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# Driving forces for the weathering and alteration of silica in the regolith: implications for studies of prehistoric flint tools.

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## Highlights

Weathering of silica responds to specific geochemical and mineralogical factors

Differential solubility of silica phases and water flux control recrystallisation

Micromorphology of siliceous materials changes over historical and geological time

Models of silica weathering proposed for paleoenvironments

**Abstract**

A range of geochemical and mineralogical factors trigger the weathering and influence the stability of various silica phases under near-surface temperatures and pressures. Based on current knowledge of the crystallochemical basis of silica behaviour in near-surface environments, the mineralogical and petrographical transformations of silica under weathering conditions in the regolith are reviewed using data from wide-ranging and detailed investigations of siliceous materials. Some of the investigations are of siliceous materials that evolved in near-surface environments over geological time and thus the weathering and alteration features are relatively clear and well expressed. Examples include weathering of tightly cemented sandstones, the formation of silica duricrusts (pedogenetic silcretes), and the weathering of flints. The various micromorphological and mineralogical forms of silica as determined by high resolution petrographic and electron-optical techniques can be related to geochemical and hydrological conditions in particular microenvironments. However, new studies have demonstrated that silica alteration and transformation mechanisms can also occur within prehistoric and historic time intervals. These are also described but are more difficult to observe, principally because of the microcrystalline character of the alteration phases and the infra-millimetric scale on which they develop.

Of many potential applications of knowledge about the near-surface alteration of silica in regolith materials and the environmental conditions under which it occurs, our studies can be used as a basis determining the provenance and post-discard history of prehistoric flint tools and artefacts, in part to determine the source of the primary raw material. We suggest that the mineralogical and petrographical characteristics of the weathering rind (cortex) of the flint (specifically the recrystallization, dissolution and deposition of the silica phases, and the spatial arrangement of surfaces that have undergone successive transformations) are related to specific and identifiable weathering environments.

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Keywords:

silica; weathering; solubility; recrystallization; flint; prehistoric artefacts;

## 1 Introduction

Rates of dissolution and precipitation of silica in weathering environments are relatively slow and few detailed investigations have been undertaken to document the outcomes of these alteration processes. Although the effective solubility of silica at room temperature was measured during the 1950's (Krauskopf, 1956; Siffert, 1967) it was twenty or more years before complementary studies were published (Marshall and Warakomski, 1980) to assist research on weathering.

Our studies undertaken over many years have examined the weathering of siliceous materials on many continents in order to illustrate the behaviour of forms of silica under different environmental conditions and go some way to explain the responsible mechanisms and the time frames in which they occurred. The alteration processes and outcomes are complex. The influence of variations that occur in microenvironments, for example the porosity of the siliceous material, the percolation rate of water through the material, and repeated mechanical shocks, are some key controls.

In this paper we review the mineralogical and micromorphological transformations of silica in regolith materials. Although these transformations have occurred in a geological time frame, new data has demonstrated that similar transformations of silica can occur much more quickly within prehistoric and historic time frames. Consequently, this information and the concepts derived may be applied in archaeological investigations where the provenance and post-discard weathering and alteration history of prehistoric flint artefacts is a recurrent question. Some initial studies have been undertaken in this context.

## 2 Crystallo-chemical basis of silica behaviour

### 2.1 *Mineralogical forms of silica*

Under near-surface conditions silica forms several minerals that differ in the spatial ordering of silica tetrahedrons. Quartz is the most common silica mineral and forms at high as well as low temperatures. Chalcedony is a microcrystalline and fibrous variety of quartz (Drees et al., 1989). Moganite (Flörke et al., 1984; Rodgers and Cressey, 2001) is a widespread microcrystalline silica-mineral (Heaney and Post, 1992) but is not commonly identified in the

descriptions of siliceous materials. Cristobalite and tridymite have a sheet-like crystalline structure (Correns and Nagelschmidt, 1933), similar to that of clay minerals, and in supergene environments they are often bound to chemical (evaporitic) deposits. Opal CT has also a sheet-like crystalline structure, with alternating cristobalite- and tridymite-like sheets (Flörke et al., 1975). It is relatively frequent in buried marine deposits and in confined continental environments. Opal is a petrographic variety of silica defined at the optical microscope level as amorphous because the crystallites are too small to be distinguished (Arbey, 1980; Folk and Weaver, 1952). It may correspond to true amorphous silica, but is most often composed of quartz, moganite, cristobalite, opal-CT, or a mix of these minerals. Amorphous silica has no crystalline organisation: silica tetrahedrons pile up in a disordered fashion and form chains limited to a few tetrahedrons.

## **2.2 Solubility of the various forms of silica**

Silica in solution forms mono-molecular silicic acid  $[\text{Si}(\text{OH})_4]$ . The solubility of amorphous silica in water is about 120 mg/L  $\text{SiO}_2$  and remains independent of the pH for values below 9 but increases strongly above 9 (Krauskopf, 1956). The solubility of all other silica varieties is lower than that of amorphous silica (Fig. 1). A fundamental law that rules geochemistry is that the most soluble phases sustain the precipitation of the less soluble ones. In this way, amorphous silica in equilibrium with a solution is able to sustain the crystallisation of every other crystalline silica variety, but these phases do not necessarily precipitate. Furthermore cristobalite, tridymite, chalcedony and all opal varieties are able to sustain the crystallisation of quartz (Garcia-Hernandez, 1981; Gislason et al., 1993; Iler, 1979; Siffert, 1967). Moreover, thermodynamic laws predict that as long as a more soluble phase is present, the less soluble phases do not dissolve, but kinetic dynamic equilibrium may partly disturb this rule. At room temperature the equilibrium between silica varieties and water is reached very slowly, sometimes only after 1 or 2 years (Dove and Nix, 1997; House and Hickinbotham, 1992; Siffert, 1967).

It should be noted that most ground waters around the world have a silica content between 12 and 18 ppm  $\text{SiO}_2$  (Garrels and Christ, 1965; White et al., 1963) that is roughly in equilibrium with clay minerals. This means that most groundwaters are oversaturated with respect to quartz (solubility 4-7 mg/L) and are thus potentially able to precipitate quartz. This

oversaturation in silica with respect to quartz is thought to result from a kinetic dynamic equilibrium since the dissolution kinetics of clay minerals are much higher than those for the precipitation of quartz (Palandri and Kharaka, 2004).

It is possible to demonstrate a specific sequence of crystallization and particular relationships between the silica phases that form in surficial regolith environments. For example, siliceous duricrusts that have formed in soils (pedogenic silcretes) and occur over wide regions of the world display several distinct horizons with systematic micromorphological and mineralogical structures (Thiry, 1999). Detailed mineralogical and petrographic studies show that silica transforms from more to less soluble phases systematically from the base to the top of the profile (Fig. 2):

opal → microcrystalline quartz → euhedral quartz

This distribution of silica phases reflects the chemistry of the solutions from which they precipitated (Williams and Crerar, 1985). Microcrystalline, amoebic and euhedral quartz in the upper horizons developed from dilute infiltrating soil water solutions that dissolved pre-existing more soluble silica phases. The leached silica migrated down towards the base of the profile and precipitated microcrystalline quartz, and ultimately opal, as a result of the progressive concentration of silica in solution by evaporation. In this sequence, each mineralogical and petrographical silica species is derived from the previous generation by in-situ dissolution and recrystallization, indicating the re-equilibration of the mineral with its environment. The recrystallizations are irreversible and ultimately favour development of quartz (Thiry and Millot, 1987).

The influence of organic compounds (i.e. humic acids, oxalic acid, alcanes) on silica solubility in the regolith is poorly known and has been generally neglected in the past. Recent studies have shown that silico-organic complexes raise silica solubility and influence dissolution kinetics (Bennett, 1991).

Additionally, the influence of temperature on the solubility of quartz is important. Quartz solubility decreases exponentially with temperature (Rimstidt, 1997, Williams et al., 1985). Between 12.5 and 0°C quartz solubility decreases to half its initial value (Fig. 3).

Also of note is the fact that structural damage in quartz caused by mechanical impact such as grinding significantly increases the potential for quartz dissolution. However, the rate of dissolution decreases exponentially as the domains of damaged quartz are selectively dissolved (Petrovich, 1981; Talbot and Kempis, 1960).

### **2.3 Stability of forms of silica vs crystallinity**

The crystallinity of the various forms of silica relates to the geochemistry of the solution from which they precipitated. Solutions with a high silica content favour the blooming of crystal nuclei and crystal defects that restrict the growth of crystals and consequently amorphous or low crystallinity silica varieties will form (Lee, 2007a). On the other hand, in dilute solutions, the number of nuclei, as well as impurities, remains limited. As a consequence, elementary crystallites form regularly and large quartz crystals develop or, under less favourable conditions, microcrystalline or fibrous silica varieties are formed.

