

THE POTENTIAL OF ROCK PATINATION ANALYSIS
IN AUSTRALIAN ARCHAEOLOGY

PART 2

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DIAGENESIS AND PATINATION OF SEDIMENTARY SILICATES

This is the second of two papers discussing mineral patinae their development antiquity and possible usefulness in serving the prehistorian.

Goodwin (1960: 302) uses the term bleaching to describe what he considers as leaching out of silica and replacement by lime salts in flint chalcedonies and certain shales. He advocates caution in eliciting chronometric clues from this form of patina.

Archaeological writers frequently attribute the familiar modified veneer on flint to the influence of alkaline groundwater. This it is suggested slowly produces an effect comparable to the removal of the 'more soluble fraction of flint' by boiling the mineral in concentrated basic solution preserving the porous lattice of 'insoluble' quartz crystals (Cornwall 1960 cf. Schmalz 1960). That several researchers are at variance over the course actually taken by this patination should not surprise us. Until recently agreemtn was equally lacking on the composition of the micro and cryptocrystalline quartzes and discord is at times evident even in the definition of flint. Essentially the term can have two meanings. It can denote a stone artefact in general but when employed in a scientific context usually designates the distinctive chert of the Cretaceous Chalk deposits in Western Europe. Tarr (1938) recommends that the usage of 'flint' be confined to archaeology arguing that flint is merely a type of chert. Petrologists have generally accepted that the term's lithological meaning is restricted by chronological and possibly geographical connotations as well as by physical attributes. Some however are prepared to define any nodular black opaque siliceous sedimentary rock occuring in limestone as such (cf. Oakley 1939: 277). The practice of describing

nodular microcrystalline and chalcedonic quartzes from other facies as flint may reflect their mode of occurrence but it is geologically invalid (Zeuner 1960: 319; Milner 1962: 256) unless they are indistinguishable from flint in every important physical aspect. Wright (1971: 52) when re-evaluating Koonalda Cave distinguished two macroscopically identifiable types of silicate a 'brown translucent glassy flint' and a 'white opaque non-glassy flint'. He observed patination only on the former and dismisses the possibility of the latter being an epigenetically altered state of the translucent type. The geologist that accompanied his 1967 expedition defined the nodules as chert (Frank 1971: 41 Table 3). The silicates of Koonalda Cave's Upper Eocene Wilson Bluff Limestone (Jennings 1963) are of a range lacking clear demarcation of varieties. Opaqueness is a function of both bulk density and proportion of connected interstitial spaces (if impurities are ignored 33.9% of presupposed total cavities are readily accessible). Optical phenomena are attributable to diagenetic factors i.e. the mode of carbonate replacement and occasionally the state of it. Identification as flint cannot be sustained because colour spectra of all forms are aberrant for flint and not acceptable to most writers 'flint meal' is absent colorant is provided by primary colour centres of readily extractable iron oxides (both of ferrous and ferric condition) and the limestone matrix is not of the geological provenience stipulated for flint. The chalcedonic silicate was satisfactorily defined by the site's initial investigator (Gallus 1971; 1977) and by Sharpe and Sharpe (1976).¹

Judd (1887) the first to attempt an explanation for the patina of flint deemed this mineral to be an aggregate of quartz and opaline matter and inferred that patina results from selective leaching of the latter. Subsequent writers (Tarr 1926 Correns and Nagelschmidt 1933 Gehrke 1935) believed they identified the colloid and some even calculated the opal content of flint (Donnay 1936 at 10%; Bosazza 1937 at 76%). Archaeological writers (e.g. Curwen 1940; Mitchell 1947) had little choice but to conform with prevalent opinion because Washburn and Navias' (1922a 1922b) papers and Taliaferro's (1934) hints remained unheeded until 1951. However there is no justification for modern archaeologists to continue

ignoring the important work done by Midgley (1951) and the Australians Weymouth and Williamson (1951) or the overwhelming evidence of Folk and Weaver (1952) which vindicated Midgley's mathematical predictions so convincingly.²

Schmalz' (1960) view on flint patination contrasted decidedly with that of Oakley (1939) who considered carbonic acid in the ionized state to be 'undoubtedly' the chief patinating agent.³ Clark (1979) noted the strikingly opposed concepts of some writers on the influence of calcareous sand. Mitchell repeatedly (e.g. 1947: 299) suggested carbonate waters to have been responsible for the leaching out of silica from the surface of 'flints'⁴ and Moore and Maynard (1929: 276) described them as the most effective solvent of silica from norite and diabase. The results of Curwen's (1940) experiments indicate the influence of both organic and calcareous matter and bring to mind an early comment (Murray and Irvine 1891) that siliceous remains are appreciably soluble in cold sea water in the presence of CaCO_3 and decaying matter (cf. Fairbridge 1964: 444-447). At the same time the tenability of the process it implies is challenged by the demonstrated tendency of many organic compounds to interact with carbonate mineral surfaces forming mono- or multimolecular layers physically isolating the carbonate from water and inhibiting even inorganic equilibrium (Suess 1970).

