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## Quaternary periglacial silicifications in the Paris Basin

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**Abstract** – In this paper, and in previous works, quartzites within the Sable de Fontainebleau are clearly shown to occur only near outcrops in Plio-Pleistocene plateau landscapes and are related to groundwater flows. These arrangements, together with dating of encased calcites, led us to consider that silicification occurred during Plio-Pleistocene glacial stages. The precipitation of silica was most likely triggered by cooling of groundwaters as they approached cold zones in the regolith close to points of discharge. We describe the arrangement and morphologies of quartzites in Tertiary sand formations in the Paris Basin to demonstrate how cold climates could have influenced hydrologic regimes and promoted silicification. The coeval precipitation of calcite and silica in gypseous formations at the edges of plateaux-bordering valleys, along with the dissolution of gypsum, also points to interactions between silica-laden groundwater and carbonate host rocks during cold periods. In parallel, the distribution and micromorphology of silicifications in associated Tertiary limestone formations suggests that they formed during cold climates in the Quaternary. These are key pointers to the role of groundwater in regolith environments in controlling silicification processes. We detail a link to palaeosurfaces of the distinctive meulière facies in the Paris Basin. Geotopic structures and micromorphological organisations are the basis of new ideas about their origin in a combination of vadose and phreatic environments and proximity to impervious cold horizons. The active zone in a permafrost landscape is a good hydrological example. All silicifications in Tertiary formations in the Paris Basin can be linked to the hydrology of Quaternary periglacial environments in a single model. This could apply more widely to similar silicifications elsewhere and be tested using new analytical techniques that date silicifications and unravel the isotopic relationships between silicification, groundwater composition and the prevailing climate.

**Keywords:** silicification / periglacial / quartzite / chert / gypsum pseudomorphs / France

**Résumé** – **Silicifications périglaciaires quaternaires du Bassin de Paris.** Dans cette note, comme dans les travaux antérieurs, il est clairement montré que les Grès de Fontainebleau sont limités à la proximité de l’affleurement dans les paysages de plateaux datant du Plio-Pléistocène et sont liés à des écoulements de nappe phréatique. Cette disposition, ainsi que la datation de calcites incluses dans les grès, nous ont amené à considérer que la silicification s’est produite au cours des périodes glaciaires du Plio-Pléistocène. Ainsi, la précipitation de la silice est vraisemblablement due au refroidissement des eaux de la nappe en se rapprochant des zones froides du régolithe en arrière des lignes de source. Nous décrivons ici la distribution et les morphologies des quartzites des formations sableuses tertiaires du Bassin de Paris pour démontrer comment les climats froids ont pu influencer les régimes hydrologiques et favoriser la silicification. De même, la précipitation concomitante de calcite et de silice lors de la dissolution du gypse en bordure des vallées, qui avait été montrée par les anciens travaux, est expliquée par l’interaction entre des eaux de nappe carbonatées chargées en silice avec les encaissants gypseux pendant les périodes glaciaires. Parallèlement, la distribution et la micromorphologie des silicifications dans les formations calcaires tertiaires suggèrent qu’elles se sont formées dans les climats froids du Quaternaire. Ce sont des indicateurs clés du rôle des eaux souterraines du régolithe dans le contrôle des processus de silicification. Les faciès particuliers de l’Argile à Meulière et leurs liens avec les paléosurfaces sont également détaillés. Le géotropisme des profils et leurs organisations micromorphologiques ouvrent une nouvelle perspective sur leur origine avec la combinaison d’environnements vadoses et phréatiques et la proximité d’un horizon froid imperméable à la base du profil.

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La zone active dans un paysage de pergélisol en est un bon modèle hydrologique. A notre avis, toutes les silicifications des formations tertiaires du Bassin de Paris peuvent être intégrées dans un modèle cohérent unique lié à l'hydrologie des environnements périglaciaires quaternaires. Ce modèle pourrait s'appliquer plus largement à d'autres silicifications similaires ailleurs et pourrait être testé en utilisant de nouvelles techniques d'analyse pour dater la silicification et démêler les relations isotopiques entre la silicification, la composition des eaux souterraines et le climat.

**Mots-clés** : silicification / périglaciaire / grès / calcaire silicifié / pseudomorphose gypse / France

## 1 Introduction

The proposition that the extensive forms of silicification described in continental environments occurred during warm and dry climates has been advanced for more than a century (Lamplugh, 1907; Woolnough, 1927; Storz, 1928; Auzel and Cailleux, 1949; Millot *et al.*, 1959; Smale, 1973; Ulliyott *et al.*, 1998; Webb and Nash, 2020). Various mechanisms for triggering silica precipitation have also been suggested, including evaporation, and mixing of fresh silica-laden waters with highly alkaline solutions and/or brines. We have argued that evaporative and mixing models are not viable because, in order to accumulate adequate precipitate from the relatively low concentrations available in surface waters, considerable volumes of incoming water are required. This would have diluted and thus ruined the evaporative and mixing systems (Thiry and Milnes, 2017). In this context, a realistic mechanism for triggering precipitation from incoming volumes of silica-containing water remained elusive.

During the last decades of the 20th century, our studies identified two principal types of silica accumulation in continental silicifications (Thiry and Milnes, 1991; Thiry, 1999), namely;

- 1 pedogenic – formed on wide piedmont/glacis surfaces and resulting mainly from the alteration of clay materials by leaching of cations (relative accumulation of silica) together with successive phases of dissolution and precipitation of silica along infiltrating rainwater pathways in vadose environments; and
- 2 groundwater – formed at depth in phreatic environments in incised landscapes and resulting from the precipitation of silica from incoming groundwaters (absolute accumulation of silica) in pores and fractures.

We focussed on describing the occurrences and morphologies of the silicifications as well as the details of their characteristics and compositions at all scales. We considered the source of the silica and the triggers for its precipitation from infiltrating waters and groundwaters and developed arguments for particular mechanisms and the environments in which they operated. We also addressed the question of the time required for their formation. Geological evidence led us to believe that pedogenic silicifications might form over very long time periods (several Ma; Thiry, 1981) whereas mass balance calculations for groundwater silicifications (amount of silica precipitated, silica content of the groundwater, groundwater flow rate) suggested that the formation of a substantial quartzite pan 2-3 m thick and a few hundred metres in extent could occur in 10,000 to 50,000 years (Thiry *et al.*, 1988a).

In this paper we assemble a substantial set of our observations and data. We concentrate on groundwater

silicifications (sandstone, Si-gypsum, chert and meulières) and, in particular, the issue of environmental conditions that triggered silica precipitation. The main sections are designed such that each silicified facies has a self-supporting section, with settings, data and interpretation. A final summary integrates the different models into a dynamic periglacial evolution. The attached Supplementary files are essentially comprehensive additional notes and observations which relate to each of the main sections of the paper. In terms of the Tertiary formations of the Paris Basin, we:

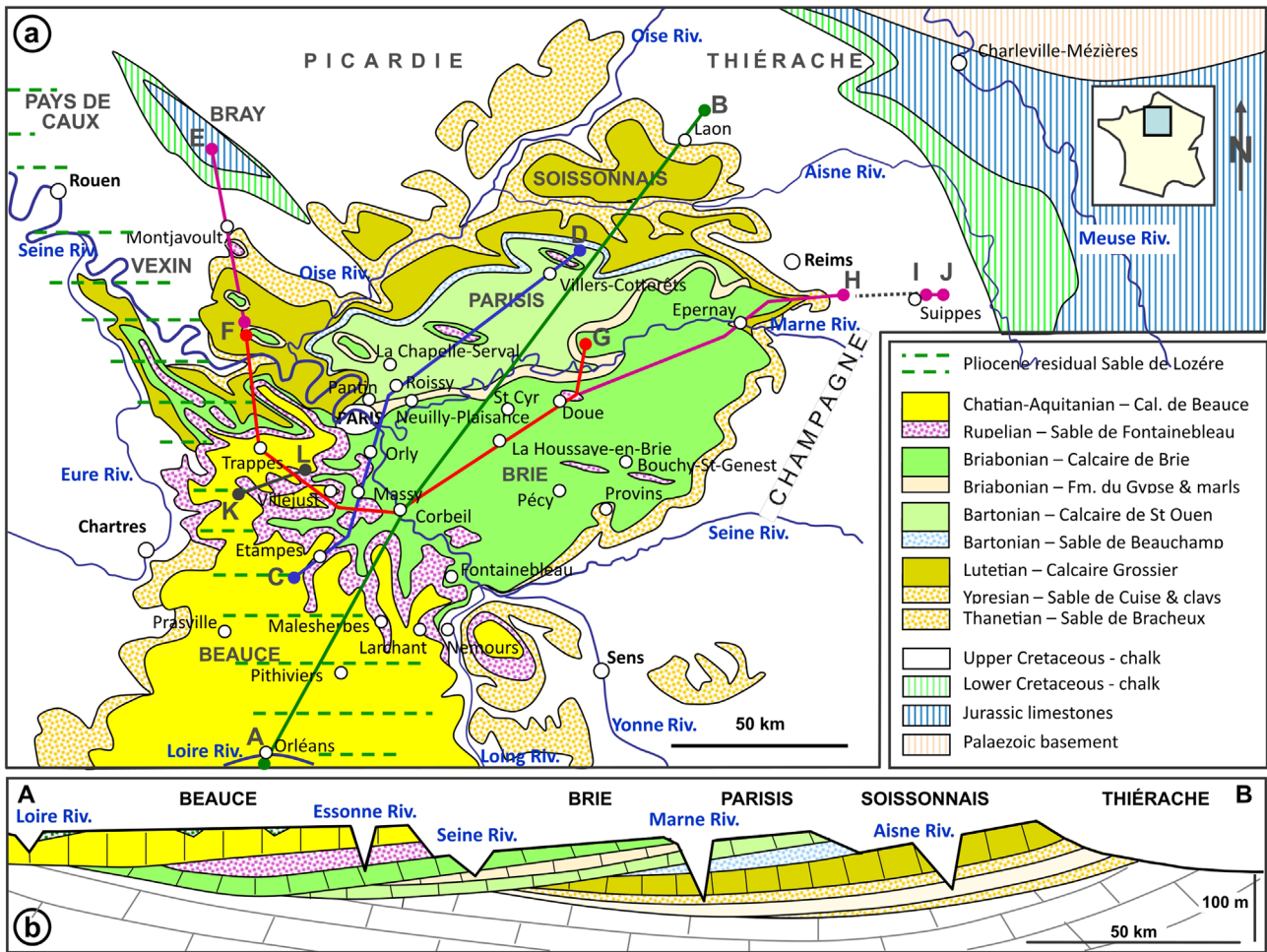
- 1 assemble all relevant observations and data relating to groundwater silicification in continental environments;
- 2 consolidate arguments for the mechanism of silicification of the Sable de Fontainebleau during the Pleistocene based on our earlier studies;
- 3 speculate that a similar mechanism probably applied in forming quartzite pans in other Tertiary sand formations in the basin;
- 4 in this same context, examine the siliceous facies that has long been described as gypsum replacement by silica;
- 5 provide arguments to suggest that the silicification of lacustrine limestones in the Paris Basin may have taken place in the same landscapes and under the same climatic regime; and
- 6 extend our understanding of these landscapes and climates to a new assessment of the development of the complex meulières facies.

## 2 Geological and geomorphological settings

### 2.1 Landscape setting

Geomorphologically, Tertiary formations in the Paris Basin form superimposed structural plateaux stacked from north to south (Fig. 1). The plateaux are armoured by resistant limestone formations which overlie clays, sands, marls and gypsum-bearing units to form cuestas.

The geology of the Basin has been well-described (see, for example, Pomerol & Feugueur, 1968). In summary, it contains successive deposits of thick limestones overlying clays, sands, marls and gypseous sediments. Overall, these are transgressive sequences advancing from the north and typically evolved towards brackish-water environments and later lacustrine sediments. The oldest sequences are restricted to the northern part of the basin, the most recent cover the southern part (Fig. 1b). Palaeocene and lower Eocene sands are capped by the thick Lutetian marine Calcaire Grossier which is succeeded by brackish-water limestones of the Marnes et Caillasses. Together they form the Soissonnais Plateau which extends to Paris. The middle Eocene marine Sable de Beauchamp is



**Fig. 1.** Geomorphological settings. (a) Geological map of the Paris Basin. (b) schematic cross-section A-B through the superimposed plateaux. Quartzites occur in all sand formations intercalated between limestones armouring the plateaux. Trace C-D links to the section in Figure 2, trace F-G to the section in Figure 4, trace E-J extends the previous section to the borders of the basin and links to the section in Figure 24, and trace K-L links to the section in Figure 6.

capped by the brackish-water Calcaire de Saint-Ouen which armours the Parisis Plateau. The upper Eocene gypsum and marls of the Formation du Gypse and the lacustrine Calcaire de Champigny are capped by the Eocene-Oligocene lacustrine Calcaire de Brie and the clayey succession of the Argile Verte that form the Brie Plateau. A later and more extensive marine transgression that produced the Sable de Fontainebleau ended with the thick (more than 100 m in places), lacustrine Early Miocene Calcaire de Beauce that forms the Beauce Plateau. The youngest formation, the Sables de Lozère, overlies the Calcaire de Beauce. This sand deposit is bound to a vast piedmont which extends from the Massif Central to the English Channel/La Manche. The piedmont is likely to be Mio-Pliocene in age and transgressed the Loire and Seine valleys before they were incised (Larue and Etienne, 2002; Cojan et al., 2007). Thus, the Beauce Plateau, covered by the Sables de Lozère, is considered to be the primordial landsurface pre-dating river incisions.

The elevations and ages of the terraces, combined with a climatic and tectonic evaluation of erosion/depositional processes, indicate that the evolution of the Quaternary landscape was driven by river incision and cuesta retreat

(Cojan et al., 2007). It is of note that the Sable de Valmont, near the Channel and considered to be a marine equivalent of the Sables de Lozère, is currently located at 125 m altitude and thus demonstrates the importance of epeirogenic movements since the Late Pliocene.

A geological section drawn through the Paris Basin illustrates the relationships between the geomorphological units (Fig. 2). There are three key zones: to the south, the ‘classical’ relationship between the Beauce and Brie Plateaux; the Paris area where the geological structure becomes more complex with numerous facies variations; and to the north, the striking emergence of the Villers-Cotterêt butte (10 km × 1 km in size and rising 110 m above the surrounding plateau). The buttes at Villers-Cotterêt and Belleville (and its twin sister the Butte de Montmartre) are capped by the Meulière (‘millstones’) de Beauce formed of silicified Aquitanian limestone and mark the position and extent of the primordial Mio-Pliocene surface prior to river incision and consequent erosion. In the southwest, at a lower level in the landscape, the Meulière de Brie caps the Calcaire de Brie (early Rupelian) on the Brie Plateau, a recently exhumed marine abrasion surface.

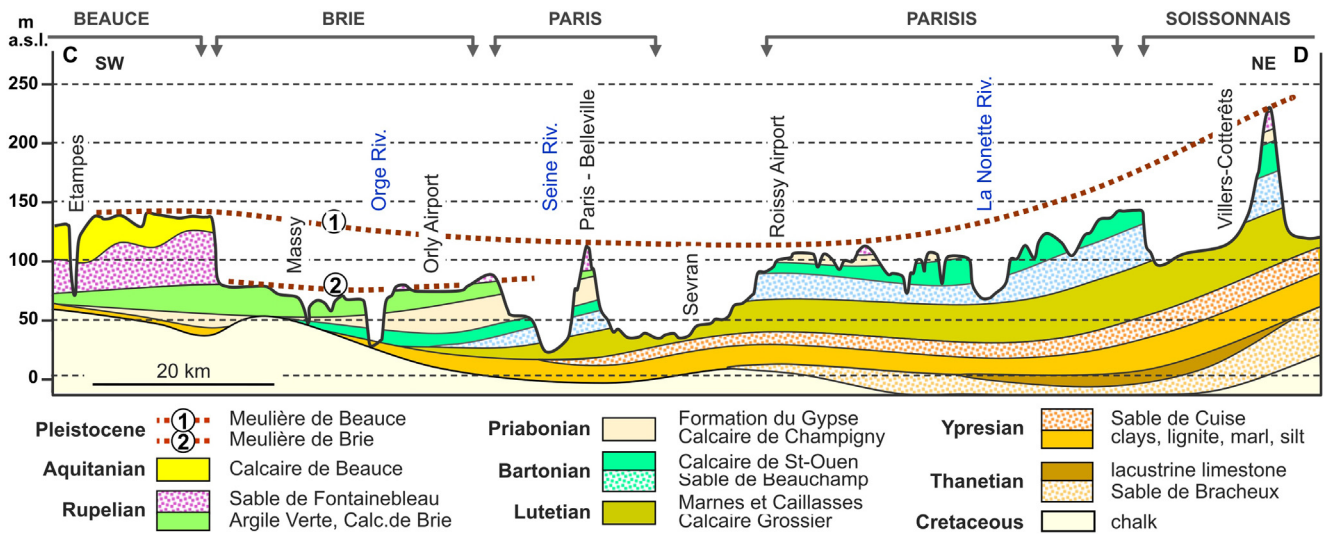


Fig. 2. Geological section through the Paris Basin Plateaux (see C–D in Fig. 1) showing the Tertiary formations and their erosion. Note the Mio-Pliocene surface marked by residuals of silicified Calcaire de Beauce: this marks the earliest stage of morphological evolution of the Basin.

### 2.2 Prevalence of silicified materials

Apart from monographs about a few of the Tertiary formations, most of the occurrences of silicified materials are recorded in the fifty or so explanatory notes of the 1:50,000 geological maps covering Tertiary deposits (InfoTerre, 2023). These are a highly valuable inventory of silicifications visible in outcrop. The occurrence of these silicifications at depth can only be determined from boreholes for which descriptions are reliable for thick quartzite pans but much less so for silicified limestones or small ‘chert’ masses. Silicified zones are recorded in all Tertiary formations in the Paris Basin, marine or continental, calcareous or siliceous (Fig. 3).

