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

Médard Thiry, Anthony Milnes

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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

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.

1 Introduction

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

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

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

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

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

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

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

In this paper we summarise our current thinking on the characteristics, landscape associations, origin and age of silcretes. We also attempt to link petrological and mineralogical features (which are of specific importance to geologists in generating hypotheses to explain the origin of silcretes) to the potential value of silcretes to prehistoric peoples for the production of stone tools,. However, we recognise that there are substantial fields of knowledge in geoarchaeology and lithic technology that rightly lay claim to the development of an understanding of the associations between prehistoric peoples and the source materials for stone tools.

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

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

Although there are several forms of silcrete that can be found and recognised on many continents, only some appear to have been suitable for stone tool making. The sites that have generated starting materials for appropriate tools can be readily recognised in the field from the litter of flakes and chips discarded during tool production. Mineralogical and micromorphological properties can explain physical appearance, hardness, lustre and potential durability of silcrete tools and, in some cases, in some regions, point to their provenance. However, archaeologists may not be particularly focussed on sources of silcrete (or other forms of siliceous rocks) that have been opportunistically exploited for the production of stone tools, but rather seek to recognise specific source materials that have been valued from a technological, aesthetic or symbolic viewpoint and which potentially have been transported long distances. Identifying provenance from this perspective permits them to potentially trace out migration patterns, exchanges, and possibly social behaviour.

2 Behaviour of silica in regolith environments

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

2.1 Silica solubility

The solubility of amorphous silica in water under earth-surface conditions is about 120 mg/L SiO_2 while the solubility of all other silica phases is significantly lower than this (Fig. 1). The most soluble phases in a geochemical system control the precipitation of the less soluble ones and, in this way, amorphous silica in equilibrium with a solution is able to sustain the crystallisation of every other crystalline silica phase. In turn, cristobalite, tridymite, chalcedony and opal in equilibrium with a solution are able to sustain the crystallisation of quartz (Fig. 1; Garcia-Hernandez, 1981; Gislason *et al.*, 1993; Iler, 1979; Siffert, 1967).

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

opal → microcrystalline quartz → euhedral quartz

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

It should be noted that most natural groundwaters around the world have a silica content between 12 -18 ppm SiO_2 (Garrels and Christ, 1965, Swanberg and Morgan, 1978; White *et al.*, 1963) that is roughly in equilibrium with clay minerals. This means that most groundwaters are oversaturated with respect to quartz (solubility 4 - 7 mg/L) and are thus potentially able to precipitate quartz when favourable physico-chemical conditions occur. As pointed out by Thiry *et al*. (2014), solutions with a high silica content favour the formation of crystal nuclei and crystal defects that restrict the growth of crystals and consequently the precipitation of amorphous or low crystallinity silica varieties. However, in dilute solutions, the number of nuclei and impurities remains limited. As a consequence, pure silica crystallites generally form and large quartz crystals can develop or, under less favourable conditions, microcrystalline or fibrous silica varieties are formed.

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

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

Increasing the concentrations of salts in solution is another efficient way to decrease silica solubility: the solubility of amorphous silica decreases with increasing salt concentration to saturation (Fig. 3), up to 96% in the case of $CaCl_2$ and up to 30% in the case of a NaCl saturated solution (Marshall, 1980). The mixing of a silica solution with chlorite- and/or sulphate-rich brine is certainly a very effective mechanism for inducing the precipitation of silica. The often advocated relation between silicification and warm and dry climates most probably results from the negative relationship between increasing concentrations of evaporite brines and silica solubility.

2.2 Key geochemical processes in regolith solutions

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

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

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

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

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

Sulfide oxidation is one possibility for the development of acid conditions. It is a consequence of weathering of sulfides present in host rocks, resulting in high concentrations of sulfur in groundwaters, abundant sulfate minerals and an oxidizing environment. Nevertheless, pyrite oxidation will only develop widespread acidity if water flow through these formations is limited. Ultimately, the acidity depends on the degree of oxidation reached:

(1) $$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{++} + 2\ SO_4^{--} + 2\ H^+$$

(2) $$2\ FeS_2 + 15/2\ O_2 + 7\ H_2O \rightarrow 2\ (Fe(OH)_3 + 4\ SO_4^{--} + 8\ H^+$$

Ferrolysis is another geochemical process that develops highly acidic environments. It relies on the oxidation of Fe^{++}-bearing solutions by incoming O_2, leading to the liberation of H^+ protons (Fig. 5).

(3) $$Fe^{++} \rightarrow Fe^{+++} + 2e^-$$

(4) $$2Fe^{+++} + 4H_2O \rightarrow 2\ FeO(OH) + 6H^+$$

It has been widely advocated in several soil environments in which clay minerals are degraded by leaching of Al from the silicate framework (Brinkman, 1970). In Western Australia, pyrite oxidation and ferrolysis have been put forward to explain the regional acid saline groundwater systems and hundreds of ephemeral saline lakes characterized by complex acid brines with a pH as low as 1.4, together with an abundance of alunite, and the large-scale mobilisation of silica and accompanying silcrete formation (Benison and Bowen, 2015; Dickson and Giblin, 2009; Mann, 1983; McArthur *et al.*, 1991).

The effectiveness of acidolysis of alumino-silicates (feldspars and clay minerals) with regard to silicification can be appreciated from the mass balance equations:

(5) $$\underset{\text{orthoclase 100g}}{2\ (KAlSi_3O_8)} + 2\ H_2O + 2\ H^+ \rightarrow \underset{\text{kaolinite 46 g}}{Si_2Al_2O_5(OH)_4} + \underset{\text{silica 43g}}{4\ SiO_2} + 2\ K^+$$

(6) $$\underset{\text{kaolinite 46g}}{Si_2Al_2O_5(OH)_4} + 6\ H^+ \rightarrow 2Al^{+++} + \underset{\text{silica 30 g}}{2\ SiO_2} + 5\ H_2O$$

The complete acidolysis of orthoclase releases 73% by weight of silica: this could remain *in situ* to contribute to the formation of a silcrete (*relative* accumulation of silica) or be released in solution to infiltrate, and initiate silicification of, specific zones or horizons in the regolith (*absolute* accumulation of silica).

2.3 Silicification in the regolith

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

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

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

3 Varieties of silcrete

Silcretes take a wide variety of forms and detailed investigations of these forms from the field scale to that available via scanning microscopy provide clues to their origin. Aspects such as field distribution, geomorphological patterns and relationships to current and former landscapes, petrology and mineralogical-geochemical characteristics have all to be considered. We group silcretes into two classes: groundwater silcretes that form mainly as a result of the absolute silica accumulation of silica in regolith environments; and pedogenic silcretes that reflect the relative accumulation of silica, as well as a complex of dissolution, eluviation and illuviation processes typical of soil environments. Nash and Ullyott (2007) have suggested a sub-classification of '*non-pedogenic*' silcretes into '*drainage-line*' and '*pan/lacustrine*' types', but these forms can be encompassed satisfactorily within groundwater silcretes from our perspective. Of particular interest in the landscape context is that volume is mostly conserved during the formation of groundwater silcretes, whereas volume is substantially lost during the formation of pedogenic silcretes, some of which can be metres thick in profile.

3.1 Groundwater silcretes

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

3.1.1 Quartzitic types

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

In the Paris Basin, flat-lying quartzitic silcrete lenses (1-8m thick) occur at different levels within the Fontainebleau Sand formation (Thiry *et al.*, 1988; Thiry *et al.*, 2013; Thiry *et al.*, 2015a). The silcrete lenses typically crop out on the edges of plateaux or in valley margins but pinch out rapidly under the limestone-capped plateaux, as shown by drill holes and observations in sand quarries (Fig. 6). This strong link between silcrete distribution and present-day geomorphology suggest that these silcretes developed relatively recently in and near outcrop zones of the Fontainebleau Sand. Sand calcite contained in the silcretes date the silicification to Pleistocene glacial periods (Thiry *et. al.*, 2013).

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

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

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

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

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

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

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

3.1.2 Silicified limestone/calcrete types

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

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

Two types of silicification coexist: deposits of quartz and chalcedony in voids; and epigenetic replacement of the limestone matrix by microcrystalline quartz, with preservation of the primary sedimentary structures. Thin sections show a systematic link between silicification and zones of high porosity, either preserved or partly infilled by silica deposits (Thiry and Ribet, 1999).

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

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

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

3.1.3 Porcellanite/jasper types

Fine grained silcretes, obviously resulting from silicification of primary clay-rich materials, form specific facies, generally of glassy appearance, and often resembling flint or chert except for their colour which is generally due to iron-oxide inclusions. Such materials have been described in several geological contexts (Boule, 1888; Millot *et al.*, 1959, Valleron, 1981).

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

These profiles have resulted from alteration under acidic conditions in a saline groundwater environment nearly saturated in gypsum (Thiry *et al.*, 1995). The bleaching was related to the lowering of the groundwater table. Arid conditions at the time restricted water flow and allowed an acidic environment to develop to leach original alumino-silicates, retain Si (as amorphous silica and quartz), but not completely lose some of the most soluble elements like K, Ca, SO_4 and Al from the system that form nodules and veins of alunite and gypsum in places. Elevated concentrations of anatase (Fig. 9) could indicate that Ti released from primary alumino-silicates has also been retained.