Although the question of patina attribution remains unresolved to the present time there appears to be complete agreement at least on the composition of the flint patina. The appearance of such altered veneers manifests an etching of the microcrystalline grain's surfaces that alters the stone's reflective properties i.e. its colour (Hurst and Kelly 1966). In preparation for subsequent deliberations some brief comments on the possible mechanics of the solution effecting the leached out lattice of silica crystallites are worthwhile. All early writers believed colloidal silica to be the only form present in natural waters. Because it was proposed only in the year of their own publication Kahlenberg and Lincoln (1898) lacked the benefit of the colorimetric silica determination method but the several later writers repeating their view including Tarr (1917: 433; 1926: 25) Twenhofel (1932: 44 510) and even

Van Tuyl (1918: 456) did not. Dienert and Wandenbulcke (1923) enlarging upon Jolles and Neurath's (1898) method were unable to detect any colloidal silica in their samples of river water and in the following year confirmed its absence by their failure to raise the molecular silicate content of water by increasing its pH which should convert any colloidal fraction present (Dienert and Wandenbulcke 1924). Harman (1926) scrutinized Kahlenberg and Lincoln's propositions and concluded that they are untenable in the light of his meticulous and varied experiments. After persuing established concepts of another discipline Roy (1945) asserted that silica of natural waters is molecularly and not colloiddally dispersed. In 1951 Aoki suggested molecular dissolving of silica in water up to a certain concentration claiming that surplus silica (which would be produced by a lowering of temperature or pH) will polymerise to the colloidal state. It appears that most if not all of the dissolved silica is in the form of monosilicic acid (Mosebach 1955). Whilst solubility in the range of pH 0-9 differs little (Krauskopf 1956) and may in fact be slightly greater in acid than in weakly alkaline conditions (White et al. 1956) - at least at low temperatures (Okamoto et al 1957: Fig. 2). Silicic acid will of course dissolve in water to the concentration and equilibrium solubility which also rises rapidly above pH 9. Iler (1955: 25) reported that in highly alkaline environments the ion H_3SiO_4^- becomes important to the point of dominating over H_4SiO_4 above pH 10 and it is generally acknowledged that ionic forms are present in appreciable amounts only at pH's over 9. Of much relevance is Walker's (1962) examination of the reversible nature of the limestone - chert replacement process.

The questions that are crucial in the archaeological evaluation of the leached cutaneous layer of sedimentary silicates remain essentially unresolved: how is the patination process effected what are the factors deciding its rate of progress and how influential are they? Parallelling natural patination with what Schmalz (1960) terms 'artificial patinas' remains unsatisfactory in the light of several writers' comments on the involvement of carbon dioxide and organic compounds. Moreover patinated flint has been noted in environments evidently devoid

of an alkaline solvent e.g. at surface level on chemically impotent sand exposed only to atmospheric influences and an attendant pH of about 5 to 7. Many chert flakes of surface accumulations are patinated only on their upper face and lightly altered flint has been observed even in faintly acid soil. One is forced to concede that several empirical phenomena have yet to be accounted for plausibly.

The failure of previous research to ponder over one seemingly conspicuous aspect perturbed me initially: acceptance of alkaline solution as the patina producing process postulates that corrosion at the patination front proceeding along granular interfaces must progress enormously faster than the total reduction of the already accessible grains despite the immensely increased surface area of the latter and the outer zone's higher penetrability to alkali replenishment which would certainly not be so easily attainable at the patination front where the 'silicic' diluents should be both nearer equilibrium and less readily transferable. Otherwise there would be no patina. Indeed if chalcedonic chert from the Koonalda Cave is immersed in sodium hydroxide solution (saturated at its boiling point) exposure for one hour will result in the almost complete slow decay of its 1 mm thick patina without significant corrosion of the structurally unmodified stone. The precariousness of the assumption proposing artificial patina to be an accelerated version of the natural mode is clear.

One of two Australian districts splendidly suited for the study of chert weathering is that huge tract of Western Australia east of Norseman where silicate nodules and pebbles are a conspicuous feature of a deflated surface for hundreds of kilometres. Samples from 25 km west of Madura are of terra rossa like but carbonate rich (48.6%) soils with dehydrated and partly ferrous iron yielding the grain distribution curve of a typical weathered loess and a pH of 7.8. Nevertheless surface fragments of chert and quartzite broken only a few decades ago already display discernible surface fading the first stage of patination.

South of Mt. Gambier the contours of both present and ancient shorelines are usually determined by ridges of washed up nodules (almost entirely of

flint⁵ and other cherts) that are often a few metres high and extend for many kilometres on both sides of Cape Northumberland. Moreover the numerous and often very extensive decortication and workshop sites of the entire Discovery Bay region permit a truly exhaustive study of flint patination. A total of 39 such sites were examined in the course of the present investigation along the coast from Portland to Douglas Point and up to 12 km inland. Witter's (1977) 'Early Prehistoric' industries represented at 53.8% of them appear to be spread over a considerable time span. Whilst a few of the abundant in situ 'Early' implements observed definitely occur in the red sand units their majority is associated with various levels of the overlying dark semi consolidated sand. Patinae of all assemblages are being surveyed and preliminary results of this inquiry are briefly reviewed here. The techniques developed are essentially based on the impropriety of Mitchell's (1947) assumption granting the core a higher S.G. than the cortex.

