeply-embedded connections with landscapes and their features.

624 5.1 *Inland Australia*

625 As is well known, pedogenic silcretes in Australia armour glacis (pediments) on the
626 edges of plateaux and around paleorelief (Milnes and Thiry, 1992; Milnes and Twidale, 1983;
627 Simon-Coinçon *et al.*, 1996; Thiry *et al.*, 1991; Twidale and Milnes, 1983a, b). At the edges
628 of scarps extending from the Arcoona Plateau in South Australia, for example, silicification is
629 restricted to thin ‘skins’, with a very high titania content, coating joint fractures and other
630 surfaces on quartzite bedrock (Hutton *et al.*, 1972; Fig. 15). On the proximal part of the Beda
631 pediment, just downslope from the scarp-foot zone of the plateau, silcrete is more extensive
632 and almost only formed of thick cappings (5 to 20 cm thick) on bouldery quartzite scree,
633 whereas in the distal areas of the pediment silcrete forms a regular horizon with columnar
634 structure within the pediment. Thicker silcretes occur in the transition zones between the
635 glacis and the lowland plains, where water discharge is still important but flow rates have
636 slowed.

637 The facies with thick cappings on scree boulders is symptomatic of the complexity
638 that can face any archaeological search for the source of silcrete tools. These cappings are of
639 very hard silcrete with a convex lustrous break and have been exploited for tools as shown by
640 the litter of flakes and chips surrounding the outcrops. They may have been sought
641 specifically because of certain characteristics. However, this particular facies is of very
642 limited extent and locating it as a source of particular stone tools would only be possible after
643 a very detailed inventory of a wide area.

644 In localities along the scarp of the Stuart Range, near Coober Pedy, in northern South
645 Australia, a comprehensive analysis of the geomorphology of the region (Simon-Coinçon *et*
646 *al.*, 1996) delineated the age relationships between the different weathering and silicification

647 features (Fig. 16). The pedogenic silcrete armours a wide paleopediment (tableland) dipping
648 from the Stuart Range near Lake Eyre to the Eucla Basin in the southwest, a distance of about
649 500 km. The weathered and bleached profiles are younger. Groundwater silcrettes,
650 specifically quartzite and diverse porcellanite horizons, post-date the bleaching. Downcutting
651 and erosion ultimately generated the breakaway scarps now characteristic of the region.

652 The large variety of silicified materials in the Stuart Range landscapes are shown
653 schematically in more detail in Figure 16. Pedogenic silcrettes may be locally buried beneath
654 younger deposits (clayey sediments and red-brown hardpans) but are omnipresent at or near
655 the surface of the widespread remnants of the Stuart Range tableland and available in
656 numerous outcrops and extensive lag gravels ('gibber plains', 'stony deserts'). The facies vary
657 according to the parent material affected by the silicification (coarse- or fine-grained;
658 abundant matrix material, or not, between the residual detrital grains). Illuviation structures
659 enriched in titania are symptomatic of these facies. To find any specific characteristics of a
660 particular facies in a particular location would seem to be difficult. On the other hand,
661 groundwater silcrettes (quartzite, porcellanite and jasper of variegated colour) are available in
662 outcrops and lag gravels along the creeklines that leading down to Lake Eyre. They have
663 more distinctive characters and a detailed inventory may provide tracers of specific materials.

664 About 700km north of Coober Pedy and the Stuart Range, in the Todd River Plain
665 near Alice Springs in central Australia, similar paleogeographic relationships occur. Here, in
666 the scarp foot zone of a formerly extensive early Cenozoic pediment developed over the
667 Amadeus Basin, mesas and buttes capped by the massive and impressive columnar facies of a
668 pedogenic silcrete overlie a bleached and weathered regolith containing groundwater silcrettes
669 (Milnes and Thiry, 1992; Milnes and Twidale, 1983). In distal parts of the pediment there
670 are plateau remnants armoured by thick groundwater silcrettes and adjacent areas of silicified
671 limestones (Fig. 17).

672 Here, also, the silicified facies are extremely varied and the associated bleached
673 profiles are rich in white kaolinic clays and Fe oxides of variegated colours. Small mesas of
674 fine quartzitic sandstone have been intensively quarried for tool-making. The steep scree-
675 slopes around the hills and parts of the plateau surface are in places buried by thick deposits

676 of discarded flakes and chips. The clear evidence of significant (and possibly long-term)
677 exploitation provides the basis for characterising the source silcrete in detail and exploring the
678 distribution of stone tools made from it.

679 However, the vast region, maybe 1 million km², stretching from central South
680 Australia to the central parts of the Northern Territory, essentially marking the western part of
681 the Lake Eyre Basin (see Alley, 1998; Fujioka *et al.*, 2005) has innumerable outcrops and
682 derivative lag gravels of pedogenic and various groundwater silcrettes, all of which could be
683 exploited by Aboriginal people. Thus, there would be a significant challenge in progressively
684 building an inventory of these materials sufficient to assist archaeological investigations in
685 attributing artefacts to sources.

686 The nature and abundance of source material for tool-making has been noted from the
687 first archaeological works in inland Australia by Aiston (1928), who stated “.. *it was so easy*
688 *to make a tool that directly one failed to work satisfactorily it was discarded and a fresh tool*
689 *made, a supply of stone material always being kept handy for this purpose...*”. The experience
690 of Australian archaeologists comes both from stone tools excavated from archaeological sites
691 and from ethnographic records of the experience of old Aboriginal people. Both types of
692 study concluded that Aboriginal people were highly opportunistic in their use of source stone
693 and took mostly varieties of local raw materials, including chert, chalcedony, jasper, silcrete
694 (‘grey billy’ in the vernacular), quartzite, basalt, silicified wood as well as other igneous and
695 metamorphic rocks (Cane, 1992; Flenniken and White, 1985). Nevertheless, small but
696 significant amounts of non-local materials have been found dispersed over long distances and
697 are thought to relate to migrations of prehistoric Aboriginal people during periods of drought
698 (Gould and Sagers, 1985; Holdaway and Fanning, 2014; Mulvaney and Kamminga, 1999).

699 5.2 Paris Basin

700 The Paris Basin is bounded by Jurassic marine limestone overlain by thick chalk
701 deposits with alternating continental and marine Tertiary deposits in the centre. The most
702 remarkable feature of the Tertiary sequence is the interbedding of sandstone formations with
703 limestones and marls. The present-day morphology of the Paris Basin, namely superimposed

704 limestone plateaux, results from major uplift during the Pliocene and Quaternary which
705 initiated downcutting and erosion of the Tertiary formations (Fig. 18). Silicified materials
706 occur in almost all formations.

707 Pedogenic silcretes extend from the peripheral basement in the Central Massif and
708 Brittany to the centre of the basin (Fig. 18). They developed along a paleosurface shaped by
709 clastic discharge during the lower Eocene (Blanc-Valleron and Thiry, 1997). Silicification
710 affects palaeoweathering profiles of clay-with-flint above Jurassic limestones and Cretaceous
711 chalks, old alluvium to form thick puddingstones, and sandy clays that become the
712 predominant silicified material at the border of the basin. The thickest silicified profiles (more
713 than 15m thick) are found in grabens and channels that formed the lowlands (Thiry and
714 Simon-Coinçon, 1996).

715 Groundwater silcretes developed in almost every Tertiary formation in the centre of
716 the basin. Tightly cemented quartzite lenses occur in all sandy formations and silicified zones
717 are present in every lacustrine and marine limestone formation (Thiry, 1999). Even the
718 weathered materials topping the limestone plateaux contain large silicified features.
719 Groundwater silcretes also developed in sandy and conglomeratic regolith materials topping
720 the Mesozoic sequences bordering the basin. Recent groundwater cementation has been
721 superimposed on former pedogenic silcrete profiles on the outer borders of the basin. It is
722 likely that 5 to 10% of the outcropping formations in the basin are silicified, and this
723 represents a considerable mass of easily accessible silcrete for potential exploitation.

724 Added to this inventory as well are Jurassic cherts and Cretaceous flints that occur all
725 over the Paris Basin. They are *in situ* in the Mesozoic formations or occur in extensive areas
726 covered by paleoweathering profiles of clay-with-flint and reworked into thick alluvial
727 deposits within valleys that dissect the plateaux. These Jurassic cherts and Cretaceous flints
728 generally account for the main component of lithic source material. Their identification was
729 essentially based on micropaleontological determinations and was consequently limited in
730 terms of pointing to source areas (Masson, 1981; Valensi, 1953).

731 Due to the predominance of cherts and flints, less interest has been applied to the
732 recognition of various silcrete facies. Nevertheless, some investigations, in particular in the

733 Paris Basin, identified several kinds of silcretes used for making tools. Fine-grained
734 quartzitic silcretes from Fontainebleau have been recognized in flakes (Robin, 1974), used for
735 polished axes (Bostyn *et al.*, 2012), and even to made into thin leaf-shaped Solutrean points
736 (Sacchi *et al.*, 1996). These silcretes correspond to the uppermost facies, directly below the
737 limestone cover, and are of glassy appearance due to the presence of microquartz together
738 with quartz overgrowths forming the cement. Bartonian silicified lacustrine limestone has
739 also been recognized (by means of its fossil content) in polished axes that are thought to have
740 been dispersed up to 250 km (Bostyn *et al.*, 2012). Elsewhere, similar Bartonian silicified
741 lacustrine limestone has been found together with artefacts made from meulière (weathered
742 silicified limestone), silicified Lutetian marine limestone and quartzitic silcretes (Augereau,
743 2008; Lanchon *et al.*, 2008; Mauger, 1985; Surmely, 2009).

744 Recent studies in and around the margins of the Massif Central, taking into account
745 the petrography of cherts, flints and silcretes, including changes in response to their colluvial
746 and alluvial reworking, made it possible to refine source areas (Fernandes, 2012; Surmely *et*
747 *al.*, 2008). It has to be stressed that it is in basement areas (Massif Central and Bretagne)
748 where the siliceous materials are scarce that the sourcing studies were the more skilful and the
749 most successful. Detailed studies of flint and chert cortices from the Massif Central made it
750 possible to consider natural dispersion of the primary materials and consequently to determine
751 more precisely the source areas (Fernandes, 2012). Silcrete deposits exist also in these
752 basement areas, although scattered and variable in facies. Detailed studies have been able to
753 track the dissemination of these materials within the massif as well as those imported from the
754 peripheral basins (Aubry, 1991; Célérier, 1990; Dabard *et al.*, 2012; Delvigne, 2012; Surmely
755 *et al.*, 2008; Wragg-Sykes, 2014).

756 **6 Identifying provenance**

757 There are certainly specific macroscopic criteria that could be used to help identify
758 sources of silcrete tools, but most of the time these investigations are ambiguous. Colour,
759 grain size and distribution, and the character and aspects of the break, are generally not
760 specific. The morphologies of silcretes are often typical at the outcrop scale, but not at the
761 artefact scale.

762 Micromorphological and petrographical features of silcretes are more reliable criteria
763 of origin and potential provenance. However, identification of provenance from these
764 features requires a comprehensive inventory of actual local and regional source materials, a
765 sound geological knowledge of these occurrences, and an accompanying database of
766 micromorphological and petrographical observations of representative samples. This is
767 conceivable on a local scale but is much more difficult to manage on the regional scale of
768 societal exchanges. Geochemical criteria, particularly the concentrations of indicator trace
769 elements, may be helpful. Dutkiewicz *et al.* (2015) have analysed major and (particularly)
770 trace elements in both opal and host rocks in Australia in order to identify the possible origin
771 of the silica. This approach could potentially be extended to silcretes although, in pedogenic
772 silcretes, the complex of silica forms and associations with microcrystalline anatase and other
773 phases, and the multiplicity of silcrete facies, even on the scale of an outcrop, would pose a
774 significant challenge. Moreover, Holdaway and Fanning (2014) and others have pointed out
775 the complexities presented by the suite of stone artefacts in archaeological sites wherein there
776 are local and foreign sourced materials representing an interplay of unknowable activities.

777 Finally, questions of the extent of post-discard alteration and degradation of
778 archaeological materials has to be addressed. Exoscopic studies of the surfaces of stone tools,
779 which are often altered in various ways by patina evolution, can provide few critical data
780 (Fernandes, 2012; Thiry *et al.*, 2014).

781 The difficulty for archaeological studies is to precisely characterize the many varieties
782 of silica-rich source rocks for stone tools. In the past, only stratigraphic characters and fossils
783 have been used to determine the provenance of tool materials (Mauger, 1984). This was of
784 limited use because the stratigraphic levels are relatively widespread. More detailed, multi-
785 criteria identification is necessary and essential for understanding trade and acquisition
786 strategies involving stone tools.

787 Progress is possible by taking into account precise micromorphological characteristics
788 that will potentially point to source sites. However, this approach requires an insightful
789 inventory and petrographic data led by archaeological studies (Fernandes, 2012). Inventories
790 of this type are yet not available. Even existing geologic and geomorphological maps do not

791 make reference to the specific characters of silcretes, silcrete profiles, or micromorphological
792 features of particular facies, that could be key to these types of investigations. The
793 foundations of such inventories exist, but a new generation of linked archaeological and
794 geological research would be a next step.

795 **7 Summary**

796 Several forms of silcrete are recognised in remnants of paleolandscapes in Europe,
797 Africa and Australia dating from the Mesozoic to the present day. Their chemical,
798 mineralogical and physical (microstructural) composition accounts for their persistence and
799 for the major influence of some silcretes in defining the unique morphology of landforms. All
800 silcretes, of which there are 4 - 6 main types, formed as a result of the introduction and
801 precipitation of silica, for example via groundwaters, or the mobilisation and precipitation of
802 silica from pre-existing minerals via alteration and the leaching of other elements, for
803 example in acidic environments. Each is characterised by a variety of silica polymorphs,
804 including quartz, various forms of microcrystalline and cryptocrystalline quartz, and various
805 forms of opal (opal-CT, opal-A), in particular micromorphological arrangements. The main
806 categories of silcrete originated in pedogenic or groundwater environments.

807 Other than their mode of occurrence and morphological appearance, it is the
808 microstructural composition of silcretes, dictated by mineralogical and micromorphological
809 features that derive from their origin, that provides the basis for understanding their physical
810 and mechanical properties (which relates to the attractiveness of some forms to prehistoric
811 peoples for the making of effective tools). However, it is well recognised that there may have
812 been other practical and even aesthetic or symbolic dimensions to such choices.
813 Investigations of the provenance of stone tools, other than in a local area, will be challenged
814 by a need for regional inventories of silcrete facies.

815 **8 References**

816
817 Aiston, G., 1928, Chipped stone tools of the Aboriginal tribes east and north-east of Lake
818 Eyre, South Australia. Papers and Proceedings of the Royal Society of Tasmania, p. 123-
819 131.