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

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

3.2 Pedogenic silcretes

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

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

A lower granular horizon consists of a sandy claystone with millimetric- to centimetric-sized granules of microcrystalline quartz and opal. TEM and electron diffraction studies of the clay matrix show that hexagonal-shaped kaolinites have corrosion embayments and are coated and welded together by a silica gel.

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

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

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

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

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

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

4 Characteristics of silcretes of relevance to tool making

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

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

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

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

4.1 'Sandstone' cementation

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

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

4.2 Silicified limestones

In silicified limestones the carbonate matrix has been replaced by silica. The substitution is mainly epigenetic, which means that primary limestone structures such as nodules and fossils are replaced by silica and conserved. For this to occur, there can be no dissolution of the carbonate before replacement: substitution occurs step by step along a clear 'alteration front' between existing limestone and incoming silica. This replacement implies concomitant leaching of the carbonate and precipitation of silica. Voids are necessary for water circulation and their shape and size determines the density and 'quality' of the silicification.

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

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

4.3 Porcellanites and jaspers

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

Crystalline varieties of silica occur also in these silcretes. They have formed by recrystallisation of opal, either preferentially in some concretions as part of the sequence of deposition, or as in response to some form of alteration front (Fig. 13). The initial opal deposits have often recrystallized to chalcedonite while the brown opal of the matrix has transformed to microcrystalline quartz.

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

4.4 Pedogenic silcretes

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

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

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

A principal criterion for recognising pedogenic silcretes is the omnipresence of illuviation structures, particularly cutans at the base of voids and cappings over quartz grains and granules. These are very clearly distinguished because they are outlined by opaque microcrystalline titania (Fig. 14). As well, the common shard-like remnants of detrital quartz grains point to significant dissolution and concomitant ‘repacking’ of the framework prior to cementation, leading to a net volume loss in the profile as a whole.

5 Silcrete in landscapes

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

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

Thus, if we want to explore the use of silcrete as a raw material for stone tools, for example to map the routes of particular source materials and thus delimit territories and exchanges between prehistoric groups of peoples, it is necessary to locate these materials in the landscapes of the studied areas and the territories of the people exploiting them. In this context, inventories of the locations of specific silicified formations, and their petrographic characteristics, would be required for both local and regional areas. This research would utilise an understanding of silcretes and silcrete facies in a landscape context because prehistoric peoples had deeply-embedded connections with landscapes and their features.

5.1 Inland Australia

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

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

In localities along the scarp of the Stuart Range, near Coober Pedy, in northern South Australia, a comprehensive analysis of the geomorphology of the region (Simon-Coinçon *et al.*, 1996) delineated the age relationships between the different weathering and silicification features (Fig. 16). The pedogenic silcrete armours a wide paleopediment (tableland) dipping from the Stuart Range near Lake Eyre to the Eucla Basin in the southwest, a distance of about 500 km. The weathered and bleached profiles are younger. Groundwater silcretes, specifically quartzite and diverse porcellanite horizons, post-date the bleaching. Downcutting and erosion ultimately generated the breakaway scarps now characteristic of the region.

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

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

Here, also, the silicified facies are extremely varied and the associated bleached profiles are rich in white kaolinic clays and Fe oxides of variegated colours. Small mesas of fine quartzitic sandstone have been intensively quarried for tool-making. The steep scree-slopes around the hills and parts of the plateau surface are in places buried by thick deposits of discarded flakes and chips. The clear evidence of significant (and possibly long-term) exploitation provides the basis for characterising the source silcrete in detail and exploring the distribution of stone tools made from it.

However, the vast region, maybe 1 million km^2, stretching from central South Australia to the central parts of the Northern Territory, essentially marking the western part of the Lake Eyre Basin (see Alley, 1998; Fujioka *et al*., 2005) has innumerable outcrops and derivative lag gravels of pedogenic and various groundwater silcretes, all of which could be exploited by Aboriginal people. Thus, there would be a significant challenge in progressively building an inventory of these materials sufficient to assist archaeological investigations in attributing artefacts to sources.

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

5.2 Paris Basin

The Paris Basin is bounded by Jurassic marine limestone overlain by thick chalk deposits with alternating continental and marine Tertiary deposits in the centre. The most remarkable feature of the Tertiary sequence is the interbedding of sandstone formations with limestones and marls. The present-day morphology of the Paris Basin, namely superimposed limestone plateaux, results from major uplift during the Pliocene and Quaternary which initiated downcutting and erosion of the Tertiary formations (Fig. 18). Silicified materials occur in almost all formations.

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

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

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

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

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

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

6 Identifying provenance

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

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

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

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

Progress is possible by taking into account precise micromorphological characteristics that will potentially point to source sites. However, this approach requires an insightful inventory and petrographic data led by archaeological studies (Fernandes, 2012). Inventories of this type are yet not available. Even existing geologic and geomorphological maps do not make reference to the specific characters of silcretes, silcrete profiles, or micromorphological features of particular facies, that could be key to these types of investigations. The foundations of such inventories exist, but a new generation of linked archaeological and geological research would be a next step.

7 Summary

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

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

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Figure captions

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

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

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

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

Figure 5 – Eh/pH diagram for Fe-O-H system showing the reaction path leading to ferrolysis after having introduced some oxygen into the Fe^{++}- rich solution. Diagram at 25°C in equilibrium with atmospheric O_2 and CO_2, and $[SO4^{--}]= 10^{-7}$ (after Garrels and Christ, 1965).

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

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

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

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

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

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

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

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

Fig 14 – Thin sections of pedogenic silcretes, Paris Basin. (A) matrix of amoeboid quartz microcrystals in net-like arrangement generates a hard and lustrous fracture on knapping (transmitted light, crossed polars). (B) and (C) nodular facies with illuviation cutans (il) recrystallized into microquartz plus titania microcrystals; nodules are rimmed by a cortex enriched in titania (arrow). Channels remain empty (v) or are cemented with sub-euhedral quartz crystals (Q). (Transmitted plane polarised light).

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

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

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

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

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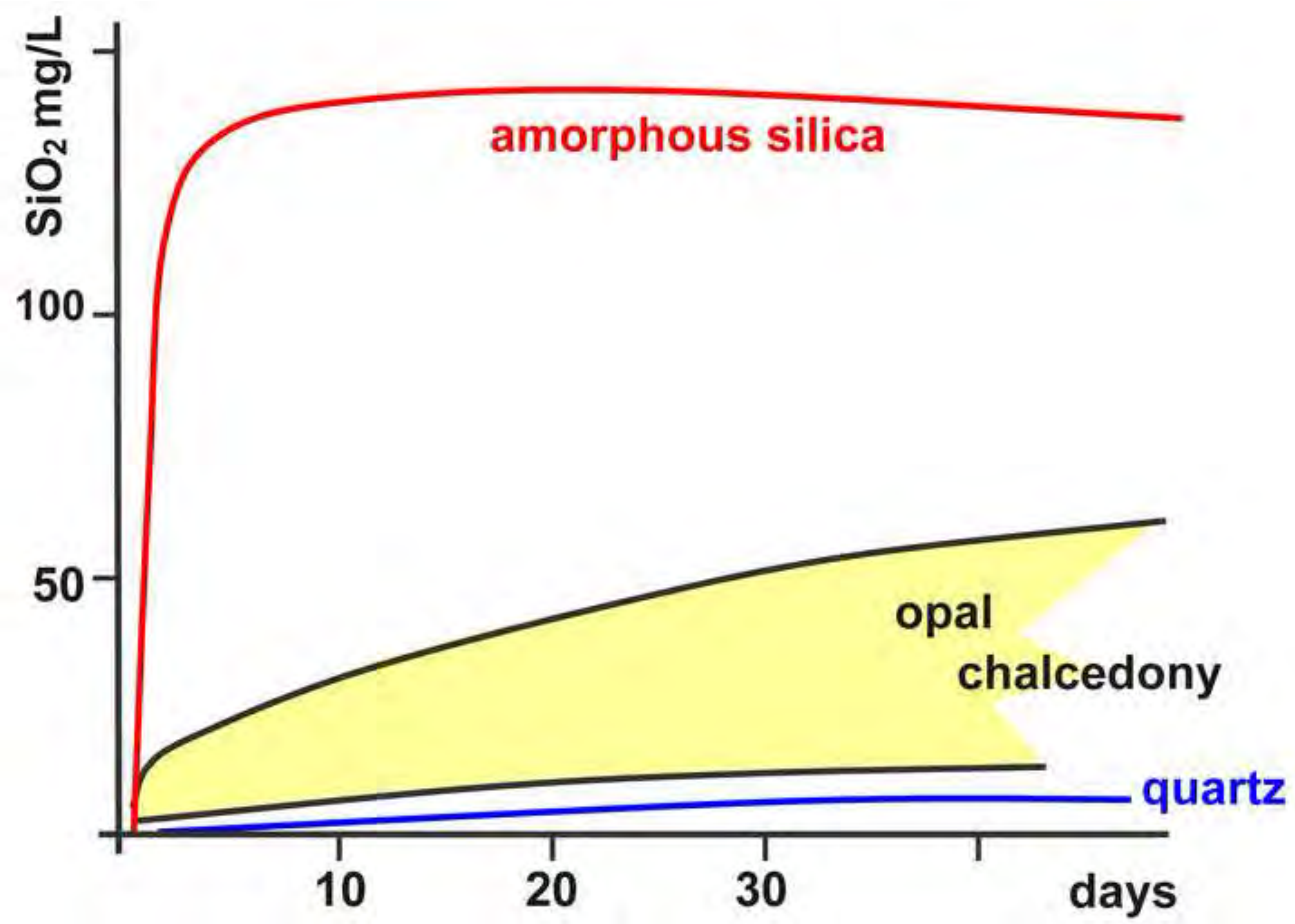