Attempts to gain some insight into the factors influencing patination rates by delineating them quantitatively succeeded in respect of some but not all of these factors. I have expressed patination progress either by patina thickness (Pt cf. Fig. 1) or by total weight loss through patination:

$$W_L \text{ (in \%)} = \frac{(2.55 V - W)}{2.55 V} 100$$

All symbols employed here are listed below.

Legend of Symbols

S.G. Specific Gravity
 Bulk S.G. S.G. inclusive of accessible pores and interstices
 L Maximum length
 V Bulk volume
 W Weight, after drying at 105°C until no further loss

Ws Weight, immersed in water at 20°C (waterproof coating already discounted, specimen fully dried)

Gs Total bulk S.G. or W/V

Ai Abplattungsindex, after Cailleux (1951)

πl Abplattungsindex, after Luttig (1956)

α Patination index; or S.G. silicate - Gs (patina)

P Percentage of patina (by volume)

Pt Patina thickness

W90 Weight of dried specimen in water at 20°C, after immersion for 90 seconds

WL Total weight loss through patination

β Porosity index, % water accepted after 90 seconds (by volume)

E Grösste Dicke, after Cailleux (1951) or $\pi l \times L \div 100$

$$P = \frac{255 - 100 G_s}{\alpha}$$

Alternatively percentage of patina (by volume) can be calculated by another approach: To eliminate the need of physically measuring Pt (which usually involves damaging the specimen) α can be estimated by an experienced observer (it can only vary from 0.5 to 0.9) and theoretical Pt determined by computer by translating the principles I have established in Fig. 1 into seven coordinates. In practice a difficulty to be taken into account is that posed by the possible presence of what I term 'grey zones' - whose consequence would remain an unknown. They are invariably present in Early Prehistoric specimens possessing a Gs > 2.2, except those of W > 100 g. In the sample analyzed bulk S.G. of 'grey zones' ranges from 1.95 to 2.20.

As readily demonstrated by Fig. 2 the index of flatness (depending on application either that of Cailleux or that of Luttig was employed) is of far more consequence than implement shape (cross sections were divided arbitrarily into circular elliptical segmentary rectangular or triangular) when relating Pt to cross section.

To assist with the estimation of α the porosity index β was designed⁶:

$$\beta = \frac{(W_{90} - W_s) 100}{V}$$

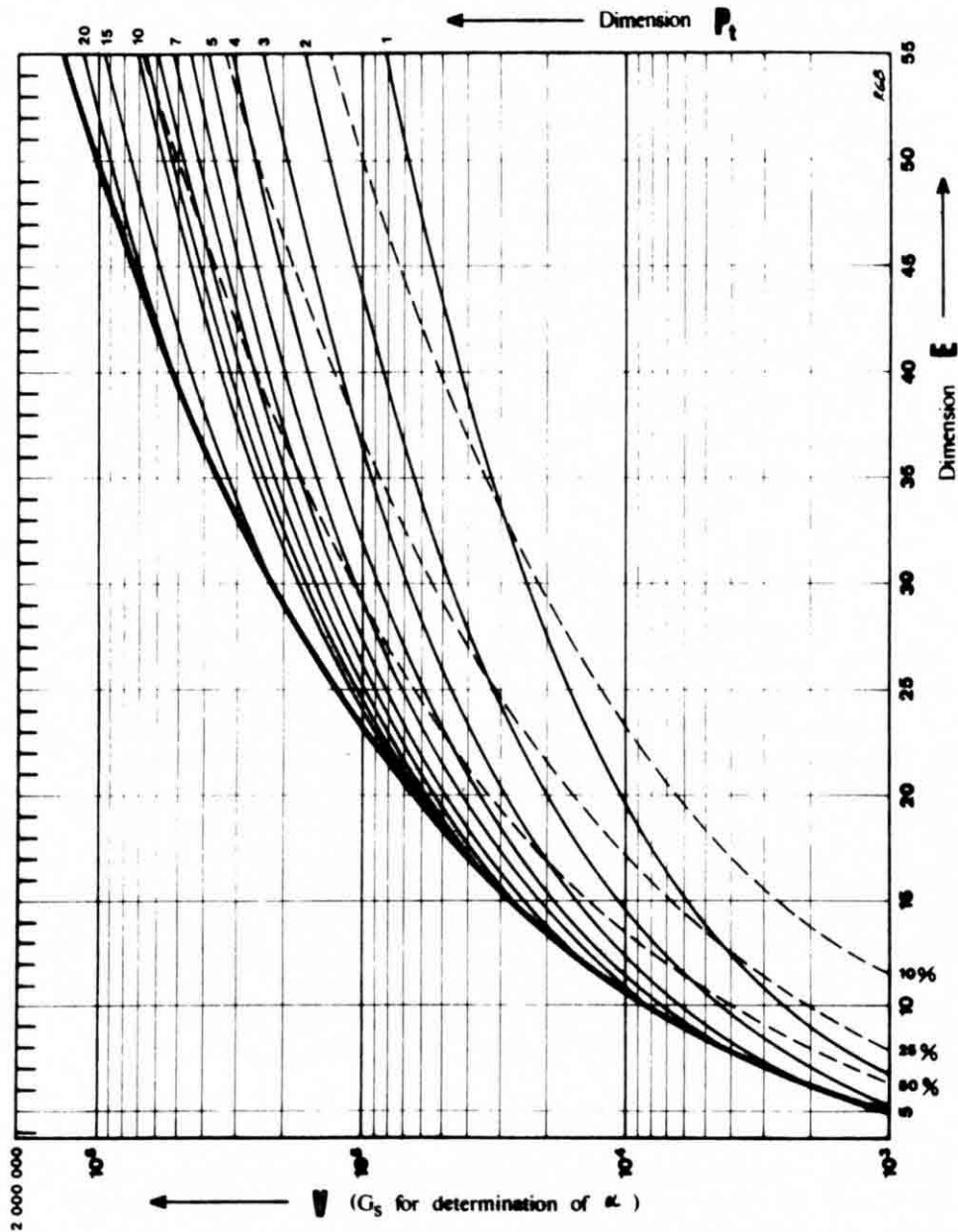


Figure 1. Relationship of G_s , P_t , and P_t , for cuboid of $l = 25$ (- being a function of $A_i = 3$).

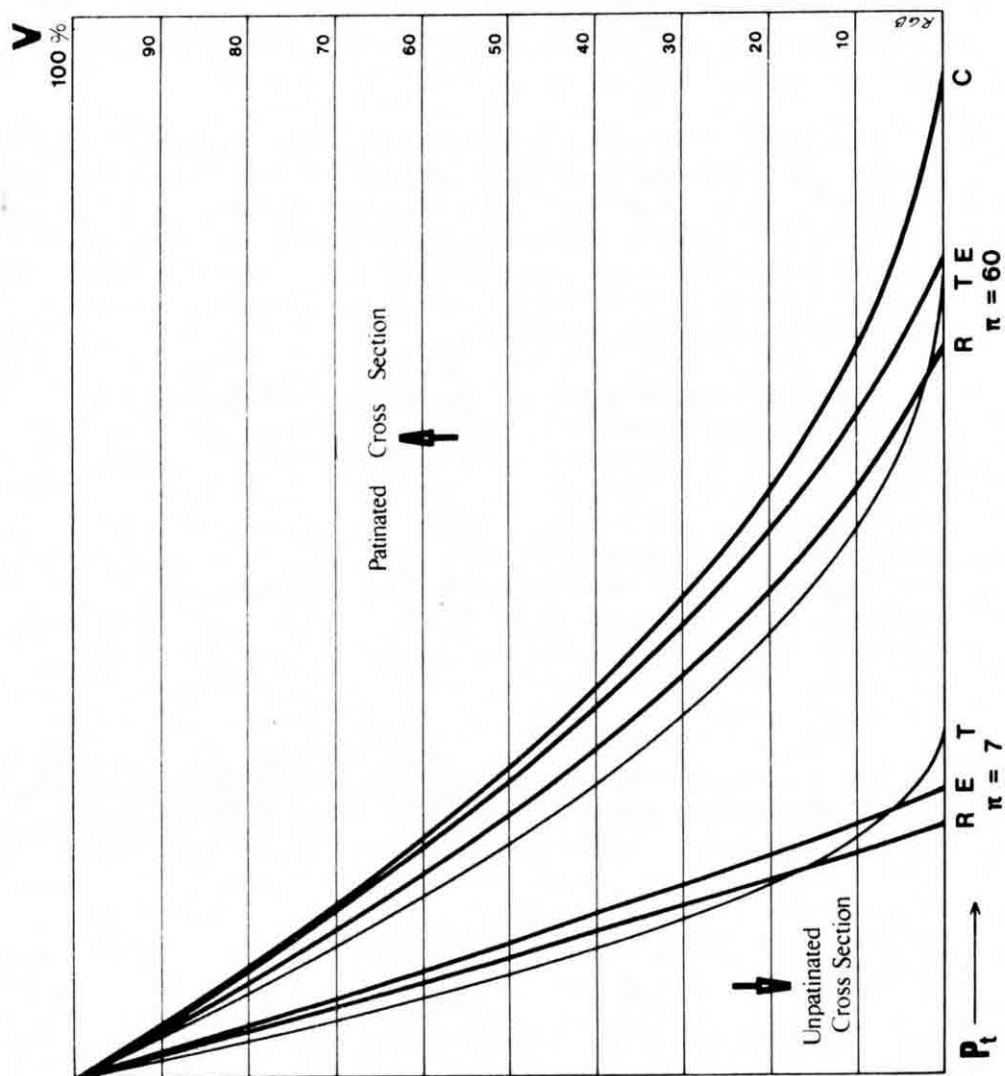


Figure 2. Influence of cross-section and index of flatness on patination progress. C = circular, E = elliptical, R = rectangular, T = triangular. Two indices of flatness are considered.

For a sample of selected Early Industry specimens (free of cortex $W < 80$ g) β ranges from 1.92 to 20.31 (mean 7.36). In general a porosity index exceeding 10 for flakes of the sizes surveyed indicates not merely patination but in fact extensive leaching and an early stage of granular disintegration. The latter always commences from the artefact's thin margins and from the remnants of cortex where these are present.