-
- 820 Alexandre, A., Meunier, J-D., Llorens, E., Hill, S.M., Savin, S.M., 2004, Methodological
821 improvements for investigating silcrete formation: petrography, FT-IR and oxygen
822 isotope ratio of silcrete quartz cement, Lake Eyre Basin (Australia). *Chemical Geology*,
823 211, p. 261-274.
- 824 Alimen H., Deicha G., 1959, Observations pétrographiques sur les meulières pliocènes. *Bull.*
825 *Soc. Géol. Fr.*, (6), 8, p. 77-90.
- 826 Alley N.F., 1998, Cainozoic stratigraphy, palaeoenvironments and geological evolution of the
827 Lake Eyre Basin. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 144, p. 239-263.
- 828 Arakel, A.V., Jacobson, G., Salehi, M., Hill, C.M., 1989, Silicification of calcrete in
829 paleodrainage basins of the Australian arid zone. *Austr. Jour. Earth Sciences*, 36, p. 73-
830 89.
- 831 Armenteros, I., Bustillo, M.A., Blanco, J.A., 1995, Pedogenic and groundwater processes in a
832 closed Miocene basin (northern Spain). *Sedimentary Geology*, 99, p. 17-36.
- 833 Aubry, T., 1991, L'exploitation des ressources en matières premières lithiques dans les
834 gisements solutréens et badegouliens du bassin versant de la Creuse (France). PhD
835 Thesis, University Bordeaux-1, 327 p.
- 836 Augereau, A., 2008, Territoires techniques et économiques au Néolithique dans le Bassin
837 parisien. *Archéopages, INRAP*, 21, p. 16-21.
- 838 Auzel, M., Cailleux, A., 1949, Silicifications nord-sahariennes. *Bull. Soc. Géol. Fr.*, (5), 19, p.
839 553-559.
- 840 Banks, N.G., 1970, Nature and origin of early and late cherts in the Leadville Limestone,
841 Colorado. *Geol. Soc. Amer. Bull.*, 81, p. 3033-3048.
- 842 Barrois, C., 1878, Sur l'étendue du système tertiaire inférieur dans les Ardennes et sur l'argile
843 à silex. *Ann. Soc. géol. Nord*, 4, p. 340-376.
- 844 Benbow, M.C., 1993, Tallaringa, South Australia. Explanatory Notes 1:250 000 Geological
845 Series – Sheet SH 53-5. Department of Mines and Energy South Australia, 40 p.
- 846 Benison, K., Bowen, B.B., 2015, The evolution of end-member continental waters: The origin
847 of acidity in southern Western Australia. *GSA Today*, 25/6, p. 4-10.
- 848 Bethke, C.M., 2002, The geochemist's workbench release 4.0: a user's guide to Rxn, Act2,
849 Tact, React, and Gtplot. University of Illinois, Urbana, IL.
- 850 Bird, M.I., Chivas, A.R., McDougall, I., 1990. An isotopic study of surficial alunite in
851 Australia, 2. Potassium argon geochronology. *Chem. Geol. (Isot. Geosci. Sect.)* 80, p.
852 133-145.

-
- 853 Blanc-Valleron, M.M., Thiry, M., 1997, Clay minerals, paleoweathering, paleolandscapes and
854 climatic sequences: The Paleogene continental deposits in France. in: Soils and
855 Sediments: Mineralogy and Geochemistry, H. Paquet, N. Clauer, (eds.), Springer, p.
856 223-247.
- 857 Bostyn, F., Couderc, J., Giligny, F., Lethrosne, H., Le Maux, N., Lo Carmine, A., Riquier, C.,
858 2012, La production de haches dans l'Ouest de l'Île-de-France (Yvelines, Val-d'Oise).
859 Approche typo-technologique et spatiale. In: Produire des haches au Néolithique, de la
860 matière première à l'abandon, de Labriffe P. A. and Thirault E. (eds), Actes de la table
861 ronde de Saint-Germain-en-Laye, 16-17 mars 2007, Société préhistorique française,
862 Paris, p. 153-172.
- 863 Boule, M., 1888, Le bassin tertiaire de Malzieu (Lozère). Bull. Soc. géol. Fr., ser. 3, 13, p.
864 341-345.
- 865 Brinkman, R. (1970). Ferrolysis, a hydromorphic soil forming process. *Geoderma*, 3/3, p.
866 199-206.
- 867 Bustillo, M.A., Bustillo, M., 2000, Miocene silcretes in argillaceous playa deposits, Madrid
868 Basin, Spain: petrological and geochemical features. *Sedimentology*, 47, p. 1023-1037.
- 869 Cane, S., 1992, Aboriginal perceptions of their stone tool technology: a case study from the
870 Western Desert, Australia. *Australian Archaeology*, 35, p. 11-31.
- 871 Cayeux, L., 1929, Les roches sédimentaires de la France. Roches siliceuses. Mém. servir expl.
872 Carte Géol. détaillée de la France, 774 p.
- 873 Célérier, G., Duchadeau-Kervazo, C., Gourdon-Platel, N., 1990, Les dalles silico-
874 ferrugineuses du Bassin de la Dronne : origine, caractérisation et utilisation
875 préhistorique. In: Actes du colloque international sur le silex, Cahiers du Quaternaire,
876 17, p 111-117.
- 877 Chartres, C.J., 1985, A preliminary investigation of hardpan horizons in north-west New
878 South Wales. *Aust. J. Soil Res.*, 23, p. 325-337.
- 879 Dabard, M.-P., Marchand, G., Monnier, J.-L., Querré, G. , 2012, Roches sédimentaires
880 siliceuses du Massif Armoricaïn. Répartition géographique, minéralogique et économie
881 au cours de la Préhistoire. In: Roches et Sociétés de la Préhistoire. Entre massifs
882 cristallins et bassins sédimentaires, Marchand G. and Querré G., (eds), Presses
883 Universitaires de rennes, p. 123-137.
- 884 Daley, B., 1989, Silica pseudomorphs from the Bembridge limestone (upper Eocene) of the
885 Isle of Wight, southern England and their palaeoclimatic significance. *Palaeogeography*,
886 *Palaeoclimatology*, *Palaeoecology*, 69, p. 233-240.

-
- 887 Delvigne, V., 2012, Petroarchaeological study of the unit F2 of the Rond du Barry cave
888 (Polignac, Haute-Loire), preliminary results. *Comptes rendus - Palevol*, 11/4, p. 293-
889 304.
- 890 Dickson, B.L., 2014, Discussion on ‘Opalisation of the Great Artesian Basin (central
891 Australia): an Australian story with a Martian twist’ by P.F. Rey (*AJES* 60, 291-314).
892 *Aust. J. Earth Sciences*, 60, p. 831-833.
- 893 Dickson, B.L., Giblin, A. M., 2009, Features of acid-saline systems of Southern Australia.
894 *Applied Geochemistry*, 24, p. 297–302.
- 895 Doelman, T., Webb, J., Domanski, M., 2001, Source to discard: patterns of raw material
896 procurement and use in Sturt National Park, northwestern New South Wales.
897 *Archaeology Oceania*, 36, p. 15-33.
- 898 Domanski, M., Webb, J.A., 1992, Effect of heat treatment on siliceous rocks used in
899 prehistoric lithic technology. *J. Archaeological Science*, 19, p. 601-614.
- 900 Domanski, M., Webb, J.A., 2007, A review of heat treatment research. *Lithic Technology*,
901 32, p. 153-194.
- 902 Domanski, M., Webb, J.A., Boland, J., 1994, Mechanical properties of stone artefact materials
903 and the effect of heat treatment. *Archaeometry*, 36, p. 177-208.
- 904 Dutkiewicz, A., Landgrebe, T.C.W., Rey, P.F., 2015, Origin of silica and fingerprinting of
905 Australian sedimentary opals. *Gondwana Research*, 27, p. 786-795.
- 906 Eggleton, R.A., (ed), 2001, *Regolith Glossary: surficial geology, soils and landscapes*.
907 Cooperative Research Centre for Landscape Evolution and Mineral Exploration,
908 Canberra, A.C.T., 144 p.
- 909 Elsass, F., Dubroeuq, D., Thiry, M., 2000, Diagenesis of silica minerals from clay minerals
910 in volcanic soils of Mexico. *Clay Minerals*, 35/3, p. 477-489.
- 911 Fernandes, P., 2012, *Itinéraires et transformations du silex : une pétroarchéologie refondée,*
912 *application au Paléolithique moyen*. Thèse Université Bordeaux I, ED Sciences et
913 Environnement, Spécialité Préhistoire, Vol. 1 Texte et figures 452 p, Vol. 2 Annexes
914 164 p. 19 juin 2012.
- 915 Flenniken, J.J., White, J.P., 1985, Australian flaked stone tools: a technological perspective.
916 *Records of the Australian Museum*, 36/3, p. 131–151.
- 917 Fujioka T., Chappell J., Honda, M., Yatsevich I., Fifield K., Fabel D., 2005, Global cooling
918 initiated stony deserts in central Australia 2-4Ma, dated by cosmogenic ^{21}Ne - ^{10}Be .
919 *Geology*, 33, p. 993-996.

-
- 920 Garcia-Hernandez, J.E., 1981. Interprétation cinétique de la géochimie d'altération de la silice
921 à basse température (25°C). INRA, Versailles, 213 p.
- 922 Garrels, R.M., Christ, C.L., 1965, Solutions, Minerals and Equilibria. Harper and Row, New-
923 York, 450 p.
- 924 Gary, M., McAfee, R., Wolf, C.L., (eds) 1973. Glossary of Geology. American Geological
925 Institute, Washington, DC, 805 p.
- 926 Gislason, S.R., Heaney, P.J., Oelkers, E.H., Schott, J., 1997, Kinetic and thermodynamic
927 properties of moganite, a novel silica polymorph. *Geochimica et Cosmochimica Acta*,
928 61/6, p. 1193–1204.
- 929 Gosselet, J., 1888, L'Ardenne. Mém. serv. exp. carte géol. Fr., Paris, 888 p.
- 930 Götze, J., Walther, H., 1995, An integrated mineralogical and geochemical study on a
931 silicified Miocene quartz sand. *Zbl. Geol. Paläont., Teil 1*, 1/2, p. 119-129.
- 932 Gould, R.A., Saggars, S., 1985, Lithic procurement in Central Australia: a closer look at
933 Binford's idea of embeddedness in archaeology. *American Antiquity*, p. 117-136.
- 934 Harwood, J., Aplin, A.C., Fialips, C.I., Iliffe, J.E., Kozdon, R., Ushikubo, T., Valley, J.W.,
935 2013, Quartz cementation history of sandstones revealed by high-resolution SIMS
936 oxygen isotope analysis. *J. Sedim. Res.*, 83, p. 522-530.
- 937 Holdaway, S., Shiner, J., Fanning, P., Douglass, M., 2008, Assemblage formation as a result
938 of raw material acquisition in western New South Wales, Australia. *Lithic Technology*,
939 33, p. 73-85.
- 940 Holdaway, S., Fanning, P., 2014, *Geoarchaeology of Aboriginal Landscapes in Semi-Arid*
941 *Australia*. CSIRO Publishing, 195 p.
- 942 Hutton, J.T., Twidale, C.R., Milnes, A.R., Rosser, H., 1972, Composition and genesis of
943 silcretes and silcrete skins from the Beda valley, southern Arcoona Plateau, South
944 Australia. *J. Geol. Soc. Australia*, 19, p. 31-39.
- 945 Iler, R.K., 1979. The chemistry of silica. Solubility, Polymerisation, Colloid and Surface
946 Properties and Biochemistry. John Wiley and Sons, New York, 866 p.
- 947 Kaiser, E., 1928, Die chemische Gesteinsaufbereitung in der Südlichen Namib. *in: Die*
948 *Diamantenwüste Südwestafrikas*, Dietrich Reiner, Berlin, Ch. 26, p. 283-316.
- 949 Kerr, M.H., 1955, On the occurrence of silcretes in southern England. *Proc. Leeds Phil. Soc.*,
950 6, p. 328-337.
- 951 Lanchon, Y., Bostyn, F., Hachem, L., Maigrot, Y., Martial, E., Boitard-Bidault, E., 2008, Le
952 Néolithique ancien dans la basse vallée de la Marne: l'habitat de Changis-sur-Marne

-
- 953 « les Pétreaux » (Seine-et-Marne). *Revue archéologique d'Île-de-France*, tome 1, p. 43-
954 94.
- 955 Lange, O., 1912, Ueber Silikatsteine für Martinofen. *Stahl und Eisen*, 32, 42, p. 1731.
- 956 Langford-Smith, T., (ed), 1978. *Silcrete in Australia*. University of New England, Armidale,
957 314 p.
- 958 Ludwig, K.R., Paces, J.B., 2002, Uranium-series dating of pedogenic silica and carbonate,
959 Crater Flat, Nevada. *Geochimica and Cosmochimica Acta*, 66(3), p. 487-506.
- 960 McArthur, J.M., Turner, J.V., Lyons, W.B., Osborn, A.O., Thirlwall, M.F., 1991,
961 Hydrochemistry on the Yilgarn Block, Western Australia: ferrollysis and mineralisation
962 in acidic brines. *Geochimica et Cosmochimica Acta*, 55, p. 1273-1288.
- 963 McCoy, Z. L. , 2011, The Distribution and Origin of Silcrete in the Ogallala Formation, Garza
964 County, Texas. Doctoral dissertation, Texas Tech University, 148 p.
- 965 Mann, A.W., 1983, Hydrogeochemistry and weathering on the Yilgarn Block, Western
966 Australia - ferrollysis and heavy metals in continental brines. *Geochim. Cosmochim.*
967 *Acta*, 47, p. 181-190.
- 968 Marshall, W.L., 1980, Amorphous silica solubilities III : activity coefficient relations and
969 predictions of solubility behavior in salt solutions, 0-350°C. *Geochim. Cosmochim.*
970 *Acta*, 44, p. 925-931.
- 971 Masson, A., 1981, *Péetroarchéologie des roches siliceuses. Intérêt en Préhistoire*. Thèse
972 Université Claude Bernard Lyon I, 111 p.
- 973 Mauger, M., 1984, L'apport des microfossiles dans l'identification des silex. Exemple du
974 Magdalénien de l'Ile-de-France. *Bulletin de la Société préhistorique française*, 81/7, p.
975 216-220.
- 976 Mikulas, R., 2002, Ichnofabric of Oligocene silcrettes at Kryry and Detan, Western Bohemia,
977 Czech Republic. *Journal of the Czech Geological Survey*, 47/3, p. 157-160.
- 978 Millot, G., 1970, *Geology of clays : weathering, sedimentology, geochemistry*. Springer-
979 Verlag, New-York, 429 p.
- 980 Millot, G., Radier, H., Muller-Feuga, R., Defosse, M., Wey, R., 1959, Sur la géochimie de la
981 silice et les silicifications sahariennes. *Bull. Serv. Carte Géol. Als. Lor.*, 12, 2, p. 3-15
- 982 Milnes, A.R., Thiry, M., 1992, Silcrettes. In Martini I.P. and Chesworth W. (eds),
983 "Weathering, Soils and Paleosols". *Developments in Earth Surface Processes* 2, Ch. 14,
984 p. 349-377. Elsevier: Amsterdam.