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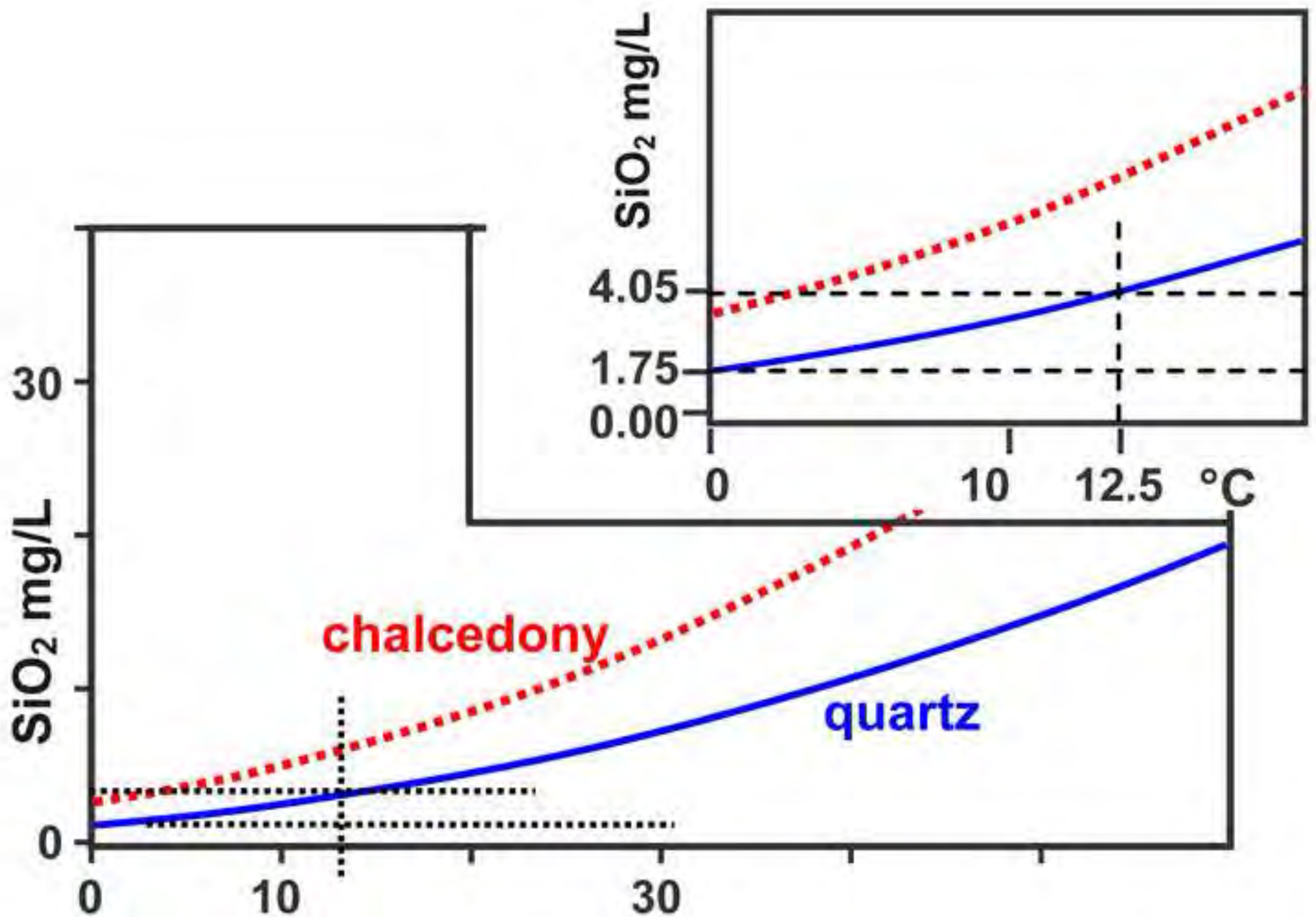

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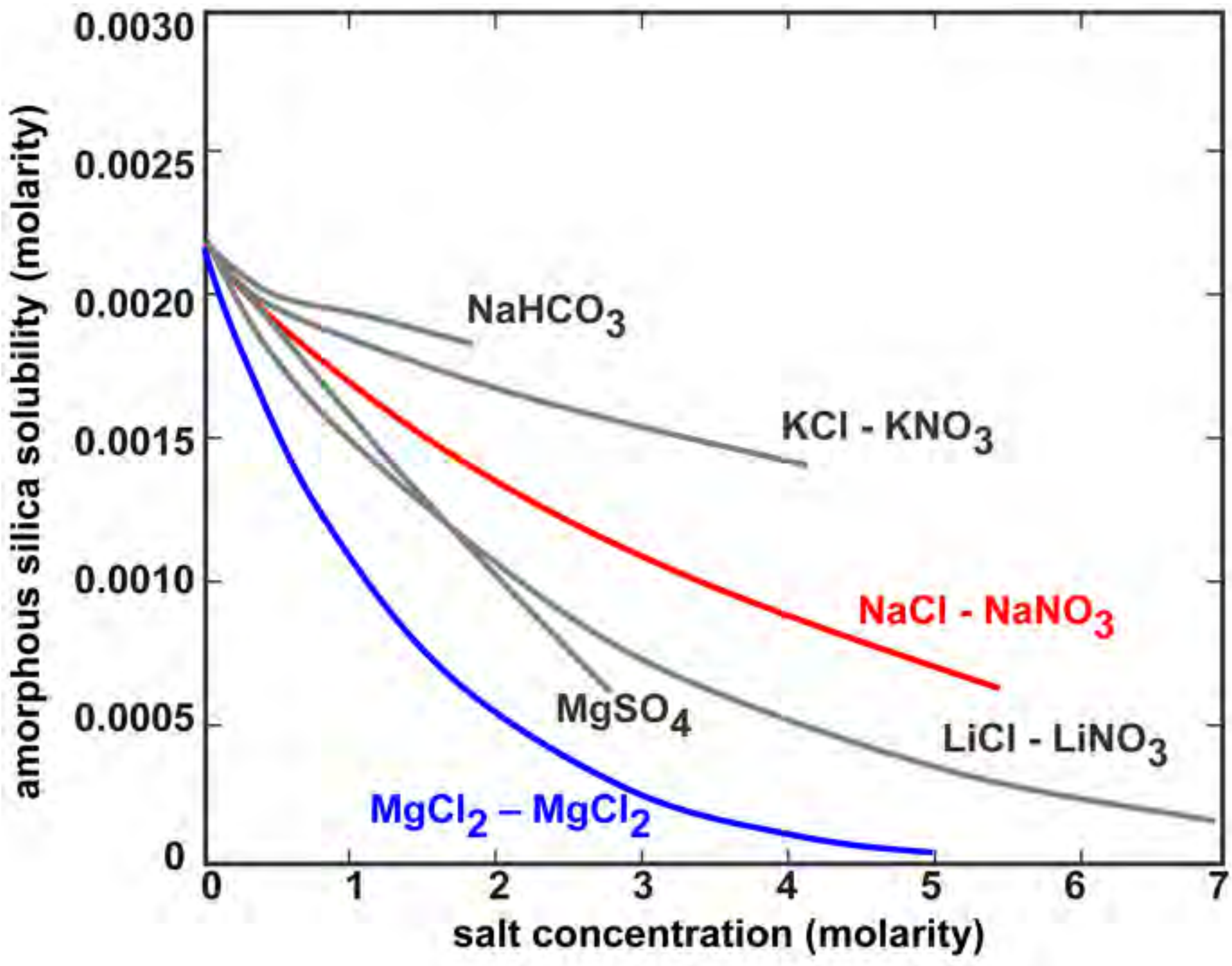