In order to understand the distribution of silicified facies in relation to geology and geomorphology, we constructed a geological section through the middle of the Plateau de Brie and the north-western edge of the Beauce Plateau where subsurface (borehole) data are plentiful. The logs in the BSS-BRGM database (InfoTerre, 2023) for this section are extensive and have good reproducibility that permits relatively reliable correlations to be made. The section (Fig. 4) consists of two domains: in the east, the Brie Plateau has a regular monoclinical structure with limited variations in the thicknesses of the various sand and limestone formations; in the west, the Beauce and Vexin Plateaux have anticlinal and synclinal structures accompanied by marked variations in thickness of the formations. In addition, the sedimentary facies in this western part of the section include more marls.

It is of particular note that no drillhole log mentioned quartzite slabs either in the Sable de Fontainebleau or in the Sable de Beauchamp: only a few occurrences of calcareous cemented sandstone were recorded. All quartzites shown on the section have either been mapped during our field surveys or reported in the notes accompanying geological maps. The section makes clear and confirms the fact that the quartzite pans in the Sable de Fontainebleau and the Sable de Beauchamp (along the flanks of the Marne and Petit Morin valleys) are restricted to outcrop areas. However, cherts occur

mainly in the Calcaire de Champigny and appear to be much more abundant beneath the Brie Plateau than beneath the Beauce and Vexin Plateaux.

Figure 4 shows that the occurrences of silicified limestone are no more related to the stratigraphy of the limestones than quartzites are to the stratigraphy of the sands. Silicification appears to be more abundant and extensive in the deeper stratigraphic horizons in the elevated eastern area of the Brie Plateau than in the shallower western area, on both sides of the Seine Valley. This is a key observation and the basis for arguments that negate prior suggestions for a primary, syn-sedimentary origin of these silicified limestones (Auzel and Cailleux, 1949; Pomerol and Feugueur, 1968).

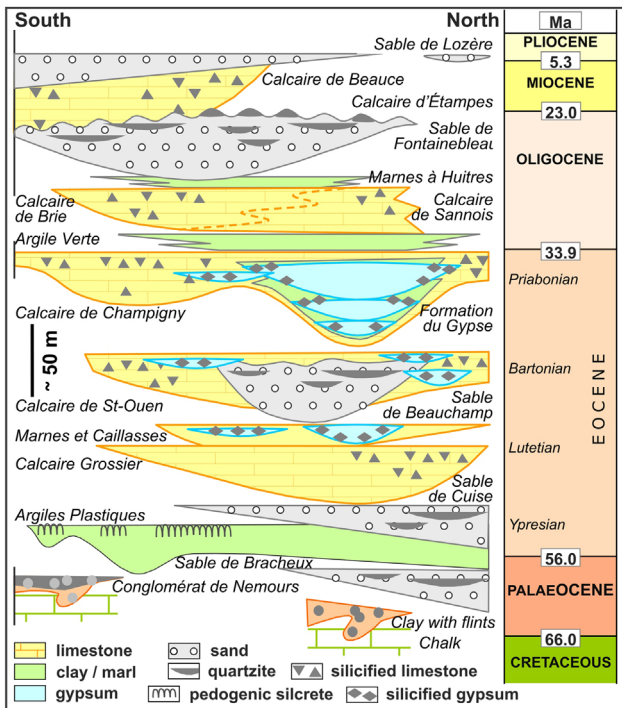
We excluded from our study the pedogenic silicifications that armour a long-lasting palaeosurface at top of the Argiles Plastiques formation at the southern border of the Paris basin (Thiry, 1981, 1999). They were not formed via absolute accumulation of silica but relative accumulation as part of which most of the other cations in the primary clayey deposits were leached. Moreover, these **pedogenic silcretes were commonly reworked** in the overlapping cover deposits, as well as in much younger formations like the Sable de Fontainebleau, **whereas clasts of groundwater quartzites and silicified limestones have never been reported** on overlying erosion surfaces, at the base of transgressive sand formations or in associated gravel beds.

Silicifications of sand formations in the Paris Basin, and particularly those in the Sable de Fontainebleau, are perhaps the most comprehensively studied examples of the discrepancy between silicification and stratigraphy/sedimentary environments.

## 3 Silicification of sands

### 3.1 Fontainebleau quartzites

The long-recognised and unique characteristics of the Fontainebleau quartzites are their occurrence as very tightly



**Fig. 3.** Schematic diagram of the lithographic succession of the Tertiary deposits in the Paris Basin. Note the wide distribution of the silicified facies within clastic, limestone and gypsum formations (after Thiry, 1999).

cemented pans and lenses ‘floating’ in unconsolidated sands (Fig. 5) and their location on dune ridges at the top of the sand formation. The frequent association between quartzite and dune ridge led to the interpretation by Alimen (1936) that silicification occurred via evaporative concentration of groundwater contained in dune sands before deposition of the Calcaire d’Étampes limestone cover. However, some key observations are important pointers to an alternative interpretation.

### 3.1.1 Link between quartzites and landscape

Although the quartzite pans are conspicuous in scarps and as valley-side outcrops, boreholes through the limestone cover and the Sable de Fontainebleau, about 1–2 km from the edge of the Beauce Plateau, demonstrate that they do not occur beneath a limestone cover exceeding 10–20 m thickness (Thiry et al., 1988b and map in Supplementary File#1). On a local scale, drill-lines established for infrastructure development confirm this. On the southern edge of the Plateau de Trappes, where quartzites are particularly abundant in the incised southern valley, drilling shows that the quartzite pans are limited in extent and are absent beneath the plateau (Fig. 6). Moreover, our mapping has shown that the quartzites are restricted to valley flanks downgradient of the groundwater. In the same area, detailed geological surveys show the thickening of the quartzite pans in thalweg closures which points to a link between quartzite and groundwater outflow. The same distribution of quartzites occurs in quarries adjacent to scarps where there can be up to 4 superimposed quartzite horizons which are seen to thin and gradually split over a distance of

250–500 m as the quarries progress into the plateaux (Thiry et al., 2013).

We deduce from these observations that:

- 1 the quartzites did not form in the sand formation before deposition of the limestone cover in the early Miocene;
- 2 there is a close link between quartzite occurrence and modern geomorphology, suggesting that silicification of the sands occurred in the general zone where outcrops are now located after down-cutting of valleys in the Beauce Plateau during Plio-Quaternary times; and that:
- 3 the arrangement of the quartzites in superposed subhorizontal pans points to silicification via groundwater with each horizon relating to an ancient water table level.

The specific arrangements of the quartzite horizons with respect to incision (down-cutting, scarps, stream valleys) of the landscape are interpreted to be a consequence of the relationship between silicification and groundwater regime. Thus, where valleys cut through a hydraulic dome, quartzite horizons were formed only in the downgradient sides of the valley where there was groundwater discharge (Fig. 6). In secondary valley and thalweg closures, where groundwater flows converged, quartzites are at their maximum thickness (Thiry et al., 1988b).

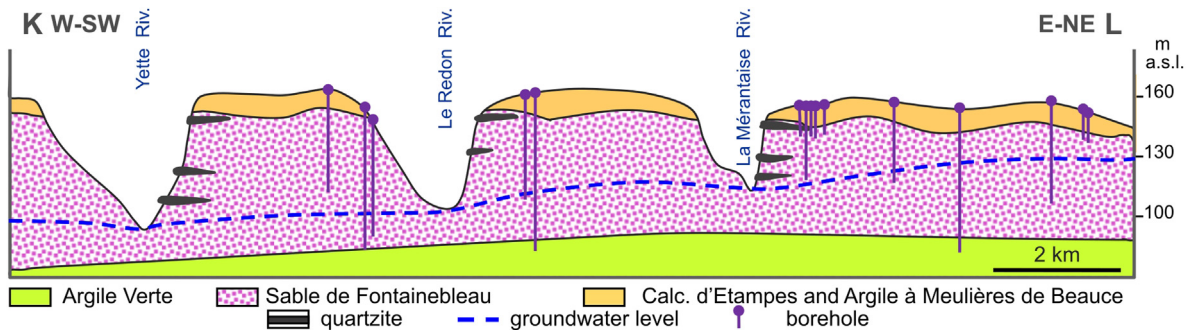
### 3.1.2 Age of silicification

The relationship between quartzites in the Sable de Fontainebleau and current landscape morphology suggests a Plio-Quaternary age for the silicification. This age is supported by dating Calcite de Fontainebleau sand calcites which are secondary calcite crystals including sand grains that formed within the host sand: they are now locally encased in quartzite pans and therefore pre-date silicification (see Supplementary File#1). <sup>14</sup>C and U-Th analyses of a total of 24 sand calcites from Tertiary sand units from various localities in the Paris Basin all yielded Pleistocene ages: most date from the latest Pleistocene (Thiry et al., 2021). Some sand calcite crystals include quartz grains with overgrowths and therefore post-date periods of silicification. Four occurrences of encapsulated sand crystals were identified:

- two sand crystal intergrowths (crystallaria), about 50 m from each other, encased in a quartzite pan near the Fontainebleau Grotte aux Cristaux formed at 44,000 and 33,630 years BP based on <sup>14</sup>C data;
- calcite crystallaria encapsulated in a quartzite lens resting on the Conglomérat de Nemours (Early Eocene) returned <sup>14</sup>C ages greater than 48,000 years BP but failed U-Th dating probably due to the sample preparation method;
- casts of sand calcite crystallaria in quartzite forming the ridge (*platière*) of the Gorge-au-Houx in the northern Fontainebleau Forest have not yet been dated; and
- sand crystals included in the Bérolots *platière* in the southern part of the Fontainebleau Forest have not yet been dated.

As a whole, and based on radiochronology, the Calcites de Fontainebleau are Pleistocene in age and their various ages coincide with regional glacial cooling stages. The intermingling of sand calcites and silicification suggests that





**Fig. 6.** Section through the incised NW Beauce Plateau (Trappes area). Quartzite pans are limited in distribution to outcrops of the Sable de Fontainebleau. The size of the quartzite lenses is exaggerated for better legibility of the drawing. After [Thiry et al. \(1988b\)](#).

### 3.2.1 Mainly horizontal pans

Extensive quartzite ridges occur west of Fontainebleau and armour palaeodunes at the top of the sand formation as spectacular multiple ridges ([Alimen, 1936](#)). They are mostly massive and average 2–5 m in thickness. Less extensive and often thinner horizontal quartzite pans occur at depth in large sand pits and average 0.3–2 m in thickness and 20–100 m width. We regard the arrangement of these horizontal pans or slabs as evidence of palaeogroundwater flows within the sands. In order to supply the silica from which the quartz overgrowths that cement the pans are derived, the palaeogroundwater table had to be in a zone of pronounced hydraulic gradient directly behind an outflow or discharge point in the landscape ([Thiry et al., 1988b](#)).

### 3.2.2 Curved and convoluted masses

Curved and spindle-like quartzite masses occur in some quarries in the southern Fontainebleau area. They consist of curved spindles 1–10 m in length arranged in divergent sheaves but are not horizontally continuous. The spindle forms are considered to reflect the flow of source groundwater at the site at which silicification occurred. Where curved, they could record silica precipitation from source groundwater subjected to ‘forced flow’ (as distinct from laminar flow), like in a duct bounded by impermeable walls. Even steeply inclined and subvertical lenses of quartzite have been observed ([Thiry and Milnes, 2024](#)).

Convoluted quartzite masses with spectacular morphologies are exposed in a quarry under a thick limestone cover in the southernmost extension of the Sable de Fontainebleau formation (Pithiviers area). These extremely tortuous bodies have relatively narrow curved and anastomosed silicified walls, only 2–30 cm thick, and surround decimetre- to metre-sized volumes of non-cemented sand. We interpret the form and arrangement of the quartzite walls as former permeable pathways around impermeable zones. Elsewhere, there are curved and anastomosed forms, including pendants and pillars, connecting adjacent horizontal quartzite slabs. These, too, are considered to represent preferential groundwater flowpaths through once-permeable (and hence non-silicified) sand masses.

### 3.2.3 Geotropic features

In addition to coalescent and amalgamated silicified masses there are locally overlapping stages of silicification. For example, we have located a younger quartzite enclosing sand calcite crystals, and thus post-dating them, encasing an older quartzite on which the sand crystals grew. Elsewhere, there are outcrops in which two episodes of silicification are recorded by an older quartzite pan (with evidence of dissolution) enwrapped by younger a less tightly cemented facies that infills the dissolution features. Although the enwrapping by the younger upper quartzite has a geopetal configuration relating to infiltrating water in a vadose environment, the younger silicification has the same petrographic characteristics as the older one.

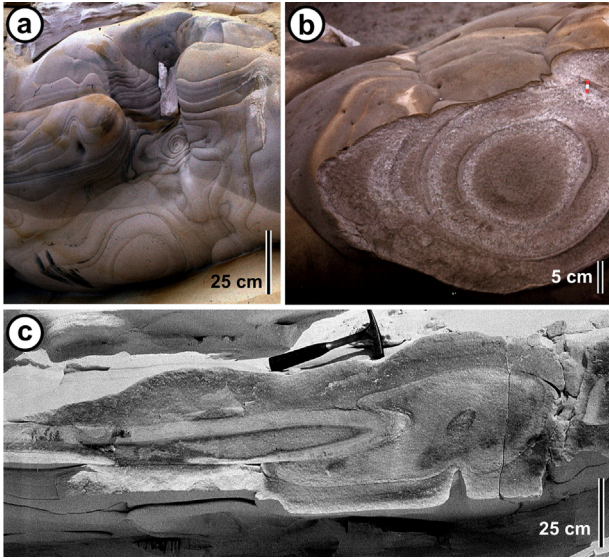
Curious concretionary masses of silica called ‘gogottes’ were collected in quarries where the Sable de Fontainebleau rests directly on the Cretaceous chalk. They display botryoidal envelopes featuring successive overlapping concretionary growths. Their in-situ orientation, particularly the downwards-projecting character of the concretionary growths, is considered to reflect a geotropic process linked to waters infiltrating through the vadose zone and meeting the watertable.

Finally, there are silica ‘skins’ coating vertical and horizontal fractures and pseudokarstic dissolution structures on thick outcropping quartzite pans. These are restricted to outcrops and have not been observed in sand quarries. The ‘skins’ are secondary silica precipitates relating to water percolating along fractures and over the surfaces of the groundwater quartzites.

### 3.2.4 Internal structures

The outer surfaces of quartzite lenses frequently have a botryoidal or mammillary ‘custard-like’ aspect ([Fig. 7a](#)). These features reflect successive layers of accretionary growth of the silicification. There is generally no internal structure although tightly cemented fringes are visible in some examples ([Figs. 7b and 7c](#)). Our interpretation is that the lenses grew by superposition of a succession of silicified layers, starting with a core and progressing by addition of discordantly cemented superposed layers. The lenses cannot have formed in a single





**Fig. 7.** Internal structures of the silicified bodies. (a) Botryoidal or mammillary ('custard-like') surface shape of a quartzite lens; sand pit Bonnevault, Larchant (Seine-et-Marne). (b) Internal growth bands with tightly cemented fringes; sand pit Villejust (Essonne). (c) Idem b, sand pit les Gondonnières (Larchant, Seine-et-Marne). After [Thiry and Maréchal, \(2001\)](#).

step because the porosity would decrease as soon as the sand became partly cemented and the source solution would be diverted, thus precluding tight cementation. Progressive centrifugal growth of the silicified bodies, such as that in concretions, had already been proposed by [Cayeux \(1929\)](#) and may explain our observations.

### 3.3 Similar quartzites in sand formations distributed more widely in the Paris Basin

Quartzite lenses in white unconsolidated sands are known in all major sand formations in the Paris Basin ([Fig. 3](#)), even extending to its peripheries. For example, in addition to the Sable de Fontainebleau, the main sand formations containing quartzite pans and lenses are the Bartonian Sable de Beauchamp and related facies, the Ypresian Sable de Cuise, and those related to the Thanetian Sable de Bracheux, Sable de Chalon-sur-Vesle and Sables du Pays de Caux (see [Supplementary File#1](#)).

Significant drilling was undertaken during and after 1970 for a geological survey of the Charles de Gaulle airport project at Roissy and drillholes passed through the Bartonian Sable de Beauchamp Formation. [Figure 8](#) is a plot of 12 fully cored boreholes located on a 2 km long section. The Sable de Beauchamp contains up to 6 superimposed silicified levels. Some of these do not exceed 5 cm in thickness but are more often 10–20 cm thick and are comparable to those exposed in the quarry of the Chapelle-en-Serval (about 15 km to the NNW of Roissy) with botryoidal or mammillary ('custard-like') features. Hard massive quartzite levels occur as well, one reaching a thickness of 2.3 m. These bands generally overlie the marl formation beneath. The most remarkable aspect of

these silicified levels is their distribution at the top and bottom of the formation in contact with or close to the low-permeability marl-limestone formations.

We interpret the discontinuous and irregular horizons of silicification, arranged in superimposed layers in places, to groundwater silicification. Their arrangement could have resulted from groundwater flowing westwards towards the valley between low permeability marls and limestones.

Exposures in sand pits developed in the Bartonian sands for the glass industry demonstrate that the silicified masses decrease in abundance from the outcrop zone into the plateaux together with a concomitant increase in the abundance of coloured sands containing brown organic matter. Similarly, drillholes which intersected the Bartonian sands beneath the Paris Plateau (along a broad strip on either side of the section shown in [Fig. 2](#)) did not intersect any quartzites whereas there are abundant Bartonian quartzite boulders in outcrops. The distribution of quartzites within the Bartonian sands thus appears to match that of the Sable de Fontainebleau: they are abundant in the vicinity of outcrops and absent away from the outcrop zone beneath the limestone plateaux.