-
- 985 Milnes, A.R., Twidale, C.R., 1983, An overview of silicification in Cainozoic landscapes of
986 arid central and southern Australia. *Aust. J. Soil Res.*, 21, p. 387-410.
- 987 Mulvaney, J., Kamminga, J., 1999, *Prehistory of Australia*. Allen & Unwin: St Leonards,
988 NSW, 480 p.
- 989 Nash, D.J., McLaren, S.J., Webb, J.A., 2004, Petrology, geochemistry and environmental
990 significance of silcrete calcrete intergrade duricrusts at Kang Pan and Tswaane, central
991 Kalahari, Botswana. *Earth Surface Processes and Landforms*, 29(12), p. 1559-1586.
- 992 Nash, D.J., Shaw, P.A., Ulyott, S., 1998, Drainage-line silcretes of the Middle Kalahari: an
993 analogue for Cenozoic sarsen trains. *Proceedings of the Geologists' Association*, 109, p.
994 241-254.
- 995 Nash, D.J., Ulyott, J.S., 2007, Silcrete. In: Nash, D.J., McLaren, S.J., (eds), *Geochemical*
996 *sediments and landscapes*. Blackwell, Oxford, p. 95-143.
- 997 Parcerisa, D., Thiry, M., Gomez-Gras, D., Calvet, C., 2001, Proposition d'un modèle de
998 silicification superficielle des grès néogènes de Montjuïc, Barcelone (Espagne) :
999 paragenèses minérales, environnements géochimiques et circulation des fluides. *Bull.*
1000 *Soc. géol. France*, 172/6, p. 751-764.
- 1001 Parkhurst, D.L., Appelo, C.A.J., 1999, User's guide to PHREEQC (Version 2): A computer
1002 program for speciation, batch-reaction, one-dimensional transport, and inverse
1003 geochemical calculations. *Water-Resources Investigations Report 99-4259*, US
1004 Geological Survey, 312 p.
- 1005 Parron, C., Nahon, D., Fritz B., Paquet, H., Millot G., 1976, Désilicification et quartzification
1006 par altération des grès albiens du Gard. *Modèles géochimiques de la genèse des dalles*
1007 *quartzitiques et silcrètes*. *Sci. Géol., Bull.*, 29, p. 273-284.
- 1008 Rayot, V., Self, P., Thiry, M., 1992, Transition of clay minerals to opal-CT during
1009 groundwater silicification. In: Schmitt, J-M., Gall, Q., (eds), *Mineralogical and*
1010 *geochemical records of paleoweathering*. *ENSMP Mem. Sc. de la Terre* 18, p. 47-49.
- 1011 Rey, P.F., 2013, Opalisation of the Great Artesian Basin (central Australia): an Australian
1012 story with a Martian twist. *Aust. J. Earth Sciences*, 60, p. 291-314.
- 1013 Rey, P.F., 2014, Remarks on the age of precious opal in central Australia: reply to comment
1014 by Bruce Dickson. *Aust. J. Earth Sciences*, 60, p. 835-837.
- 1015 Robin, A.-M., 1974, Une industrie moustérienne en forêt de Fontainebleau. *Bull. Soc. Préhist.*
1016 *Fr.*, 71/3, p. 67-69.

-
- 1017 Sacchi, C., Schmider, B., Chantret, F., Roblin-Jouve, A., Bouysonne, M., Drapier, S., 1996,
1018 Le gisement solutréen de Saint-Sulpice-de-Favières (Essone). Bull. Soc. Préhistorique
1019 fr., 93/4, p. 502-527.
- 1020 Siffert, B., 1967. Some reactions of silica in solution: formation of clay. Translation of:
1021 Mémoires du Service de la Carte géologique d'Alsace et de Lorraine, n°21, Published for
1022 the U.S. Department of Agriculture and the National Science Foundation, Washington,
1023 D.C., 100 p.
- 1024 Simon-Coinçon, R., Milnes, A.R., Thiry, M., Wright, M.J., 1996, Evolution of landscapes in
1025 northern South Australia in relation to the distribution and formation of silcretes. J.
1026 geol. Soc. London 153, p. 467-480.
- 1027 Skarpelis, N., 2006, Lateritization processes of ultramafic rocks in Cretaceous times: the
1028 fossil weathering crusts of mainland Greece. Journal of Geochemical Exploration, 88(1),
1029 p. 325-328.
- 1030 Smale, D., 1973, Silcretes and associated silica diagenesis in southern Africa and Australia. J.
1031 Sedim. Petrol., 43, p. 1077-1089.
- 1032 Storz, M., 1928, Die sekundären authigenen Kieselsäuren in ihrer petrogenetisch-
1033 geologischen Bedeutung. Monogr. z. Geologie und Pal., Ser. II, Heft 4, 481 p.
- 1034 Summerfield, M.A., 1980, The silcretes of Southern England: their paleoenvironmental
1035 interpretation with reference to other silcretes. In: The shaping of Southern England,
1036 (Jones E.K.C. ed.), Inst. Br. Geogr. Spec. Publ., Academic Press, London, 11, p.71-100.
- 1037 Summerfield, M.A., 1983, Petrography and diagenesis of silcrete from the Kalahari Basin and
1038 Cape coastal zone, Southern Africa. J. Sedim. Petrol., 53, p. 895-909.
- 1039 Surmely, F., 2009, Recherches sur les haches polies des départements de la Seine-et-Marne et
1040 du Loiret. Bulletin de la Société préhistorique française, 106(3), p. 593-596.
- 1041 Surmely, F., Boudon, P., Briot, D., Pin, C., 2008, La diffusion des silex crétacés dans le
1042 centre du Massif central durant la préhistoire (Paléolithique, Mésolithique, Néolithique).
1043 Contribution à l'étude de la circulation des matières premières lithiques sur de longues
1044 distances. PALEO. Revue d'archéologie préhistorique, 20, p. 115-144.
- 1045 Swanberg, C.A., Morgan, P., 1978, The linear relation between temperatures based on the
1046 silica content of groundwater and regional heat flow: a new heat flow map of the United
1047 States. Pure and Applied Geophysics, 117/1-2, p. 227-241
- 1048 Teichmüller, R., 1958, Die Niederreihnische Braunkohlenformation. Stand der
1049 Untersuchungen und offene Fragen. Fortschr. Geol. Rheinland und Westf., 2, p. 721-750.

-
- 1050 Thiry, M., 1981, Sédimentation continentale et altérations associées: calcitisations,
1051 ferruginisations et silicifications. Les Argiles Plastiques du Sparnacien du Bassin de
1052 Paris. *Sci. Géol. Mém.*, 64, 173 p.
- 1053 Thiry, M., 1999, Diversity of continental silicification features: examples from the Cenozoic
1054 deposits in the Paris Basin and neighbouring basement. In *Palaeoweathering,*
1055 *palaeosurfaces and related continental deposits* (Thiry M. and Simon-Coinçon R., eds),
1056 *Spec. Publ. Intern. Ass. Sediment.*, 27, p. 87-128.
- 1057 Thiry, M., Ben Brahim, M., 1997, Silicifications de nappe dans les formations carbonatées
1058 tertiaires du piedmont atlasique (Hamada du Guir, Maroc). *Geodynamica Acta*, 10, p. 12-
1059 29.
- 1060 Thiry, M., Bertrand Ayrault, M., Grisoni, J.-C., 1988, Ground-water silicification and
1061 leaching in sands: Example of the Fontainebleau Sand (Oligocene) in the Paris Basin.-
1062 *Geol. Soc. Am., Bull.*, 100, p. 1283-1290.
- 1063 Thiry, M., Fernandes, P., Milnes, A., Raynal, J. P., 2014, Driving forces for the weathering
1064 and alteration of silica in the regolith: Implications for studies of prehistoric flint tools.
1065 *Earth-Science Reviews*, 136, p. 141-154
- 1066 Thiry, M., Millot, G., 1987, Mineralogical forms of silica and their sequence of formation in
1067 silcretes. *J. sedim. Petrol.*, 57/2, p. 343-352.
- 1068 Thiry, M., Millot, R., Innocent, C., Franke, C., 2015, The Fontainebleau Sandstone:
1069 bleaching, silicification and calcite precipitation under periglacial conditions. *Rapport*
1070 *de Recherche, RS150901MTHI, Centre de Geosciences, Ecole des Mines de Paris,*
1071 *Fontainebleau, France*, 26 p.
- 1072 Thiry, M. Milnes, A.R., 1991, Pedogenic and groundwater silcretes at Stuart Creek opal field,
1073 South Australia. *J. Sedim. Petrol.*, 61, p. 111-127.;
- 1074 Thiry, M., Milnes, A.R., Ben Brahim, M., 2015, Pleistocene cold climate groundwater
1075 silicification, Jbel Ghassoul region, Missouri Basin, Morocco. *Journal of the Geological*
1076 *Society*, 172/2, p. 125-137.
- 1077 Thiry, M., Milnes, A.R., Rayot, V., Simon-Coinçon, R., 2006, Interpretation of
1078 palaeoweathering features and successive silicifications in the Tertiary regolith of Inland
1079 Australia. *Journal of the Geological Society*, 163, p. 723-736.
- 1080 Thiry, M., Ribet, I., 1999, Groundwater silicifications in Paris Basin limestones: fabrics,
1081 mechanisms, and modelling. *J. Sedim. Petrol.*, 69/1, p. 171-183.
- 1082 Thiry, M., Schmitt, J.-M., Innocent, C., Cojan, I., 2013, Sables et Grès de Fontainebleau : que
1083 reste-t-il des faciès sédimentaires initiaux? 14ème Congrès Français de Sédimentologie,

-
- 1084 Paris 2013, Trois excursions géologiques en région parisienne, Livre d'excursions, Publ.
1085 ASF, n°74, p. 37-90.
- 1086 Thiry, M., Schmitt, J.-M., Rayot, V., Milnes, A.R., 1995, Géochimie des altérations des
1087 profils blanchis du régo-lite tertiaire de l'intérieur de l'Australie. C. R. Acad. Sci.
1088 Paris, t. 320, serie II, p. 279-285.
- 1089 Thiry, M., Simon-Coinçon, R., 1996, Tertiary paleoweatherings and silcretes in the southern
1090 Paris Basin. *Catena*, 26(1), p. 1-26.
- 1091 Twidale, C.R., Milnes, A.R., 1983, Slope processes active in the scarp retreat cycle. *Z.*
1092 *Geomorph.*, 27, p. 343-361.
- 1093 Twidale, C.R., Milnes, A.R., 1983b, Aspects of the distribution and disintegration of siliceous
1094 duricrusts in arid Australia. *Geol. Mijnbouw* 62, p. 373-382.
- 1095 Valensi, L., 1953, Microfossiles des silex du Jurassique moyen, remarques pétrographiques.
1096 Mémoires de la Société géologique de France, 68, 100 p.
- 1097 Valleron, M.M., 1981, Les faciès calcaires du Lutétien à Planorbis pseudoammonius dans le
1098 Bas-Languedoc. Argilocénèse et silifications associées aux encroûtements calcaires.
1099 Thèse 3ème cycle, Univ. Louis Pasteur, Strasbourg, 108 p.
- 1100 Webb, J.A., Domanski, M., 2008, The relationship between lithology, flaking properties and
1101 artefact manufacture for Australian silcretes. *Archaeometry*, 50, p. 555-575.
- 1102 Webb, J.A., Golding, S.D., 1998, geochemical mass-balance and oxygen-isotope constraints
1103 on silcrete formation and its palaeoclimatic implications in southern Australia. *Journal of*
1104 *Sedimentary Research*, 68, p. 981-993.
- 1105 White, D.E., Hem, J.D., Waring, G.A., 1963, Chemical composition of subsurface waters. in:
1106 . Fleischer, M. (Ed.), *Data of Geochemistry*, 6th ed., U.S. Geol. Survey Professional
1107 Paper 440-F.
- 1108 Wragg-Sykes R., Chomette D., Defive E., Delvigne V., Lafarge A., Fernandes P., Liabeuf R.,
1109 Piboule M., Raynal J.-P., 2014, Sondages sur le gite-atelier de Saint-Pierre-Eynac
1110 (Haute-Loire) et son environnement géologique. in: J.-P. Raynal, M.-H. Moncel, eds.,
1111 Programme collectif de recherche Espaces et subsistance au Paléolithique moyen dans le
1112 sud du Massif central. Ministère de la Culture et de la Communication , DRAC
1113 Auvergne., rapport DRAC 2014-142, vol. 2, p. 1-52.
- 1114 Wright, M.J., 1983, Red-brown hardpans and associated soils in Australia. *Trans R. Soc. S.*
1115 *Aust.*, 107, p. 252-254.

1116 **Figure captions**

1117

1118 Figure 1 - Rate of dissolution and asymptotic solubility of the different silica varieties at 25°C
1119 (after Siffert 1967). Opal and chalcedony show variable solubility according to their
1120 respective crystallinity.

1121 Figure 2 - Quartz and chalcedony solubility versus temperature (computed from geochemist's
1122 workbench program; Bethke, 2002). Quartz solubility decreases to more than half of its
1123 initial value between 12.5 and 0°C.

1124 Figure 3 – Solubility of amorphous silica in aqueous salt solutions at 25°C (after Marshall,
1125 1980)

1126 Figure 4 – Alumina and silica solubility versus pH (computed from PHREEQC program, U.S.
1127 Geological Survey; Parkhurst and Appelo, 1999). Silica is insoluble at acidic and neutral
1128 pH that appear favourable for development of silcretes, whereas alumina stability is
1129 restricted to neutral pH.

1130 Figure 5 – Eh/pH diagram for Fe-O-H system showing the reaction path leading to ferrolysis
1131 after having introduced some oxygen into the Fe⁺⁺- rich solution. Diagram at 25°C in
1132 equilibrium with atmospheric O₂ and CO₂, and [SO₄⁻⁻]= 10⁻⁷ (after Garrels and Christ,
1133 1965).

1134 Figure 6 –Schematic geological section through the Beauce Plateau. Quartzitic silcrete pans
1135 are limited to the outcrop zone of the Fontainebleau Sand. The size of the silcrete lenses
1136 (black wedges) is exaggerated for illustration.

1137 Figure 7 – Schematic model of successive cycles of groundwater-related quartzitic silcrete
1138 formation in the Fontainebleau Sand. The thickness and the slope of quartzite pans are
1139 exaggerated for illustration.

1140 Figure 8 - Schematic diagram of the Calcaire de Champigny Formation (upper Eocene)
1141 showing the distribution and shapes of silicified zones (Plateau of Brie, France). Note
1142 similarity between the distribution and shapes of the silicified zones and dissolution
1143 features of the limestone.