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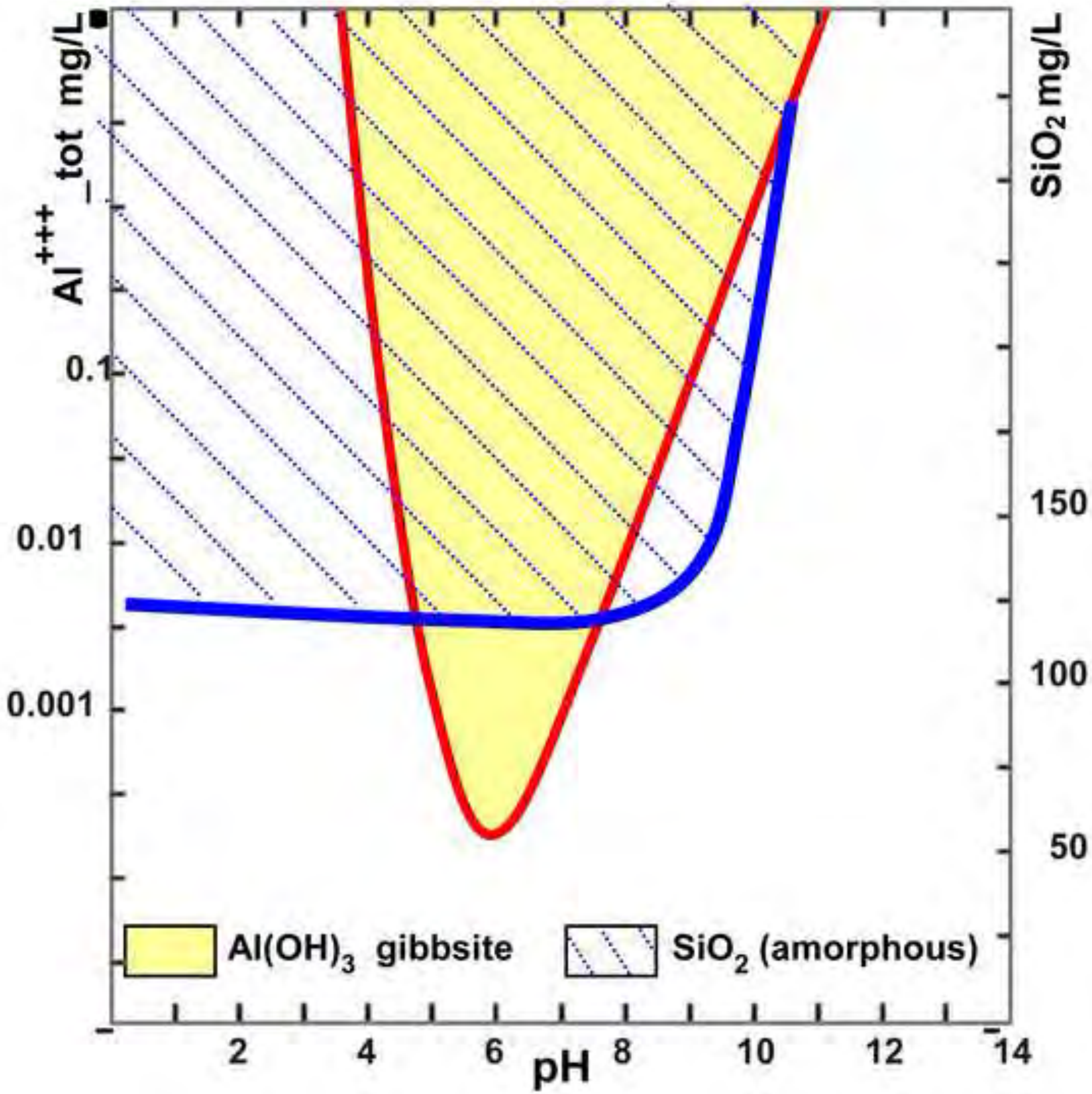

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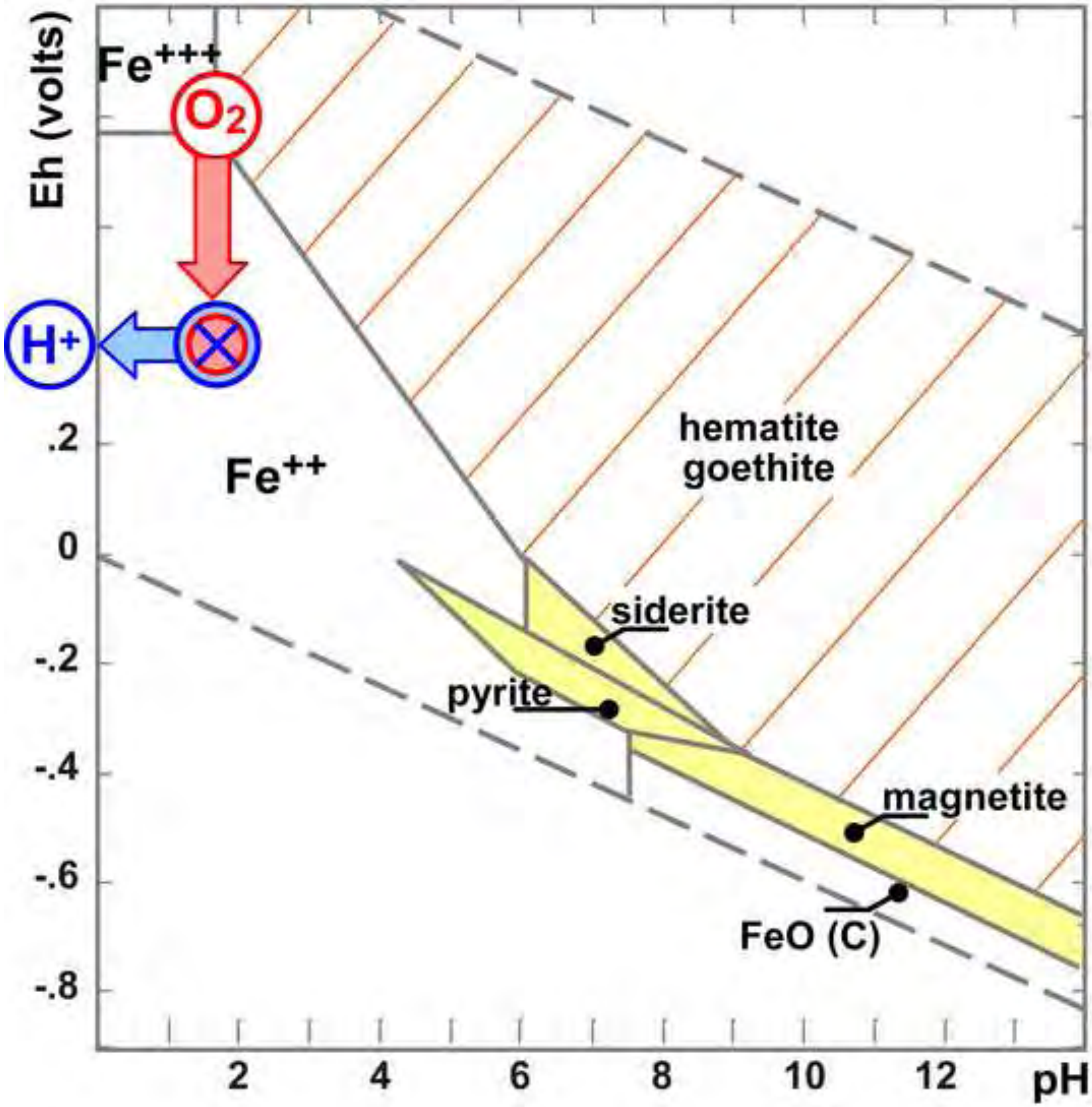

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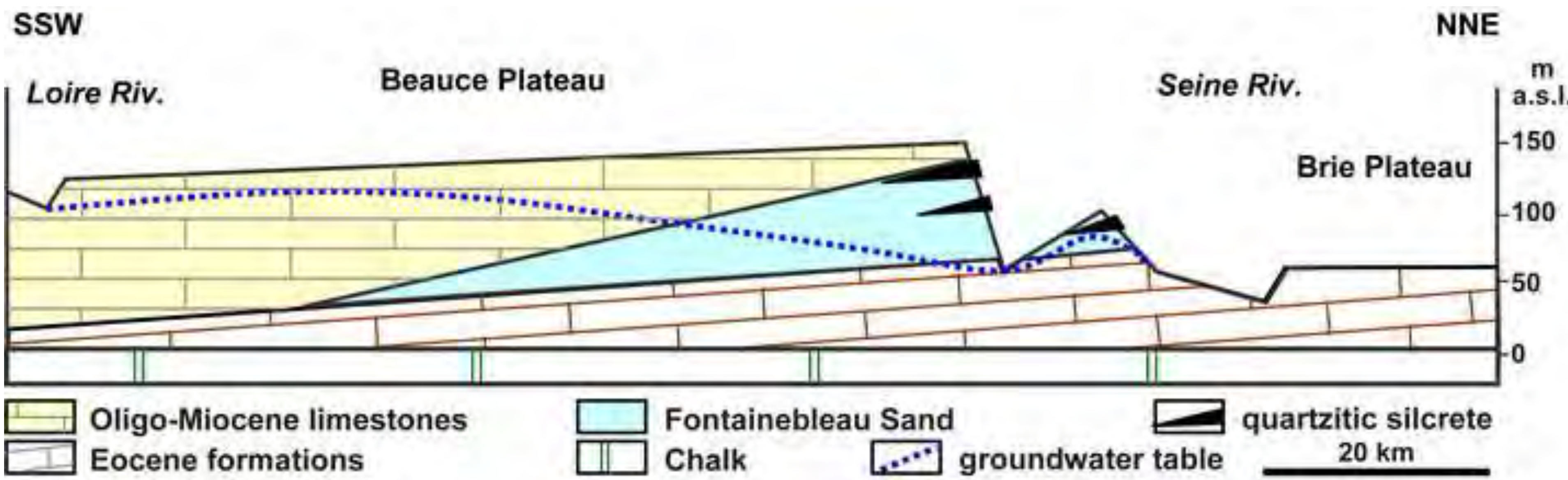