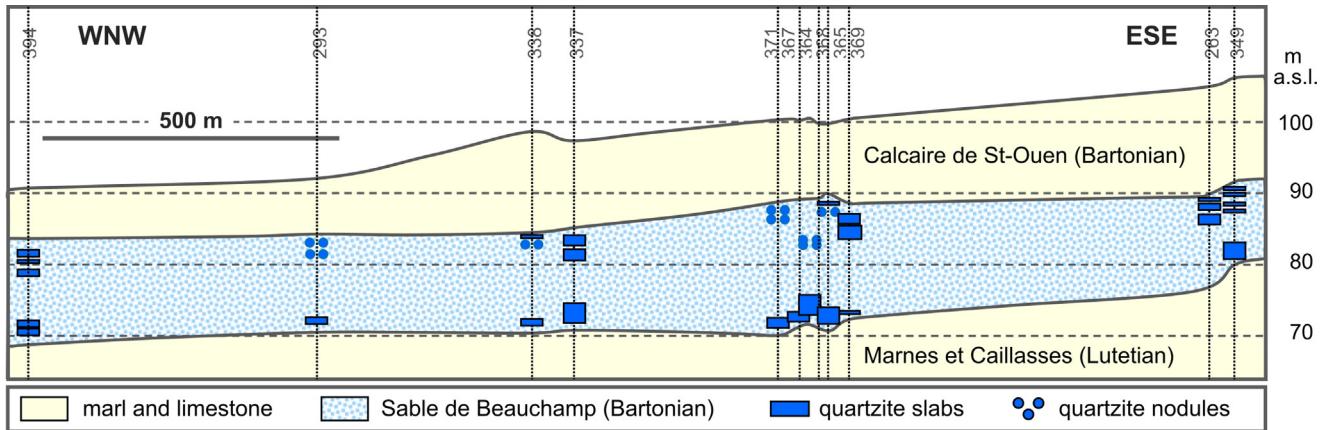
All of these quartzites have the same characteristics, namely:

- an association with bleached sand;
- an occurrence as discontinuous layers within loose sand, sometimes superimposed; and
- an internal configuration showing concretionary growth that ultimately merges to form massive slabs.

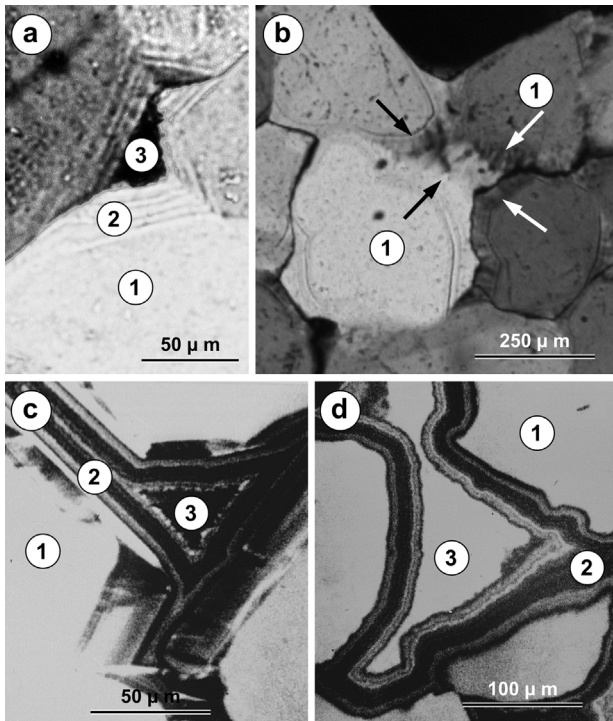
### 3.4 Petrography

The tightly cemented quartzite lenses have a secondary quartz content varying between 30–35%, leaving a residual porosity which may be as low as 2% ([Cooper et al., 2000](#)). Under the petrographic microscope, quartzite fabrics display subhedral overgrowths sutured with polygonal contacts. In places, mainly in the uppermost quartzite horizon, the overgrowths are not homogeneous in a crystalline sense ([Thiry and Maréchal, 2001](#)). Some contain very thin ribbons ([Fig. 9a](#)) and others display laminae of silica with a feathery or a likely flamboyant palisadic quartz grafted onto the inherited quartz grain ([Fig. 9b](#)). Cathodoluminescence analyses identify two main habits in the quartz cement, namely: (1) sub-euhedral quartz crystals that are syntaxial overgrowths on detrital quartz grains and sutured along straight lines ([Fig. 9c](#)); and (2) unrelated uniform quartz cutans covering detrital quartz grains ([Fig. 9d](#)).

The laminae coating the detrital grains are not related to the quartz overgrowths because this phase of silica deposition would have led to euhedral quartz. Instead, the cutans are successive deposits of amorphous or poorly ordered silica that progressively recrystallized to quartz. Electron Back-Scatter Diffraction (EBSD) analyses demonstrate that the cutans are microcrystalline and have variable orientations with regard to the underlying detrital grains ([Haddad et al., 2006](#)). [Haddad et al.](#) concluded that cutans did not form in crystallographic continuity with the substratum (non-syntaxial) but display zonal arrangements that indicate that the final stage of growth was not random.



**Fig. 8.** Selected drillholes along a section through the Sable de Beauchamp formation at Charles de Gaulle airport in Roissy-en-France (Val-d’Oise). The thickness of the silicified layers (especially the thinner layers) has been exaggerated. See position on general geomorphological section in [Figure 2](#). Drillhole numbers must have the prefix 01545 × 0 to match the national geological data bank (BSS-BRGM – [InfoTerre, 2023](#)).



**Fig. 9.** Interstitial silica cement in quartzites. (a) Ribboned syntaxial overgrowths (thin section, crossed nicols). (b) Silica laminae with feathery or flamboyant quartz arranged perpendicular to the detrital quartz grains (arrows). Thin section, crossed nicols. (c) Syntaxial ribboned overgrowth (cathodoluminescence image). (d) Concentric cutans progressively filling pores (cathodoluminescence image). (1) detrital quartz grain; (2) quartz layers; (3) residual pore. After [Thiry and Maréchal, \(2001\)](#).

The different habits of the quartz cement can coexist in a single quartzite lens and occur in a sequential fashion. Sub-euhedral overgrowths may be coated by silica cutans which may be succeeded again by euhedral overgrowths ([Thiry and](#)

[Maréchal, 2001](#)). These microscopic sequences match the macroscopic ‘layers’ or fringes observed in some quartzite bodies ([Fig. 7](#)).

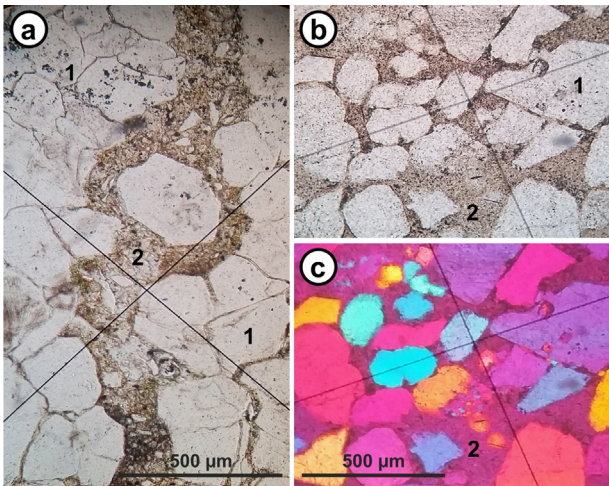
Silica skins on fractures, as well as silica filling dissolution structures, is generally opal ([Fig. 10](#)), sometimes microcrystalline quartz, but never as overgrowths, or euhedral quartz. In places, the quartz grains cemented by opal have only residual overgrowths and are deeply corroded ([Fig. 10](#)). Thus, the two weathering stages succeeded each other: firstly, the dissolution of overgrown quartz grains broken away from the fracture surface, and then deposition of the cementing opal.

The various petrographic facies are the result of specific physico-chemical conditions during cementation, particularly in the degree of oversaturation of the source groundwater with respect to quartz due to changing conditions in the physical environment ([Thiry and Millot, 1987](#); [Thiry et al., 2014](#)). In particular:

- amorphous or weakly crystallized silica precipitated from strongly oversaturated water;
- quartz precipitated from weakly oversaturated and mineralized water that was close to equilibrium with quartz; and
- previously precipitated silica was dissolved by dilute (with respect to silica in solution) water that may have infiltrated the zone of precipitation or source groundwater that was under-saturated.

### 3.5 Suggested model for the silicification of sands

We argue that in the Paris Basin, silicification of sand formations occurred in a regolith environment via precipitation of silica from groundwater in comparatively recent times. Most natural groundwaters in the Paris Basin ([Barteau and Thiry, 2001](#)), and globally ([White et al., 1963](#); [Garrels and Christ, 1965](#)), have a silica content between 12 and 18 ppm SiO<sub>2</sub>, which is roughly the concentration in equilibrium with clay minerals. This means that most groundwaters are oversaturated with respect to quartz (solubility 4–5 mg/L) and are thus potentially able to precipitate quartz when favourable physico-chemical conditions occur. Thus, key factors in a model that would



**Fig. 10.** Thin sections of silica deposits in fractures. (a) Horizontal fracture developed by breakage along syntaxial overgrowth contacts and filled with opal cementing tiny quartz splinters (polarised light). (b) Thin section cut parallel to a glossy silica coating a vertical fracture; the quartz grains are corroded and cemented by opal (polarised light). (c) As for (b) with quartz wedge plate. (1) Quartz grain; (2) Opal cement.

account for precipitation of silica include the triggering mechanism, the general character of the regolith environment in which the precipitation occurred, and evidence for an association between the form of the silicification and the prevailing hydrological regime.

Various mechanisms for triggering silica precipitation have been proposed in the literature, including, in general, evaporation, reduction of pH of highly alkaline solutions, highly acidic environments, and mixing brines with fresh silica-laden waters. None of these proposed mechanisms is realistic for groundwaters in the aquifers in the Paris Basin during the paleoclimatic conditions in the Pleistocene. However, there is one characteristic of the solubility of silica in natural groundwaters that is particularly relevant: lowering of temperature can cause an exponential decrease in the solubility of silica (Walther and Helgeson, 1977, Williams and Cregar, 1985; Rimstidt, 1997). This property has common application in research on deep hydrothermal systems up to 300 °C (Fournier, 1985) and prevails in the deposition of silica sinters from hot springs in the temperature domain between 80 and 25 °C (Herdianita *et al.*, 2000). For example, under surficial conditions, a fall in temperature from 25 to 12.5 °C or from 12.5 to 0 °C actually decreases the solubility of silica by more than half of its initial value (Fig. 11a) and, as such, is likely to be a very efficient mechanism for triggering its precipitation from natural waters. During cold periods, for example, silica dissolved in groundwater could thus precipitate if the water cools significantly by moving closer to the land surface.

We suggest that the field characteristics and petrography of the Fontainebleau quartzites, the known periglacial to glacial environments in the Paris Basin at the time of their formation (Van Vliet-Lanoë and Lisitsyna, 2001), and our recent studies of sand calcites (see Fig. 7 in Thiry *et al.*, 2021), provide the

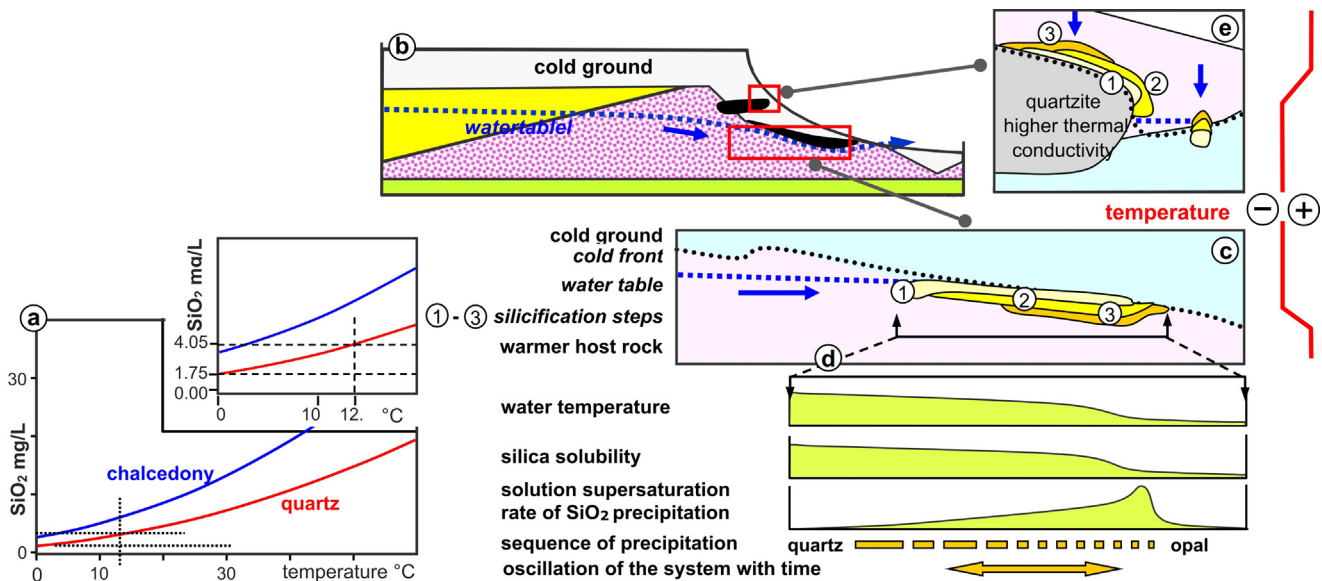
basis for our model. During Pleistocene glacial periods, the ground temperature in northern France was probably 18 °C colder than today as testified by ice wedge structures that point to deep seasonal ground freezing (Andrieux *et al.*, 2016). Discontinuous and extensive permafrost may have existed (Van Vliet-Lanoë and Lisitsyna, 2001). Early modelling of permafrost in the Paris basin suggested that it might have reached 300 m depth (Lebret *et al.*, 1994). During the last glacial stage there was a zone of continuous permafrost in the northern half of the Paris basin and in eastern France (Jiraková *et al.*, 2011). Recent reworking of the permafrost model showed a similar distribution of continuous permafrost in the northern half of the Paris basin, but without any indication of depth (Bertran *et al.*, 2022). Additionally, it is of note that the transmission of air temperature to aquifers in the regolith can be relatively rapid. In south-east Germany, for example, a temperature increase has been recorded in aquifers 20–60 m deep over the last 30 years (Hemmerle and Bayer, 2020).

In the Paris Basin, during periglacial to glacial environments, a marked temperature gradient would have existed between surface waters around 2 °C (mean value of the thawed active layer) and the deeper ground water with a temperature beneath the chilled ground probably only slightly lower than at the present day, around 12 °C. In our model, groundwater that flowed at depth from plateaux to valleys in the local landscape came into contact with a cold near-surface zone on approach to valley landforms where it would have discharged (Figs. 11b and 11c). This would have generated the physico-chemical changes that led to precipitation of contained silica and concomitant alterations (Fig. 11d), namely:

- a reduction in temperature of the groundwater solution;
- a decrease in silica solubility and concomitant supersaturation of the solution; and,
- the precipitation of a specific sequence of silica forms in response to progressive cooling of the groundwater solution and the correlative increase in oversaturation.

In these environments, most of the silica would have precipitated from slightly supersaturated groundwater and so the growth of primary quartz was dominant, probably constituting 90 to 95% of the precipitated silica.

It is well known that the presence of permafrost in a landscape affects the prevailing hydrological regime (Lemieux *et al.*, 2008; Dobiński, 2012). Firstly, near-surface lateral groundwater flow can be severely restricted by continuous permafrost which acts as an impermeable upper boundary. Secondly, an increase in pore water volume by freezing leads to increasing groundwater pressure. If permafrost forms to significant depths, it can tend to force lateral groundwater flow to greater depths, even far below the hydrostatic level. Under these conditions, groundwater flows are no longer driven by gravity and flow paths can become very tortuous and narrow, bypassing not only less permeable materials but also frozen aquifer volumes (Yoshikawa and Kane, 2021). Nevertheless, if the ground is frozen as permafrost, groundwaters would continue to discharge in valleys through non-frozen structures (taliks) because the warm water can maintain the ground in an unfrozen state. If the permafrost continues to develop, outflows in the valleys may gradually freeze, causing over-



**Fig. 11.** Geochemical model of sand silicification during glacial periods. (a) Quartz solubility according to temperature. Silica solubility decreases by lowering temperature. Hytec geochemical modelling (Van Der Lee *et al.*, 2003). (b) Hydrological and thermal conditions at a plateau edge. (c) Silica precipitates from groundwater on meeting cold ground. (d) The degree of oversaturation of the water is proportional to the rate of water cooling and results in a sequence of silica minerals arranged along the flowpath. (e) Silica precipitates in the active layer above permanent cold ground or even permafrost.

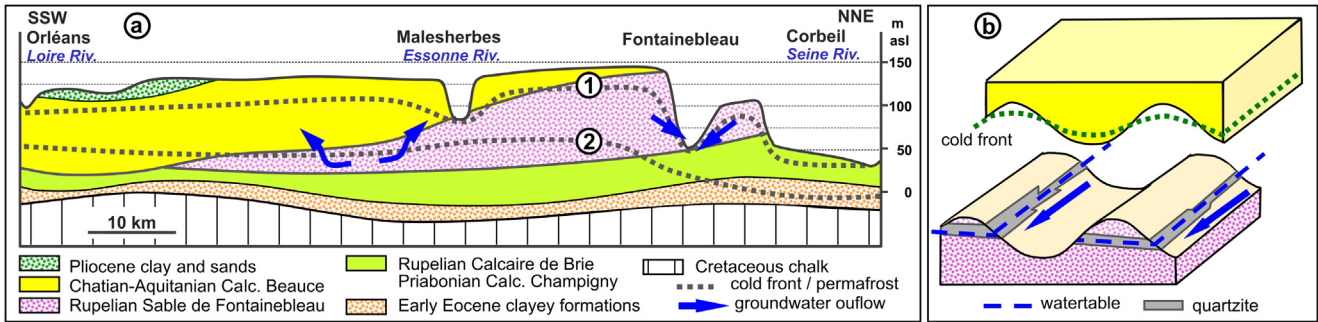
pressure to rise and generate hydraulic fracturing, and thus groundwater escape to the plateau surface. In northern Canada, water has been recorded discharging at 16.8°C in a river (Clark *et al.*, 2001) and elsewhere through 600 m-thick permafrost (Andersen *et al.*, 2002).

Above the permafrost there can be an ‘active layer’ in which surface water infiltrates during summer thaw and shallow groundwater may form. The active layer may reach over 20 m in depth during periods of global warming (Dobiński, 2020). If the regional groundwater level drops as a result of thawing permafrost, infiltration can penetrate deeper into the permafrost following specific pathways along non-frozen zones like taliks and thermokarsts (Fig. 11e). This infiltrating water may cool down by 5–10° from its temperature at the surface as it comes into contact with the permafrost (Boike *et al.*, 1998). The active layer may operate both seasonally and perhaps perennially, depending on conditions, as a shallow zone of flow of a perched supra-permafrost aquifer (Walvoord and Kurylyk, 2016).

