28 July 1961, Volume 134, Number 3474

SCIENCE

CURRENT PROBLEMS IN RESEARCH

Patination of Cultural Flints

Flint artifacts can be dated by cortical changes in mineralogy and texture.

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Certain flint artifacts have undergone cortical decomposition since they were fashioned several hundred to several thousand years ago and are now invested with a rind or patina. A rough correlation between the thickness of the patina and the age of the artifact has been noted (*1*).

However, many artifacts which are known to be old exhibit little or no cortical change. It is apparent, therefore, that age is not the sole variable on which patination depends. Before patination can be utilized chronometrically the other variables must be determined and their relative effects must be evaluated.

For obsidian, Friedman and Smith (*2*) have shown that only two main variables must be evaluated: composition and mean temperature.

Flint is a more complex material. Its microstructure is more variable and is an important patina-controlling factor. The kind, size, and manner of distribution of impurities profoundly influence flint's susceptibility to attack and the rate of penetration by water and other weathering agents. Even limited study suffices to show that the patination rate may vary more with microstructure and mineralogical impurities than with age. The number of variables is greater for flint than for obsidian, but with careful use of evaluation techniques and a fuller understanding of the processes involved, flint patination can be made to yield useful chronometric data.

Two general types of flint patination can be distinguished. In one type the patina is some shade of brown and is darker than the core. In the other type the patina is a chalky white and is lighter in color than the core. The patina is visible primarily as a color difference in both cases. Before considering in detail the origin of the patina, let us review the properties of flint, such as composition and texture, which are modified during patination and on which the color differences depend.

Composition and Texture of Flint

Flint is composed mainly of small crystallites of silica. The individual crystallites may be so small that their boundaries are invisible even at high magnification, or they may be large enough to be seen by the unaided eye. Their shapes range from needles or fibers to equant (nearly equidimensional) grains. The size and shape of the grains may be regular within a given specimen, or they may vary greatly (Fig. 1). Radiating spherulitic and oölitic textures are common (Fig. 2). Many flints originated as siliceous replacements of fossiliferous carbonate rocks, and outlines of fossils or fossil fragments are commonly preserved (Fig. 3). The mineral impurities in flint include carbonates, iron and manganese oxides, clay minerals, carbonaceous matter, and iron sulfide. The carbonates are typically in the form of rhombs 0.01 to 0.1 millimeter across, distributed unevenly through the flint and often imparting to it a mottling or banding. Less frequently the carbonate is in the form of granular patches or partially replaced fossil fragments. The other mineral impurities are generally distributed unevenly as "dust" or clay-size inclusions which are not individually visible to the eye but which impart a haziness, milkiness, or other color change.

Color of Flint

The color of flint is determined by the grain size, the texture, and the kind and number of impurities.

Grain size and texture largely determine how much of the incident light enters the specimen and passes through and how much is reflected back to the observer by a series of refractions and reflections at grain intersurfaces. The ratio of transmitted light to diffused and reflected light fixes the diaphaneity of the specimen and the *value* of its color (according to the Munsell color system). A flint composed of coarse even-grained quartz, for example, has relatively few refracting and reflecting surfaces, so that most of the incident light enters and passes through (unless it is absorbed by impurities) and the specimen appears colorless-to-light-gray and transparent-to-translucent. A flint composed of fine crystallites, on the other hand, particularly if they vary in size and are irregular in shape, has numerous intersurfaces. Most of the light incident on such a specimen is diffused and reflected out. Consequently the specimen is white and opaque.

The impurities in flint affect the

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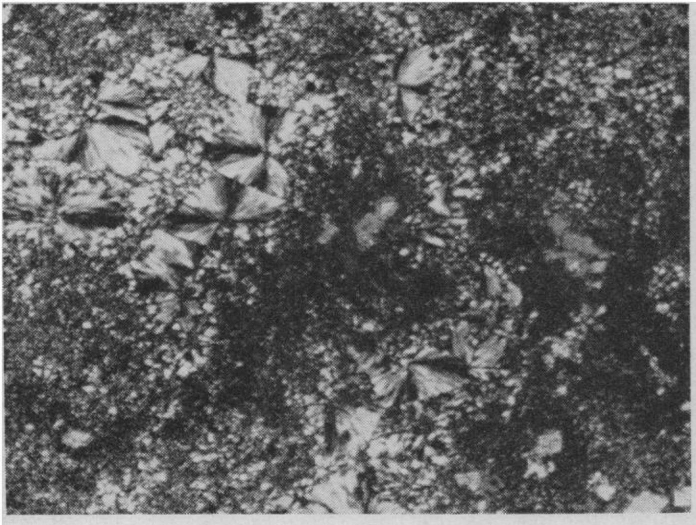