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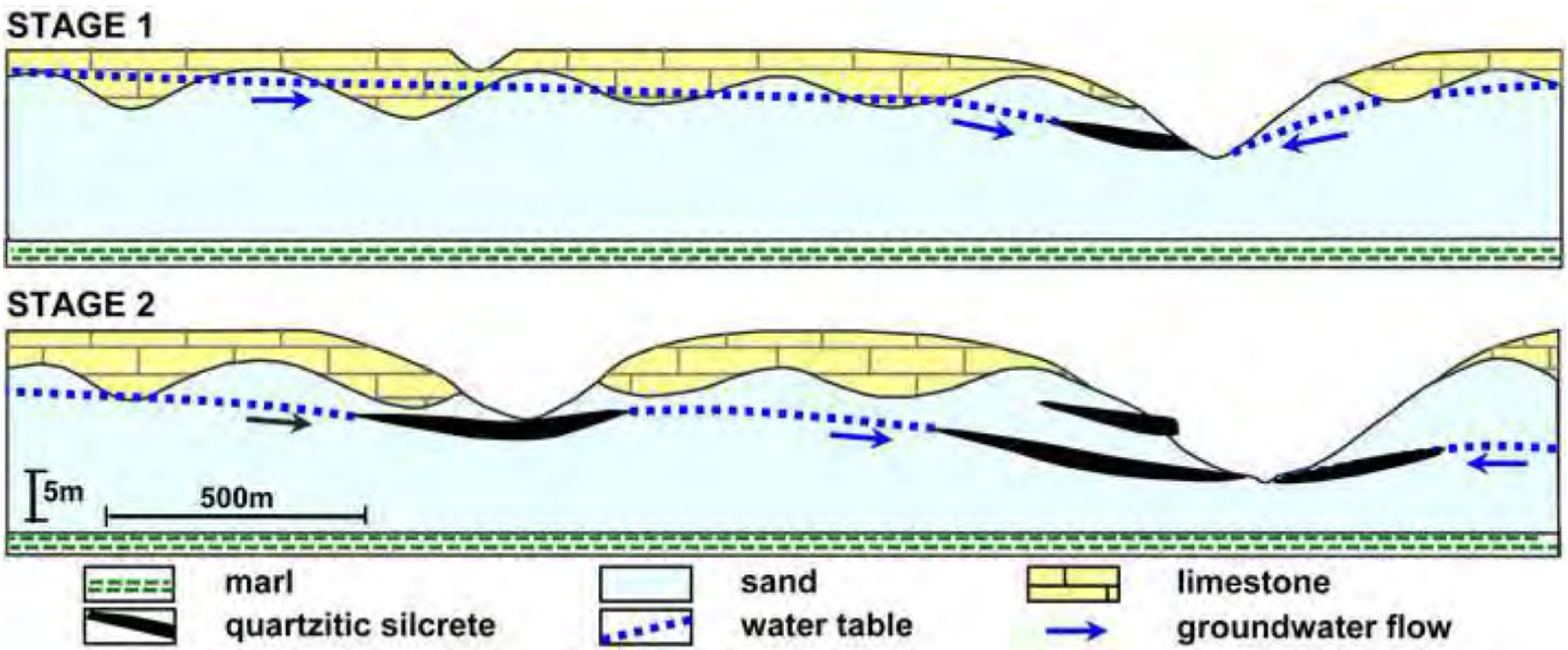

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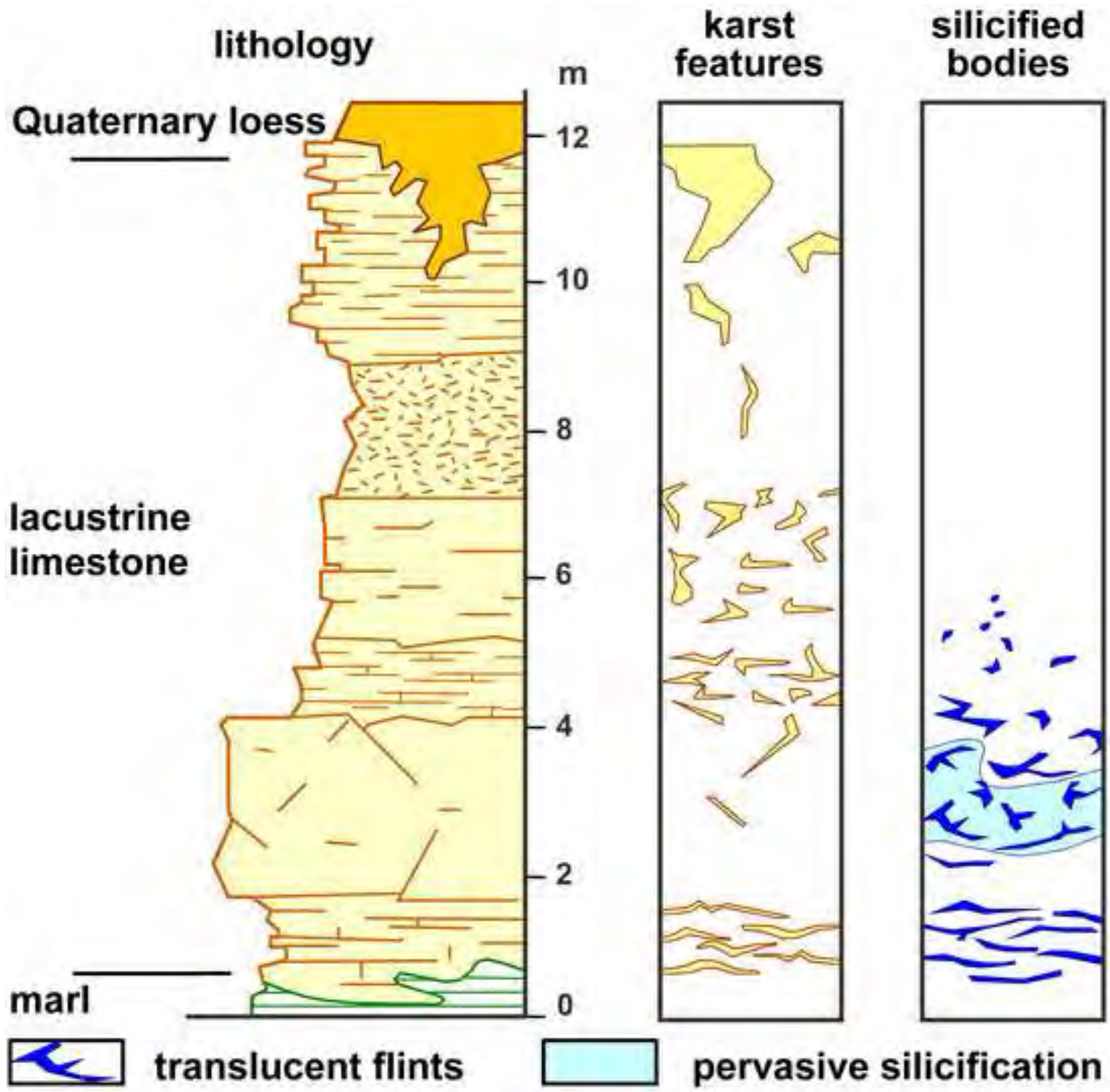

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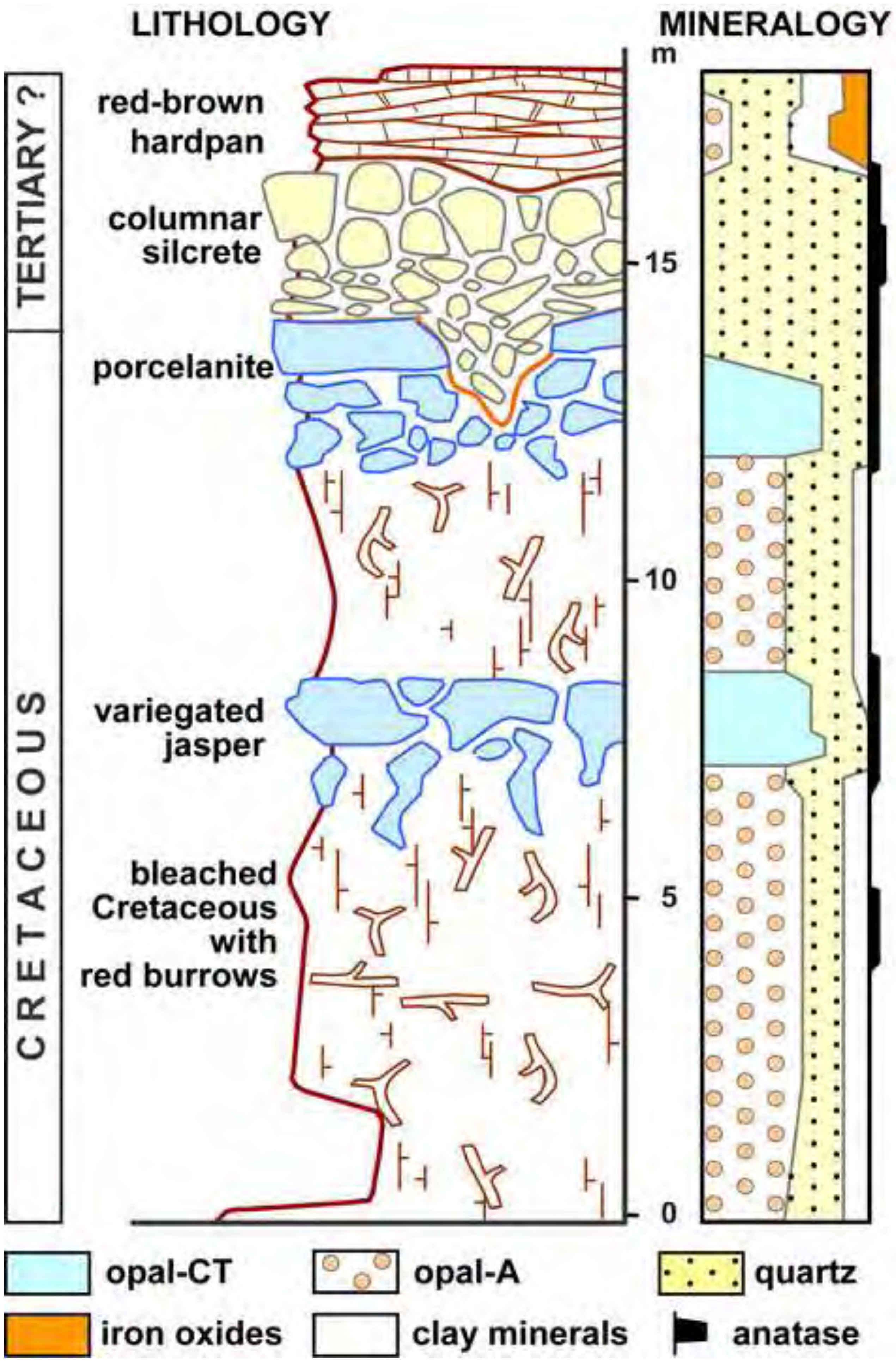