The variation in quartzite morphologies we have described is superimposed on the structural arrangement of the Sable de Fontainebleau (Fig. 12a). In the north, in the vicinity of the outcrops of the Sable de Fontainebleau along the edge of the Beauce Plateau, there are horizontal quartzite slabs at the landsurface or under a thin limestone cover. More irregular quartzite masses with curved shapes and concavities crop out along the valleys that incise the Beauce Plateau from beneath a 10m thick limestone cover (Fig. 1). There are also convoluted quartzite masses in the southernmost extension of the Sable de Fontainebleau formation (Pithiviers area) where the limestone cover is 20–40 m thick.

We suggest the following.

- 1 At the beginning of the cold period there was no permafrost but the regolith cooled to depths of 5–10 m. The hydrology of the Fontainebleau sand unit was not disturbed, with flows discharging at the valley edges. Silica precipitated from groundwater when the cold front encroached on the flow paths, resulting in mainly horizontal quartzite slabs formed at the water table.
- 2 As permafrost formed and thickened to 10–20 m, drainage lines along the valley walls may have frozen and so most of the discharge from the sub-permafrost aquifer occurred in the valleys through taliks below the streams. The flows would mostly have been proximal to the lower limit of the permafrost and under high hydraulic gradients because of an increase in pressure due to the freezing of part of the pore water. It is under these particular aquifer discharge conditions, namely through irregular frozen areas at the base of thick permafrost, and probably along non-frozen domains (taliks) along the valleys, that quartzites with curved and spindle like morphologies likely formed.
- 3 With deepening of the permafrost (beyond 30–40 m), the taliks in the valleys would gradually shrink, increasing the pressure within the aquifer and causing groundwater to discharge through hydraulic fractures. At this stage, silica would have precipitated against fracture walls, forming quartzite shells around zones of frozen sand. These are the sites in which the convoluted quartzites with spectacular hollows (originally frozen sand, later exported on exposure) formed. Larger quartzite bodies may also have formed, depending on the groundwater flow rate and water temperature. Some sort of dynamic equilibrium would have



**Fig. 12.** Geological section through the Sable de Fontainebleau in relation to the cold front. (a) Progressive deepening of the cold front over time. (1) No permafrost or limited discontinuous permafrost in the early glacial period leading to the formation of horizontal quartzite slabs at the groundwater table. (2) Thick permafrost during the glacial maximum. The groundwater is confined and under pressure, leading to the formation of irregular quartzite masses. (b) Schematic of the spatial disposition of the watertable and a cold front versus paleodune ridges incised by a perpendicular valley leading to preferential silicification of these paleostructures.

been established between silica precipitation and cementation in relation to the cold of the encased quartzite (relatively high thermal conductivity) and the thawing of the slightly less conductive adjacent frozen permafrost.

- 4 In thick active layers (which develop during periods of climate warming, as in boreal countries), surface water infiltrated during summer thaw can cool 5–10°C on contact with the permafrost or on contact with quartzite masses encased in the top of the permafrost. Thus, chilling could have triggered the precipitation of dissolved silica along specific infiltration pathways or even in non-frozen zones within the permafrost, and so led to the formation of geopetal ‘gogotte’ structures and silica skins on the walls of fractures in earlier-cemented sands. The silica in these younger silcretes is typically opal, which is indicative of highly silica supersaturated solutions. This mode of formation has recently been proposed for speleothems within fractures in a Miocene sandstone in Spain in which the silica had depleted  $\delta^{18}\text{O}$  values indicating precipitation from partially frozen meteoric waters (Cantarero *et al.*, 2020). We suggest that: (1) the sand within an aquifer was silicified during an initial glacial period, (2) exposure and fracturing of the resulting quartzite occurred as a result of erosion and scarp retreat during a subsequent interglacial period, accompanied by silica dissolution by infiltrating warmer, dilute rainwater, and (3) secondary silica was deposited in response to subsurface cooling during a later glacial period.

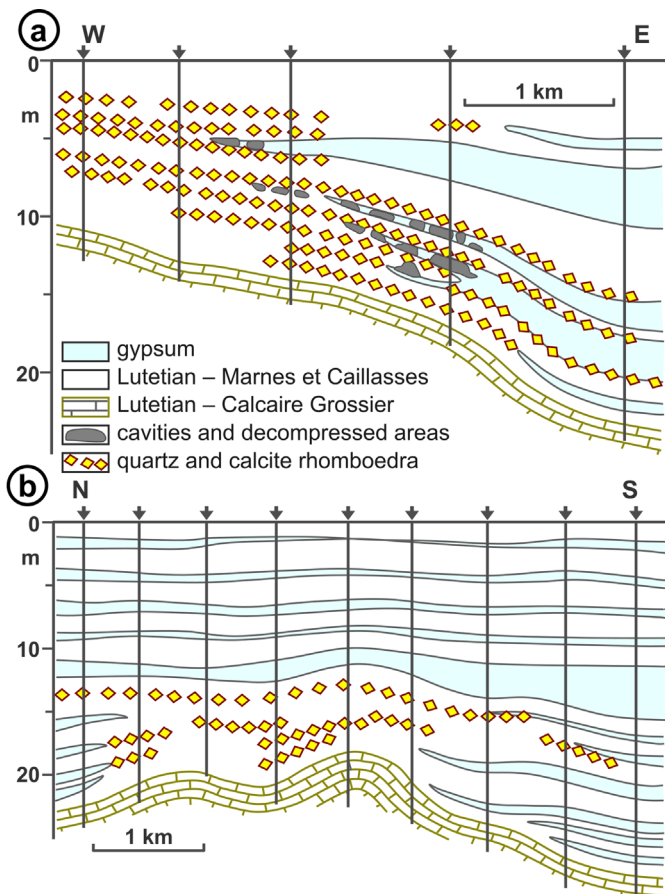
As well, in places, the geometrical relationship between paleodunes and valleys resulted in a specific hydrological structure and the preferential silicification of the paleodunes. This was promoted by the relatively high permeability of the dune sands, preferential flow and discharge of groundwater at the intersection of paleodunes with valleys, and a cold front that ‘enwrapped’ the paleodunes due to the higher thermal conductivity of the marly limestone cover compared to the underlying unsaturated (porous) sands (Fig. 12b).

## 4 Silicification of gypsum

In Paris and its surroundings, silicified gypsum occurrences are probably as common as silicification in calcareous formations. Pseudomorphs are seldom visible in quarries: their occurrence is always related to alteration/dissolution of the gypsum layers. Observations and sample collections were mainly made in the 19th century, especially in Paris, thanks to urban development work (Munier-Chalmas, 1890; Lacroix, 1901). The petrographical studies by Cayeux (1929) focussed on the spatial arrangement between gypsum and silicification and the origin of the silica. The question was taken up by Toulemont (1982) who surveyed sinkholes relating to gypsum dissolution.

### 4.1 Review of prior studies

Munier-Chalmas (1890) was the first to describe the geological occurrence of silica pseudomorphs of gypsum and propose a genetic model. He pointed out that “*the gypsum has often disappeared completely following its outcrop lines in the Quaternary valleys and has been replaced by siliceous and calcareous deposits*”. He noted an association between the silica pseudomorphs of gypsum, bipyramidal quartz, calcite of inverse rhombohedron habit and common small fluorite crystals. Thus, he recognised the conjunction of dissolution and precipitation and their association with Quaternary valley incision. The excursion of the Société géologique de France of 1889 visited some of the gypsum pseudomorph sites. Participants agreed with the idea of pseudomorphosis and its connection with the current valleys. Lacroix (1901) confirmed the geometric relationships between siliceous features and gypsum layers and noted that bipyramidal quartz and inverse rhombohedral calcite were “*neogenic minerals, contemporaneous with the formation of siliceous pseudomorphs*”. He spoke of “*decalcification and degypsification*”.



**Fig. 13.** Quartz pseudomorphs and calcite rhombohedral aggregates in the Late Lutetian Marnes et Caillasses Formation. (a) Seine syncline at Sevran (Seine-Saint-Denis), (b) synclinal trough at Massy (Essonne). After Toulemont (1982).

Additionally, he provided numerous detailed descriptions of the relationships between gypsum and silica pseudomorphs and the mineralogy of the specific silica varieties. He pointed out that all gypsum layers (about 20 distinct ones) in the Lutetian, Bartonian and Priabonian formations in Paris area contain gypsum pseudomorphs.

Lucien Cayeux (1929) provided complementary descriptions and interpretations. In relation to Priabonian gypsum, he warned: “*Siliceous concretions, formerly collected in the saccharoid gypsum of the upper gypsum layer of the Masses du Gypse in Montmartre (Paris) and Pantin (suburb NE Paris) quarries, appear to be completely lacking in current quarries*”. In thin sections, “*the flint of the gypsum deposits, analyzed in white light, with lowered condenser, testify to a colloidal primitive state, highlighted by countless zones of extremely fine concentric growth*”.

Toulemont (1982) benefited from information from numerous drillholes established in a project to prevent land collapse over cavities formed by dissolution of gypsum. He noticed that decimetre-thick layers of siliceous and calcitic aggregates (called ‘candy sugar’ or ‘salt bank’ by the quarrymen) had lateral extensions over a few hundred metres in the gypsum horizons (Fig. 13). The association of these altered facies with the sedimentary units led him to conclude

that “*these materials bear witness to the early onset of diagenetic silicification and calcitization phenomena affecting not only the sulphated phase itself, but also the associated carbonates*”. He showed thin sections including euhedral quartz crystals with very distinct ribbons marking successive zones of growth, similar to those described above in the quartzite cements in the sand formations.

## 4.2 Description of alteration products

Gypsum levels have long been accessible only in large open-pit quarries or in underground workings and it is no longer possible to observe and collect the siliceous pseudomorphs described by the early authors. We turned to samples from mineralogy collections where, even if the context of the samples is lacking, their exceptional quality permits detailed observations that indicate their mode of formation (see details in [Supplementary File#1](#)).

### 4.2.1 Gypsum crystals replaced by silica

Pseudomorphism of ‘sand roses’ of lenticular gypsum crystals by quartz are the most common samples in the many Paris Mineralogical museums. Such replacement had to occur step by step, flake by flake, otherwise the interleaved crystals would not have been preserved. In some specimens, pseudomorphism is restricted to fine casings around curved gypsum crystals, showing that silica deposits were limited to surfaces that were accessible to silica-bearing waters.

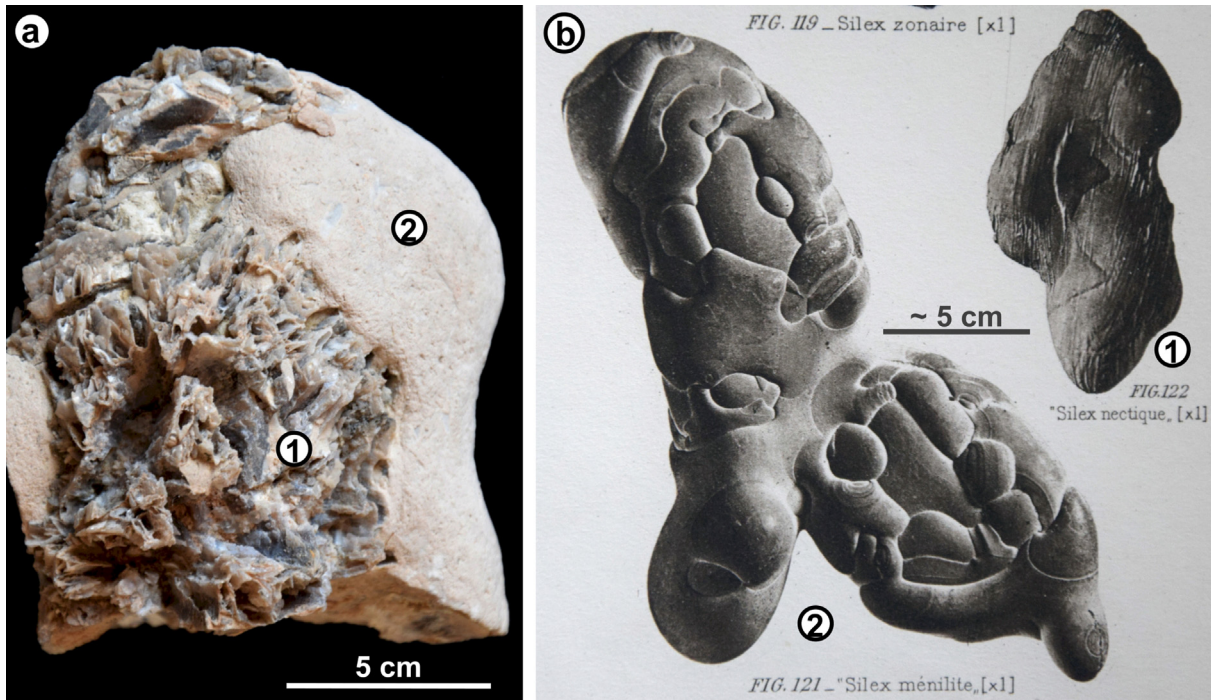
There are also hollow moulds of gypsum crystals. Here, fine walls of silica originally encasing gypsum crystals remain as moulds after the remaining gypsum was dissolved

(Fig. 14a). In this sample, silica moulds have a smooth outer surface but mammillary deposits towards the inside of the former gypsum crystal, indicating that silica replacement started along cleavages and that gypsum dissolution and silica deposition occurred concomitantly. Silica casts were subsequently embedded in a silicified mass (gogotte) prior to dissolution of the residual gypsum. The casts of gypsum crystals are composed of botryoidal quartzine (length slow chalcedonite) and the gogotte has a microcrystalline quartz matrix with small inverse rhombohedral calcite crystals.

Concretionary siliceous masses are common in the Calcaire de St-Ouen and the Masses du Gypse (Lacroix, 1901; Cayeux, 1929). These include concretions and tubercular kidney-shaped mammillary bodies, 1–10 cm in diameter, and with original marl bedding laminations preserved in some examples (Fig. 14b, 1). Concentric growth layers around one or several centres are common (Fig. 14b, 2). The contact between the encasing rock and the siliceous masses is sharp: replacement appears to have been initiated in specific locations with outgrowth expanding gradually.

### 4.2.2 Calcite of inverse rhombohedron habit

Interpretations of the origin of the mineral assemblages made up of bipyramidal quartz, gypsum replaced by silica, and rhombohedral calcite were discussed in the earliest studies. Munier-Chalmas (1890) and Lacroix (1901) considered that



**Fig. 14.** Siliceous pseudomorphs of gypsum. (a) Siliceous moulds of gypsum showing that (1) gypsum crystals were cast by silica deposits, then (2) embedded in a silicified mass (gogotte) before residual gypsum was dissolved. Sample from altered/dissolved gypsum layers in the vicinity of outcrop in ancient gypsum quarries of the Plateau d'Avron, Neuilly-Plaisance (Seine-Saint-Denis). (b) Gogotte-like siliceous concretions with mamillary protrusions; (1) silex nectique ('float-stone') in gypsum deposit, (2) silex melinite (brown flint) interspersed in magnesium-rich clays, with geotropism indicated by overlapping concretionary growths. Extracted from Cayeux (1929).

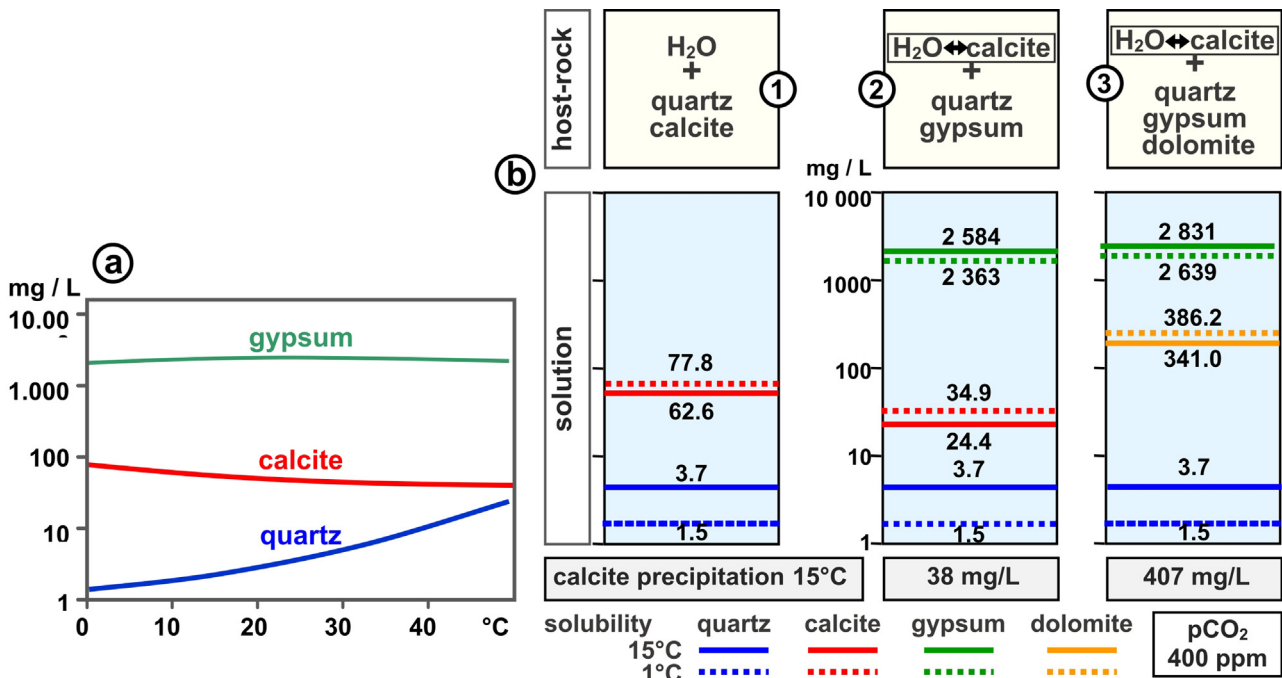
this association was paragenetic, whereas Cayeux (1929) refuted that the three components were related and suggested that the nature of the parent rock of bipyramidal quartz and inverse rhombohedral calcite could not be determined. Following this, Toulemont (1982) linked them to sedimentary facies formed as lateral equivalents of the gypsum deposits.