Some prehistorians accustomed to the concept of almost indestructable lithic implements may find this somewhat surprising if not disconcerting: chert flakes could totally disintegrate within a few tens of millenia in environments quite common in nature - such as exposure to a continually renewable alkaline buffer combined with ample moisture.

The 'grey patina zones' mentioned appear to be either intermediate stages of modification or - especially when arranged as (usually one or two) pseudoconcentric rings - strata indicative of environmental variations. Such fluctuations could have been of pH temperature precipitation or caused by burial exposure or deviations in the availability of buffers (e.g. withdrawal of the sea) and other agents. Their manifestations may well prove to be of at least as much importance as dating attempts via silicate patina.

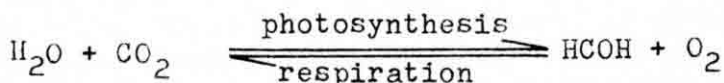
In summary the quantitative relationship of patina thickness and proportion total and specific gravities flatness index and implement shape - albeit rather complex - is well understood and can be demonstrated. Three other factors governing patination rates are still subject to further investigation:

1. Mineralogical composition of specimen. Essentially predominantly cryptocrystalline silicates are altered more slowly than microcrystalline forms. Conversely presence of cortex tends to accelerate the rate of patination in the stone beneath it presumably because leaching proceeds more readily from the porous contact seam than from the initially smooth surface of a fresh fracture.

2. Water availability. Significance is demonstrated at the four cave sites surveyed. Whilst implements from their interior are almost unpatinated despite the mostly alkaline sediments those from just outside the cave entrances are without exception substantially altered.
3. Chemical environment. Its influence must be understood before its effectiveness can be appreciated.

Precision abrasion pH measurements on extensively weathered silicate nodules from Madura offer a somewhat surprising circumstance: the high reading of the unaltered core (pH 9.61) and a slightly lower result for the outermost rind of 2-3 mm thickness (pH 9.07) contrast with readings of the intermediate zones which decline to below pH 8.77. However these variations need not restrict the silica solution's outward movement even if it is saturated. Some of the silica would polymerize to the colloidal state if the solubility limit decreased as a function of reduced pH in some of the layers traversed. Abrasion pH values for similar minerals are in the same order of magnitude and as the readings for the unaltered stone are only marginally below those for CaCO_3 the ability of the silicate to - in the presence of water - itself create a micro-environment requisite to its dissolution transpires. However to ensure the unrestrained continuation of crystalline dismantlement to tendency of the aqueous solution to almost instantaneously attain equilibrium in such restricted spaces as interstitial pores must be arrested.

The role played in this context by carbon dioxide is intriguing. It is of fundamental importance in short term pH variations in nature (Pytkowicz 1965) and the CO_2 system is intimately connected to biologic activities:



Similarly consumption of oxygen by decaying organic matter and activity of microorganisms result in the production of CO₂. The ion exchange effected by this gas and CaCO₃ in the presence of water is one of the geomorphologically most important reactions:



Thus solution of limestone by carbonic acid will not only provide an alkaline buffer calcium bicarbonate it will also decrease the log of the hydrogen ion concentration's activity i.e. increase the pH.

It is via these simple agencies that I propose to explain the basic phenomena associated with the patination of cherts and similar stone. The predicted system is being tested by long term experiments. The striking optical alteration achieved by patination is probably assisted by the polyhedral grains' propensity to surface repulsion causing lack of cohesion between them. It dates from their diagenesis when the closely spaced crystallization centres tended to form a negatively charged skin on the randomly oriented micro crystals by pushing the highly polarizable anions to their surfaces. The solvent attacks primarily along these contact planes where less regular molecular arrangements may form less resistant zones and where water was often trapped during replacement. Compact silicates patinate only hesitantly and randomly if at all in comparison to those of sedimentary origin. Since constituent removal will always be slower on a smooth surface their often evenly knit orderly atomic arrangement will retard alteration.

In a highly favorable environment chert will be subjected to pronounced surface leaching in the course of a few years. Under quite dry or permanently acid conditions patination should not develop over geological epochs. Since it appears impossible to accurately establish the conditions implement surfaces have been exposed to throughout their life one is forced to concede that quantitative evaluation of patinae from different localities will remain futile for the purpose of absolute dating.

One more proposition requiring elaboration in this context adds a cautionary note. What is without fail described as the patina of chert nodules by some archaeologists may not be a surface alteration at all. It may represent a gradational zone of the carbonate replacement process or of its reversal. Such laminae of incomplete silicification of the limestone (or incomplete carbonatization of the chert) are obviously of no relevance whatsoever in dating stone surfaces. Silica filled fractures on chert nodules at Eight Mile Creek (near Port MacDonnell) amply demonstrate that the cortex present is not a recent phenomenon. Many specimens show re-cemented cortex bearing fragments that were displaced up to 10 mm before silica deposition ceased and they break across such ancient fractures.