1144 Figure 9 - Larkins Folly section exposed in bulldozer costeans in Coober Pedy opal field. The
1145 bleached Cretaceous formations contain termite burrows and alunite nodules. There are
1146 two superposed levels of groundwater silicification. In addition, at the top is a
1147 pedogenic silcrete disrupted by vertical pipe-like structures, and an overlying laminar-
1148 structured red-brown hardpan.

1149 Figure 10 – Sketch of the macromorphological organisation of a pedogenetic quartzose
1150 silcrete and distribution of secondary silica and dissolution structures.

1151 Figure 11 – Thin sections of groundwater silcrettes (transmitted light, crossed polars). (A)
1152 Fontainebleau quartzitic silcrete in which original detrital quartz grains are overgrown
1153 by secondary silica, producing triple-point junctions and thus a compact mesh that
1154 results in a rough fracture. (B) Stuart Creek quartzitic silcrete with chalcedonite deposits
1155 in pore spaces produces a lustrous break on knapping.

1156 Figure 12 – Thin sections of silicified limestone (Paris Basin): two views (A) and (B):
1157 transmitted light, crossed polars. The larger crystals are euhedral quartz that crystallized
1158 in voids (v) by precipitation from water, the speckled areas are microcrystalline quartz
1159 (μ Q) replacing primary carbonate and the black areas are remnant carbonate (Ca). The
1160 images show the nature of the silicified “front” (dotted line).

1161 Figure 13 – Thin sections of porcellanites (transmitted plane polarised light). (A) Stuart
1162 Creek, South Australia. The dark granular matrix (Op1) is silicified silty claystone.
1163 Voids (v) and channels contain successive silica deposits (Op2), firstly brown opal then
1164 chalcedonite. The latter also impregnates the matrix and results in a compact material
1165 with a lustrous fracture. (B) Sancerre, southern Paris Basin. The dark opal matrix (Op1)
1166 has recrystallized into clear homogeneous microquartz (μ Q); the opal deposits in the
1167 voids (Op2) remain unaffected. This type of porcellanite provides sharp flakes, like
1168 flints, on knapping.

1169 Fig 14 – Thin sections of pedogenic silcrettes, Paris Basin. (A) matrix of amoeboid quartz
1170 microcrystals in net-like arrangement generates a hard and lustrous fracture on knapping
1171 (transmitted light, crossed polars). (B) and (C) nodular facies with illuviation cutans (il)
1172 recrystallized into microquartz plus titania microcrystals; nodules are rimmed by a

1173 cortex enriched in titania (arrow). Channels remain empty (v) or are cemented with sub-
1174 euhedral quartz crystals (Q). (Transmitted plane polarised light).

1175 Figure 15 - Schematic view of the Beda pediment showing the distribution of pedogenic
1176 silcrete facies. Facies change completely at a 100 m scale (after Milnes and Thiry,
1177 1992).

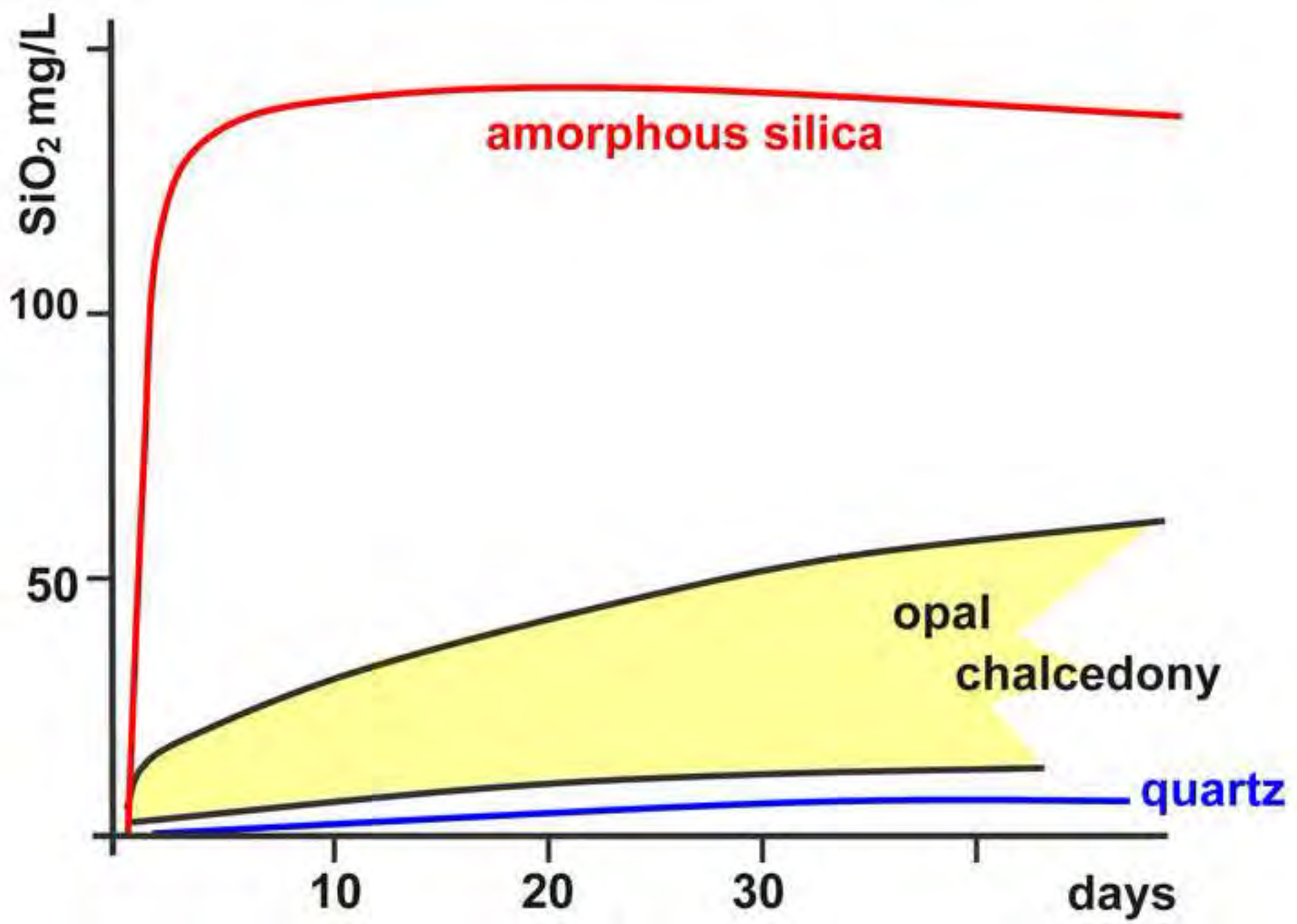
1178 Figure 16 - Schematic morphostratigraphic sketch of landscapes from the Davenport Range,
1179 across the Stuart Range, to the Eucla Basin, South Australia, showing silicification in
1180 relation to different weathering features and their distribution in relation to landsurfaces
1181 and geology (after Simon-Coinçon *et al.*, 1996).

1182 Figure 17 –Schematic section across the Todd River Plain, southeast of Alice Springs, central
1183 Australia, showing the location of different silcrete facies (after Milnes and Thiry,
1184 1992).

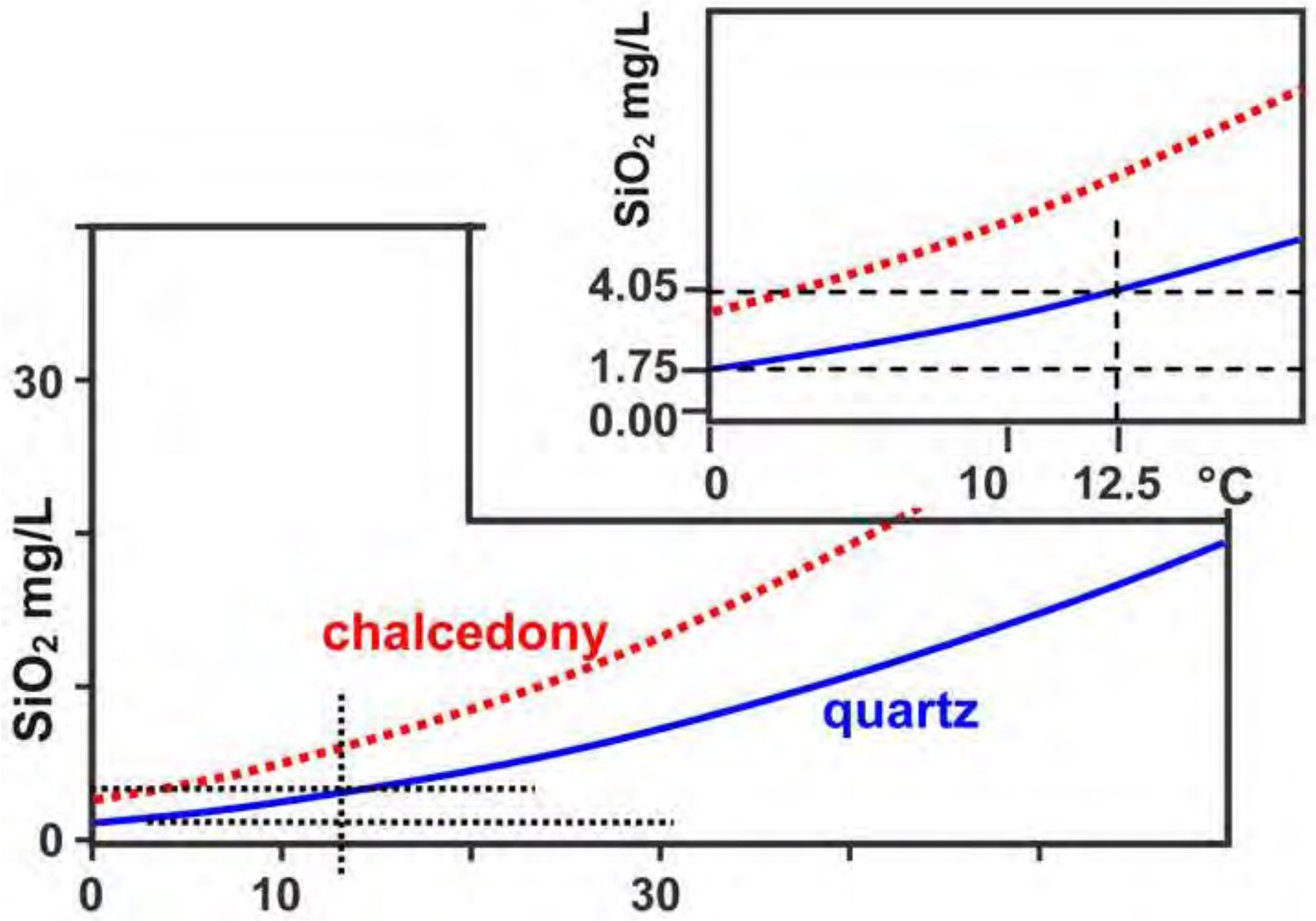
1185 Fig. 18 – Schematic geomorphological section across the Paris Basin, showing the
1186 distribution and relationships of silcrete facies.

1187

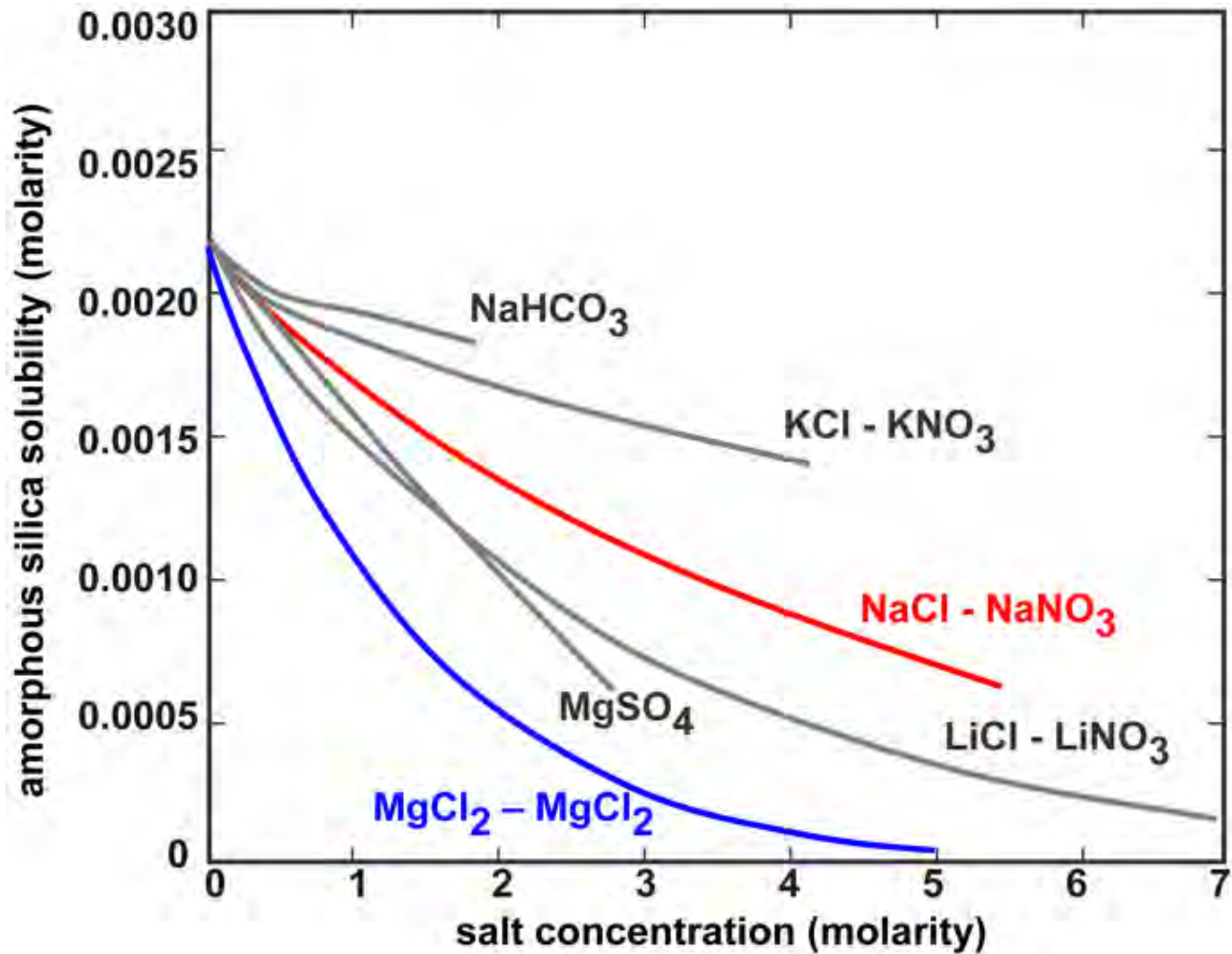
Figure_01_8cm
[Click here to download high resolution image](#)