An empirical relation exists between the stability (the reverse of solubility) of silica varieties and their degree of structural order and crystallinity. Large silica crystals, which have few structural defects, are the most stable; for example euhedral quartz and quartz overgrowths on matrix grains. Silica varieties such as opal (formed of nanoquartz), microcrystalline quartz, moganite and fibrous silica varieties with numerous structural defects form small elementary crystallites (coherent crystal domains). They are relatively more soluble than quartz, in terms of thermodynamic solubility and kinetics (Gislason et al., 1993; Williams et al., 1985), and so the microcrystalline silica varieties, especially moganite, are preferentially dissolved in the first stages of weathering (Gislason et al., 1997) (Fig. 4).

Silica solubility may even vary within a single crystal due to domains of various degrees of crystallinity: increased crystallinity correlates with a larger size of the coherent (without defect) domains of its atomic arrangement, or is inversely proportional to the frequency of crystal defects. The variation in crystallinity of quartz, for example, can be evaluated by several methods (Graetsch et al, 1987; Herdianita et al., 2000b; Lee, 2007a; Moxon et al., 2006; Murata and Norman, 1976; Smykatz-Kloss, 1972) including the full width at half-maximum intensity of an X-ray diffraction band, the intensity of peaks in X-ray diffraction patterns (quantitative



analyses), and the sharpness/intensity of the thermal transformation of quartz- $\alpha$  into quartz- $\beta$ <sup>1</sup> as determined by Differential Thermal Analysis (DTA).

Detailed studies of the quartzite pans of the Fontainebleau Sandstones show the relationship between solubility and crystallinity. These pans are tightly cemented and have a friable rim that results from partial dissolution of the quartzite (Thiry, 1999). As clearly indicated in thin sections (Fig. 5), the dissolution preferentially affects overgrowth quartz aureoles: primary quartz grains are hardly ever corroded (Thiry et al., 1984). This contrasted dissolution behaviour highlights the occurrence of two different kinds of quartz crystals in the quartzite, although there appears to be no distinction between primary quartz grains and secondary quartz overgrowths in the optical microscope. The overgrowth quartz, which precipitated at low temperature within a near-surface water table, has a higher solubility than the inherited magmatic quartz grains, presumably because the former has a lower crystallinity and more structural defects than the primary quartz.

It is widely observed in diagenetic and weathering environments that successive transformations of silica phases generally results in increasing crystallinity and decreasing solubility (Goldstein and Rossi, 2002; Graetsch and Grünberg, 2012; Knauth, 1979; Lee, 2007b; Willey, 1980; Williams et al., 1985). Once precipitated the silica crystal begins to increase in size, resulting in a decrease in surface defects and a more compact structure (Moxon et al., 2006).

Understanding the relationship between crystallinity and both stability and solubility of the various forms of silica, based on laboratory data, provides the basis for interpretations of the behaviour of silica in natural systems.

### **3 Spatial and temporal aspects of weathering and alteration of silica in near-surface environments**

In natural systems silica generally behaves in a much more complex way than in laboratory experiments. This is mostly due to the specific spatial distribution of the various forms of silica in relation to water flows and because weathering and alteration reactions occur

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<sup>1</sup> Quartz- $\alpha$ , the form of quartz at normal temperatures, transforms reversibly into the high temperature form, quartz- $\beta$ , at 573°C and the nature of this transition reflects the crystallinity of the original quartz.

according to changes in ground water (and soil water) chemistry and conditions. Thiry and his colleagues have undertaken detailed investigations of several examples of the development, weathering and alteration of siliceous materials in the regolith in Europe and Australia, focussing particularly on mineralogical and micromorphological features (Thiry, 1999; Thiry and Maréchal, 2001; Thiry and Milnes, 1991; Thiry et al., 1988; Thiry et al., 2006). Here we review examples of weathering and alteration in France that illustrate the complex of spatial and temporal processes.

### **3.1 Weathering and alteration of silica in outcropping sandstones**

Numerous outcropping sandstones around the world show specific weathering features at their surface and provide invaluable information about weathering of siliceous materials (Willems et al., 2002; Wray, 1997; Young and Young, 1992).

For example, in outcrop, quartzite pans in the Fontainebleau Sandstone break down and yield quartzite blocks that progressively acquire rounded dome-like morphologies (Thiry, 2005; Thiry et al., 1984). The domal structures are often coated with a 0.5 to 2 cm-thick hardened silica crust (Fig. 6a). The crust is restricted to the top of the domes, and does not occur on lower parts or on overhanging surfaces. The crust appears in relief as a result of differential alteration at the periphery of the domes. Thin sections across this hardened silica crust show that quartz overgrowths on original grains are split off by tiny cracks filled by brown opal (Fig. 6b).

Polygonal groove patterns about 5 to 10 cm in diameter develop on the flanks of the domes and on overhanging surfaces (Fig. 6c). Such grooves are never observed in the silica crusts on the top of the blocks. The layout of the overhanging structures clearly indicates that they are related to a former soil that has been stripped off by erosion. Thin sections across the grooves show the development of large intergranular voids that are related to preferential dissolution of the quartz overgrowths (Fig. 6d & 6e) that occurred within the former soil.

These typical quartzite weathering morphologies result mainly from concomitant and contrasted weathering processes, in particular silica dissolution and, to a lesser extent, silica deposition. It is important to recognise that even on the relatively small scale represented by individual quartzite domes, silica dissolution and precipitation do not occur in the same place or at the same time in weathering environments. Silica dissolution is enhanced on the flanks of the

dome where there is contact with humid and organic-rich soils, and is probably due to complexation with organic compounds. Silica deposition occurs on the top of the domes and originates from pore waters from the quartzite blocks that are in equilibrium with quartz and which concentrate by evaporation during warm sunny days (Fig. 7). All quartzite blocks display these features, even those on very steep and unstable sandy slopes. Quartzite weathering is thus a current and rapid phenomenon and a millennium time scale (10 to 100 ka) is envisaged for its development as sandy slopes date back to the last glacial period (Thiry et al., 2010).

### **3.2 Weathering and alteration of silica in siliceous duricrusts**

Siliceous duricrust profiles in France, Australia and elsewhere (Dubroeuq and Thiry, 1994; Thiry and Milnes, 1991; Thiry and Simon-Coinçon, 1996) display macroscopic and mesoscopic vertical and horizontal joints that determine their unique columnar structure (Fig. 8a). The voids linked to horizontal joints show specific features of successive reorganisation (Fig. 8b) (Thiry, 1981; Thiry and Millot, 1987). As seen in thin section, silica accumulates in fine illuviation laminae at the base of the joints. The youngest laminae, at the top, always consist of opal. The oldest laminae, at the base, commonly have a nodular structure and are formed of microcrystalline quartz. This sequence indicates a progressive recrystallization of the opal. The recrystallization is accompanied by a loss of silica which induces the destruction of the primary structures. Also in thin section, the ceilings of the joints are seen to be lined with mammillary deposits of titania resembling stalactites. Preferential dissolution of microcrystalline quartz takes place in the ceilings of voids but coarse quartz grains are preserved and the resistant titania and impurity traces of the former microcrystalline quartz matrix have remained and accumulated in the mammillary deposits.

The bases and ceilings of voids behave in different fashions according to the hydraulic regime. Opal deposits form in the base of the voids where water flows slowly or is stagnant and is concentrated by evaporation, while the microcrystalline matrix dissolves in the ceilings through which water seeps as a consequence of the percolation of soil water through the profile.

However, it is important to recognise that this close link between leached and confined environments does not imply a strict synchronism of degradation and construction. In fact, the two systems work alternately between humid (wet) periods during which silica dissolves and is

leached downwards and dry periods during which the solutions that have accumulated at the base of the profile are concentrated by evaporation and opal crystallises. In between these fluctuations of the soil water regime, the secondary silica deposits may undergo partial dissolution, and successive dissolution-precipitation may trigger recrystallization into various microcrystalline petrofacies. Again, as in the studies of sandstone weathering and alteration, a complex of spatial and temporal conditions is implicated.