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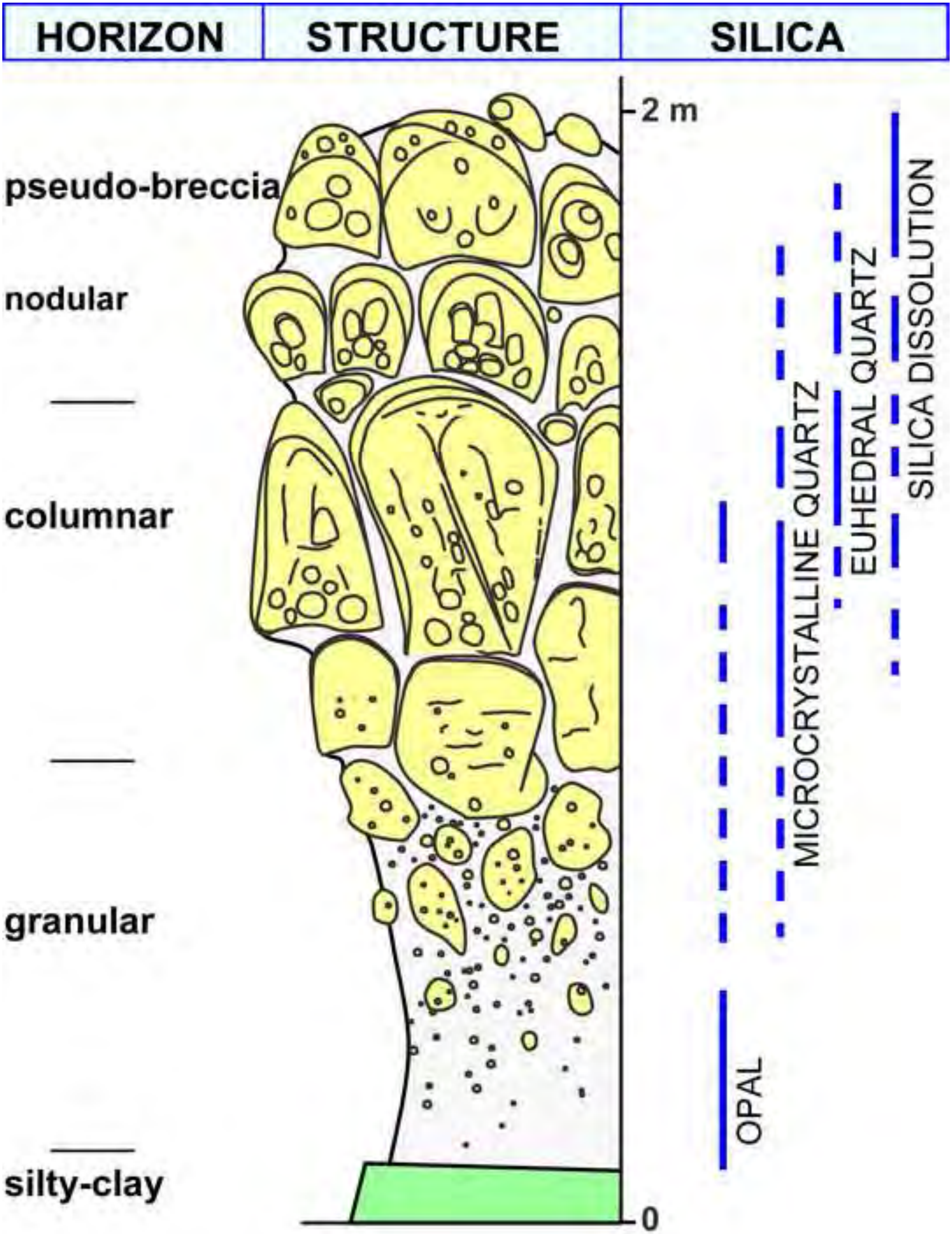

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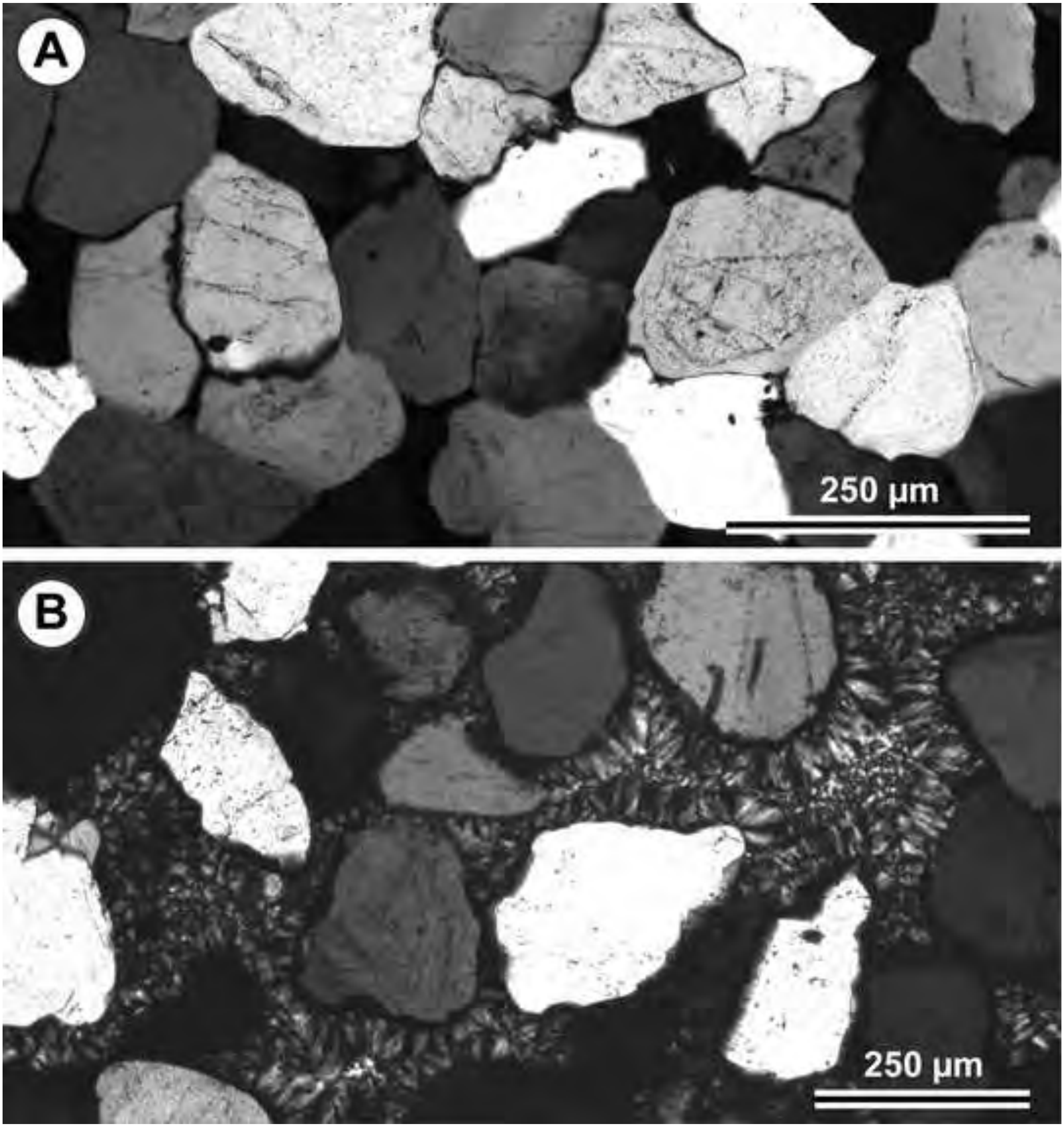