Figure_02_8cm
[Click here to download high resolution image](#)

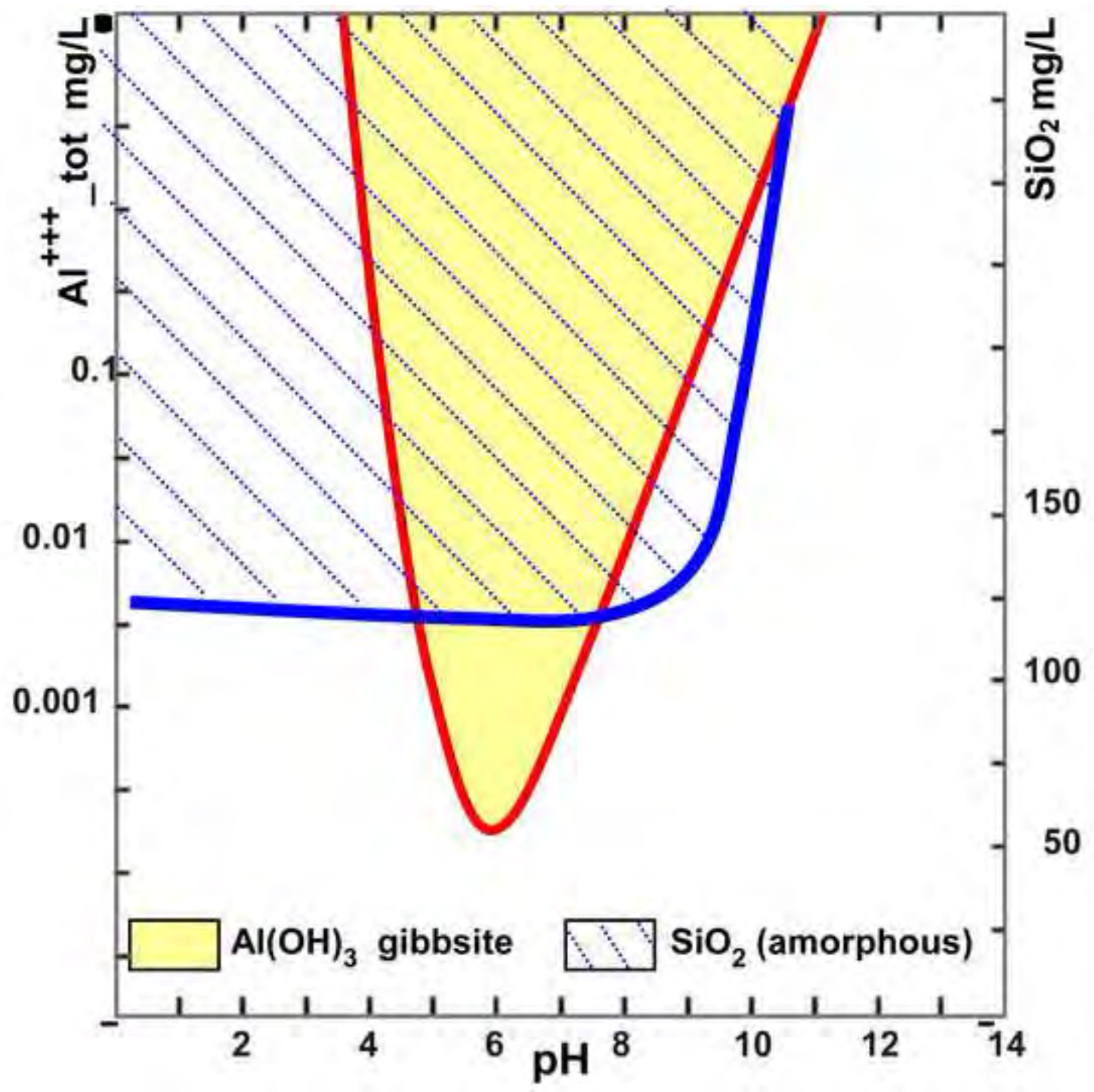


Figure_03_9cm
[Click here to download high resolution image](#)



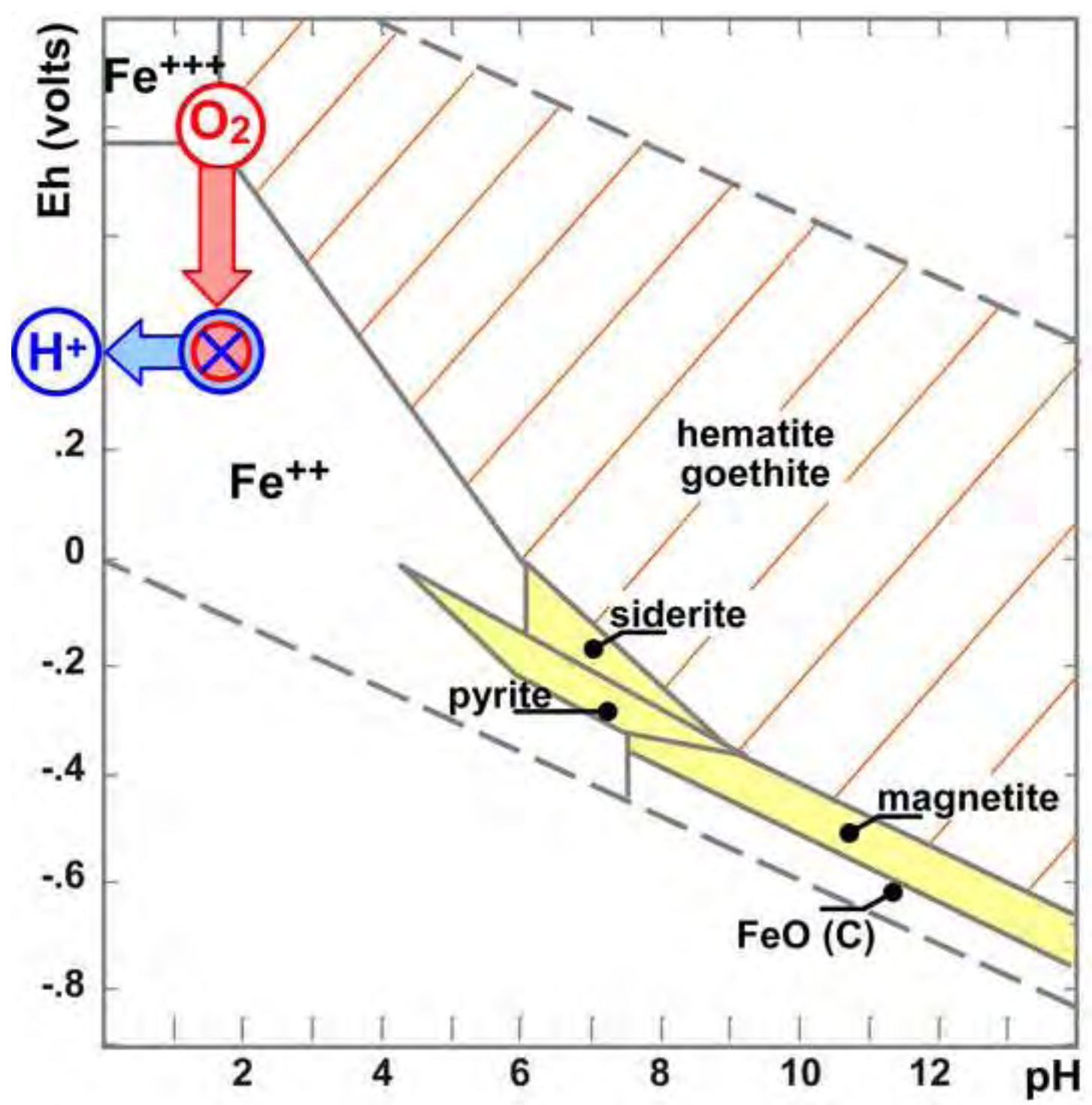
Figure_04_8cm

[Click here to download high resolution image](#)

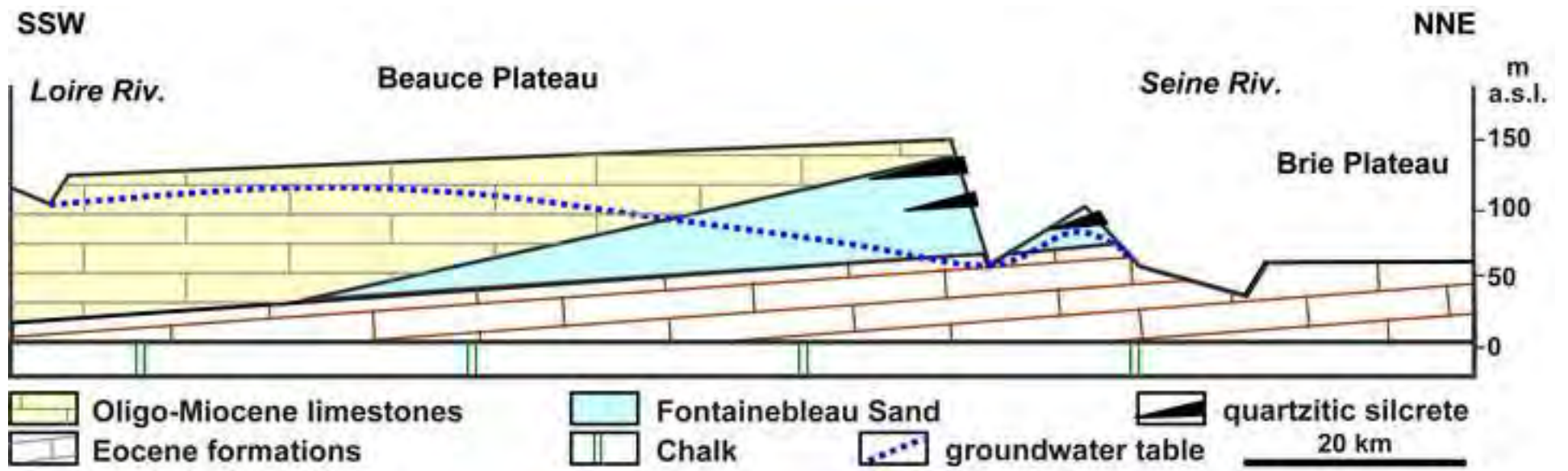


Figure_05_8cm

[Click here to download high resolution image](#)

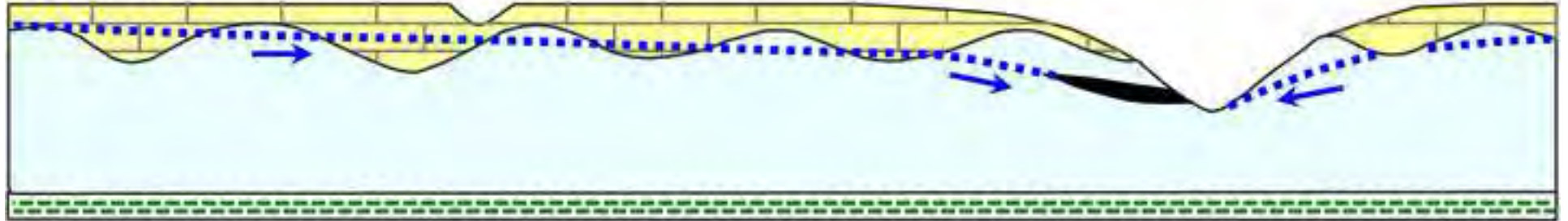


Figure_06_15cm
[Click here to download high resolution image](#)

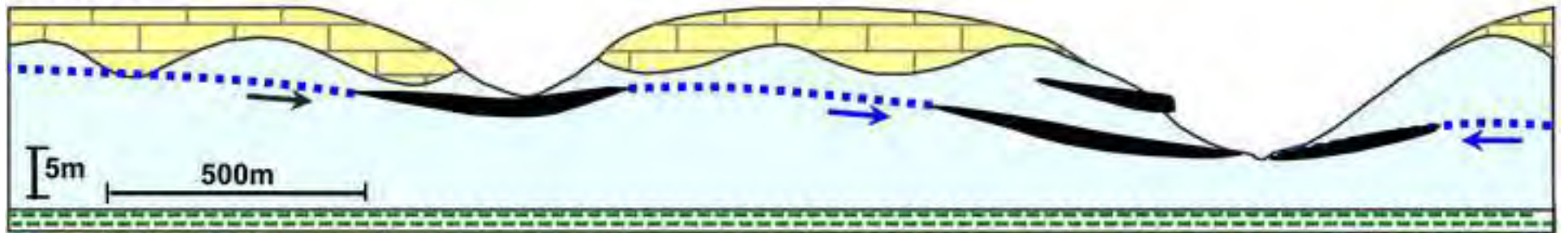


Figure_07_13cm
[Click here to download high resolution image](#)