The difficulty is that the collected samples were treated with HCl to remove marl gangue and ubiquitous calcite crystals (Lacroix, 1901) and so there is no clear indication as to whether the calcite crystals were residual or small neogenic rhombohedra. As the curved primary gypsum crystals in gypsum roses are most often clear and without inclusions, it is possible that the small calcite crystals that were scattered within the silica are secondary and precipitated at the same time as the silica. In addition, geodic nodules lined with euhedral quartz and inverse rhombohedral calcite are suggestive of groundwater flow along pipes that were probably karstic structures and in which the precipitation of calcite and silica were concurrent. So, if the silicification is thought about in the context of groundwater silicification, then valley incision, groundwater flow and silicification facies could all be a response to lithological discontinuities in shoals rather than in the more impervious massive gypsum and calcareous marl deposits in ponds.

### 4.3 Suggested model for the silicification of gypsum

The disposition of silicified gypsum in weathered and/or dissolved gypsum layers and karst dissolutions, its disappearance away from the outcrop, as well as the presence of quartz and calcite crystallization in dissolution voids, led us to consider a link to groundwater flows. The mass balance of silica substituting for gypsum has also to be considered, as well as the occurrence of calcite of inverse rhombohedron habit. Calcites with inverse rhombohedron habit (sand calcites as well as translucent calcites) are common in the Sable de Fontainebleau and in the lacustrine limestone formations south of Paris. They are Pleistocene in age and their occurrence and isotopic composition suggest crystallization from groundwaters in cold and partly frozen paleo-environments (Thiry *et al.*, 2021).

The above inferences are that silicification of gypsum could have occurred in a regolith environment via precipitation of silica from groundwater in comparatively recent times. Thus, we suggest that silicification of gypsum occurred in conditions comparable to those in which silicification of sands produced the quartzites described earlier. To support this hypothesis we examined the geochemical mechanisms likely to have been involved.



**Fig. 15.** –Geochemical behaviour of groundwater within gypsum series. (a) Solubilities of gypsum, calcite and quartz according to temperature. (b) Mass balance of groundwater in equilibrium with (1) a calcareous aquifer, (2) contact with gypsum leads to calcite precipitation and which (3) is even higher in the presence of dolomite. Silica precipitation may occur at any step if the temperature falls. HYTEC geochemical modelling (Van Der Lee *et al.*, 2003).

4.3.1 Gypsum versus calcite solubility

Gypsum is characterized by its high solubility, about 2.5 g/L, and if calcite is about 10 times more soluble than quartz, gypsum is about 250 times more soluble than quartz and about 25 times more soluble than calcite (Fig. 15a). Its solubility increases almost linearly between 0 and 20 °C from 2.35 to 2.53 g/L (1% increase), which is negligible compared to the solubility of quartz which increases about three times (from about 2 to 6 mg/L SiO<sub>2</sub>) over the same temperature range.

HYTEC geochemical modelling (Van der Lee *et al.*, 2003) shows that the solubility of calcite decreases in the presence of gypsum (Fig. 15b 1 and 2). Thus, carbonated water in equilibrium with calcite that encountered gypsum would induce the dissolution of gypsum and the precipitation of more than half of its initially dissolved calcite content (Fig. 15b 2). Calcite precipitation would remain low, about 40 mg/L at 15°C, and the mass balance very low compared to the concomitant dissolution of gypsum (about 2.5 g/L at 15°C). Precipitated calcite and dissolved gypsum would be in a volume ratio of about 1/50. In the presence of dolomite, the solubility of gypsum would increase slightly and about 600 mg/L of dolomite dissolve, whereas 400 mg/L of calcite would precipitate: that is, about 10 times more than in the absence of dolomite (Fig. 15b 3). This is due to the remarkably high solubilities of the Mg sulphates (about 350 g/L for epsomite) which destabilize the dolomite, which in turn releases Ca<sup>++</sup> that feeds calcite precipitation. A temperature drop from 15 °C to 1 °C has no significant effect on mineral solubilities, except silica, the solubility of which is reduced by

about 3 times over that temperature range. Calcite would precipitate even if the solution was chilled.

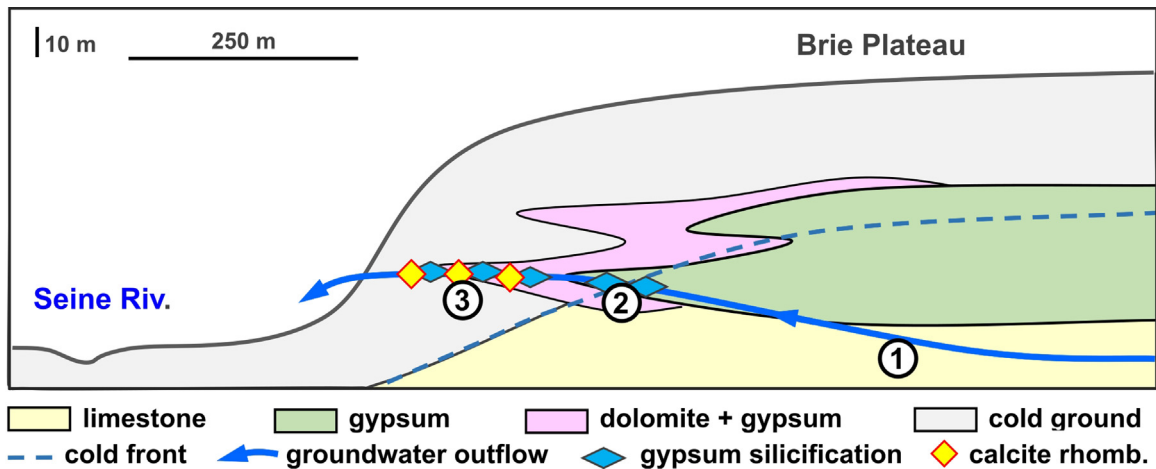
Thus, calcite precipitation occurs when groundwater from a limestone aquifer encounters gypsum. This is exacerbated in the presence of dolomite, which is the geological facies in proximity to the gypsum masses. If, at the same time, the temperature falls, there will be concomitant precipitation of calcite and silica. This is in line with our observations: pseudomorphosis of gypsum by silica together with calcite of inverse rhombohedron form, the latter typifying cold environments (Evszkova, 1958; Thiry *et al.*, 2021).

4.3.2 Siliceous pseudomorphism of gypsum via groundwater

The relationship between epigenetic silica layers in the Marnes et Caillasses and the morphology of the Seine valley in Paris was clearly recognized and established by Munier-Chalmas (1890) and Lacroix (1901). Cayeux (1929), who did not see the classical sites where silica had replaced Lutetian gypsum, did not accept this relationship. Toulemon (1982) linked silicification to sedimentary environments and, consistent with the silicification models proposed at the time, suggested that it was a syn-depositional evaporative process.

We cannot identify a realistic syn-depositional or immediately post-depositional model for the silicification. The major difficulty is the mass balance: the subdued landscape of the sedimentary basin could not have generated a hydraulic gradient and thus sustained groundwater flows sufficient to provide the required large volumes of water





**Fig. 16.** Sketch of the suggested hydrological and thermal arrangements in the Seine River valley during a cold period in the Quaternary. (1) Limestone reservoir groundwater flowing through (2) cold ground interface in presence of gypsum leads to silica precipitation and minor amounts of calcite. If it encounters gypsum + dolomite layers (3) it brings about precipitation of silica + large amounts of calcite. 1, 2 and 3 refer to the equilibrium geochemistry in [Figure 15b](#).

needed to supply the silica. Moreover, it is not because gypsum precipitates via concentration of water by evaporation that makes it possible to precipitate silica by evaporation. Indeed, the solubility of silica in surface water is about 20 mg/L while the solubility of gypsum is about 2.5 g/L, about 100 times higher ([Fig. 15a](#)). Thus, no (or only small and diffuse amounts of) silica could precipitate in an evaporative environment where gypsum and silica were being concentrated.

In contrast, it is remarkable that the relationships proposed in the earliest studies match those we describe between the silcrete pans and lenses in the Fontainebleau Sand and the scarps of the Plateau de Beauce and the sides of valleys that incised it. These observations are key to silicification at a late stage. Our suggestion is that the field relationships, distribution, and macro- and micromorphology of the silicified gypsum formations evoke groundwater silicifications observed elsewhere in the Paris Basin and can be explained by precipitation of silica and the replacement of pre-existing gypsum under specific local groundwater conditions during Quaternary cold periods. The geochemical evolution of groundwater flowing through gypseous formations bordering the Seine River valley during cold periods, as suggested in our model, also makes it possible to explain the association between silicification of gypsum and the precipitation of inverse calcite rhombohedra ([Fig. 16](#)) described by [Munier-Chalmas \(1890\)](#) and [Lacroix \(1901\)](#).

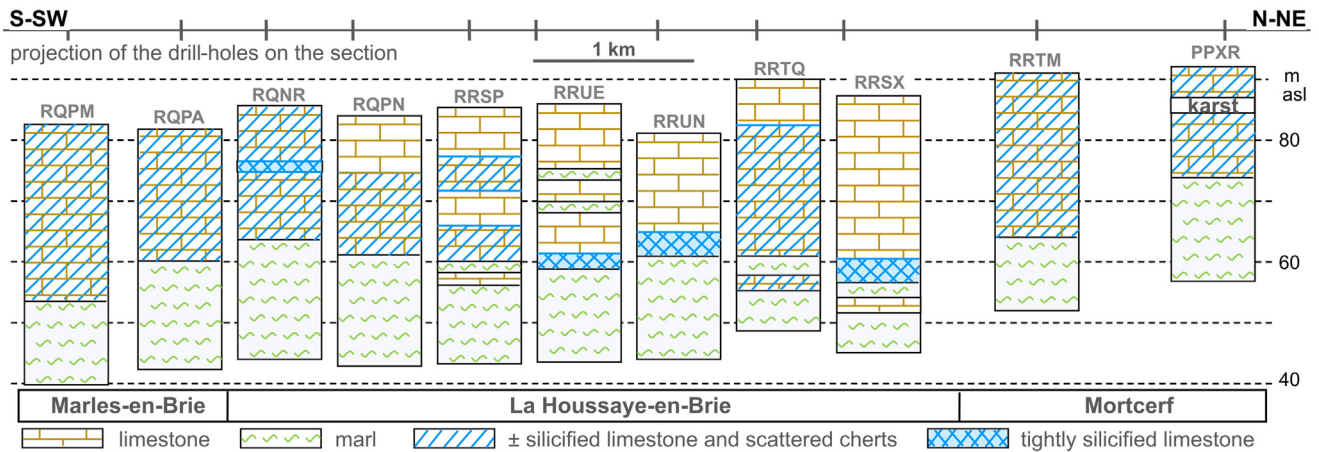
The scarcity of the silicification of the Priabonian gypsum in the Montmartre butte in Paris and in the NE Paris suburb Pantin ([Lacroix, 1901](#)) could be related to a lack of groundwater flow within isolated buttes and/or the impermeability of the massive gypsum deposits. On the other hand, the abundance of silicification in the older gypsum quarries relative to its paucity in more recent quarries ([Cayeux, 1929](#)) might relate to the fact that the more recent quarries have penetrated further into the formation, away from the original groundwater discharge zones where silicification occurred, as is the case for the quartzites in the Sable de Fontainebleau.

## 5 Silicification of limestones

Almost all Tertiary limestones in the Paris Basin contain siliceous masses ([Cayeux, 1929](#) and [Fig. 3](#)) that are commonly called ‘chert’ ([Cayeux, 1929](#)). Although these so-called ‘cherts’ were described more than 200 years ago their origin has remained obscure. Many local observers suggested that they were formed during a late, post-exhumation process. For example, [Lacroix \(1901\)](#) described chalcedonic stalactites, up to a few millimetres in diameter, indicative of silicification in a vadose environment. [Cayeux \(1929\)](#) clearly showed that silica replaced calcareous facies while preserving sedimentary structures and fossils. He raised a question about the origin of the silica.

Despite some of these early insights, ‘chert’ masses in the Paris basin limestones were subsequently considered, without question or comment, to result from the concentration of silica in syn-depositional evaporative environments ([Auzel and Cailleux, 1949](#); [Pomerol and Feugueur, 1968](#)). But in a comprehensive review of the silicified lacustrine limestones in the Paris Basin, [Ménillet \(1988\)](#) suggested that, although there were some clues for early epi-diagenetic silicification, much of the silicification was related to successive periods of karst development while some was geometrically related to paleoweathering surfaces and residual sand covers. However, **no reworking of the silicified zones in limestones has ever been reported** on the erosion surfaces where sand formations unconformably overlie the limestones, for example in the Sable de Fontainebleau above the Calcaire de Brie and the Calcaire de Champigny on the Brie Plateau and in the Sable de Beauchamp above the Marnes et Caillasses around the Paris Plateau. The absence of ‘chert’ lags in association with these erosion surfaces may be taken to indicate that the limestones had not been silicified at this time.

There are one or more peculiar silicified horizons in the Bartonian Calcaire de Saint-Ouen. They were intensively mined during the Neolithic period ([Imbeau \*et al.\*, 2018](#)) while the common ‘cherts’ in the limestones have almost never



**Fig. 17.** Drillholes showing silicified facies within the Calcaire de Champigny in the central Brie Plateau, La Houssaye-en-Brie area (Seine-et-Marne). Tightly silicified layers occur above the basal marls. In the absence of distinct tightly silicified layers, silicification occurs in smaller patches randomly through the whole limestone unit. There is no obvious correlation of silicification with specific sedimentary horizons. Karst features are locally noted in the boreholes.

been used for flaking. These peculiar silicified Calcaire de Saint-Ouen cherts used by prehistoric people are mainly composed of opal-CT. They may have originated from an early or late relative accumulation of silica but not an absolute accumulation, as are the ‘cherts’ that are the subject of our studies (see [Supplementary File#3](#)).

Elsewhere, in continental realms, calcretes and lacustrine limestones display forms of silicification that are commonly interpreted to be the result of primary silica deposition in alkaline environments ([Pittman, 1959](#); [Wheeler and Textoris, 1978](#); [Daley, 1989](#); [Bustillo et al., 2002](#)) and have been compared to opal deposition in the present-day Coorong Lake ([Peterson and Von der Borch, 1965](#)). However, in a few studies, dilute solutions, mainly groundwaters, have been suggested as the source of silicification of some lacustrine limestones, especially those that contain no evaporitic minerals and have not been deeply buried. [Banks \(1970\)](#) suggested that silica precipitated from groundwater after initial lithification and prior to or during karst erosion. [Conrad \(1969\)](#) showed that cherts in the Mio-Pliocene lacustrine limestones in southeastern Morocco are more abundant in the cliffs along the valleys where groundwater discharges and concluded that the cherts formed after valley incision. [Thiry and Ben Brahim \(1997\)](#) noted that in the same Moroccan successions most of the silica deposits were related to karst-like pipes and voids and so linked the occurrences to groundwater outflows. In central Australia, [Arakel et al. \(1989\)](#) showed that silicification in paleodrainage basins in both vadose and phreatic hydrological zones from dilute alkaline pore solutions of the carbonate host occurred in a remarkably short time span (of the order of some tens of thousands of years). Similar features have been described in calcretes in South Africa ([Netterberg, 1982](#)) and Kuwait ([Khalaf, 1988](#)). Recently, [Khalaf et al. \(2020\)](#) suggested a groundwater origin for cherts in Eocene limestones from Kuwait. These have never been deeply buried and were reworked on the unconformity with overlying Mio-Pliocene formations. They occur in horizons that are discordant with bedding, exhibit karst-like dissolution features and relate to absolute accumulation of silica.

Similarly, [Thiry et al. \(2015\)](#) suggested a groundwater origin for limestone silicifications in a Miocene lacustrine sequence in southeastern Morocco. These absolute accumulations of silica are almost exclusively limited to a 10–40 m zone from the edges of scarp and mesa landforms as seen in dozens of mine galleries.

### 5.1 Occurrence and distribution of the ‘cherts’

The distribution of silicified zones in the limestones is typically very irregular and the size of the silica masses varies from millimetric dots to bodies several tens of metres long. (see details in [Supplementary File#3](#)). Locally, they can form up to 50% of the faces in some quarries (10 m extent and 3 m height) but be absent 5-10 m away. Some silicified slabs can vary from a few tens of metres to a kilometre in length and more than 2 m thick ([Ménillet, 1988](#)) and are reminiscent of quartzite pans in sand formations. An estimate made in the southern Paris Basin indicated that they constitute about 5% of the volume of the Beauce Plateau lacustrine limestone ([Aubert and Lorain, 1977](#); [Ménillet, 1980](#)). In the eastern Paris Basin, quarrymen select areas of Calcaire de Champigny where the silica content is limited to about 2%, but the actual levels of silicification in the limestones, on a regional scale, are probably 2 to 5 times higher.

Lacustrine limestones have often been drilled for geotechnical or hydrogeological studies and often described in metric intervals with notes as to whether the limestone is compact or not and if chert chips are present in the cuttings. Our geological section through the southern edge of the Paris Basin ([Fig. 4](#)) shows in detail the distribution of the various silicified facies in various limestone formations based on these comprehensive borehole data. The cherts appear to be much more abundant beneath the Plateau de Brie than beneath the NW Plateau de Beauce and the Vexin. It emerges from this section that: (1) the most abundant silicified limestone facies occur in the Calcaire de Champigny, which is a hard limestone about 25 m thick, that overlays 10 m of marly limestones; (2) the Calcaire de Saint-Ouen is similar in that cherts appear to be

limited to the upper calcareous part but, except in one drillhole, are not identified in the lower marly part; and (3) there are cherts contained within the Calcaire de Brie which occurs above a thick impervious unit that is part of the Argile Verte and Marnes Supra Gypseuses. Impervious marls and claystone units are devoid of silicifications.