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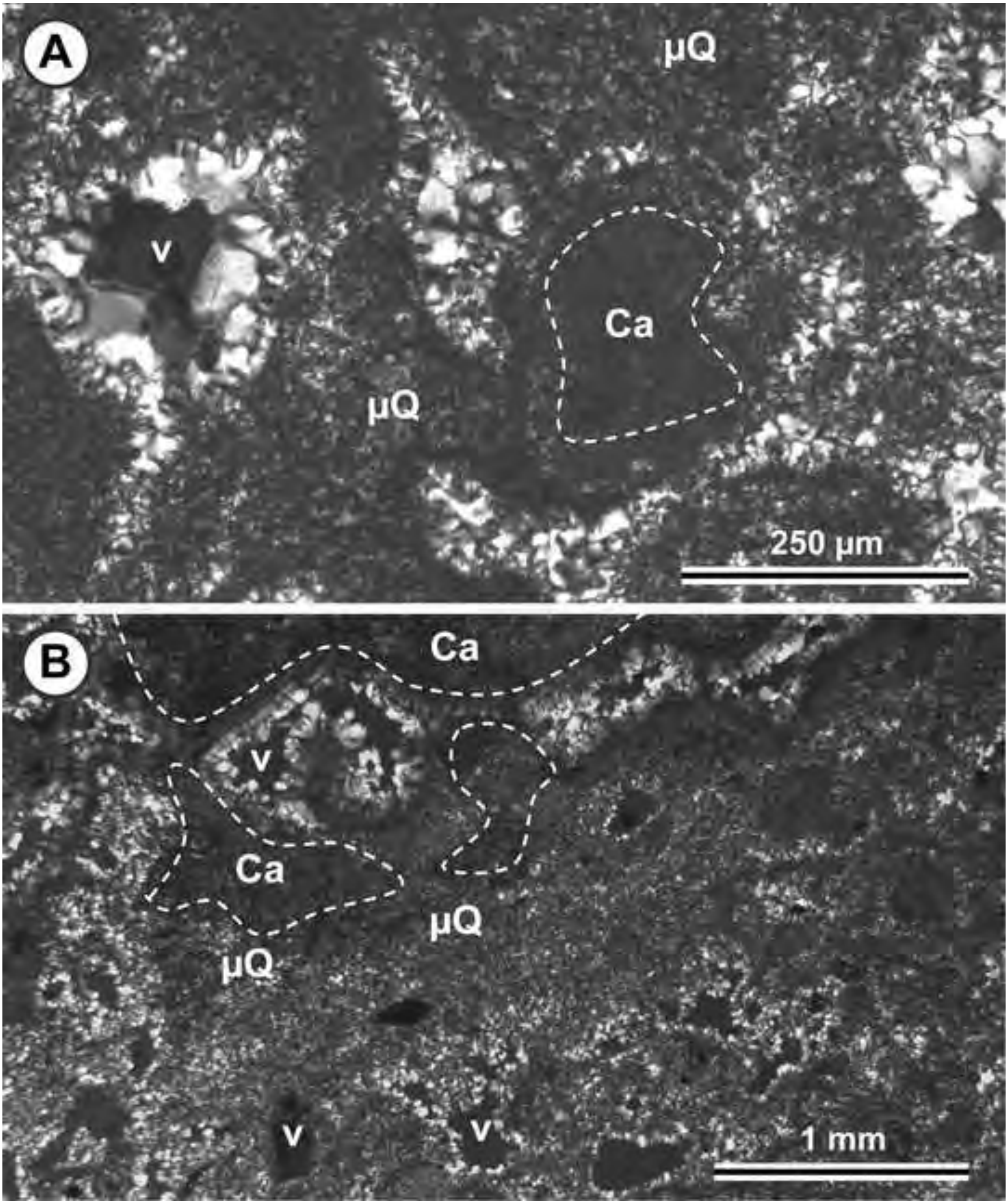

Figure_13_9cm
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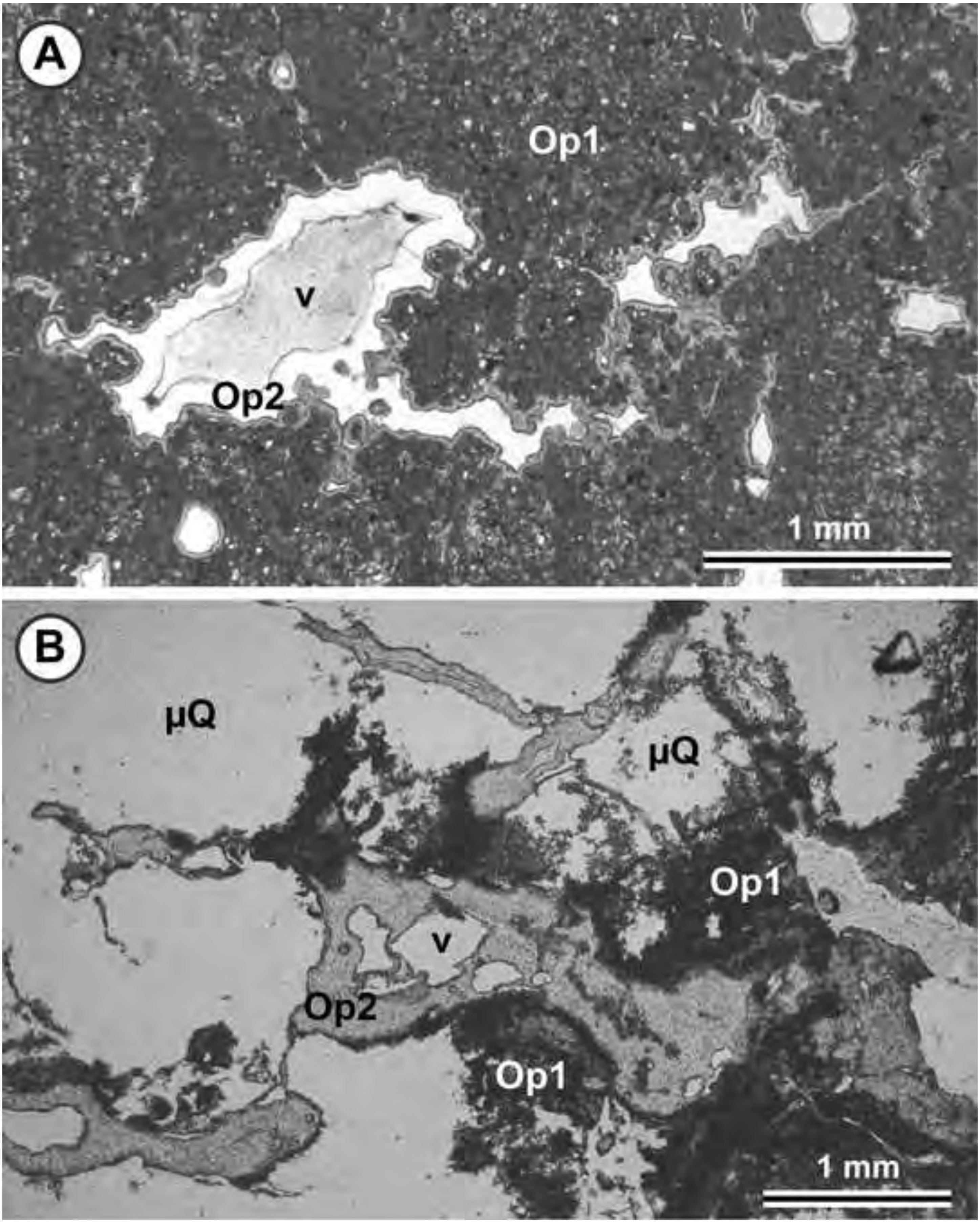