OTHER PATINAE

Minerals consisting entirely of crystallized silica do not patinate at an archaeologically significant rate nor does similar stone containing only chemically stable impurities. However the intimations of some writers suggesting complete inertness of quartz in water are still fallacious. Although the equilibrium solubility of crystalline silica is somewhat lower than that of the amorphous state (certainly below 100p.p.m. - Krauskopf 1956; no higher than 6p.p.m. for quartz - Gardner 1938; cf. Siever 1957; the equilibrium constant for the reaction of quartz with water to H_4SiO_4 at 25 degrees celcius was determined at 1.7×10^{-4} - Siever 1962) and the reaction very much slower the mineral will still experience surface retreat in the course of geological periods. Thus (in addition to not 'consisting of amorphous silica') quartz is not 'entirely stable' (Kamminga 1971: 43-44). The practice of some prehistorians not to consider clear quartz lacking visibly developed crystal facets as rock crystal also requires comment: despite the absence of smooth growth planes such a stone has fully identical internal crystal structure i.e. its atoms lie in a similar symmetrical arrangement. It is chemically and physically indistinguishable from rock crystal except for the lack of crystal faces and since these need not necessarily be present on a culturally fractured fragment of a rock crystal I feel that in an archaeological context the only discriminating

criterion is immaterial.

The alteration resistant nature of 'pure' quartz⁸ is demonstrated by the twenty or so fragments excavated at Choukoutien (Pei 1931: 120-121; Breuil 1931: 149). An Acheulian flake from the oldest known occupational layer of Austria one of the many rock crystal implements of the Gudenus Cave has no trace of surface alteration on its ventral face. Several milky quartz artefacts from the same habitation level and the succeeding Middle Palaeolithic horizon show a similar resistance to chemical weathering. Despite its inferior fracturing qualities white quartz is frequently used for the manufacture of stone tools especially in regions where accessible deposits of crypto- and microcrystalline silicates are scarce or amongst population groups whose ecology places no emphasis on the virtues of superior stone implements. The white colour of milky quartz is a function of the high ratio of transmitted light to diffused and reflected light and the effected low diaphaneity the result of microscopic liquid and gaseous inclusions. Archaeologically significant time spans are not adequate to cause surface deterioration in other than most exceptional environments unless unstable impurities are present.

Of the two remaining types of mineral patination described by Goodwin (1960) the first induration of exposed surface affects quartzitic sandstones in novel environments. It is a surface redeposition of leached out silica and apparently unsuitable for dating purposes. The more promising limonite staining can affect any sufficiently porous stone under favorable conditions but 'iron oxide staining' would be a preferable locution. Not only is much 'limonite' in fact cryptocrystalline goethite with merely absorbed or capillary water both these minerals are metastable intermediate forms under possibly all geological conditions (Berner 1969: 272; cf. Scheffer et al. 1957: 57-60). That limonite is a stable weathering product following oxidation and subsequent hydration of iron minerals is yet another myth. Soil investigators are well aware that even magnetite may be quite immutable in poorly aerated soils (e.g. Cornwall 1958: 167; for more detailed discussion cf. Schellmann 1959: 134; Van Houten 1964: 654; Van Houten 1968: 406-407; Metzger 1974: 16) and may

form from hematite through reduction (Betremieux 1951: 193; Bloomfield 1964: 661-662; Bednarik 1979: 29).

Patina rinds of crystalline sedimentary silicates readily accept iron oxides. Whilst evenly distributed throughout their matrix in some situations they tend to concentrate in a cutaneous layer in others. Field observations suggest the former mode to be indicative of stable environmental conditions (e.g. subterranean) whereas the latter may manifest climatic extremes. The thin iron free zone contiguous with the unaltered rock of some otherwise impregnated specimens (e.g. samples from Koonalda Cave) represents the patina advance since that infiltration ceased. A climatic change could conceivably have effected the cessation - however farfetched such a notion may appear: the reversible replacement relationship of carbonate and silicate would seem equally applicable to iron oxides and silicate. It could further be argued that deposition of Fe_2O_3 would retard subsequent patination by partially obstructing the migration of dissolved silica. Having been precipitated during a period of environmental pH lower than that of the patina's interstitial spaces iron would find itself even less mobile after a reversal in that relationship. The tendency of prehistorians to overrate the significance of the presence or absence of iron oxide accretion in already patinated artefacts from the Portland - Mt. Gambier region requires mention. The stain should not be considered adequate proof of stratigraphical situation.

Stone tools are frequently found coated with an accretionary deposit of mineral matter that fails to penetrate previous aspects and is often fairly discontinuous. Though perhaps not a patina in the strict sense this is included here for completeness. Carbonate and iron oxide encrustations are established comparatively rapidly silicates perhaps less so. All such coatings involve postulation of a considerable supply of moisture for their formation and their occurrence at presently very dry locations (e.g. Sites 13 14 and 15 Tom Price Western Australia) could infer that these have experienced quite wet climates since such artefacts were deposited.

The hydrated rind of volcanic glasses remains the most thoroughly investigated type of mineral surface alteration but due to the abundance of literature on this subject (e.g. Clark 1961; Friedman et al. 1963; Michels 1973) it is not pursued here. Patination of man-made glass (which has been knapped extensively by Australians since its introduction; Newall 1913; Dickson 1971; Bednarik 1977) by hydrolysis (Brill and Hood 1961; Brill 1963) is not reviewed in the present paper on natural stone.