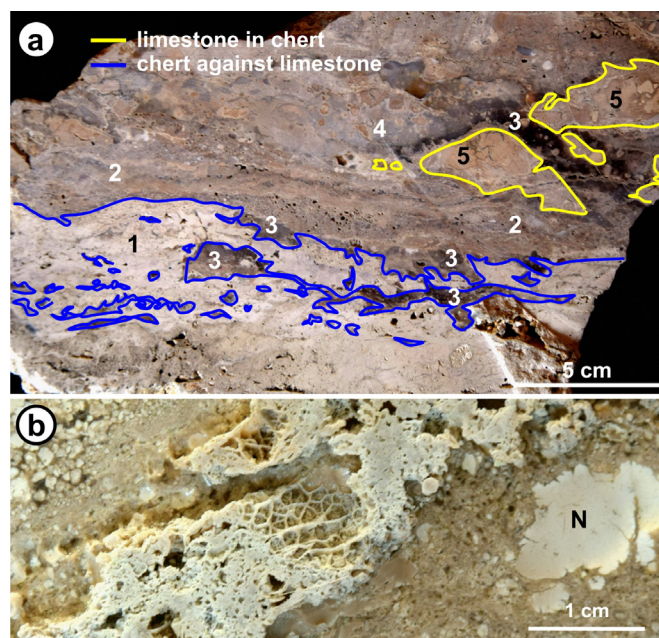
The Argile à Meulière de Brie (Fig. 4) results from weathering of the silicified Calcaire de Brie which, in several places, exceeds 10 m in thickness. This points to the importance of silicification in the Calcaire de Brie. In addition, monolithic Meulière layers more than 5 m thick are known in the old grinding-stone quarries. These show that the silicification in the former Calcaire de Brie was not scattered throughout but rather concentrated in masses, some of which were over 5 m thick and several tens of metres in extent. The geological section in Figure 4 shows that the intense silicification of the Calcaire de Brie on the surface of the plateau is not repeated in the west where the Calcaire de Brie beneath the Sable de Fontainebleau and the Marnes à Huitres is not silicified. Nevertheless, notes on the geological maps indicate cherts in the Calcaire de Brie in outcrop on the flanks of the Yvette and Seine Valleys.

Closely-spaced drillholes show that, at a 500 m spacing, there is no correlation between silicified limestone units intersected in adjacent drillholes (Fig. 17). The description of homogeneous units as more or less silicified has been interpreted as containing scattered occurrences of chert nodules or fine silica laminae. In contrast, the logged 20–80 cm thick individual tightly silicified horizons are surely intensively silicified zones. Only the silicified horizons immediately above the lower marls might possibly be correlated one with another. However, the overall distribution of silicification in the Calcaire de Champigny is not related to bedding in the formation.

## 5.2 Configuration and composition of the cherts

Silicification in limestones includes irregular, amoeboid or pseudopodic morphologies and is most often found in more or less dense horizontal layers (see Supplementary File#3). Most of the silicified zones are distributed randomly and are often discordant with respect to sedimentary structures, including bedding. Field relationships clearly show that the silicification occurred after initial lithification of the limestones. In particular, there is never any differential compaction around the ‘chert’ masses. The silicification occurs on the one hand as barely altered limestone with a substantial residue of carbonate fabric and on the other as a silica-rich mass in which there are virtually no traces of limestone. However, there are gradations between these two extremes.

The boundary between silicified domain and limestone is always deeply interpenetrating and quite different from that observed for classic flint masses in chalk. It has the appearance of an alteration ‘front’ which is somewhat indented but nevertheless sharp (Fig. 18a). Ahead of this ‘front’ are small outliers of chert in the limestone whilst behind are remnant limestone patches within the chert. This arrangement occurs at all scales from outcrop to thin section. The ‘silicification front’ can cut across primary features in the limestone as well as bypass certain elements by respecting the detail of millimetric sedimentary structures (Fig. 18b).

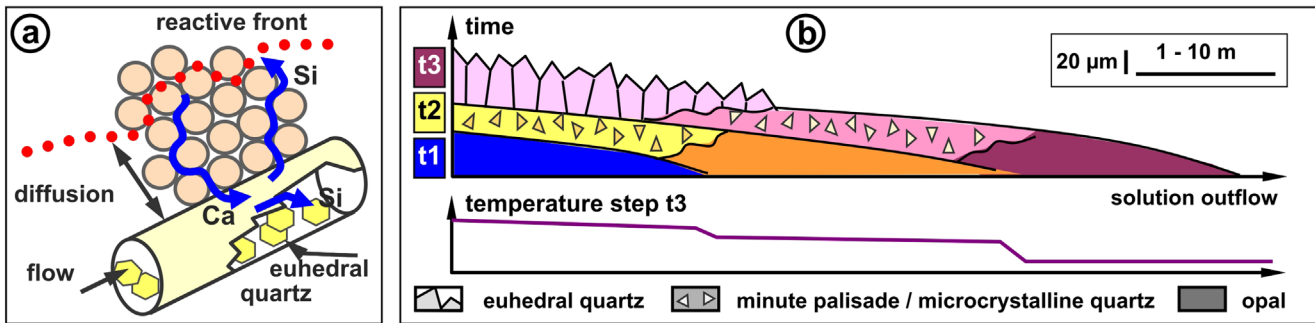


**Fig. 18.** Relationship between silica and carbonate. (a) Interpenetrating boundaries between silicified domain and host limestone (highlighted in blue). (1) Nodular limestone; (2) dull chert containing remnant limestone structures; (3) vitreous segments; (4) opalescent reflection; (5) residual limestone. Prasville (Eure-et-Loir). (b) Chert – limestone boundaries etched by hydrochloric acid. Moulds of shrinkage cracks like those in limestone nodule N (right) and finely porous texture due to former calcite inclusions; Pécy (Seine-et-Marne).

Petrographic analysis provides key observations on the various silica phases and their distribution and sequence of formation (see Supplementary File#3). Two types of silica are always associated with each other: (1) void fillings with growths of quartz crystals making up most of the silica accumulation; and (2) replacement of limestone matrix, mainly by microcrystalline silica, surrounding the void fillings in a more or less important halo (Thiry and Ribet, 1999). The distribution of voids and the nature of their infillings are key indicators of the silica importation mechanisms, its deposition and its transformation/recrystallization.

Voids infilled by silica average 0.1–3 mm in size, have irregular shapes and are often linked in the form of anastomosed networks. The irregular shapes and the layout of the networks are reminiscent of karst dissolutions in the form of micro-karst, quite distinct from large dissolution structures which locally affect these limestones in outcrop.

A general feature of silicified carbonate matrix is its relationship with silica-filled voids. Silicification of carbonate matrix does not occur where there are no silica-filled voids, in contrast to the typical situation in Chalk flints. Thus, initially, all silicified zones had important porosity. Where initial porosity was less well developed, silicification of the matrix is usually restricted to a 10–50  $\mu\text{m}$  wide fringe around the voids and rarely extends more than 0.5–1 mm from the edge of a void, joint or fracture. Where porosity was pervasive the whole matrix has been silicified.



**Fig. 19.** Silicification mechanisms. (a) Schematic showing phenomena that could account for replacement of limestone matrix by silica as well as precipitation of quartz on walls of the voids or fractures carrying groundwater. After [Thiry and Ribet \(1999\)](#). (b) Development of observed mineralogical sequence along the flow path of incoming silica-laden groundwater solutions. After [Thiry et al. \(2014\)](#).

Quartz is the dominant silica phase observed in thin sections of the silicified domains. Chalcedony is sparse. Opal is only a minor component and, where associated with fine microcrystalline quartz, it cannot be identified with confidence. Quartz crystal sizes range from tiny microcrystals <1 μm in size to euhedral crystals up to 500 μm. Clear silicified zones devoid of calcite inclusions are composed of microcrystalline quartz, or larger flamboyant crystals of poorly crystallized quartz (as determined by XRD), the undulose extinction of which indicates lattice distortion. On the other hand, larger euhedral crystals with straight extinction have sharp diffraction lines typical of well crystallised quartz. In places, the euhedral quartz exhibits striking brown ribbons with low refractive index that mark successive zones of growth and which have optical characteristics of remanent opal within quartz. They may relate to layers of opal or nanocrystalline quartz that precipitated periodically within the growth stages. The overgrowths interlayered with ribbons are like those described in the quartzites of the Sable de Fontainebleau ([Fig. 9a](#)) and other sand formations. They also recall quartz crystals occurring in chert which, in scanning electron images, exhibit growth steps of compact quartz texture separated by bands of tiny opal nanoglobules ([Khalaf et al., 2020](#)).

Additionally, it should be noted that secondary calcite crystals with inverse rhombohedron habit were precipitated in some voids both before they were infilled with silica, as well as after silica had been deposited. These are linked to the same groundwaters that deposited the silica and indicate that the precipitation of silica and calcite may have occurred concomitantly.

### 5.3 Origin and distribution of silica

The volumetric importance of silica filling pre-existing voids demonstrates an absolute accumulation of silica. The limestones hosting the silicification do not contain clay or sand interlayers, or siliceous fossils, and were never deeply buried ([Cayeux, 1929](#)). Thus, the silica was imported from elsewhere, most likely originating in other formations (for example, overlying sandstones, loess or soils), and introduced in groundwaters. As we have argued in the case of quartzites in sand formations and silica pseudomorphism of gypsum, sustained flow of incoming

groundwaters would have been required to continuously replenish the silica precipitating from solution.

#### 5.3.1 Silicification vs hydrology

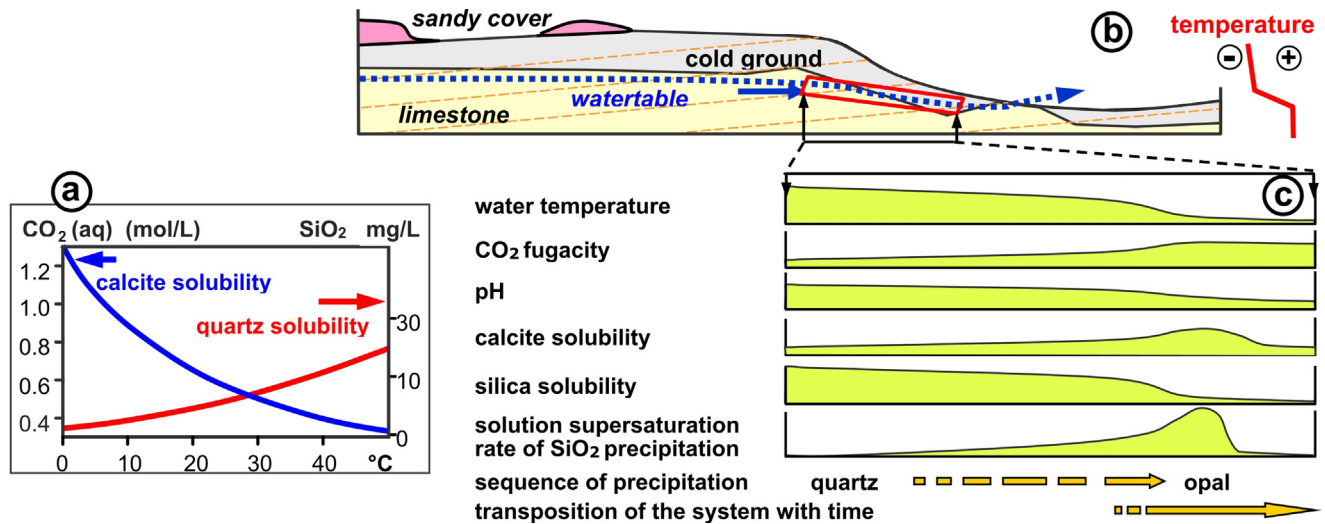
Our petrographic observations indicate that silicification was most intense in wider fractures and voids where the groundwater flow rate was significant and less intense in restricted fractures and smaller voids where the flow rate was constrained. At the regional scale, silicification appears to be more intense towards the base of the limestone units or, more precisely, just above marly and clayey units. The latter, which currently support a perched water-table with sustained flow rate, could well have done so in the past ([Fig. 4](#)).

The formation of silica cutans completely lining voids points to a water-saturated environment. We suggest that silicification occurred in the water table along drowned flow paths. However, as distinct from silicification in the sand formations, silicification does not form extensive horizontal levels because karst features in the limestones have complicated the groundwater flow paths.

#### 5.3.2 Replacement of limestone matrix

Replacement of the matrix by silica, with conservation of texture and fabric, indicates that the precipitation of silica and dissolution of calcite occurred simultaneously. Whatever the geochemical trigger mechanism, the incoming solution must have been undersaturated with respect to calcite and saturated with respect to quartz at the same time and in the same place. This suggests that a particular coupling or feedback mechanism was operating ([Fig. 19a](#)). The crystallization pressure of quartz on calcite is a likely driving force for this replacement, as argued by [Maliva and Siever \(1988\)](#) and [Dewers and Ortoleva \(1990\)](#). This does not prevent local precipitation of secondary calcite crystals, such as those with inverse rhombohedron habit, in some voids.

The transfer of chemical species between the voids and the replacement front probably proceeded via diffusion along fluid films on grain boundaries. The extent of the diffusion would have limited the extent of silica replacement. The longer the distance between the void and the silicification front the lower the diffusion gradient, ultimately leading to slowing and cessation of the process ([Thiry and Ribet, 1999](#)). In some samples void



**Fig. 20.** Geochemical model of limestone silicification during glacial periods. (a) Opposite solubilities of quartz and calcite in water in relation to temperature. (b) Conceptual model of hydrological and thermal arrangements. (c) The interface between cold subsurface and warmer groundwater triggers both precipitation of silica and concomitant microkarstic dissolution of the matrix in the host limestone. Several self-organizing processes explain numerous field and petrographic characteristics of the chert layers.

infillings are well developed and matrix replacement is limited whereas in other samples the opposite is true. This may relate to local variability in the porosity of the limestone matrix as well as the state of silica saturation in the solution.

### 5.3.3 Silica deposits in voids

All deposits of silica in pores and fractures follow a similar mineral succession starting with cryptocrystalline forms and progressing towards better developed crystals and, ultimately, euhedral quartz. This mineral sequence is likely to reflect the changing degree of silica supersaturation in the incoming groundwater solution (Thiry *et al.*, 2015; Khalaf *et al.*, 2020).

Amorphous forms of silica precipitate from source solutions that are supersaturated in silica and generate abundant nuclei that have a high growth rate (Fournier, 1985; William and Crerar, 1985). Precipitation of silica from solutions that are less supersaturated generate a limited number of nuclei and thus the slow growth of large quartz crystals is favoured (Delmas *et al.*, 1982; Williams and Crerar, 1985). The composition of the solution plays an important role: incoming groundwaters can become charged with cations and anions from interaction with regolith materials and so precipitate ‘poorly’ crystalline silica. As this silica progressively fills pores and fractures, the abundance of impurity ions from limestone dissolution are reduced and more crystalline forms of silica are formed (Thiry and Millot, 1987; Thiry *et al.*, 2015). High degrees of supersaturation reflect large and rapid changes in the physico-chemical properties of the solution whereas low degrees of supersaturation indicate more subtle and progressive changes. The striking brown opal ribbons that mark successive zones of growth appear as testimonies of successive short lived and recurrent episodes of rapid changes in the physicochemical properties of the solution.

Although the content of impurity ions and supersaturation both affect the sequential development of silica mineral forms,

this pattern in time will also relate to a pattern in space in response to a gradient in geochemical conditions along the flow path of the groundwater, especially in terms of host rock temperature variations (Fig. 19b). This would explain why the silica deposits systematically progress towards more crystalline and less soluble phases, rather than fluctuate in crystallinity as would be expected if the composition of the incoming solutions was the primary control.

### 5.4 Geomorphological context and environmental conditions

Our model for silicification of limestones in the Paris Basin assumes that the silica was introduced in appreciable volumes of water passing through the limestone formations. The hydrodynamic conditions required for a sufficient silica supply could only be met if a consistent groundwater through-flow was achieved after the limestone formations were uplifted and the landscapes incised by streams. These environmental and geomorphological conditions are the same as proposed for formation of quartzite pans within sand formations in the Basin. However, whereas quartzites in the sand formations were restricted in their development to scarps and valleysides where groundwaters discharged into the stream networks, the disposition of the scattered silicified zones in the limestones in relation to geomorphology is more difficult to determine. Firstly, karst hydrology in the limestones is likely to account for the distribution of silicified domains at the outcrop and thin section scale. On this basis, because karst hydraulics are characterised by tortuous and complicated flow paths compared with homogenous and linear flows in sand aquifers, it is not possible to assign relative age relationships to the silicified limestone masses or to determine if there are one or more episodes of silicification. Secondly, compared with quartzite pans, for example in the Sable de Fontainebleau, silicified domains in the limestone formations are difficult to recognize in outcrop and not easy to map.

Nevertheless, some geological studies linked silicified limestone and landscape morphology long before the relationship of quartzite pans with outcrops in the Sable de Fontainebleau was described. In the eastern Paris Basin, [Hatrival et al. \(1988\)](#) stated that silicification of the limestone in the northeast of the Brie Plateau was more significant along plateau edges because it had been outcropping for a longer time. [Turland \(1974\)](#) also noted that silicification of limestone on the southern edge of the Brie Plateau appeared to be better developed near outcrops on the plateau escarpments and in the upper parts of the limestone. Moreover, [Cayeux \(1929\)](#), who considered Meulières to be weathered silicified limestones, recognised that the maximum development of Meulières occurred east of Paris on either side of the Marne valley and along the Ile-de-France cuesta, as shown in [Figure 4](#). In the western Paris Basin, the notes on geological maps indicate that cherts in the Calcaire de Brie crop out on the flanks of the Yvette and Seine Valleys, whereas there is no mention of chert in this formation in logs of drillholes beneath the neighboring plateaux ([Fig. 4](#)). Thus, there could potentially be a link between silicification of limestone and the depth of landscape incision.