### **3.3 Influence of mechanical stress on weathering and alteration of silica**

Prehistoric polishing features are known on numerous quartzite blocks associated with abundant Neolithic polished flint axes in the Fontainebleau area (Bénard, 2009; Loiseau, 1970; Soulier, 1972). They are polished V-shaped grooves and abraded surfaces that are strikingly hardened and in relief, raised above the non-polished sandstone by resistance to weathering (Fig. 9a). This arrangement clearly points to the “worked” surfaces being indurated and probably re-silicified. Such polishing features with a protective silica ‘varnish’ that is resistant to weathering are known on a variety of siliceous rocks used by prehistoric peoples (Fisk, 1971; Fullagar, 1991; Hamon, 2003; Howard, 1994; Nouel, 1961; Pope and Miranda, 1999). Archaeologists have generally considered these surface varnishes to have formed from plant phytoliths and to be indicative of the grinding of plant products by prehistoric peoples. However, it is well known that rubbing surfaces together with a fine powder between them develops a “vitreous” film of amorphous character that coats the irregularities of the materials and gives the shiny aspect akin to a “Beilby layer” (Bowden and Hughes, 1937; Jones and Uehara, 1973; Nakamura et al., 2012). In the case of the polishing features described here, the mechanical grinding and polishing of stone tools in grooves and across the quartzite blocks would have generated the structurally damaged quartz that is susceptible to dissolution and later recrystallization leading to hardening of the surface.

One of us (Thiry, unpublished work) has found that similar surface hardening is also developed on paving stones made of Fontainebleau quartzite. The paving stones can be found at several historical sites (courtyards in castles and barracks) and show a convex surface due to wear (Fig. 9b). This surface is indurated with a millimetric crust that flakes off. Thin section studies show that quartz grains within the crust are intensely crushed and display microfractures

spaced at about 10  $\mu\text{m}$  and to a depth of 2 to 4 mm beneath the surface (Fig. 10a). This is the effect of repeated mechanical shocks from the shod wheels of carts and carriages and horses hooves. With such fractured grains one would expect that the exposed surface may be friable, but it is not. This is due to concomitant cementation and hardening as the microfractures have refilled with brown opal (Fig 10b & 10c). The opal has formed from silica dissolved from amorphous fracture edges in the crushed quartz and cements the quartz splinters together to form the hardened crust.

Whatever the crystallo-chemical mechanisms in detail, it is obvious that the mechanical shocks have had an effect on the quartz grains and that the hardening of the exposed surfaces can occur within a few decades, as testified by the history of the paving stones which had to be turned over every 20-40 years to avoid excessive roundness. The development of an indurated crust on prehistoric polishing stones may also have occurred in a relatively short time: although the polishing stones may have been used by several generations of prehistoric peoples, they were probably only used intermittently. The secondary silica patina would have developed concomitantly with the mechanical abrasion generated during the times of working.

### **3.4 Weathering and alteration of silica in flints**

The microcrystalline texture of flint makes it very difficult to observe and analyse its weathering and alteration in near-surface environments. Nevertheless, there are specific case studies of flint deposits that provide evidence of the geochemical and mineralogical mechanisms at play (Burrone et al., 2002; Bustillo et al., 2009; Catt, 1986; Fernandes, 2012; Glauberman and Thorson, 2012; Hurst and Kelly, 1961; Fayolle, 1979; Laignel and Meyer, 2000; Rodgers et al., 2004; Rottlander, 1975).

#### **3.4.1 Alteration after reworking of flint from chalk deposits**

A comparison of more than a hundred samples of flints in-situ within chalk deposits, and a similar number of samples of flints inherited in clay-with-flints and reworked into alluvium and sedimentary deposits, in France, was undertaken by Trauth et al. (1978). From a strict mineralogical point of view, flints embedded in chalk contain quartz as well as tridymite, cristobalite and opal-CT. These minerals are easily identified by X-ray diffraction (XRD) and differential thermal analysis (DTA) (Fig. 11). In contrast, flints reworked from chalk deposits

and exposed to weathering are exclusively composed of quartz. In addition, all relevant indexes show that quartz in reworked flints is of higher crystallinity than quartz in flints embedded in chalk (Fig. 12).

The mineralogical composition of flints starts to change after they are removed from the host chalk, even if the changes are not visible by means of petrographic techniques. The changes always favour a more stable secondary mineralogical structure, less soluble and of better crystallinity than the primary one. This process involves recrystallization triggered by the external environment of the flint and physico-chemical mechanisms like Ostwald ripening through which the smallest crystallites dissolve and contribute silica for the growth of larger crystals (Crerar et al., 1981). The mass balance exchange is minimal and there are no dissolution features. Recrystallization probably occurs through water films between the crystals and exchange by diffusion rather than by convection (Cady et al., 1996). Such recrystallization of silica phases may occur in a relatively short time as shown by primary opal deposits that have transformed to microquartz over periods of 20 to 50 000 years (Herdianita et al., 2000a).

### 3.4.2 Dissolution of flints

Often flint cobbles have a friable white rind (cortex)<sup>2</sup>. Flints altered in this way are common at the top of clay-with-flints weathering profiles (Laignel and Meyer, 2000; Quesnel et al., 2003) and in fluvial (riverine) terrace gravels (Coutard and Ozouf, 2008). Similar alteration affects some flint gravels interlayered in sand formations (Thiry et al., 1988). The friable white cortex is generally about 1 to 10 mm thick and the shape of the flint cobble is generally preserved. However, in some regolith environments the flints are more extensively weathered and altered and have contorted shapes (Fig. 13), with obvious solution features (cavities and hollows), and can be easily broken by hand. The friable white cortex is associated with progressive dissolution and development of porosity which may reach 35%, and a concomitant increase of the pore size and specific surface area, which may reach 15 m<sup>2</sup>/g in the most altered, powdery samples (Coutard and Ozouf, 2008).

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<sup>2</sup> We use the terms 'weathering rind' and 'cortex', whatever the origin (primary or secondary), interchangeably in reference to millimetric to centimetric zones of alteration developed in the outermost parts of siliceous materials, especially flints. We use the terms 'patina' for the very thin layers of weathering or alteration that form at the surface of siliceous artefacts.

These weathering features illustrate the sensitivity of the flints to silica leaching, with the progressive development of a friable white cortex. As reworked flints are primarily exclusively composed of microcrystalline quartz (in contrast with primary flints in chalk that contain some tridymite and cristobalite), the development of the friable texture reveals the preferential or relatively rapid dissolution of some of the microquartz varieties. These are most probably quartz microcrystals that have the lowest crystallinity and the smallest grain size (and thus the highest specific surface area). Once the dissolution has started, porosity develops, promoting water penetration into the flint and enhancing dissolution. The less soluble quartz microcrystals remain and are preserved, or at least partly preserved. These have the greater grain size with less structural defects and thus better crystallinity.

A few occurrences of flint cobbles embedded in geological formations allow us to estimate the rate of development of the friable white cortex. In the Paris Basin, leached and bleached sandstone profiles that contain weathered flints are related to valley incision, and thus the duration of the alteration producing the cortex is probably several 10 ka (Thiry et al., 1988). Elsewhere, along the Channel shore in Normandy, flints with a thick, friable cortex are found in association with wave-cut platforms of Saalian (c. 350 - 130 ka) and Eemian (c. 130-114 ka) ages, and are considered to have developed in less than 130 ka (Coutard and Ozouf, 2008).

### **3.4.3 Recrystallization of flints**

Studies of geological formations that contain flints show that silica alteration and recrystallization phenomena occurred over long time periods. Weathering and alteration features no doubt occur in shorter time frames but are incipient and difficult to recognise.

Flint cobbles embedded in silcrete profiles of Lower Eocene age in the Paris Basin have been weathered and altered in-situ (Thiry, 1981; Thiry and Simon-Coinçon, 1996). In the upper parts of these silicified formations the flints show peripheral dissolution with a white and porous centimetric cortex and a dull core: only small primary translucent zones of the original flint remain. In thin sections the altered flints show microcrystalline quartz forming a microspherulitic texture with spherules about 10µm in diameter (Fig. 14). The microspherulites become more pronounced progressively from the core of the flint towards the cortex. Voids occur within the porous cortex and even larger voids can be observed at the outer rim.

The microspherulites are not visible in thin section in unweathered, translucent flints formed of very fine microcrystalline quartz. Nevertheless, it is obvious that these microspherulites are primary constituents of the flint. They have been described in fresh flints within chalk deposits (Cayeux, 1897; Knauth, 1994). The microspherulites become progressively more distinct because they have a lower solubility than the matrix between the spherulites that is composed of a different form of microcrystalline quartz, possibly mixed with opal. This is more soluble and dissolves preferentially.

These features reveal two successive transformations of silica in flints: (1) the presence of microspherulites show that recrystallization of the flint to microcrystalline quartz after it has been reworked from the chalk nevertheless preserved at least some of the primary petrographic features; and (2) weathering of flints results not only from simple dissolution processes but progresses as a result of differential dissolution and reorganisation of silica phases progressing from the surface inwards towards the core of the flints.