ON THE PATINATION OF STONE IMPLEMENTS

A sizable portion of all patinated stone artefacts does not possess a comparatively uniform coating and Goodwin (1960: 301) coined three designations for anomalous forms:

1. Differential patination by disproportionate exposure of an object to patination may be of significance in rare instances e.g. where the patina on a spearhead preserved the outline of the long decayed shaft or hafting resin because organic acids have retarded conversion and subsequent removal of silica. Australian implement types suspected of having been hafted should be closely scrutinized for analogous conditions.
2. Anachronistic patination diagnoses the state of a stone that prior to having been subjected to an environment identical to the rest of an assemblage was already patinated through previous exposure.
3. 'Double patination' is a term that could more aptly be broadened to multiple patination. Specimens with two or more accentuated temporally separate phases of superficial modification occur particularly where rich sequence of occupation layers has enabled the more recent habitants to procure stone from lower strata and quarry the earlier artefacts for re-knapping. The number of scholars confounded by the ensuing typological puzzles can only be conjectured. European workers have brought to light modified hand axes from Perigordian Aurignacian and Magdalenian

living floors (Bordes pers. comm.) and Mousterian flakes re-worked by some Upper Palaeolithic peoples. When cryoturbation or fluvial abrasion have not produced adequate means to assist differentiation of typologically incompatible aspects of such an artefact multiple patination may provide the only corroborative evidence. The inadmissibility of silicate patinae for absolute dating which I have attempted to demonstrate in a previous chapter does not extend to certain relative chronometric use or to the illumination of events or processes in a specimen's history especially through elucidating multiple patination. Of the many examples where this was accomplished convincingly the most dramatic I am acquainted with is provided by item No. 22351 from the Gudenus Cave. Head Breuil and Obermaier (1908) deduced the existence of more than two Lower or Middle Palaeolithic levels suggested by their own comments on the specimen's patination and wear they would have invited much criticism for proposing such a poorly supported hypothesis. Nevertheless they would have been proven right 68 years later (Bednarik in prep.).

Without wishing to encourage unrestrained use of patina for postulating otherwise unfounded premises the import of appreciating however guardedly the hints to be derived from patina assessment must still be emphasized. It is unfortunately true that the great majority of descriptive treatises dealing with lithic assemblages fail to record postfabricational alterations (micro wear and patination) after so generously committing space to fabrication aspects (knapping and retouch). Admittedly there are some notable exceptions in respect of patination (Burkitt et al. 1939; Krueger 1956; Valoch 1970 are some instances).

Silicate patina analysis is not in widespread use in Australia. Witter's (1977: 56 58 60) profitable comments on the seemingly clear differentiation achievable by patina appraisal of typologically separable industries in the Discovery Bay area seem

almost hesitant and yet they are most material. His assertion that the Early Prehistoric implements are always extensively altered in contrast to the thinly patinated Late Industries found ample support in our work and that of others. In addition none of the many Discovery Bay specimens with multiple patination displays an intermediate patina thickness. Accentuation is in fact so profound that one cannot resist the temptation of proffering the following speculation: would it be too far fetched to suggest that the withdrawal of concentrated population indicated by the apparent large temporal hiatus between occupations coincides with the withdrawal of the sea? Naturally a greater antiquity than that implied by the few Early Holocene dates so far available for the Gambieran would be stipulated but evidence of preceding occupation seems forthcoming (Bednarik in prep.).

CHRONOMETRIC POTENTIAL OF PATINAE: A SUMMARY

The utility of flint patina as an expression of antiquity was realised soon after flint implements themselves were first identified in Europe. Prestwich (1859: 55-56) engaged by Falconer to report on Boucher de Perthes' finds not only employed patination to demonstrate the authenticity of stone tools but already went as far as linking differing patina compositions to certain matrices. This was in the year of Darwin's main publication and despite the labors of dozens of scholars over the many years since the potential of flint patination for dating purposes still remains obscure. I am aware of only two Australian archaeological treatises solely concerned with patination and its quantitative appraisal has been almost totally neglected. Hossfeld (1965) is preoccupied with terminology and his proposition to limit the use of the term 'patina' to a very thin surface film cannot be supported. The acceptance of the originally Italian patina is not necessarily restricted to thin veneers. Adoption by all three main scientific languages of the French archaeological usage would seem to render such an emendatory attempt both insular and futile. Hossfeld's exclusion of desert varnish from patinae is inconsistent with his own definition because its thinness is one of desert varnish's most pronounced characteristics. However

this does not detract from the contribution's great significance which lies mostly in the one observation: 'Some (patinated flint) specimens give evidence of temporary cessation and subsequent renewal of weathering indicating environmental changes.' In compliance with Hossfeld's concluding request for a uniform denominative system of patinae the following scheme is offered for discussion. The varieties listed are those discerned by me and they are accompanied with comments on their apparent significance to the prehistorian:

1. SOLUTION and removal of one or more components producing a distinct layer of altered chemical and/or optical character:
1A - Removal of silica especially in sedimentary silicate rocks: Thickness of patina is considered to be more a function of chemical environment than of time and therefore not relevant for absolute dating. It is advantageous for relative dating at a single locality in most circumstances. 1B - Removal of iron or other cations: Comments for 1A probably apply.
2. ALTERATION (CHEMICAL): 2A - Oxidation or reduction (e.g. of iron components): Are certainly environmental indices. 2B - Hydration (volcanic glasses): Its diffusion rate is believed to be controlled by known factors and rind thickness is used for absolute dating. 2C - Hydrolysis: Laminated layers have been suggested to represent annual cycles on man-made glass. 2D - Glazing of silicate: Product of momentary or brief reaction. Possibly of advantage in distinguishing chronologically discrete components or for documenting a past event. 2E - Others.