STAGE 1



STAGE 2



marl



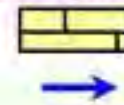
quartzitic silcrete



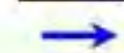
sand



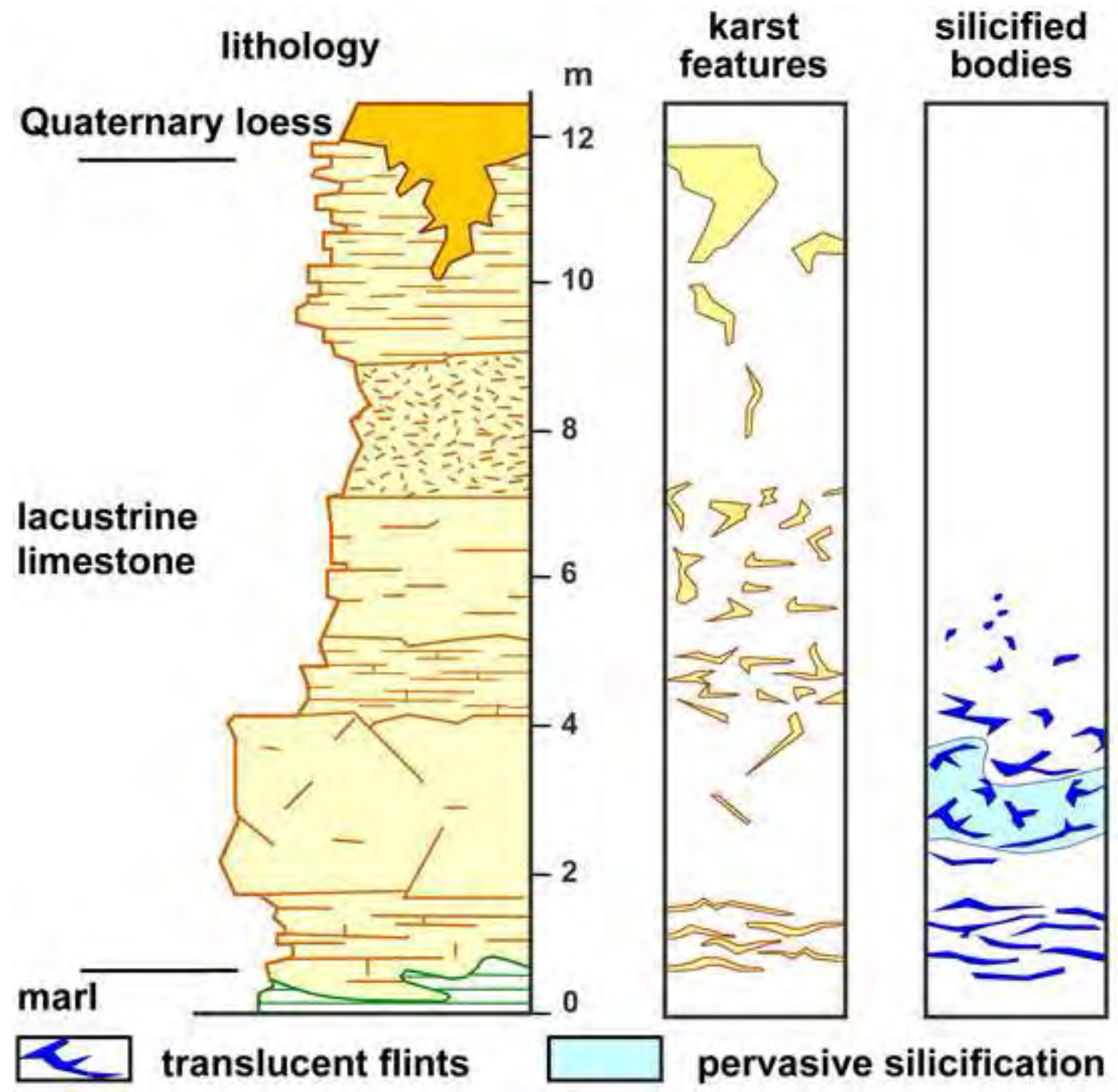
water table

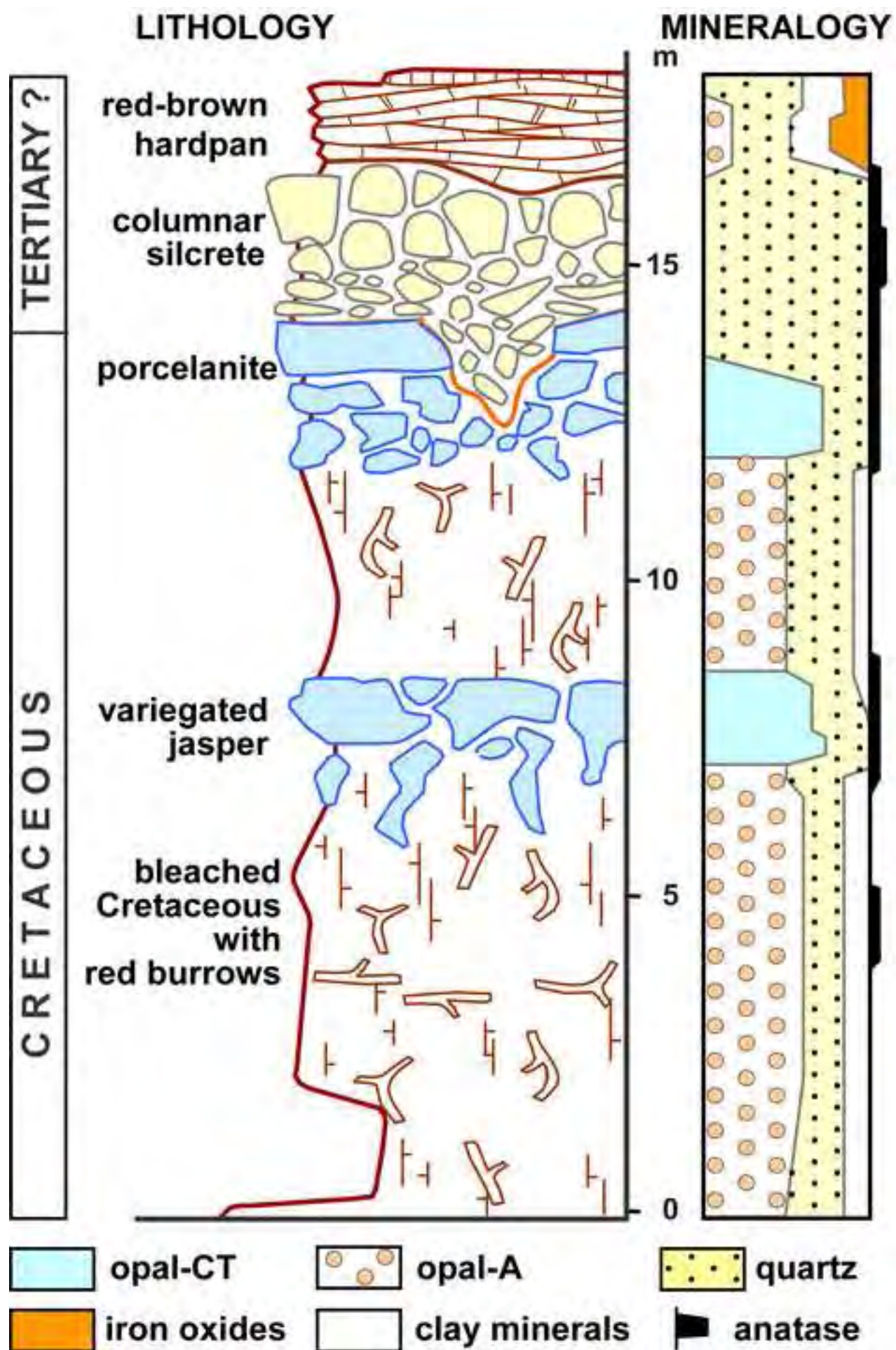


limestone



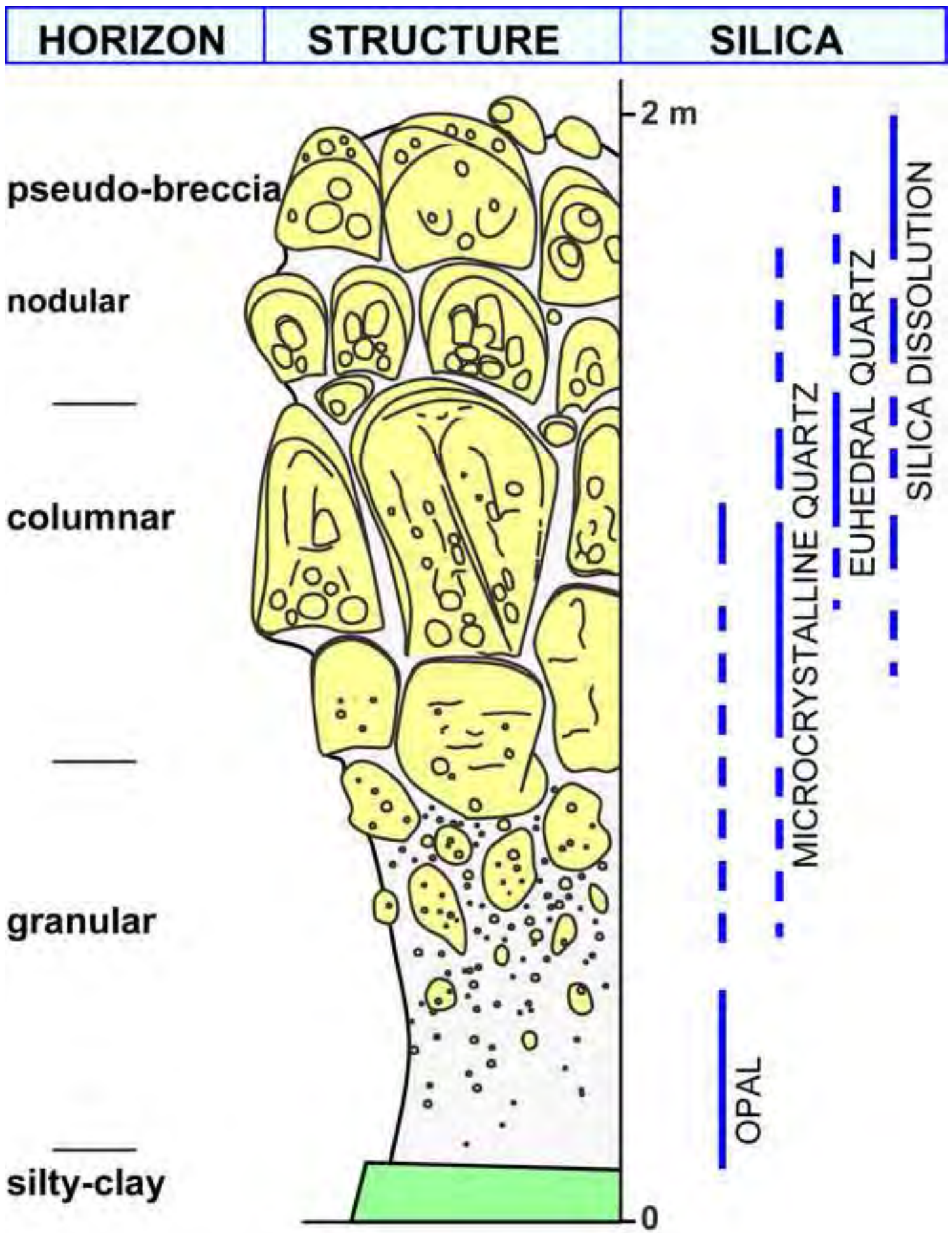
groundwater flow

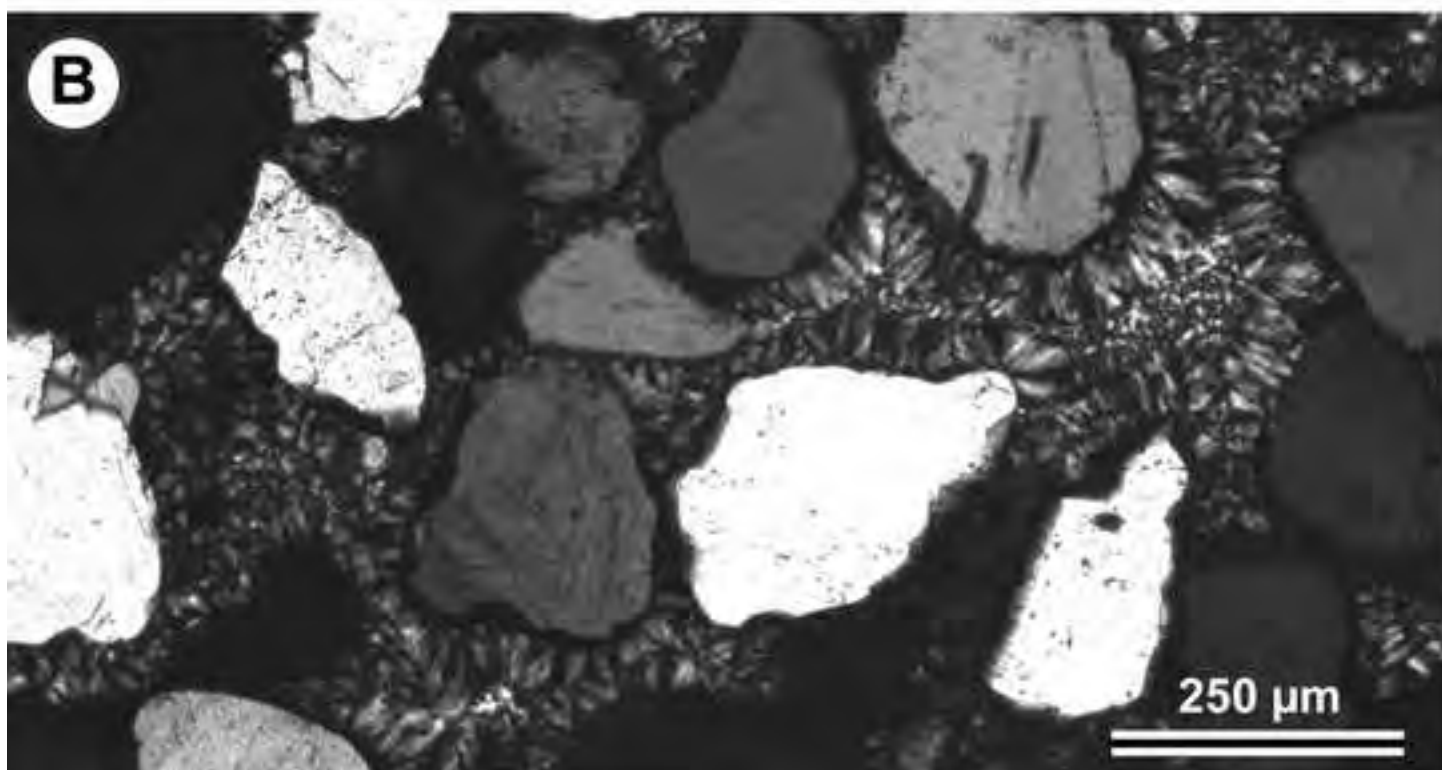
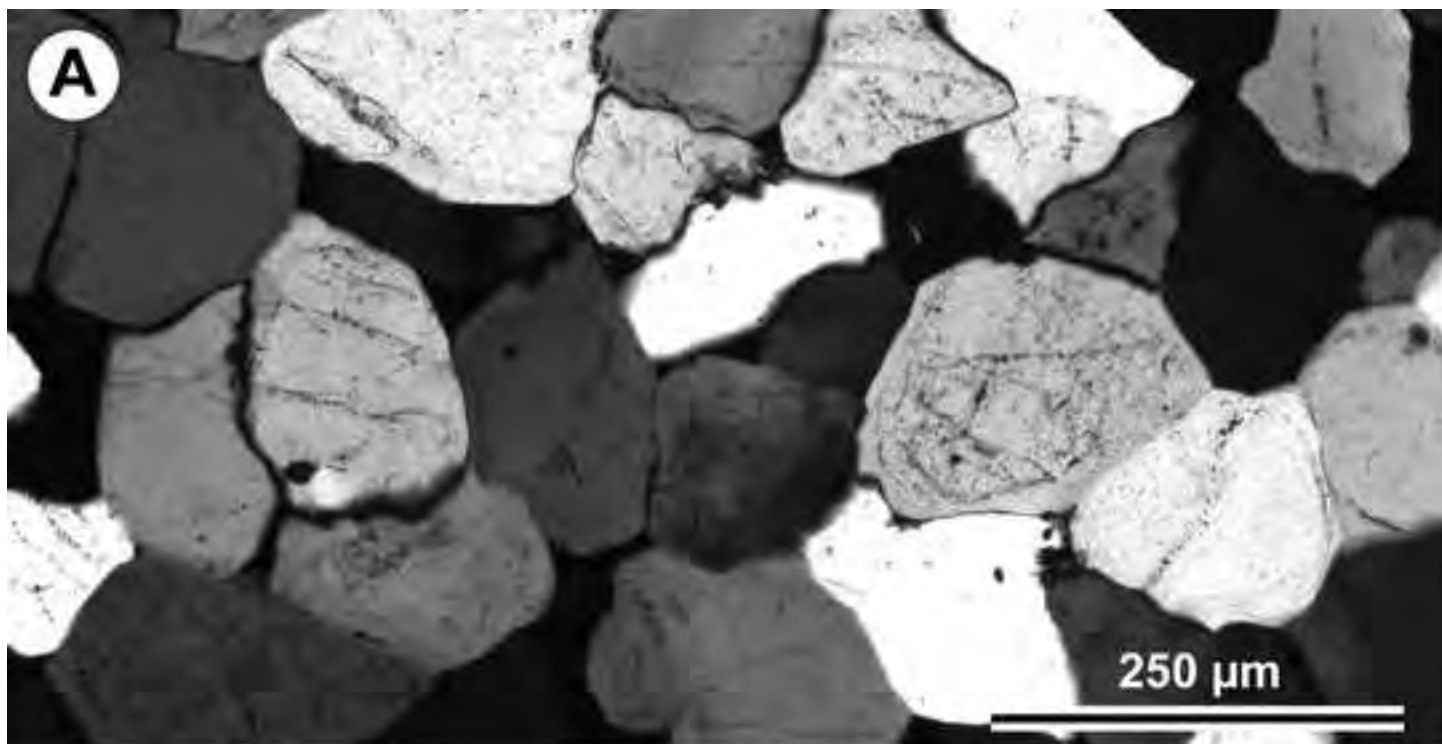