We suggest that the limestones were silicified under similar conditions and at a similar time to quartzite formation in the Sable de Fontainebleau and that the precipitation of silica from inflowing groundwaters was triggered by a fall in temperature (chilling) during cold climate periods. We have noted that secondary calcite crystals with inverse rhombohedron habit precipitated in some voids before they were infilled with silica, as well as after silica had been deposited (see [Supplementary File#3](#)). As shown in [Figure 20a](#), silica and calcium carbonate behave in opposite ways under these conditions, the solubility of silica decreasing with decreasing temperature whereas that of calcite increases because of the increase in solubility (fugacity) of CO<sub>2</sub> gas. This opposite behaviour explains how calcite can be replaced by quartz and reflects the antagonistic behaviour of calcite and quartz which has long been observed by petrographers ([Cayeux, 1929](#); [Hesse, 1987](#)).

Our hypothesis is that groundwater flowing through the lower parts of the limestone just, above an aquiclude formed by underlying marly and clayey formations, encountered cold ground at or near local or regional discharge zones ([Fig. 20b](#); *cf.* [Fig. 11b](#)). This led to (1) a drop in temperature of the groundwater solution; (2) a decrease in silica solubility and supersaturation of the solution; (3) a slight increase in aqueous CO<sub>2</sub> and a correlative decrease in pH; and (4) microkarstic dissolution of limestone ([Fig. 20c](#)). In detail, we suggest the following.

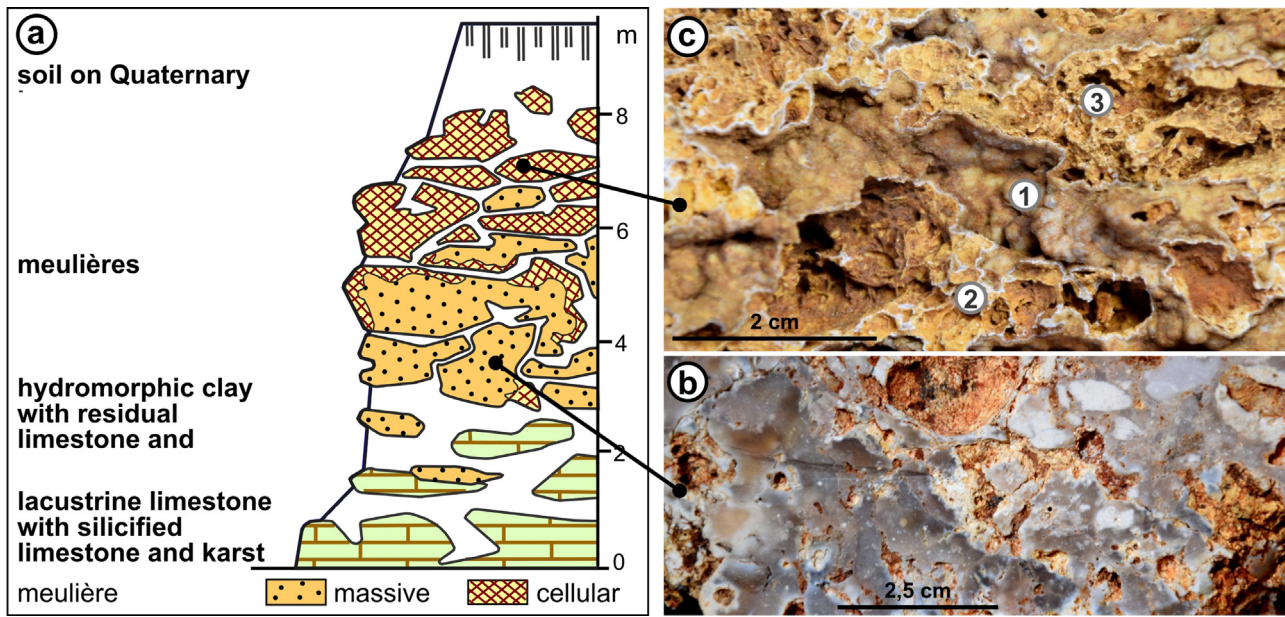
- Groundwater cooled progressively as it approached the cold ground. Cooling was rapid as it entered the cold front but probably ameliorated as a temperature equilibrium was established between the heat carried by groundwater flow and the thermal inertia of the cold ground.
- Quartz precipitated progressively from groundwater that was weakly supersaturated in silica as it approached the cold ground. Downstream, amorphous silica or poorly ordered silica minerals precipitated as supersaturation of silica increased as a consequence of increasingly rapid cooling of the groundwater at the cold front. Further downstream the groundwater became exhausted in silica and it was no longer precipitated.

- Subsequently, as groundwater flow continued, the groundwater warmed the host limestone and the supersaturation gradient moved downstream. Precipitation and growth of quartz crystals coated former opal deposits (*cf.* [Fig. 19b](#)).
- Opal ribbons inter-laminated within successive quartz growth zones may reflect some rapid and short-term upstream shift of the cold front likely due to a diminution of the groundwater flux, which in turn could have led to a decrease in the thermal input.
- A slight decrease of the pH at the cold front triggered some microkarstic dissolution of the limestone matrix. This additional porosity maintained groundwater flow and further silica precipitation that helped to achieve limestone replacement by silica. Leaching of limestone re-equilibrated the solution and microkarstic dissolution did not continue downstream.

A coupled mathematical reaction-transport model was developed by [Thiry and Ribet \(1999\)](#) to simulate the silicification. It specified physico-chemical conditions in order to examine the influence of the various interrelated factors and generate a quantitative explanation of the phenomenon. The modelling established a mass-balance listing of all imports and exports of a chemical species either by advection (flow) diffusion or precipitation (dissolution). Kinetic laws of calcite dissolution and quartz precipitation were considered to govern the rate of the process. Several points were clarified.

- The kinetics of quartz precipitation define the limits of limestone replacement by quartz whereas the diffusion of the dissolved species seems to restrict calcite dissolution. There is a feedback mechanism that limits calcite dissolution and the development of voids in the limestone matrix.
- When only the kinetics of quartz precipitation and calcite dissolution are taken into account, the balance between calcite dissolution and quartz precipitation occurs if the solution is close to equilibrium with calcite. The thickness of the zone in which replacement of calcite by quartz is possible depends on the calcite dissolution rate.
- A calculation made with plausible values of different parameters (number of nuclei, kinetics, solution geochemistry, and no major supersaturation and opal precipitation) suggests that the development of a halo of silicification about 500 μm wide around a void could take between 10,000 and 100,000 years. The model also suggests that the void would be filled with precipitated quartz in approximately the same time as it takes to form the silicified halo. This time span is compatible with the geological constraints for the development of a groundwater flow capable of bringing silica into the limestone formation.

In summary, ‘cherts’ in Paris Basin lacustrine limestones were originally thought to result from the concentration of silica in evaporative environments, mostly during limestone deposition, but the absence of any reworked material in younger formations was never expressly raised. The difficulty in explaining syn-depositional silicification from geochemical and hydrochemical points of view has often been raised informally. However, questioning the syn-depositional idea has always stumbled at the need for an alternative model. Even though the limestones represent different environments of



**Fig. 21.** Weathering features within the Argile à Meulières profile. (a) Macromorphological organisation of the Argile à Meulières profiles. The meulières develop from the silicified limestone by dissolution of the residual limestone domains to form the highly porous ‘cellular’ facies. Modified from [Thiry \(1999\)](#). (b) Lower massive meulière with secondary silica coating (vitreous-waxy quartzose lustre) on a fracture through micronodules of silicified limestone parent; Bouchy-St-Genest (Marne). (c) Upper cellular meulière facies showing: (1) primary concretionary silica lining voids of silicified limestone to form (2) thin contoured walls, and (3) porous and powdery infilling of hollows resulting from the dissolution of discontinuously silicified limestone matrix; Brie Plateau, St-Cyr-sur-Morin (Seine-et-Marne).

deposition, paleoclimate and age, all silicified limestones are remarkably similar in terms of form and appearance in the field, facies and fabric. Only after linking the formation of quartzite pans and lenses in the Sable de Fontainebleau to groundwater silicification during glacial periods, as in our model, has it been possible to consider this hypothesis for silicifications in other outcropping formations in the Paris Basin, including the limestones.

## 6 Meulières: weathered silicified limestones

*Meulières* (millstones) is the name given to a particular facies of cavernous siliceous rocks that formed as a result of weathering of silicified lacustrine limestones in the Paris Basin. The most intriguing feature of the meulières is their cellular aspect. The typical meulières consist of a framework of thin (less than 1 mm) siliceous plates that surround empty centimetre-sized cells and result in a rock having a very low density. Despite the size of the cells, and more than 50% porosity, meulières have a low permeability because most of the cells are sealed or are linked only to a few of their neighbours. Meulières are generally embedded in variegated clay and the formation as a whole is called ‘Argile à Meulières’. The Argile à Meulières is generally considered to be a Plio-Pleistocene weathering product of silicified lacustrine limestone. The most recent review of this facies was by [Ménillet \(1987\)](#) and we refer to much of his work here.

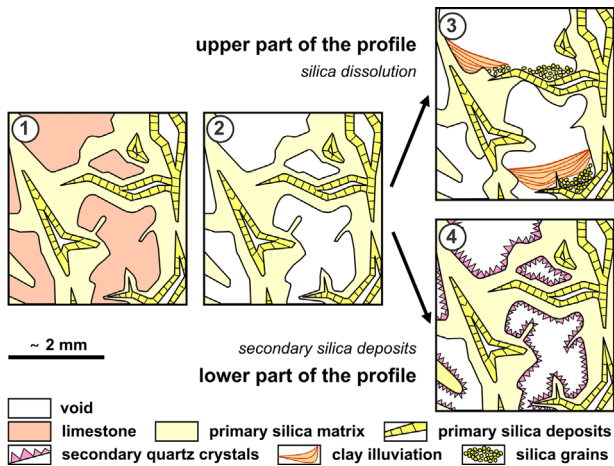
## 6.1 Field relationships

### 6.1.1 Geological setting

The Argile à Meulières Formation marks old plateau surfaces in the southern Paris Basin ([Figs. 1, 2 and 4](#)): (1) the Plateau de Beauce, armoured by Calcaire de Beauce (Miocene); and (2) the Plateau de Brie, where the Argile à Meulières rests on the Calcaire de Brie (early Rupelian) and cuts eastwards across the underlying Argile Verte and then the Calcaire de Champigny (Priabonian). The Beauce Plateau, together with the outliers on its northern extension, form the primordial surface of the Paris Basin. The Brie Plateau is a former marine abrasion surface (Sable de Fontainebleau, Rupelian) that has only relatively recently been exhumed from its sedimentary cover ([Lutaud, 1948](#)). West of the Seine, at the foot of the Beauce Plateau escarpment, the exhumation is younger and continues today.

On the Plateau de Brie, the Argile à Meulières is discontinuous and missing in areas where the Calcaire de Brie is at its maximum thickness ([Fig. 4](#)). On the other hand, it is well developed where it rests on underlying clayey facies (Argile Verte and marls of the Calcaire de St-Ouen). There are generally thicker profiles and more mature facies of the Argile à Meulières on outliers of the Beauce Plateau which has a longer period of regolith evolution than the more recently exhumed Brie Plateau ([Ménillet, 1987](#)).

On the outliers of the Plateau de Beauce in the northwest, the meulières locally include sand grains of the Late Pliocene



**Fig. 22.** Schematic showing development of the meulière facies. Dissolution of residual limestone patches (1) generated at first a cellular facies (2). There are two subsequent evolution paths. In the upper part of the profile (3), the silica framework inherited from the silicified limestone was progressively dissolved, voids enlarged, and illuviated clay infiltrated some hollows. In the lower part of the profile (4), secondary euhedral quartz was precipitated in the voids. Adapted from Thiry (1999).

Sables de Lozère (Ménillet, 1987) and thus post-date the deposition of the Sable de Lozère. On the Brie Plateau, the Argile à Meulières Formation is consistently missing beneath the Sable de Fontainebleau indicating that it post-dates exhumation of the plateau (Cholley, 1960; Grisoni, 1979; Turland, 1974; Ménillet, 1987). The Argile à Meulières Formation on the residual buttes of Sable de Fontainebleau in the centre (Paris) and northern edge of the Paris Basin is related to the Beauce Plateau meulières (Fig. 4).

The Argile à Meulières is a heterogeneous formation, rather discontinuous and from 2 to 10 m thick. The meulières occur as siliceous blocks from decimetre to several tens of metres in diameter, irregularly shaped, within a clay or sand matrix that is variegated red, ochre or grey in colour. The blocks often have cell-like hollows infilled with brown sandy clay (see Supplementary File#4). The precursors of all Argile à Meulières facies are the silicified lacustrine limestones of the Paris Basin. Weathering and karst development within these limestones has exposed the meulières. As the limestones generally have very little insoluble residue, the host brown sandy clay has been either derived from the overlying loess and sand or inherited from the underlying clay and marl formations.

### 6.1.2 Profile description

In most localities, the Argile à Meulières overlies a lacustrine limestone which contains numerous microkarst dissolution features. Elsewhere, it can overlie clay formations, such as the Argile Verte, or even sand formations like the Sable de Fontainebleau, where all of the parent limestone has been removed by dissolution. A systematic vertical arrangement of macro-morphological features can be distinguished in profiles (Fig. 21a).

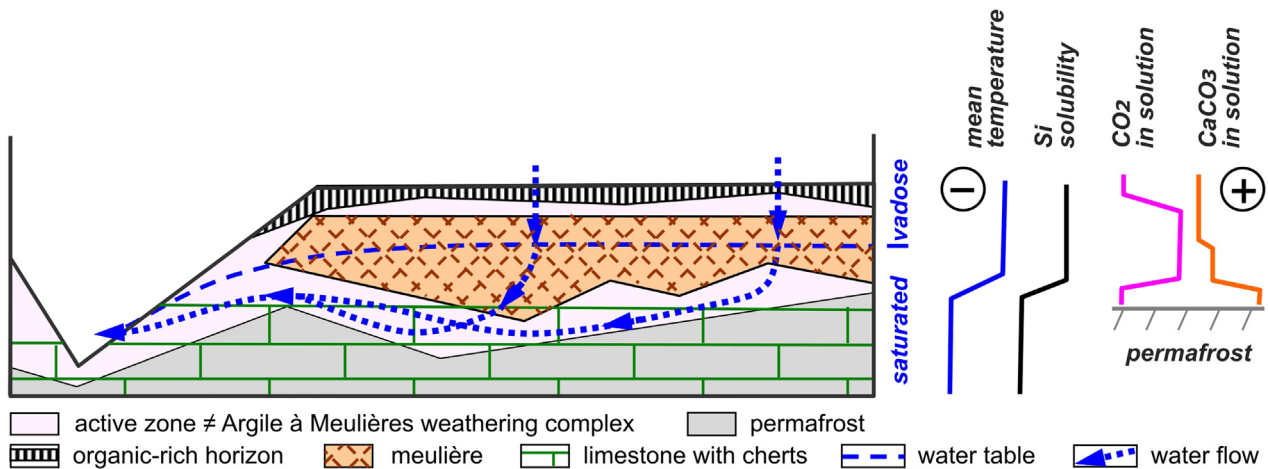
- At the base there is generally a clay horizon with residual limestone boulders and silicified limestone masses. Metre-size collapse structures relating to karst dissolution features in the underlying limestone are common.
- The lower part of the siliceous horizon (massive meulières) is made up of compact silica-rich masses in brown clay: they are of irregular shape and vary from 0.5 to several metres in diameter. They generally have a dull lustre but can be slightly translucent and are light in colour (white, yellowish or even greenish). A scoria-like rim surrounds the siliceous masses and also occurs along joints (Fig. 21b). The brown clay displays numerous illuviation features.
- The upper part of the siliceous horizon (cellular meulières) consists of porous or cellular siliceous masses (pale yellow to ochre in colour) within variegated illuvial clays (Fig. 21c). The siliceous masses are horizontally elongated slabs, 0.5–1 m thick at the base of the horizon but smaller (0.1–0.5 m in diameter) and irregularly shaped towards the top.
- The meulières do not usually crop out at the landsurface but are covered by a blanket of Quaternary loess and soil, or even an organic-rich and iron-stained hardpan (*grisons*) containing weathered silica-leached clasts of meulières.

### 6.2 Successive weathering steps

Petrographic data from Thiry (1999) indicates that the first stage of weathering produced karst features in the silicified limestone. The residual silicified domains, enclosing some remnant limestone, became surrounded by sands and clays infilling the karst voids. The resulting complex constitutes the Argile à Meulières Formation. Ongoing alteration has expression at various scales from top to bottom of the profiles as well as from the outer fringes of the silicified masses towards their inner cores (Fig. 22; see Supplementary File#4).

- In the first instance, in the upper parts of the profiles, there was progressive decalcification of remnant limestone within the silicified domains leaving numerous irregularly shaped secondary voids and thus very porous siliceous masses (Fig. 22, 2).
- In the upper parts of the profile there was also some dissolution of the primary silica matrix. It started with the least well crystallised silica phases (opal and micro-cryptocrystalline quartz) and resulted in the formation of micropores. Progressively, weathering dissolved almost all the silica matrix leaving only palisadic quartz lining primary voids (Fig. 22, 3). This produced a very porous siliceous mass of cellular appearance. Further dissolution led to breakage and collapse of the primary silica framework and available voids were infiltrated with sand.
- In the lower parts of the profile, the inherited silicified limestone structures have been further modified by new deposits of secondary silica (most obviously euhedral quartz crystals and sometimes chalcedony) in the secondary voids (Fig. 22, 4). There is no evidence of precipitation of secondary quartz in primary voids which are lined with palisadic quartz that form a sealed siliceous shell.





**Fig. 23.** Conceptual model of hydrological and thermal conditions within the Argile à Meulières during Quaternary glacial stages. The interface between a warmer near-surface zone and permafrost at depth could account for precipitation of silica. Concomitant limestone dissolution in the saturated zone could be related to acidity enhanced by bogs and podzols of the tundra environment.

Microcrystalline silica is likely to have precipitated in the matrix of the siliceous masses but we have not observed this.

- Clays were illuviated into hollows in the outer fringes of the resulting meulières blocks and setts forming distinctive laminar deposits. Initially, clays were illuviated into primary voids rimmed with palisadic quartz but later infiltrated large dissolution hollows where clay laminae covered and sealed residual deposits of sand grains in the base (Fig. 22, 3).