ALTERATION (PHYSICAL): 2F - Polishing (aeolian abrasion or by movement of snow or soil): Should be expedient for relative dating in some instances.

3. SECRETION where leached out cations are unable to remain in solution upon reaching the stone's surface and precipitate possibly

due to decrease in pressure different pH in the soil matrix hydration/dehydration differentials or micro-electrochemical and organic influences: 3A - Iron oxides: Schutzrinden that are not subjected to cycles of alternative stabilization and disbandment appear useful where their differing properties combined with insolation induced (-or other) fractures may permit the establishment of a sequence but much detailed investigation is required here. Constancy of crust formation rate can be better relied upon where a surface has been exposed to atmospheric agents only. For certain rock types 'full patination' will be accomplished only in the course of millenia especially in arid environs.

3B - Silica: 'Induration of exposed surface' (Goodwin 1960) possibly also the 'superficial layer of flint patina' of Sollas (1913).

4. ACCRETION either by penetration of pervious aspects or by superficial precipitation:

4A - Iron oxide staining of porous stone: Usefulness possibly overrated because deposition besides being a function of time is significantly affected by several environmental factors.

4B - Desert varnish (thin ferro manganese veneer): Although formation may depend primarily on climatic factors its presence commonly implies great antiquity. Suitable for chronological separation of cumulative components of a surface assemblage.

4C - Surface accretions (of iron oxides carbonates silicates): Their precipitation postulates certain chemical conditions whereas time appears to be a far of relatively little bearing.

It is important to realize that combinations of two or more of these types are very common and their end products can be distinguished only with difficulty in many instances.

What transpires is the very limited utility of any endeavours to relate the absolute thickness of an altered cutaneous layer to antiquity. The results of such correlation are encouraging in the case of the hydrated skin of volcanic glass whilst the potential of leached out layers beneath the secretion rinds of specific rock types has yet to be demonstrated (Bednarik 1979). In particular the influence time has on the thickness of chert patina is so insignificant that it can be disregarded unless exposure to identical environments can be proposed for specimens. That relative dating may in such circumstances be effected from silicate patina study has been suggested by many writers and positively confirmed by my own work.

The value of patinae as palaeo-climatic or other environmental indices implied by the above classification system has been reflected upon only by few writers (Hunt 1954: 184; Hossfeld 1965: 170; Curwen 1940: 435) and not examined in any detail at all since the days of de Perthes. Once patina was branded as a mark of antiquity its other potential remained neglected and as attempts of absolute dating via patina thickness or intensity emerged as mostly futile patination itself fell into disrepute. This may have been justified in earlier years but as the prehistorian's resources continue to move towards increased sophistication as he gains access to electronic computing equipment capable of processing immensely complex data re-considering the potential of patina analysis becomes relevant.

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NOTES

1. The archaeologist's tendency to extend the term flint to other cherts is reminiscent of his frequent misuse of petrological designations: e.g. opal is substituted for chalcedony obsidian for tachylyte (cf. Cochrane's 1977 criticism) patina for cortex clay or ochre for Montmilch desert varnish for dunkle Rinden oxidisation for solution quartzite for silcrete.
2. It is a practice comparable to that of continuing to advocate Tarr's flint genesis hypothesis long after Van Tuyl (1918) Correns (1926) and Wroost (1936) had pioneered the replacement origin thesis (cf. also Krauskopf 1956; Audley-Charles 1965: 1189; for some interesting exceptions cf. Peterson and von der Borch 1965; and Liss and Spencer 1970).
3. Schmalz misunderstood the crucial passage of Weymouth and Williamson's article and since he was apparently unaware of both Midgley's and Folk and Weaver's papers he held the genuine belief of being the first to demonstrate the absence of opal in flint.
4. Mitchell's assumption that the specific gravity of the flint core is higher than that of the 'cortex' is however contradictory to his stated espousal of the interstitial opal theory: removal of colloid silica would increase not decrease the S.G. What is in fact decreased is the bulk density.

5. In the absence of any chauvinistic preference I accept this term for stone possessing characteristics almost identical to those of European flint.
6. Porosity as such or void content can be ascertained by several methods. Although the McLeod porosimeter is employed in my palaeo-climatic work on carbonates the wax coating method was used in the present context because it is readily accessible to prehistorians.
7. The theoretical pH of pure deaerated water in equilibrium with CaCO_3 is between 9.9 and 10.0 (Garrels 1960: 50) in contrast to other values reported.
8. Like other crystals it usually contains microscopic bubbles mostly of water but also of numerous other impurities (Wahler 1956; Kvenvolden 1971). In addition some rock crystal displays crystal inclusions e.g. the black longitudinally striated forms at some Wilsons Promontory sites which I believe to be schorlite.

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