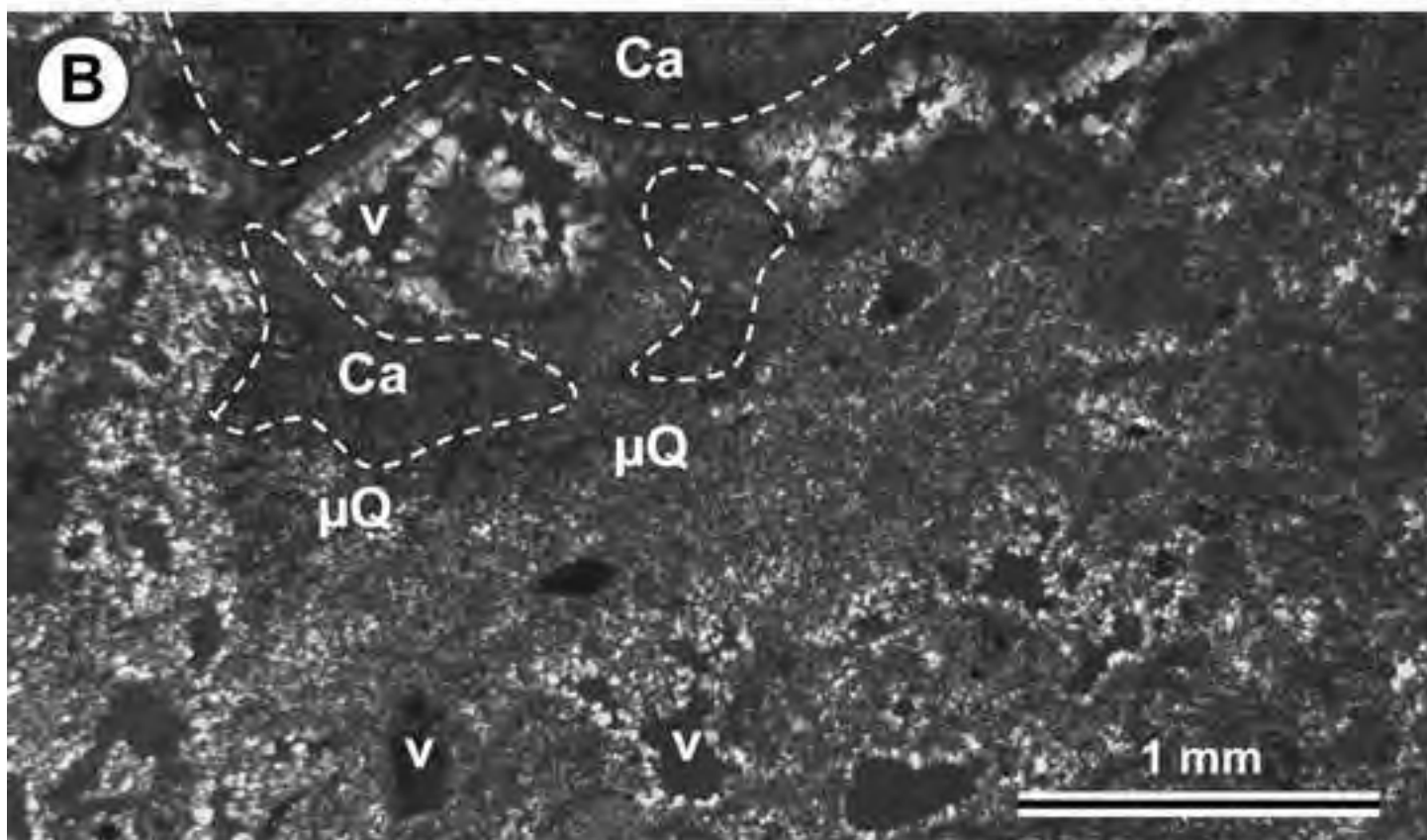
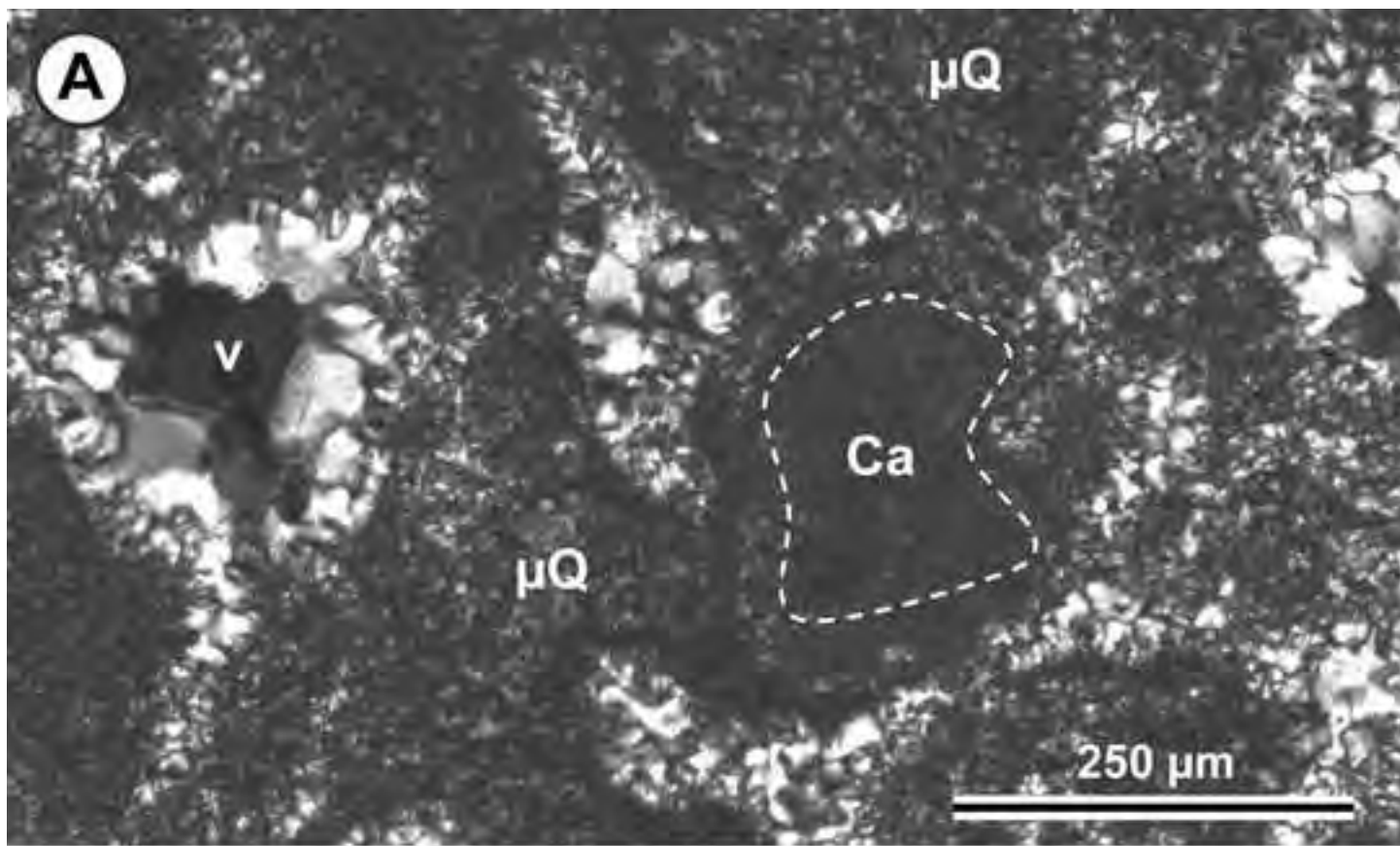
Figure_10_8cm

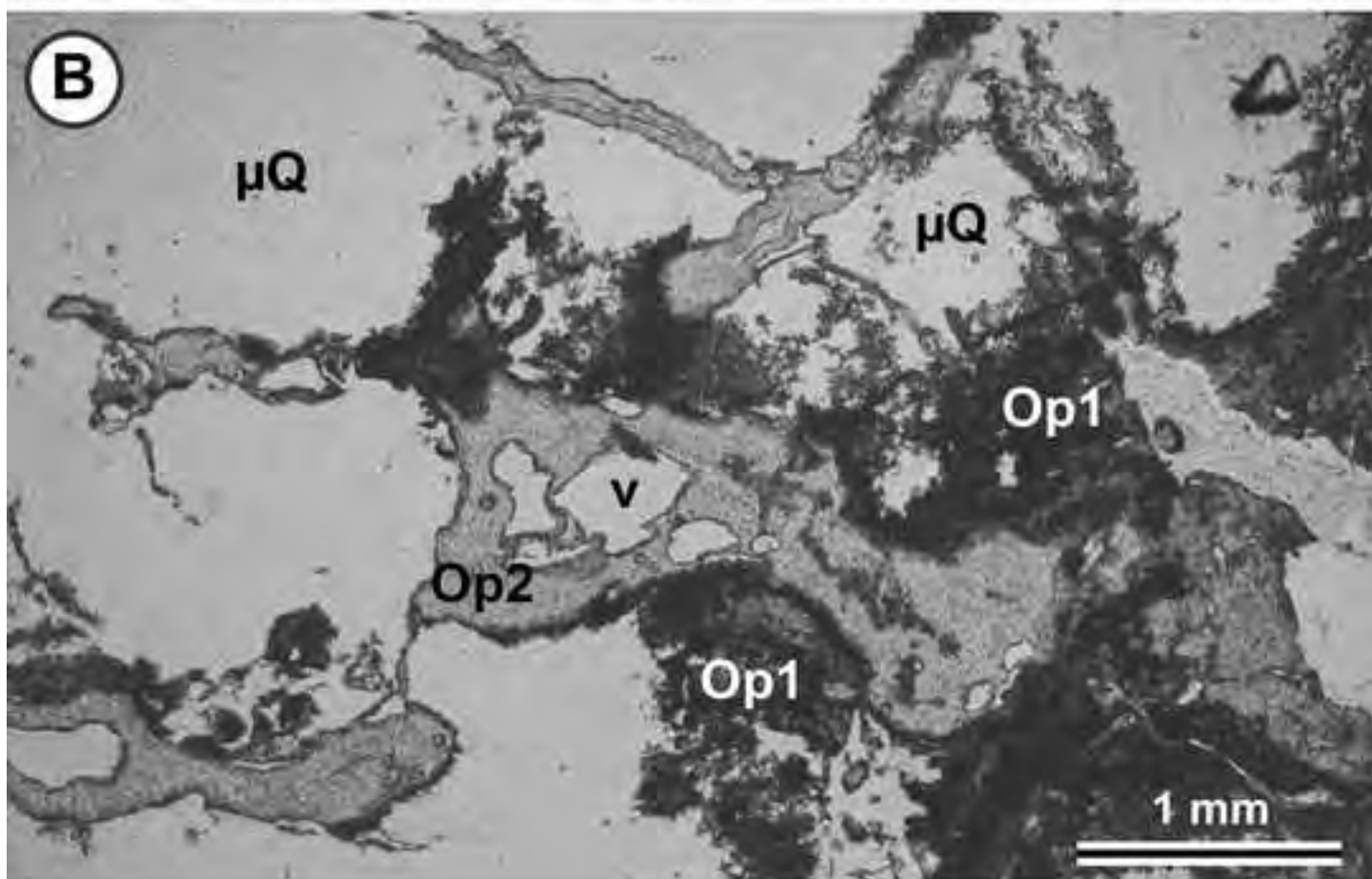
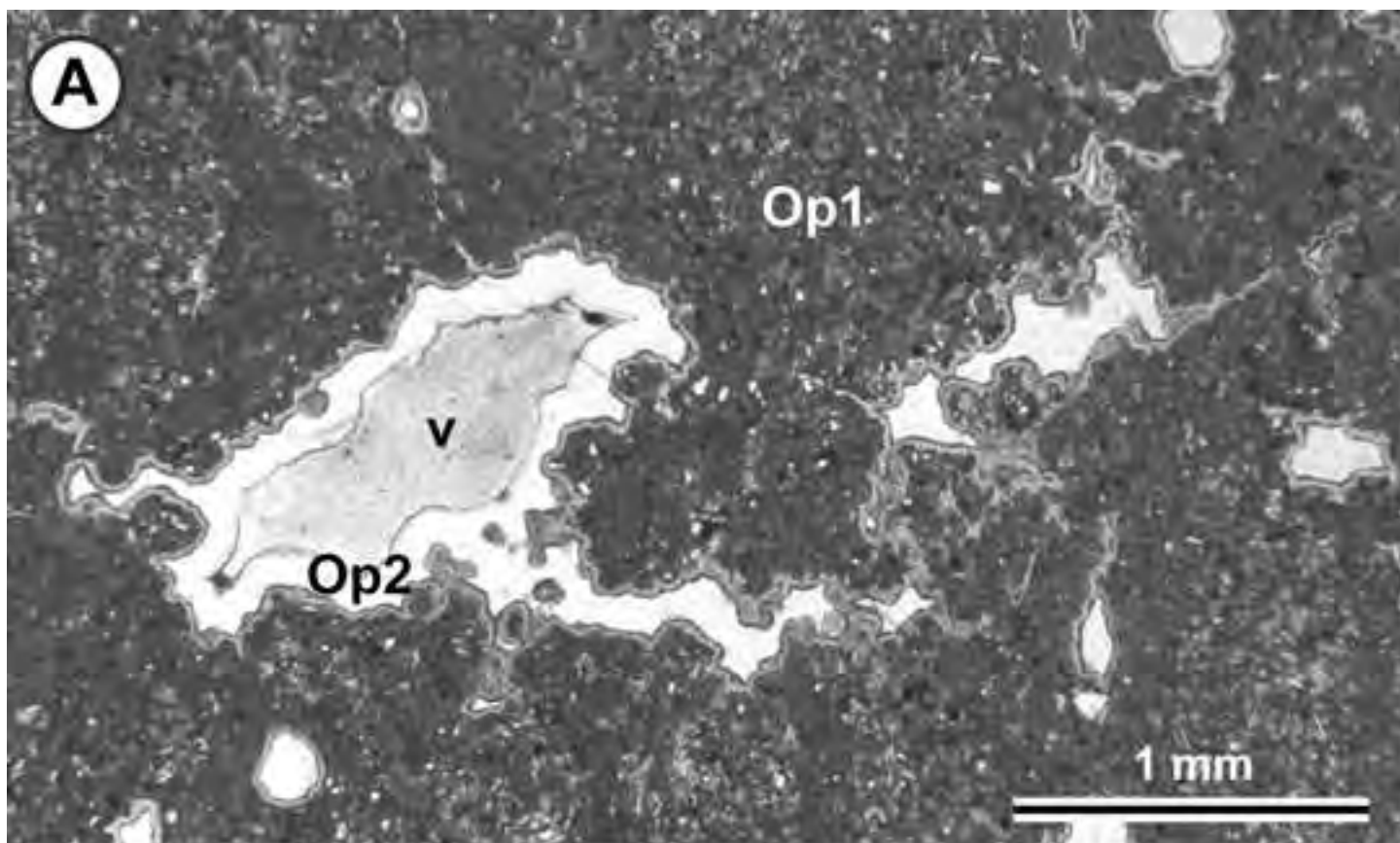
[Click here to download high resolution image](#)