#### **4 Application to investigations of flint artefacts**

The alteration of flint artefacts has been under investigation from the earliest days of archaeological studies. For example, in a letter written in 1846, Boucher de Perthes specified the main factors relating to the development of patinas on artefacts, namely: the nature and the origin of the flint, its localisation at depth within the water-table or near-surface in well-drained sites, and the duration of the alteration, while also warning not to "*.. determine the age at glance ..*" (Boucher de Perthes, 1865). In subsequent studies, experiments were undertaken to reproduce patinas on flint artefacts (especially white ones) by chemical attack. These include the research of Meillet (1866), Chedeville *et al.* (1907) and especially the important work of Hue (1929) who put varieties of flint in contact with diluted solutions for a duration of 20 years. Petrographic studies were also undertaken early and the differential dissolution of silica varieties was recognised as well as some of the agents influencing these alterations (Cayeux, 1929; Curwen, 1940; Hurst and Kelly, 1961; Meillet, 1866; Schmalz, 1960; Rottländer, 1975; Stapert, 1976).

A renewal of research on flint artefacts, and especially their surface features and characteristics, was initiated by analyses of their use (Arrighi and Borgia, 2009; Burrone *et al.*, 2002; Howard, 1999; Levi-Sala, 1986). Recently, taphonomic studies of artefact deposits led to



dynamic models of flint alteration taking into account the nature, hydrodynamics, geochemistry and other properties of the flint and the host deposits (Glauberman and Thorson, 2012; Fernandes, 2012; Howard, 2002). Our work builds on this research.

#### **4.1 Overview of the alteration of flint artefacts**

Determining the origins of lithic raw materials has long been considered essential to understand the collection behaviours of prehistoric societies. Petro-archaeological studies of flints have difficulty in establishing a correlation between the artefact material and the potential sources of that material (Bressy, 2002; Briggs, 2001; Deflandre, 1935; Kars et al., 1990; Masson, 1981; Mauger, 1985; Sieveking et al., 1972; Valensi, 1957). Studies have been mostly on primary (in situ) and/or sub-primary sources, whereas gatherings of flints by prehistoric peoples were often probably made from secondary, redeposited materials such as glacial till and water-laid gravels (Fernandes and Raynal, 2006; Hughes et al., 2010; Lavin and Prothero, 1987, 1992; Stapert, 1976; Verri et al., 2004; Williams-Thorpe et al., 1999). Transformations of the flint cortex that can be identified from detailed petrographic studies are specific to some sedimentary environments (Fernandes, 2012; Fernandes et al., 2007). Recognition of these petrographic characteristics may be the key to characterizing secondary flint deposits and could help to locate such deposits worked by prehistoric peoples and permit the drawing of maps of subsistence areas and potential itineraries (Fernandes et al., 2008).

As in the case of flints reworked from their sedimentary host, the silica minerals in tools made from flints and later buried when discarded by their users are affected by dissolution and precipitation (Fig. 15) (Arrighi and Borgia, 2009; Burrioni et al., 2002; Glauberman and Thorson, 2012; Hurst and Kelly, 1961; Masson, 1981; VanNest, 1985; Vignard and Vacher, 1964). Silica dissolution in flints buried within soils or sediments commonly occurs at the periphery due to water seeping through the surrounding material. On the other hand, silica precipitation may occur either by concentration of pore waters during dry periods (seasons), or by cooling of warmer groundwater rising to near-surface, for example at times of periglacial environments in Europe during the cold periods of the Quaternary (Woo et al., 2008).

When transported flint clasts or worked tools are buried, a gradient of percolation is established between the essentially impermeable core of the flint and the host sediment or soil.

Reactions within the margins of the flint occur via diffusion processes through water films between component silica crystals. Any primary interstitial water bound within the flint core will be in contact with the silica minerals for a long time: in the outer rim, which is in contact with percolating water in the surrounding soil or sediment, the contact time will be shorter. This equates to a gradient of silica concentration in the solutions. Whereas the interstitial solutions and the water films between crystals within the core of the flint are in equilibrium with the silica minerals and no mineralogical change occurs, solutions at the surface of the flint are renewed by percolation and are thus undersaturated in silica so that the silica phases in the flint are dissolved. Beneath the surface of the flint, in the cortex, solutions have intermediate silica concentrations that may trigger recrystallization (Fig. 16). Flint weathering always leads to a loss of silica. However, in turn, the crystallinity and therefore stability of the silica minerals increases, leading to more stable phases.

## **4.2 The concept of successive alterations**

### **4.2.1 Chronology**

Of particular importance in unraveling the petrographic evolution of flint tools in near-surface environments in relation to the geochemical and kinetic behaviour of silica minerals is recognition of the remnant natural surfaces that are inherited from the primary chalk deposits. The detailed characteristics of these natural surfaces will reflect the environments in which the flints were deposited and contained before they were collected for tool-making. The first step in determining the provenance of flints is to decipher the spatial arrangement of the successive natural surfaces (flat surfaces, edges, depressions, cupules, etc) and their relative chronology (Fig. 17). Secondly, the wear marks and the weathering rind formed when the sample was exposed, removed and transported have to be characterized for each surface. This requires a multi-scale approach by macroscopic and binocular observations, then examination of the microfacies, textures and porosity by optical microscopy, and finally a clarification of various phases of the silica dissolution and precipitation by scanning electron microscopy (SEM) (Fernandes, 2012).

#### 4.2.2 Pre-gathering weathering and alteration

Successive transformations to form the weathering rind (cortex) occur during the geological reworking process, for example in flints from colluvial deposits downslope from flint-bearing limestone outcrops and, further downstream, flints bound within a mature alluvial conglomerate. Studies so far have been undertaken on about 3500 flint cobbles and 8000 flint artefacts, and included 200 thin sections, and Scanning Electron Microscope (SEM) analysis of 80 specific samples originating mainly from Massif Central, Rhône Valley and Aquitaine Basin in France and from several sites of Morocco (Fernandes, 2012).

The first stage of alteration after release of the flint from the source limestone consists of the development of three differentiated zones which constitute the weathering rind (Fig. 18a). An inner micro-porous zone develops as a result of dissolution of the most soluble and less crystalline phases (diverse opal). An outer friable zone with large pores develops with further dissolution. In between, a tight zone cemented by secondary crystalline silica (mainly microquartz) has formed.

In colluvium, most of the surface of the flint is remoulded by a thin layer of silica underneath which quartz grains remain visible (Fig. 18b & 18c). The silica layer is thicker in surface depressions and frequently shows shrinkage cracks. The most soluble mineral phases like calcite and opal CT have disappeared from the matrix. The cortex of the flint thus contains secondary silica deposits, abrasion on bulges and split features (Fig. 18d).

This complex alteration ultimately ends in the development of a thick silica layer that completely changes the surface morphology of the flint. The surface becomes smooth and the grains that form the flint underneath the silica layer are no longer visible. Sometimes, the silica coats biogenic elements, like diatom frustules, that record deposition in a quiet environment.

The development of silica coatings appears to be characteristic of flint weathering. It is a consequence of differential alteration: the most soluble silica phases are dissolved whereas more stable phases and of better crystallinity than in the primary one are preserved and/or precipitated (Graetsch and Grünberg, 2012). The silica coating remains partial and discontinuous on flints contained within colluvium. It thickens up and the flints become somewhat rounded in downgradient fluvial networks, until they become cemented entirely as well rounded pebbles in alluvial conglomerates. There appears to be a relationship between the thickness of the silica

coating and the intensity and duration of the weathering and reworking processes. It is possible that mechanical stresses due to repeated friction, abrasion and impact of the flints during fluvial reworking gave rise to amorphous silica that has reorganised into silica coatings that harden the surface of the pebbles, in a similar way to that demonstrated above in paving stones and polishing stones.

#### **4.2.3 Alteration of worked flint flakes**

The patina formed after knapping is the most demonstrative example of the alteration of flints. The alteration is obvious and, in the case of archaeological excavations, a maximum age can be attributed to it which allows an assessment of a minimal rate of development. The alteration may also indicate the sedimentary and climatic processes that acted on the archaeological unit. Most commonly there are three zones superposed from the surface to the interior (Fig. 19): (1) an outer tightly cemented rim of a few tens of microns thickness, without porosity, which consists of a film of secondary silica that coats the microquartz and blurs entirely the granularity of the matrix; (2) a more or less regular underlying zone formed of microquartz without fibrous silica phases (chalcedony) that has relatively highly interconnected porosity and; (3) an inner zone in which the primary fibrous texture of chalcedony is preserved.

These alterations are frequent on flint flakes and are always characterised by a very fine silica phase covering the microquartz of the matrix. This is separated from the primary flint matrix by a network of open pores that indicates dissolution and recrystallization of the matrix as testified by the disappearance of the fibrous silica phases in the primary flint facies. This zonal arrangement may not have developed simultaneously but possibly successively or even in alternative fashion. The outer silica casing has most probably developed from amorphous silica compounds resulting from the knapping of the flints, or later mechanical shocks.