Figure_14_9cm
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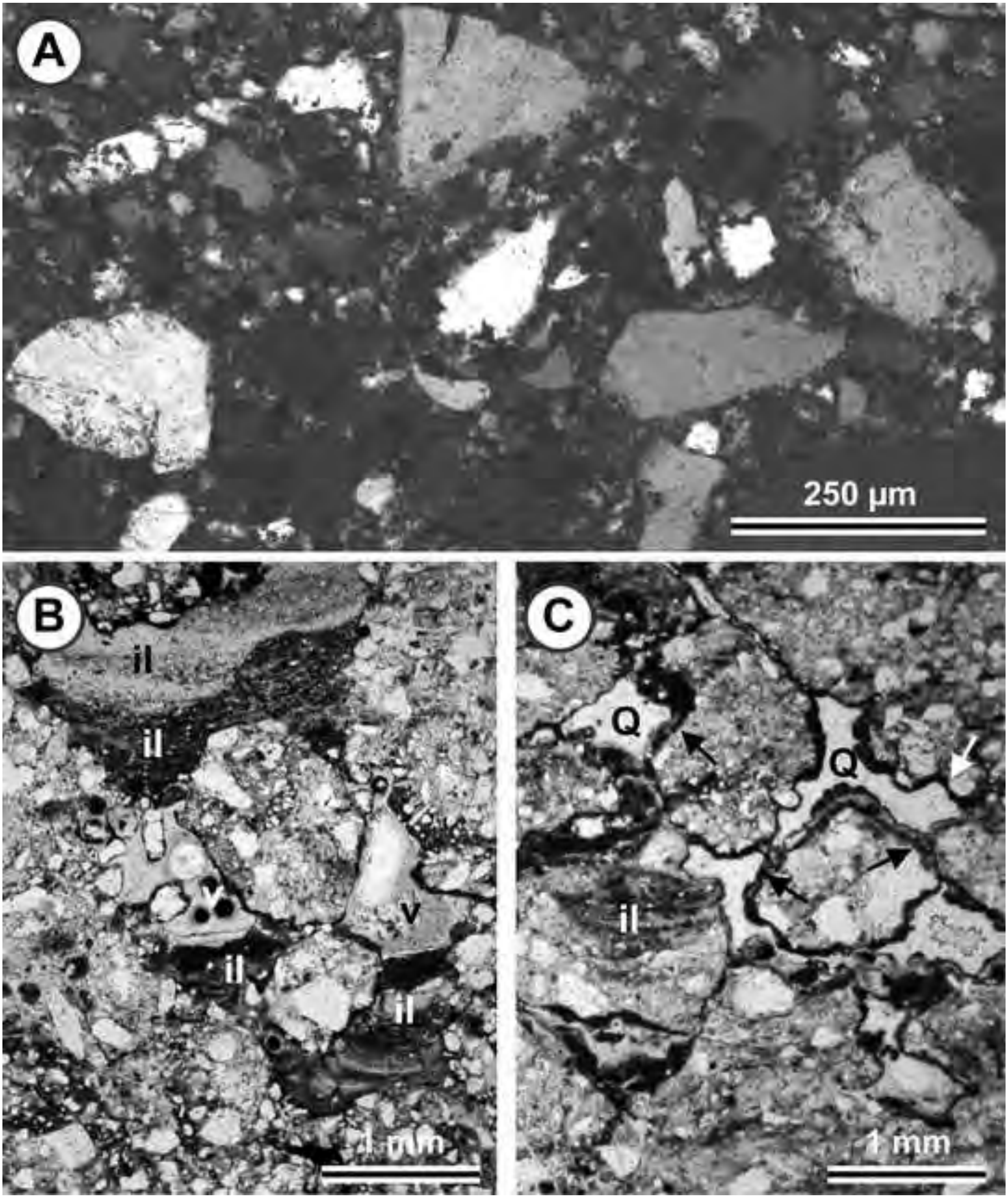

Figure_15_16cm
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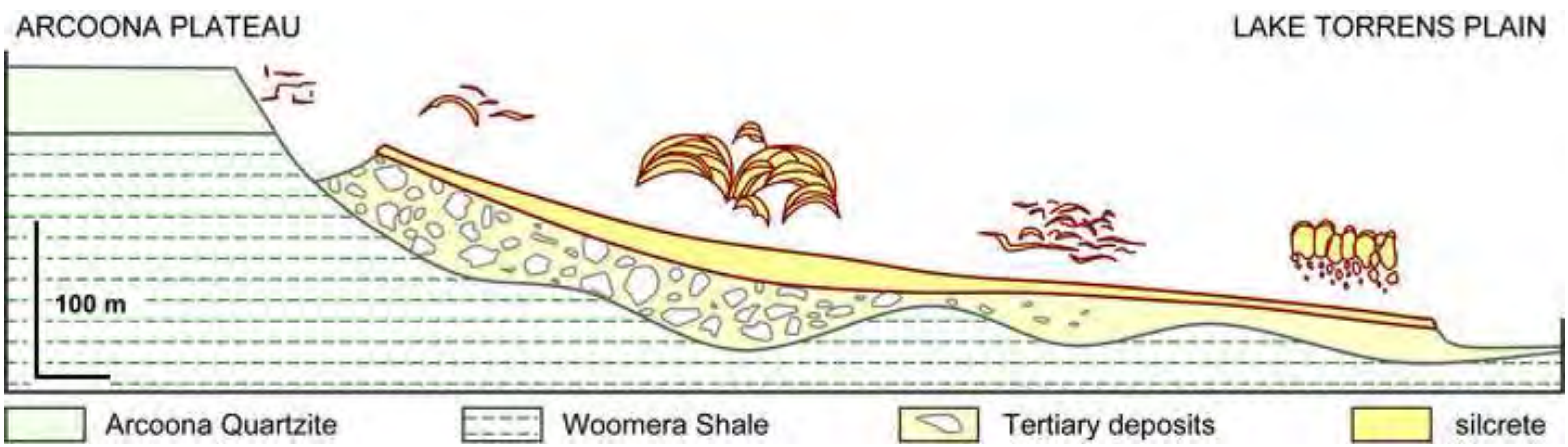

Figure_16_16cm

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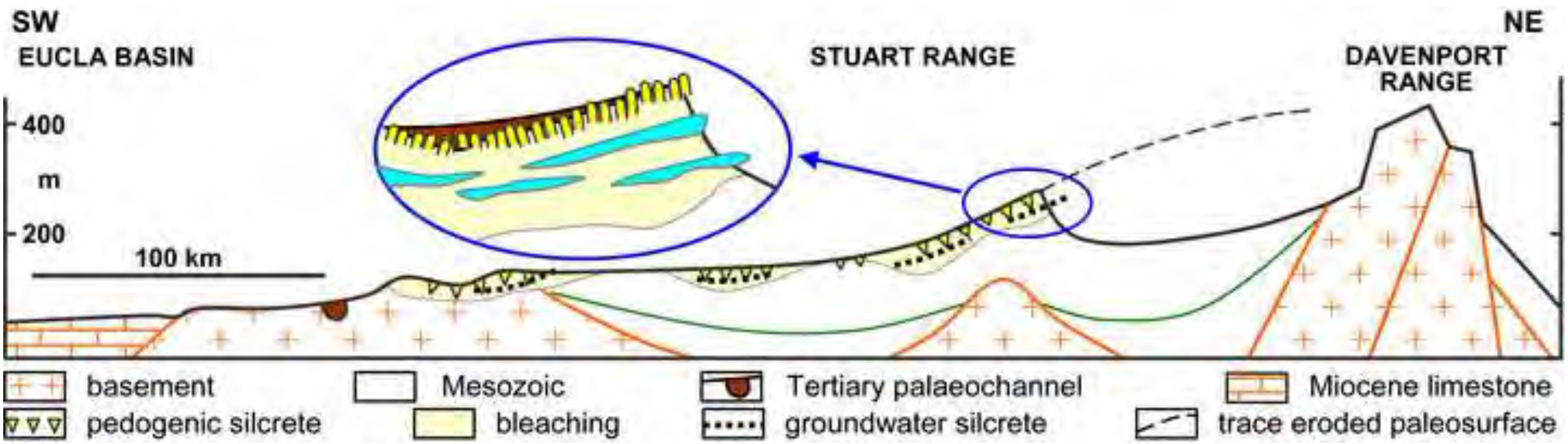

Figure_17_16cm

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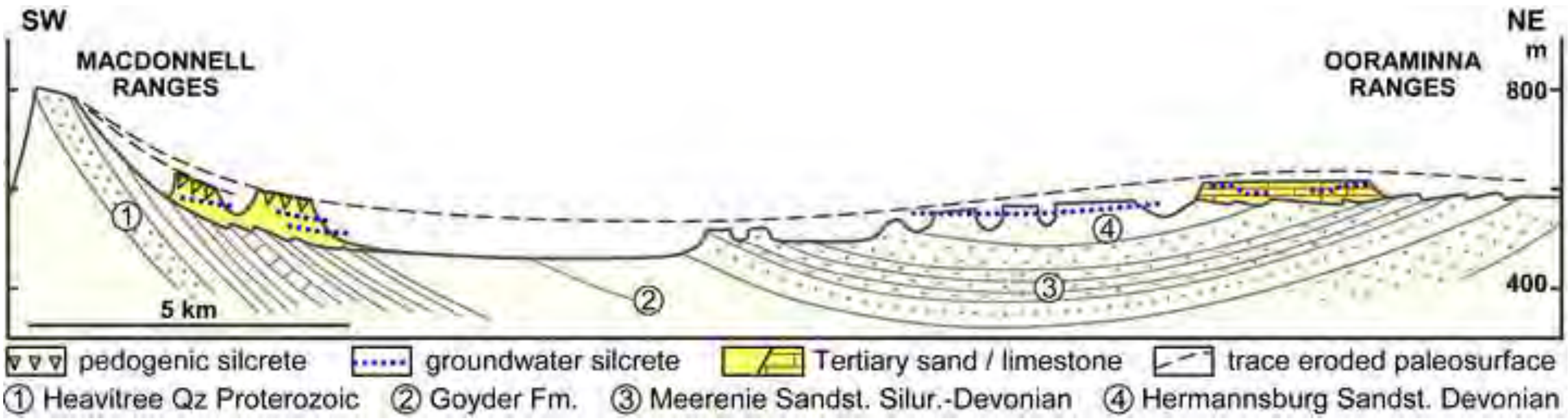

Figure_18_17cm

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