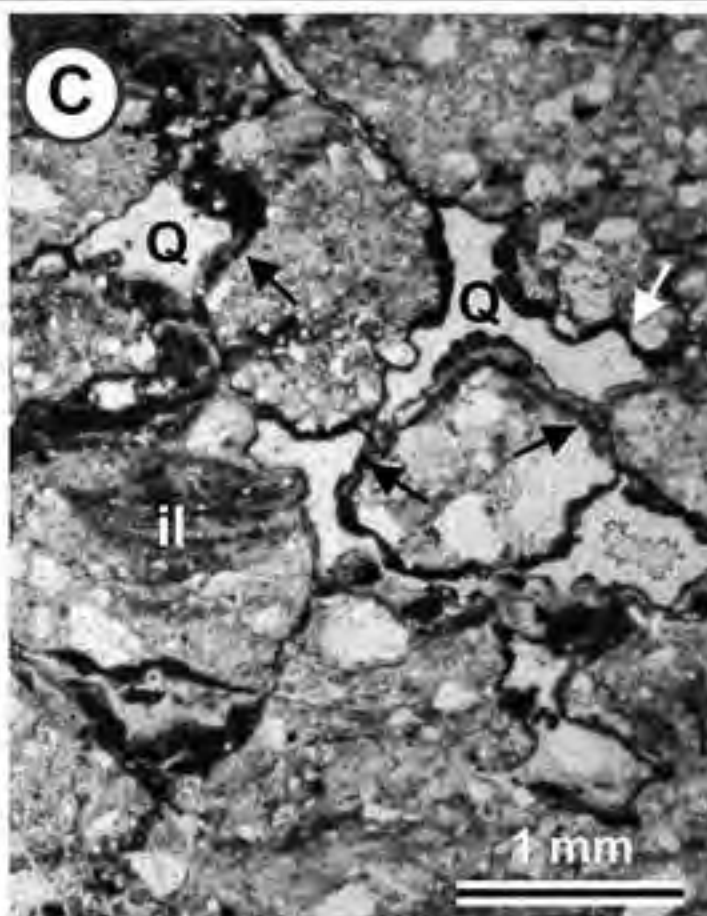
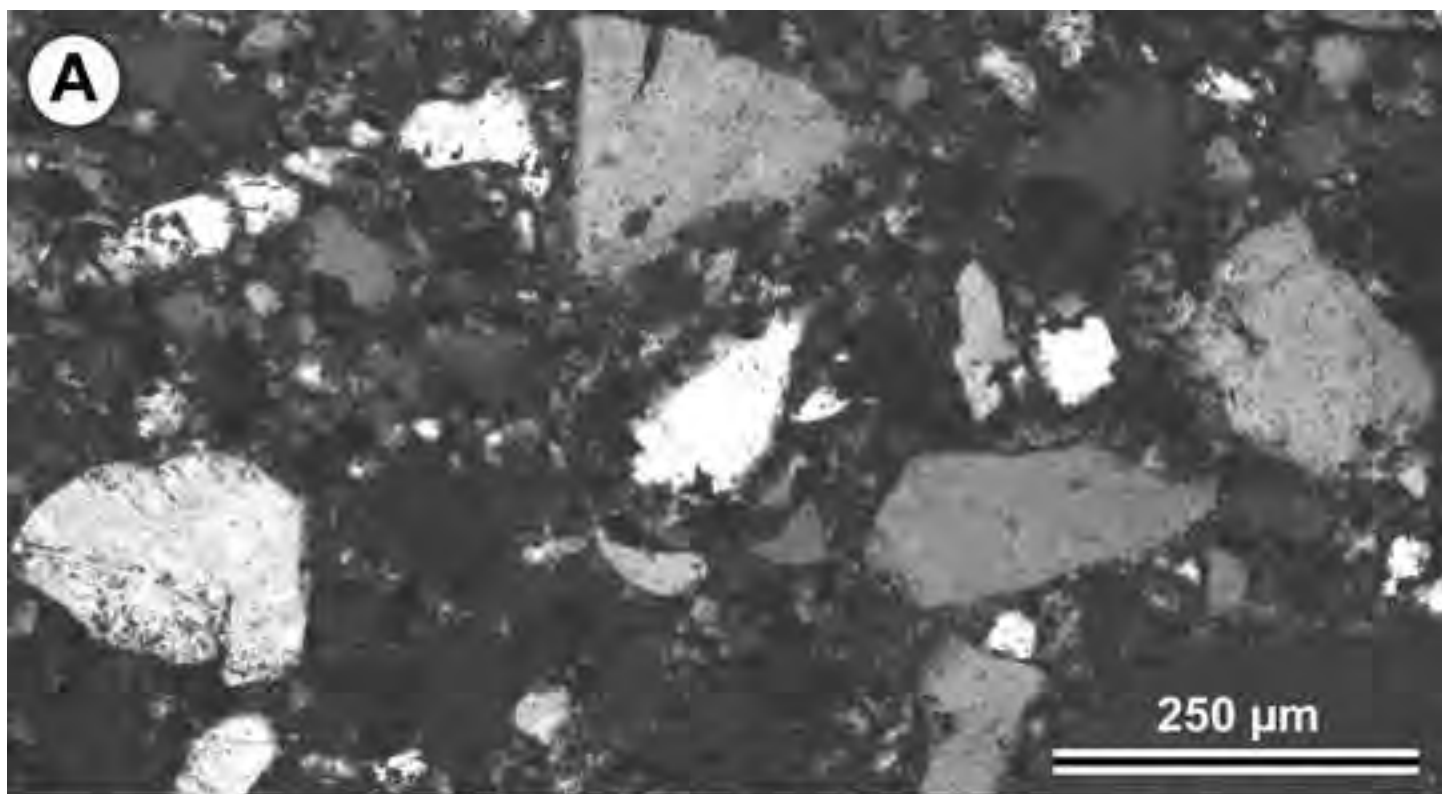




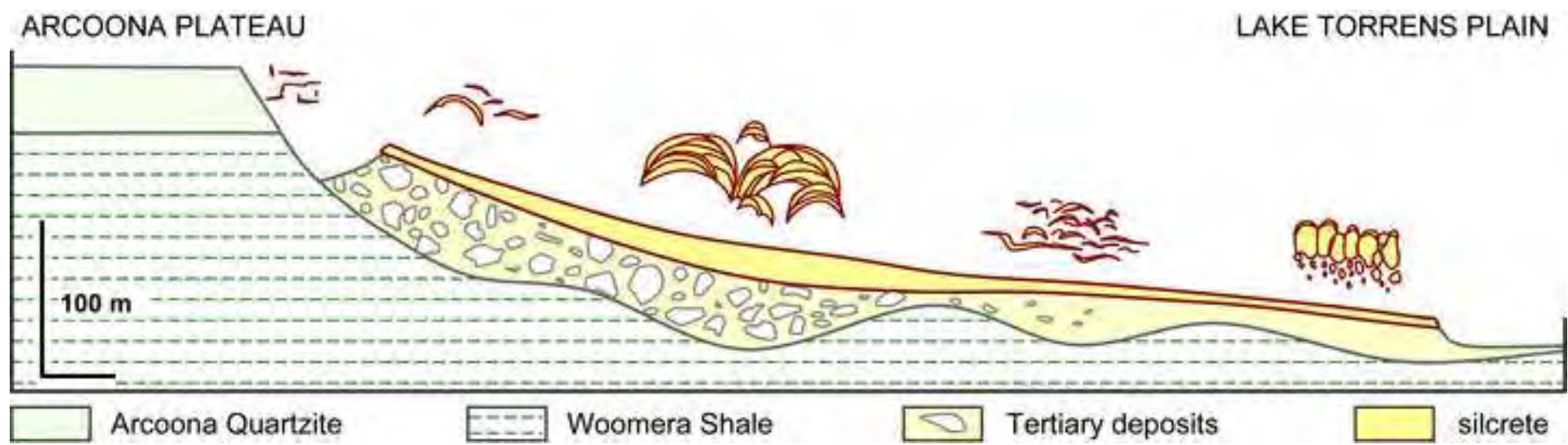
Figure_12_9cm
[Click here to download high resolution image](#)



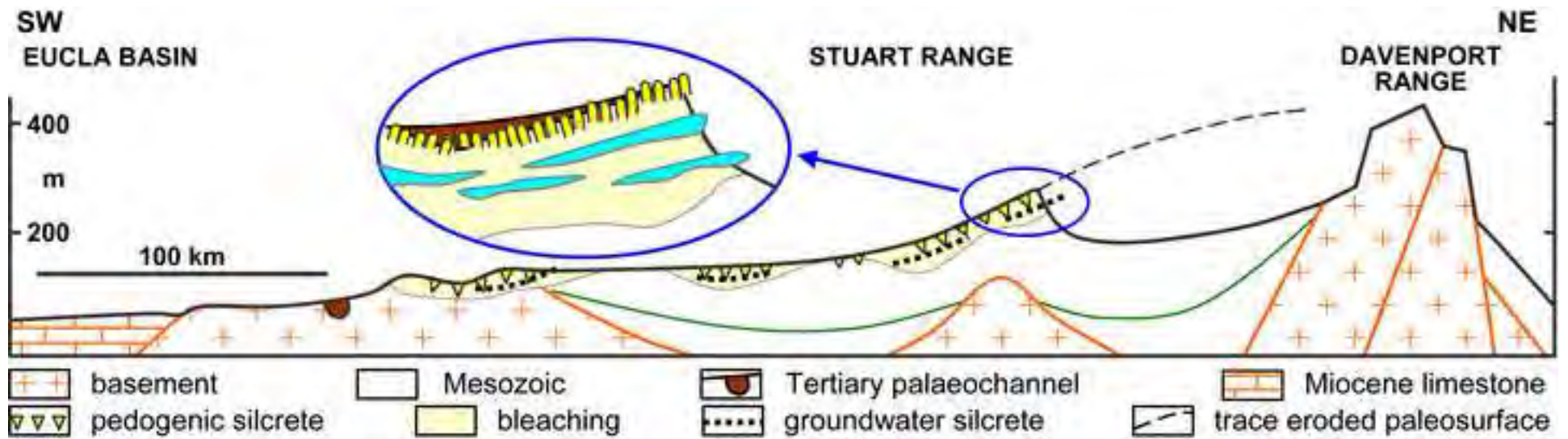




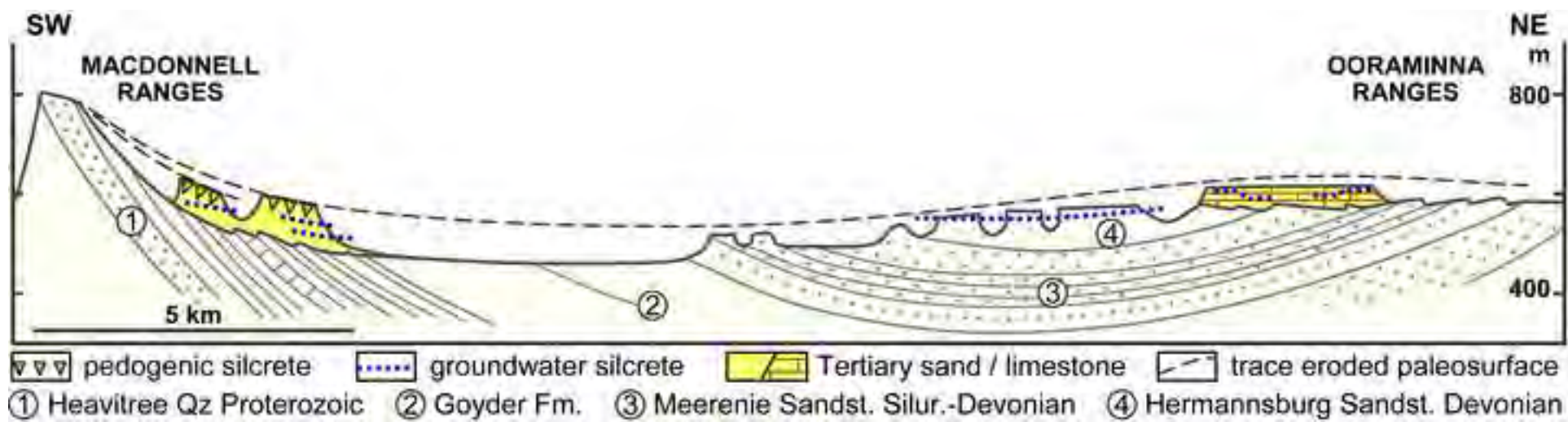
Figure_15_16cm
[Click here to download high resolution image](#)



Figure_16_16cm
[Click here to download high resolution image](#)



Figure_17_16cm
[Click here to download high resolution image](#)



Figure_18_17cm
[Click here to download high resolution image](#)