### **4.3 Implications**

Weathering and alteration of silica in regolith environments has specific relevance to studies of the alteration of flint tools in near-surface environments. In particular, interpretations of the geochemical and kinetic behaviour of the constituent silica phases permits the forecasting of changes that may occur at the surface of a flint during its history (Fig. 20). For example: (1) dissolution always occurs at its surface; (2) percolation rates of soil water or groundwater

through the core are very slow, and changes probably occur over geological time-scales (Ma); and (3) the intermediate zone (sub-cortical zone) is the site of adjustment between the flint and its surrounding geochemical environment. This scheme is very similar to that proposed independently by Glauberman and Thorson (2012). Here, recrystallization and ultimately deposition of silica record the various environmental conditions experienced by the flint during its history and can be interpreted and characterised using petrographical and micromorphological techniques to provide clues to the source of the worked flint materials.

Flint alteration and cortex development are mainly triggered by the nature of the component silica phases that have differing solubilities. The most soluble phases dissolve first and at the highest rate resulting in relative accumulation of the most stable phases. This is the first process of alteration. The crystallinity of the silica phases also plays a main role: it controls solubility which decreases with increasing crystallinity. Significant parts of the alteration process are the recrystallizations that occur in the solid state via diffusion in water films between crystal grains. Silica solubility is also temperature dependent: if groundwaters rise to the surface during cold periods they may precipitate silica and re-silicify cortex textures as they cool down.

The chemistry of interstitial water depends on the host material and on the water flow regime. In soils and in the zone of aeration, percolating water always remains under-saturated due to the low kinetic rate of silica dissolution: consequently dissolution will prevail during flint alteration. Groundwaters generally have a higher silica content and may be saturated with respect to the quartz varieties: dissolution of flint cortices will be limited in these environments. In clay-rich host rocks, such as clay-with-flints, percolating water flow rates are reduced and the silica content of the pore waters is even higher, favouring deposition of secondary silica.

Specific flow rates and water chemistry may be ascribed to sedimentary characteristics of flint deposits. For example, colluvium on slopes has intermittent drainage. Young alluvium may be permanently drowned whereas old alluvium may have the form of emerged terraces and undergo silica leaching for long periods. Flints at the soil surface, constituting an easy supply of materials, are exposed to severe temperature changes, desiccation, overheating in the sun, and exposure to the winds, and may undergo very specific alterations. Leaching conditions may even be different between the upper and the lower faces of a flint: the upper faces may undergo

leaching but may also be subject to silica precipitation when the percolation rate slows down or even stops, whereas the lower faces always experience outflows and thus leaching conditions.

## 5 Conclusions

High resolution petrographic and electron optical investigations of weathering and alteration of the various forms of silica in materials that are exposed to near-surface regolith environments provide the basis for assigning micromorphological and mineralogical features to geochemical and hydrological conditions in particular micro-environments. The materials studied over many years and on several continents include sandstones, siliceous duricrusts, and flints. Where the weathering and alteration of silica occurs over geological time, as in the case of siliceous duricrusts, or a millennium time scale, as in the case of the Fontainebleau Sandstone, features are generally clearly observed and comparatively easily interpreted. However, the weathering of silica can be a relatively rapid and current phenomenon. In the case of flints, there are examples of transformations of silica that occurred over periods of 20,000-50,000 years, thick weathering cortices have developed in less than about 130,000 years, and friable cortices have formed in several decades. In addition, we describe examples of polishing and surface hardening of rock surfaces initiated by abrasion and repeated mechanical working followed by subsequent silicification that has occurred within a few decades. Details of the alteration features produced over shorter time periods are progressively less easily examined. However, the outcomes of studies of these alteration features can be used to investigate the provenance of flint tools in an archaeological context.

As well as flints, worked flint flakes exhibit various weathering rinds that are due to changes in the texture and mineralogy at their surface forced by physico-chemical exchanges during working and weathering. And, as in the case of our geological and mineralogical studies in regolith environments, the textures (component particles, geometric aspects, size, mutual relations among the components, granularity) of the weathering rinds result from changes that occurred under specific microenvironmental conditions and thus reflect evidence of these conditions. Firstly, the remnant primary cortex on flint tools may provide information that identifies the deposits from which prehistoric peoples obtained the flints. Secondly, worked flint flake patinas retain information that may aid in the reconstruction of the environment of the

archaeological site. An inventory of flint cortex textures forms the basis for elucidating the mechanisms that triggered the formation of the textures. Three main influencing factors are the nature of the silica components, the pore water of the host sediments or soils and water flow or percolation regimes. Each flint registers its own history, and each type of environment lays down certain characteristic features on its surface, so that morphological and mineralogical changes recorded in the flint cortex can be used to reconstruct the successive environmental conditions experienced by that flint. Thus, a flint flake is not only a petrographical and archaeological entity; it also wears clues of alterations that, once deciphered, potentially reveal a chronology of sedimentary, diagenetic and archaeological events.

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## Figure captions

**Figure 1** – Rate of dissolution and asymptotic solubility of the different silica varieties at 25°C (after Siffert 1967). The solubility equilibrium of the silica phases in water is reached slowly.

Opal and chalcedony show variable solubility according to their respective crystallinity.

**Figure 2** – Macro- and micromorphological structures of a pedogenic silcrete profile. The siliceous matrix is the location of successive silica dissolution and deposition leading to relative accumulation of crystalline quartz.

**Figure 3** – Quartz and chalcedony solubility versus temperature (Bethke, 2002). Quartz solubility decreases to more than half of its initial value between 12.5 and 0°C.

**Figure 4** – Schematic relation between stability and crystallinity (size of the individual crystallites) of the different petrographic varieties of quartz.

**Figure 5** – Petrography of the Fontainebleau Sandstones. a – Quartzite pans are cemented by subeuhedral quartz overgrowths. b – Quartzite rims show preferential dissolution of overgrowth aureoles, but primary quartz grains are not corroded. Thin sections, cross-polarized with quartz wedge.

**Figure 6** – Weathering morphologies of quartzite blocks. a - Dome-like shaped boulders capped with a silica crust. b - Brown opal deposits between dislocated quartz grains in silica crust; thin section, polarized light. c - Polygonal network on dome flank. d - Dissolution of quartz overgrowths along polygonal grooves; thin sections, polarized light. e – Similar as d, cross-polarized with quartz wedge.

**Figure 7** - Sketches of silica mobility during weathering of quartzite boulders. Silica dissolution is enhanced in contact with soils while silica deposition (opal) occurs at the top of the dome.

**Figure 8** – Schematic diagram of a pedogenic silcrete. a – Characteristic vertical organization and large illuviation structures. b – Thin section through a planar void that shows Si dissolution (together with accumulation of residual titania) in the ceiling through which water seeps, an Si accumulation in form of opal in the base of voids where solutions concentrate during dry periods.

**Figure 9** – Quartzite surfaces hardened by mechanical pressures. a – Indurated crusts of "worked" surfaces of a Neolithic polishing stone, Fäy-les-Nemours (Seine-et-Marne), photo

J.-P. Hofstetter. b - Paving stones of Fontainebleau sandstone in a paved yard around old military buildings. Abraded surfaces are hardened by a siliceous crust that flakes off. Photo M. Thiry.

**Figure 10** – Petrographic images of hardened silica crusts developed on quartzite paving stones.

a – Thin section perpendicular to surface of paving stone. Note intense fracturing of quartz grains at the surface progressively decreasing with depth. b & c –Details of fracturing of quartz grains, showing 5 to 10  $\mu\text{m}$  quartz splinters cemented by brown opal. Thin section, polarized light.

**Figure 11** – Mineralogical composition of flints embedded in chalk and those reworked from chalk and weathered. Reworked flints are always only composed of quartz, whereas other silica varieties coexist beside quartz in the flints in-situ within chalk (after Trauth et al. 1978).

**Figure 12** – Crystallinity of quartz (proportional to the size of coherent crystal domains) is lower in quartzose flints than in magmatic quartz. Moreover, reworked and weathered flints show quartz of a higher crystallinity than in flints in-situ in chalk (after Trauth et al. 1978).

**Figure 13** – a – Selected flints showing progressive alteration and dissolution from base to top of a bleached sandstone section (Thiry et al., 1988). b - Detail of extensively altered flint from upper part of the section

**Figure 14** – Petrography of flint undergoing alteration in the upper part of a silcrete profile. Microspherulites become more distinctive through differential dissolution but are not visible in the unweathered flint. Silica is in each case formed of very fine microcrystalline quartz. Thin sections, polarized light.

**Figure 15** – Reworked or worked flints may undergo dissolution by seeping waters but also be the focus of silica deposition by way of concentration or cooling of waters.