### 6.3 Geomorphological context and environmental conditions

It is well established that the Argile à Meulières Formation on morpho-structural plateaux in the Paris Basin is of post-Pliocene age (Cholley, 1943; Lutaud, 1948; Ménillet, 1987). However, the mechanism for precipitating the silica has never been adequately identified. Post-Pliocene paleoclimatic conditions as well as field observations negate a mechanism of silica concentration by evaporation. A concept of releasing silica by weathering of illite and smectite into kaolinite has also been proposed (Prost, 1961) but is not convincing because the mass balance between weathered clays and secondary silicification in the lower horizon of the Argile à Meulières Formation is not satisfied. It has also been proposed that a redistribution of silica between silica leaching in the upper part of the profile and re-silicification in the lower part could be a likely mechanism (Ménillet 1987) but the trigger for precipitating silica was not addressed. If silica redistribution is a response to lower and higher degrees of saturation of groundwaters, proximity to a cold front could be the trigger for silica precipitation.

The hydrology of the Argile à Meulières formation exhibits a combination of features typical of both vadose and phreatic environments. The upper part of the profile contains illuviated clay deposits which indicate downward percolation of infiltrating waters through a non-saturated, vadose realm. On the other hand, palisadic quartz cutans lining dissolution voids in the lower part of the profile are

characteristic of a water saturated phreatic groundwater environment. This combination of features could correspond to the arrangement of an active zone composed of a non-saturated zone, with summer infiltrations, and a deeper frozen zone (therefore a permanent aquitard at a relatively regular level) likely to cut across the lithological units (Walvoord and Kurylyk, 2016).

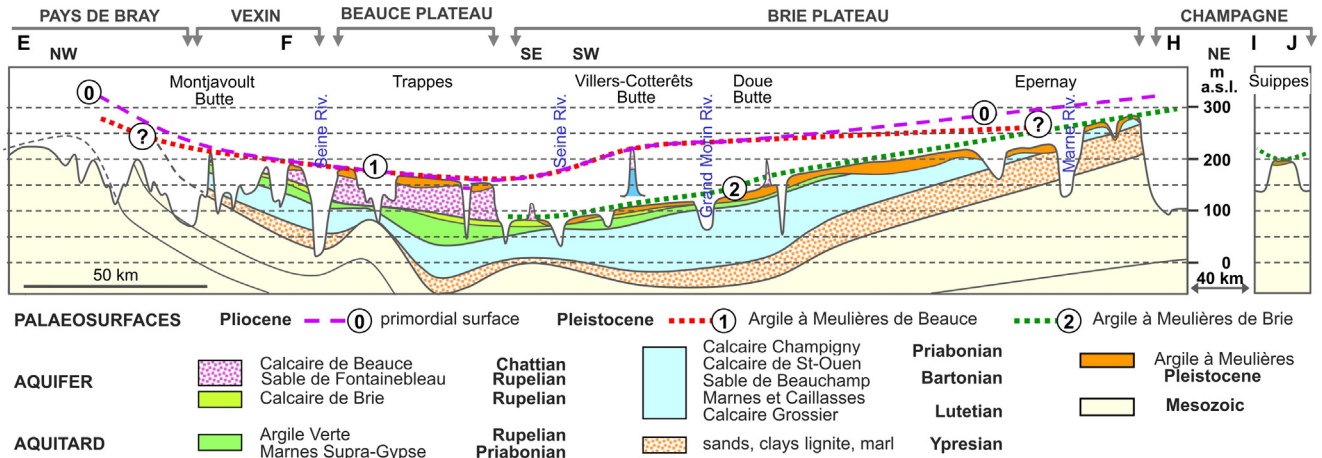
Silica redistribution, specifically dissolution in the upper parts of the profile and precipitation near the base, could have been a response to infiltration in the upper unsaturated parts of the profile and precipitation below induced by proximity to the cold front bound to permafrost (Fig. 23).

The masses of silicified limestone at the base of the meulières profiles in areas that have been exploited for the manufacture of grinding wheels are commonly very large and up to 2-4 m thick and contrast with the relatively disparate silicified masses in limestone in quarries. This is conceivable if the top of the limestone formation was part of the active zone of permafrost and was silicified supra-permafrost by groundwater flow. Such masses would thus have the same characteristics as groundwater silicified limestones below the permafrost.

These hydrological conditions and related weathering phases may have repeated and their effects accumulated over successive glacial periods. The thicker profiles on the NW of the Plateau de Beauce and the NE of the Plateau de Brie plateau occur on the oldest exposed surfaces.

### 6.4 Structural and hydrological arrangement

A geological section equivalent to that of Figure 4 but extended to the western and eastern edges of the Paris Basin allows us to delineate the extension of the Argile à Meulière surfaces and to discuss their evolution and their hydrological behaviour (Fig. 24). The current geomorphology was formed after deposition of the Sables de Lozère during the Pleistocene, at least in the southern part of the basin (Larue and Etienne 2002, Cojan *et al.*, 2007). It is possible that in the north the basin had experienced earlier erosion.



**Fig. 24.** Geological section through southern edge of the Paris Basin to western and eastern borders (extension of section Fig. 4) showing the hydrological characteristics of the Tertiary formations and the extent of the geomorphological surfaces related to the Meulière units. Data sources: InfoTerre (2023); Alloué (2016).

The thickness of the Argile à Meulière is directly related to the uplifted edges of the basin. The Argile à Meulière de Beauce disappears with distance southward from the northern edge of the Beauce Plateau and reaches its maximum thickness (more than 8 m at Trappes) on the NW edge of the plateau, that is to say on the piedmont of the Bray anticline (Fig. 24). Similarly, the Argile à Meulière de Brie is the thickest on the eastern edge of the basin (La Ferté-sous-Jouarre), near the raised edge of the basin, and decreases in distal parts against the escarpment of the Beauce Plateau. The Argile à Meulière is discontinuous and thinner in this area but also younger, according to the timing of exhumation of the Brie Plateau (Fig. 24). There is likely to be an impact of hydrological flow dynamics induced by recharge from the raised regions of the plateau edges. In other words, we suggest that the thickness of the Meulière profiles is related to the mass balance of the nourishing groundwater, probably starting with the formation of the silicified limestones and their later secondary silicification within the Argile à Meulière.

It should also be noted that both the upper and lower level Argile à Meulière seem to record opposite hydrological characteristics: pervious Sable de Fontainebleau for the upper Meulière de Beauce and impervious Argile Verte for the lower Meulière de Brie. In fact, placed in a periglacial context, both Argile à Meulière levels could have surmounted a frozen horizon that acted as an impervious layer.

## 7 Summary

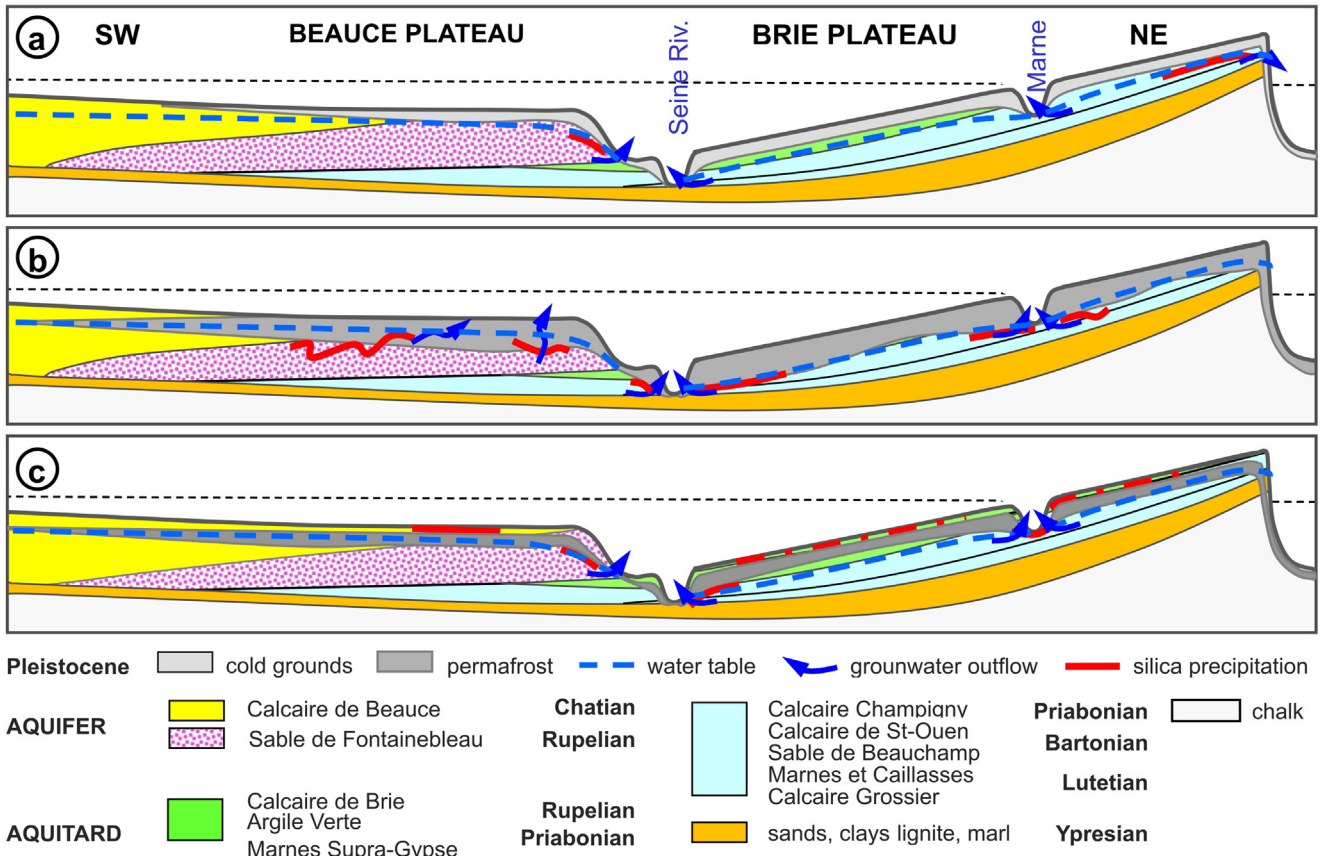
In the first instance we confirm that all silicifications within the Tertiary formations of the Paris Basin that are the subject of this study were formed as a result of absolute accumulation of silica manifested by deposition and crystal growth in pores and voids. This required a continuous flow of solution containing silica, part of which precipitated cumulatively over a relatively long period of time, depending on the flow rate and the amount of precipitated silica per unit volume. The links we identify between silicification of sands, gypseous formations and

Quaternary geomorphology, as well as the links between Meulière and extensive post-Miocene plateaux, promote a mechanism related to cooling of groundwaters in regolith environments. This causes an exponential decrease in the solubility of silica and is a very efficient mechanism for triggering its precipitation. In this context, water flowing from a warmer to a cooler aquifer could continuously deposit silica against the cold front.

### 7.1 The various kinds of silicification

Figure 4 shows the distribution of the various types of silicification in a geological section through the southern edge of the Paris Basin. Our studies originated from work on the tightly cemented quartzite pans within uncemented Sables de Fontainebleau. A relationship between the quartzites and landscape morphology indicates a Plio-Quaternary age. This is supported by studies of Fontainebleau sand calcite crystals, some of which are locally encased within the quartzite pans and therefore predate the silicification (Thiry et al., 2021). Coherence of our data on the Sables de Fontainebleau and observations made in different sand formations elsewhere in the Paris Basin reinforced our arguments for silicification by groundwater flows during well-documented Pleistocene cold periods. Several particular and peculiar structures (convoluted and spindle-like quartzite masses) have previously been difficult to explain but we now consider that the silicification responsible could be linked to constrained groundwater flows beneath permafrost. Other unusual forms (gogottes and silica deposits on fractures) appear to be due to precipitation of silica from percolating water in vadose environments, possibly in periodically thawed active zones above permafrost.

Our model for silicification of sands can be applied to the silicification of gypsum in that it could account for the spatial distribution of silicified gypseous formations and be related to glacial periods. It could also explain the paragenesis of dissolution of limestone formations and concurrent precipitation of calcite together with silica and is reinforced by the association with calcite of inverse rhombohedron habit ('cold calcite'; Ezikova, 1958).



**Fig. 25.** Conceptual model of hydrological and thermal arrangements within Paris Basin plateaux during Pleistocene glacial periods. (a) At the beginning of the cold period the chilled grounds remained relatively thin and approached the water table level only in its shallowest areas, near springs. (b) With the cold period ongoing, permafrost developed, and the upper parts of the aquifers froze, resulting in overpressures causing ‘forced’ flows along the undulating base of the permafrost and through cracks and taliks. (c) With climate warming the permafrost thawed at its base and at its top. The active layer thickened. A superficial groundwater formed above the permafrost and flowed towards the lowland area. Note that the gradient of the water table and thickness of the permafrost appear reduced on plateau edges due to an extended vertical scale vs horizontal scale.

In terms of the lacustrine limestones, the large volume of silica crystallized in voids demonstrates that significant amounts of water containing silica in solution must have flowed through them. The omnipresence of isotropic cutans around voids points to phreatic environments. We suggest that these conditions could only be fulfilled after the limestones were uplifted and incised to create the necessary hydraulic gradient for groundwater flows. As in the case of quartzites formed by silicification of sands, the absence of an appropriate trigger mechanism to induce silica precipitation in the limestones led us to propose a model in which there was significant cooling of groundwater solutions close to a cold front during glacial periods. It is thus possible to conceive of the dissolution of limestone during silicification and to explain how the ‘compactness’ of the cherts was achieved. We suggest that the groundwaters may at times, or in certain locations, have been confined by impervious permafrost.

For Meulières, the question of the origin and mode of precipitation of silica remained open. From our perspective, these forms of silicification occurred in glacial environments and, more particularly, in the active layer above a permafrost. The dissolution of the silica at the top of the profiles and its

precipitation at the base is simply explained by cooling of meteoric water in contact with the underlying permafrost. As well, groundwater silicification above impervious permafrost possibly explains the exceptionally large monoliths that have been exploited: they are actually overprints of the cherts (prior silicification of the parent limestones) inherited from beneath the permafrost. In addition, groundwater flow over permafrost would have resulted in ‘planar’ decalcification that explains the systematic absence of vertical collapse, except in late and local circumstances.

## 7.2 Dynamics of the periglacial model for silicification

A schematic NE-SW section through the Brie and Beauce Plateaux (Fig. 25) is a synthesis of our model of the spatial-temporal relationships between geomorphology, hydrology and the various forms of silicification in periglacial environments. It could represent conditions during the last ice age when the geomorphology of the Paris basin was not fundamentally different from that of today. Three stages in the evolution of cold regolith are envisaged: (a) an initial stage in which the thickness of the cold ground is limited to 10–30 m;

(b) a period of maximum cooling when permafrost may have reached 50 m or more in thickness; and (c) a period of warming. We suggest that the latter would have involved thawing of the upper part of the permafrost accompanied by an increase in the thickness of the active zone and a concomitant thawing of the base of the permafrost. The genetic axiom is that silicification occurred in zones of groundwater flow to satisfy the mass balance and in response to contact between groundwater and cold ground that cooled it and triggered precipitation of silica.

- Under peri-glacial conditions, before permafrost developed, we suggest that groundwater continued to flow through the spring lines at the base of the valleys (Fig. 25a) and silica precipitated at the contact of the water table with the cold ground. This configuration is considered to be the origin of the regular and flat quartzite pans in the sand formations. Superposed levels of quartzite could reflect fluctuations of the base of the cold ground in the regolith and/or the water table. However, in limestones, groundwater flow paths were complex and heterogeneous, linked to karst structures, and silicification was sporadic and discontinuous.
- The development of permafrost led to important hydrological changes, in particular: more or less complete occlusion of groundwater outflows due to permafrost sinking below valley bottoms, and a concomitant increase in pressure within the aquifer due to volume expansion by groundwater freezing. Pressurized water flows could have occurred beneath the undulating basal surface of the permafrost, and upward through pipes and hydraulically-fractured frozen zones (Fig. 25b). These pressurized flows would explain some of the complex quartzite morphologies, particularly fusiform, spindle-shaped and tortuous quartzite walls. We suggest that these morphologies are indicative of deep permafrost below the water table. Such forms are never observed in limestones because concomitant karst drained groundwater flows.
- Climate warming and melting of the permafrost led to hydrological conditions comparable to those at the time of initiation of the glacial period in terms of groundwater outflow and silicification of horizontal quartzite slabs. But conditions would have been significantly different at the landsurface (Fig. 25c). With time and an increasing in air temperature after the glacial maximum, the thawed layer would have progressively thickened at the expense of the uppermost permafrost while substantial groundwater bodies could have existed above the underlying impervious permafrost. Significant silica deposition and limestone dissolution probably occurred along outflow zones at this time. Such supra-permafrost reactive zones are considered to have been responsible for the development of thick Meulière layers, together with the concomitant dissolution of the limestone substrate along regular horizontal surfaces.

On the basis of our studies, the disposition and evolution of permafrost in the landscape could explain most of the morphological characteristics and spatial arrangements of the diverse silicifications in the Paris Basin. All of the silicifications of the Tertiary formations in the Paris Basin can be integrated into a single coherent scheme taking into account their geochemical and geomorphological aspects and their distribution. They are

linked to the hydrology of the superimposed limestone plateaux landscapes and the associated confined or free aquifers.

The robustness of our model is yet to be established but there are many opportunities to test it on other examples of Late Cenozoic to modern continental silicifications for which there is published information on relationships and characteristics. The viability of the model will need to withstand geochemical and isotopic analysis data obtained by increasingly refined new techniques that can investigate, with increasing accuracy, ages of silicification and their links to cold environments.

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## Supplementary material

**Supplementary File#1:** Occurrences and morphologies of sand silicifications in Tertiary deposits, Paris Basin.

**Supplementary File#2:** History of the discovery of silica pseudomorphs of gypsum in the Paris region and studies of museum samples described at that time.

**Supplementary File#3:** Configuration and composition of silicified limestones ('cherts') in Tertiary deposits, Paris Basin.

**Supplementary File#4:** Meulières: weathering and secondary silicification of silicified limestone.

The Supplementary Material is available at <https://www.bsgf.fr/10.1051/bsgf/2024008/olm>.

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