**Figure 16** – Relationship between solution concentration and rate of percolation through flints. Interplay between flow rate of solutions and silica concentration steers the mineralogical and petrographical transformations in the flint cortex.

**Figure 17** – Spatial arrangement of the successive surfaces on a flint cobble. (1) Primary flint cortex relating to chalk host; (1a) and (1b) early cupulae with a secondary cortex; (2) later cupula with a more recent cortex; (3) recent developing cryojoint.



**Figure 18** –Weathering rind on reworked flints. a – Section from flint cortex in colluvial deposit (Cruas, Ardèche, France): (C1) Porous outer zone, microquartz with pore diameters up to 100  $\mu\text{m}$ ; (C2) tightly cemented zone, mainly composed of microquartz; (P) porous inner zone with dissolution of finest silica matrix and preservation of microquartz and chalcedony (bioclasts); (M) flint matrix without porosity, very fine silica phases including chalcedony and most probably poorly crystallized phases like varieties of opal and moganite. Thin section, cross polarized. b – Secondary silica coating in colluvial deposits (Cruas, Ardèche, France). Zone beneath coating shows pores and granular texture typical of outer zone of flint cores with dissolution and recrystallization of more soluble silica compounds. SEM picture. c – Details of secondary silica coating with shrinkage cracks (arrows) resulting from loss of volume during transformation and dehydration of silica coating. Beneath is granular and porous zone of flint cortex. SEM picture. d – Tight silica coating on flint from alluvial deposit (Tertiary conglomerate from Naussac, Lozère, France). Thickness of coating seen in left upper corner of picture. Shock fracture affects the coating (arrow). SEM picture. After Fernandes (2012).

**Figure 19** - Section of patina from artefact worked from a Lower Cretaceous (Barremian) flint (Cruas, Ardèche, France). (C) tightly cemented by secondary silica without any granulation, overlaying a porous and granular zone formed of isometric microquartz (P) that developed above the primary flint matrix in which the lengthening textures of chalcedony remain (M). SEM picture after Fernandes (2012).

**Figure 20** – Conceptual sketch of changes in sub-cortical weathering rind of flint. Changes are consequent upon geochemistry of pore water in host sediment and provide the basis for reconstructing these environments. a – Thin section of cortex on flint from colluvial deposit (Cruas, Ardèche, France). Cross-polarized light. b - Conceptual sketch of the petrographic changes that occur in cortex of a flint during alteration.

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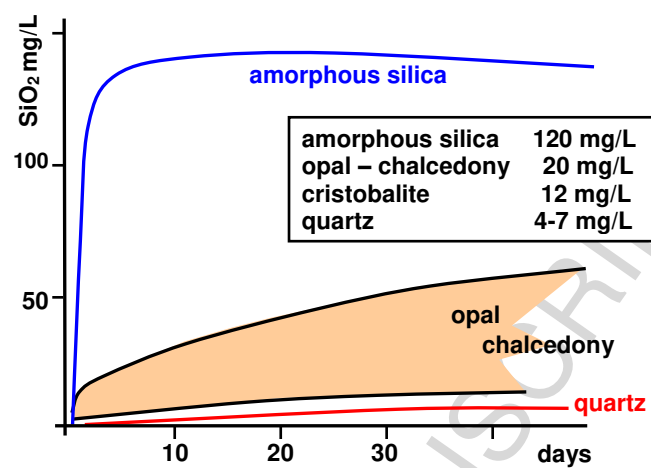


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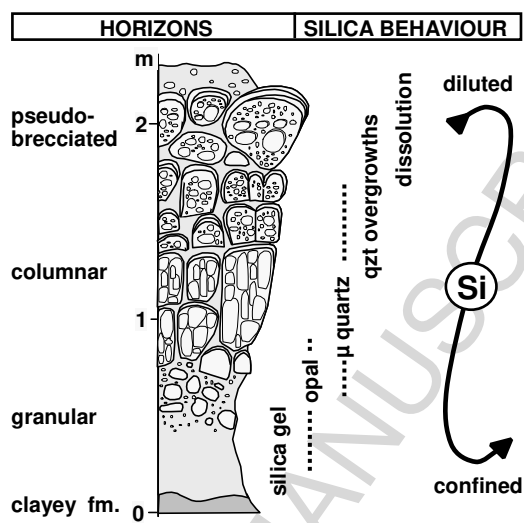


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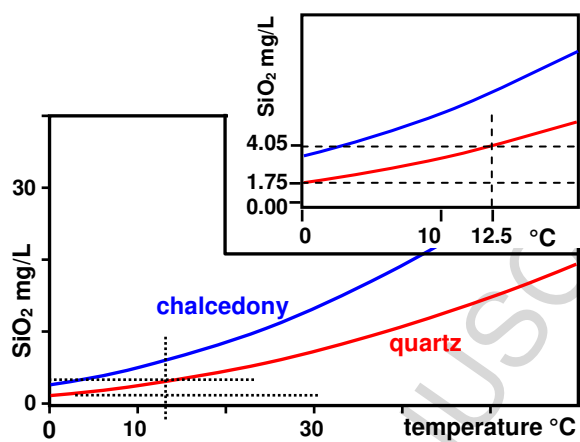


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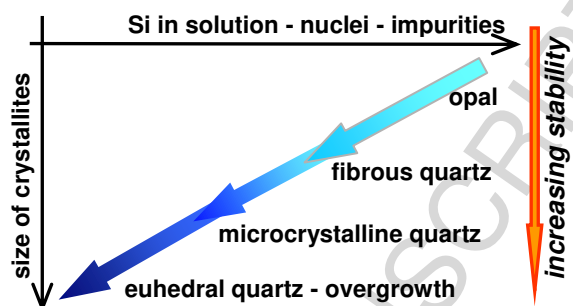


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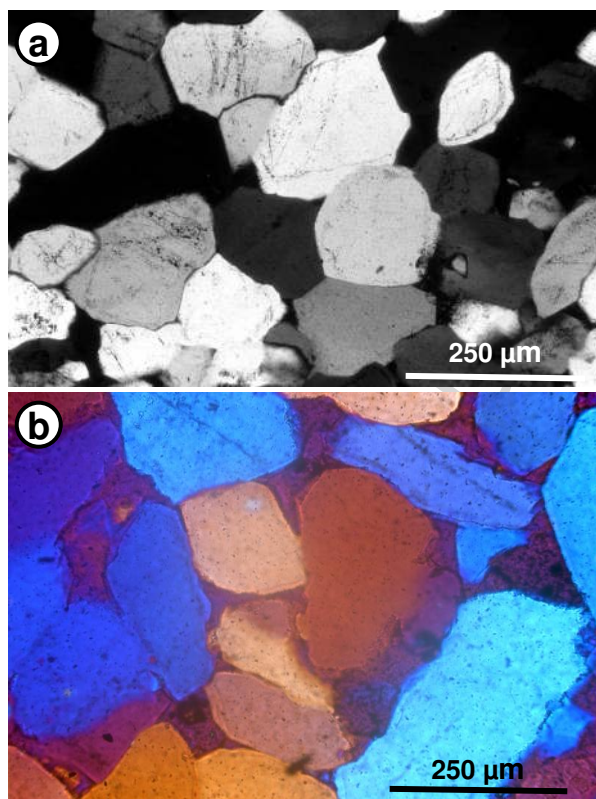


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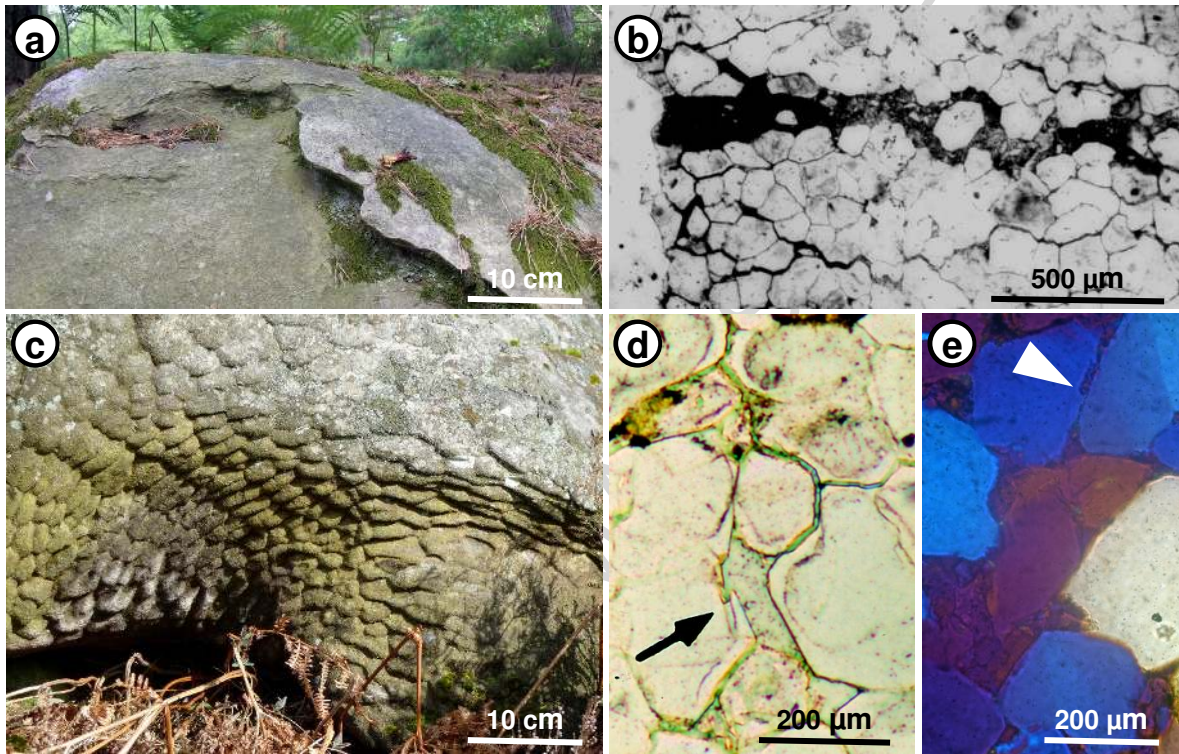


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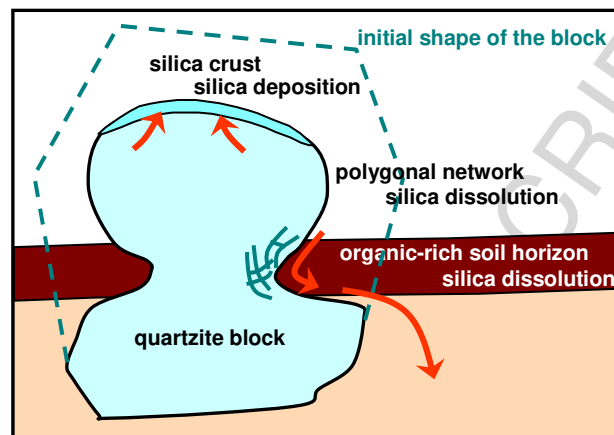




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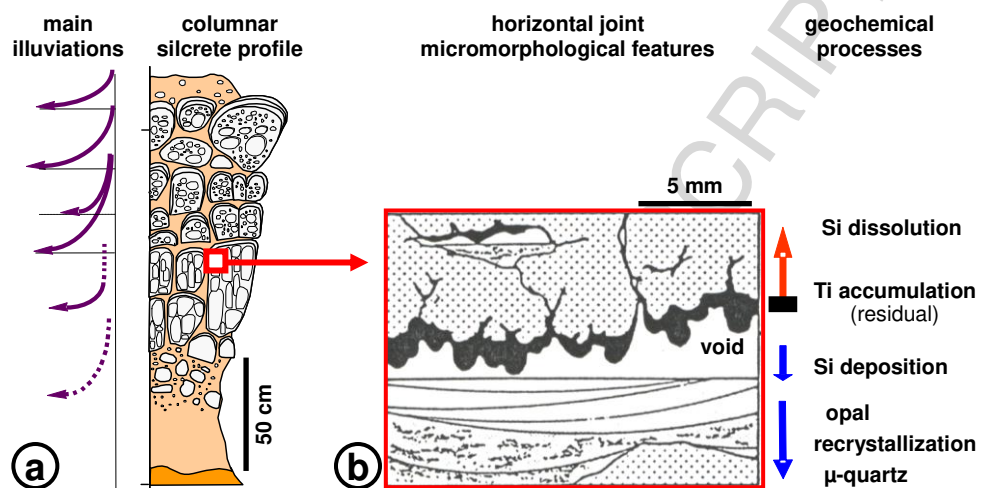


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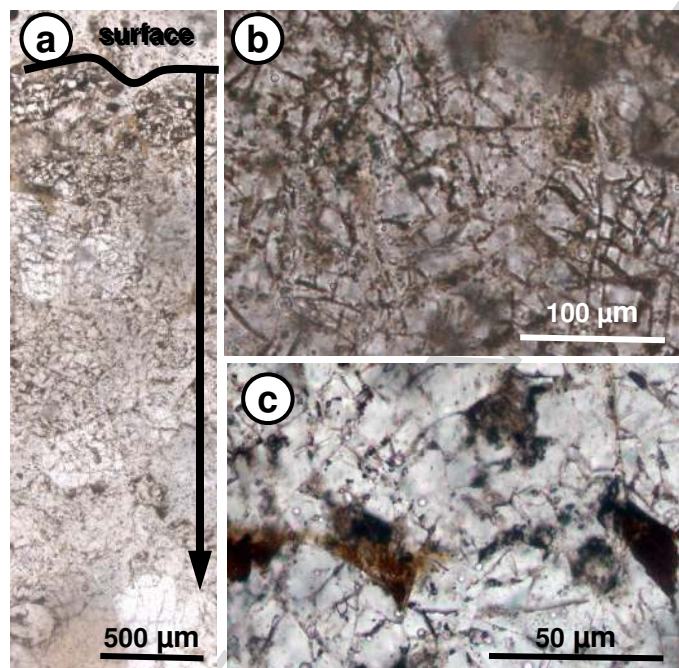


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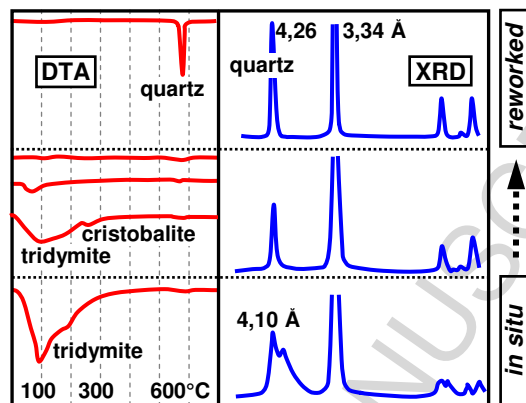


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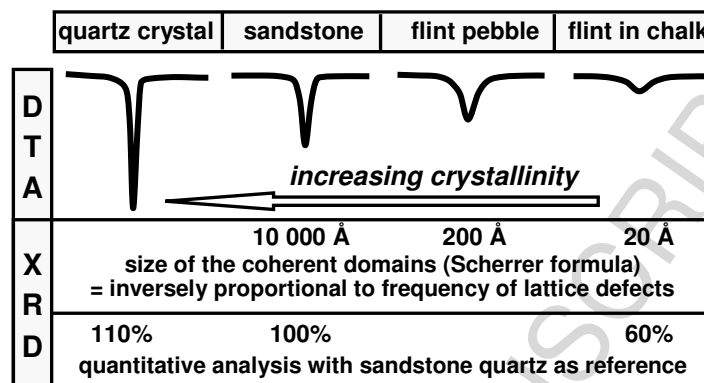


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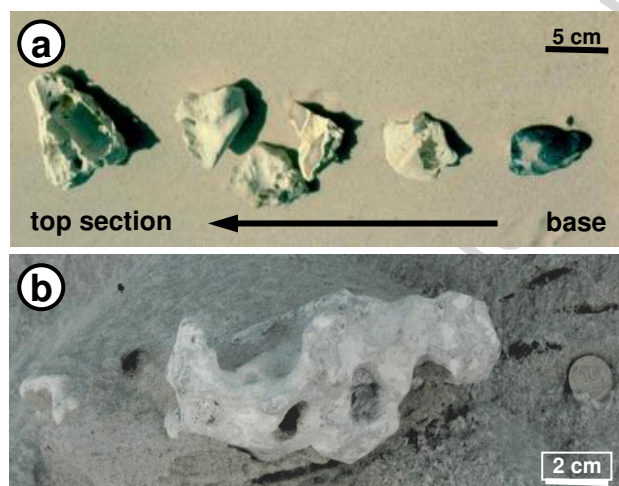


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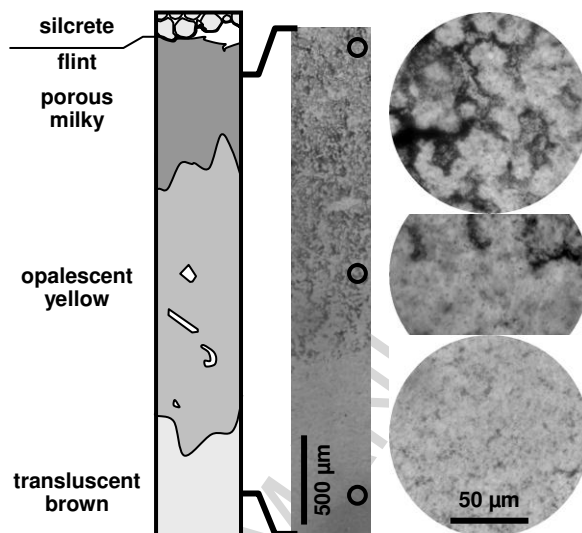


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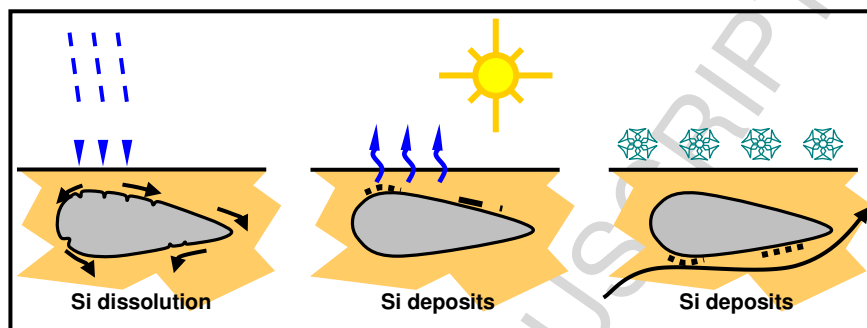




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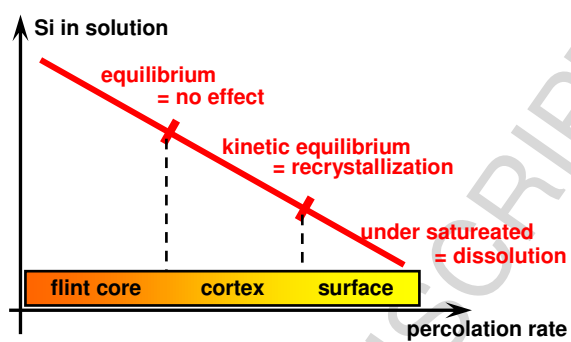


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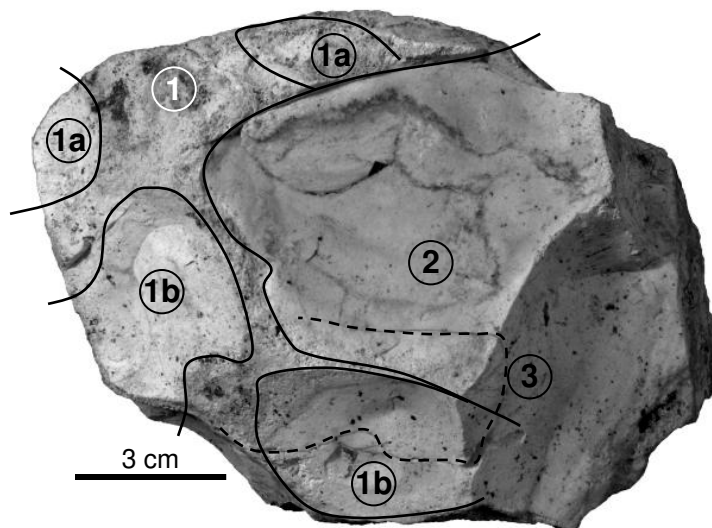


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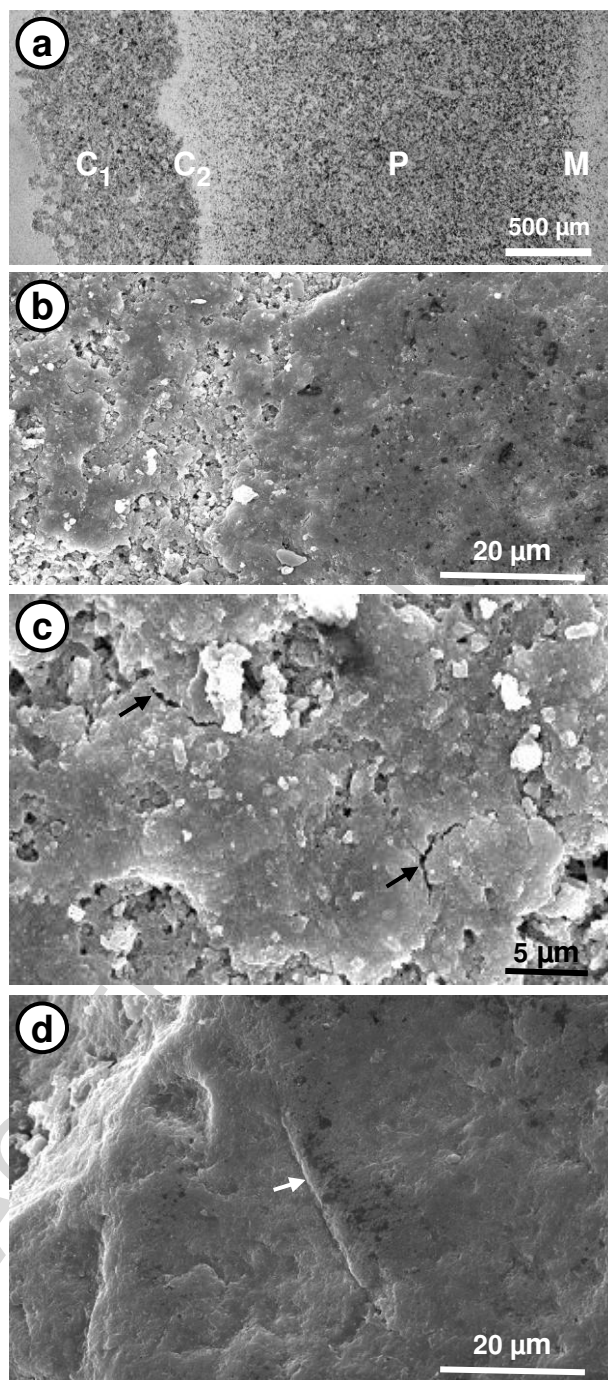


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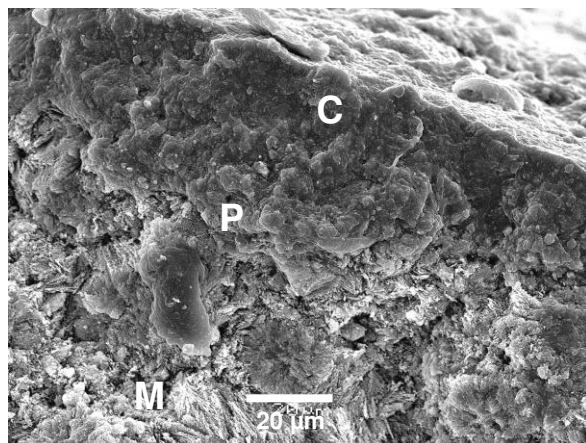
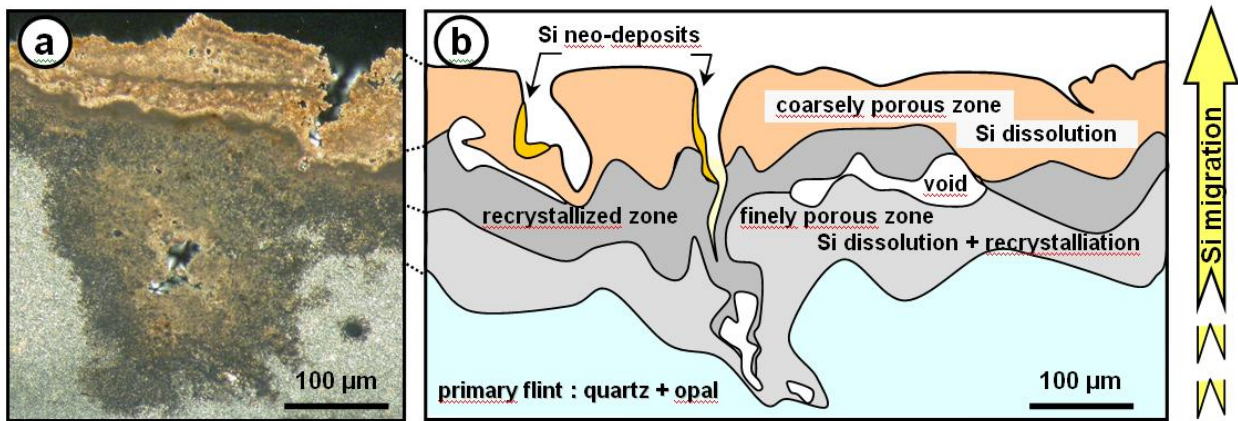


Figure 20 – 2 columns



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