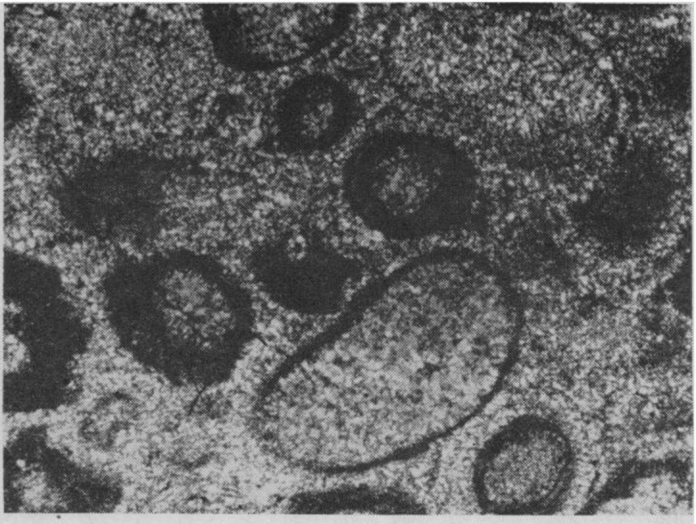


Fig. 1 (left). Photomicrograph of flint, in thin section, showing the variation in grain size and the radiating texture. Fig. 2 (right). Photomicrograph of flint with relic oölitic texture thin section. [Polarized light; about × 73]

color in two ways: (i) by their influence on the ratio of transmitted light to reflected light, and (ii) by their absorption of light. The surfaces between impurities and the enclosing quartz are more effective in refracting and reflecting light than the surfaces between the quartz crystallites themselves. A fractional percentage of impurities may reflect or absorb, or reflect and absorb all the incident light. Whether the flint appears white, gray, black, or some other color depends on how much of the light is reflected and how much is absorbed, and on whether all wavelengths are absorbed equally. Specimens that reflect all the incident light are white. Those that absorb all the light are black. Those that absorb a part of the light are some shade of gray, if all wavelengths are absorbed equally, and are red, brown, or some other color if certain wavelengths are absorbed more than others. The grain size and the texture strongly influence the ratio of reflected light to transmitted light and therefore affect the property of lightness—the *value* of the color. The kinds of impurities determine which wavelengths are absorbed —that is, they determine the *hue* of the color. The amount of the impurity affects the degree of saturation of the color, or its *chroma*, as well as its *value*.

These generalizations are illustrated by Figs. 4, 5, and 6, which are photomicrographs, made with transmitted light, of thin sections of flints. The light gray areas are silica. The moderate gray areas are silica clouded by clay inclusions. The gray rhombic shapes are carbonate minerals. The black areas are opaque impurities in the flint. The proportion of opaque matter is not as great as it appears, inasmuch as the photograph is a projection onto a single plane of all the opaque matter in the body of the section, which is 0.035 millimeter thick. Most of the opaque matter is white—that is, it reflects all visible wavelengths of light. Some of it absorbs all visible wavelengths equally, and is black. Light can penetrate these three flints for only a fraction of a millimeter before a part of it is reflected out and the remainder is absorbed.

The flint shown in Fig. 4 contains abundant white opaque matter which reflects out the incident light before much of it has been absorbed; consequently the flint is light gray. The flint shown in Fig. 6 contains much less opaque matter than that of Fig. 4 and a greater proportion of the opaque matter is black. Incident light penetrates deeper and is largely absorbed; consequently the upper half of this flint is black. A flint with the same

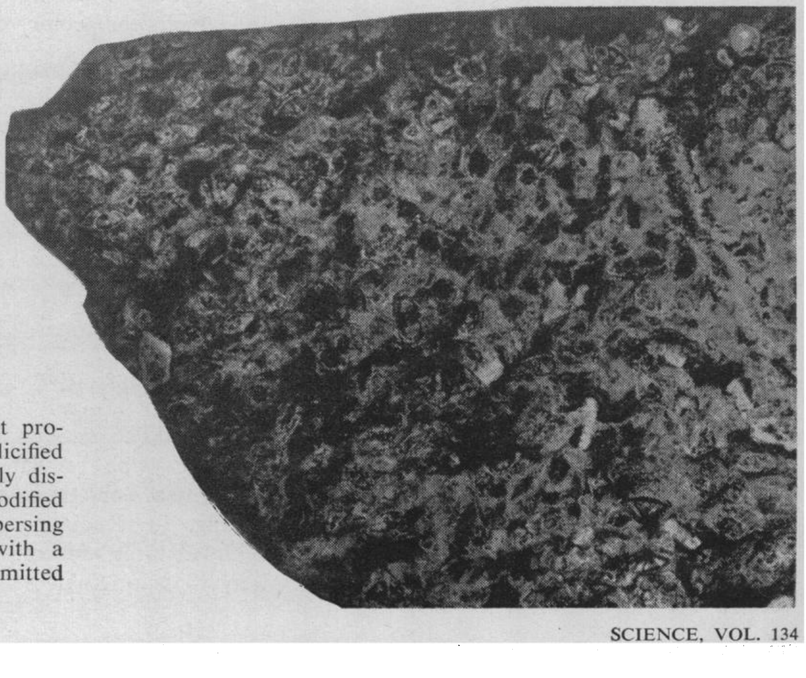


Fig. 3. Photomicrograph of a portion of a brown flint projectile, in thin section. The flint is composed of silicified foraminiferal tests and is colored red brown by unevenly distributed ferruginous matter. Patination processes have modified the exterior distribution of the ferruginous matter, dispersing it more or less evenly and investing the projectile with a continuous smooth rind of hydrous iron oxide. [Transmitted light; about × 9.3]

impurity content but with a finer, uneven texture would be light gray because light would be scattered more at the surface and a greater proportion would be reflected. The opaque-impurity content of the moderately gray flint (Fig. 5) is greater than that of the light gray flint (Fig. 4) and still greater than that of the black flint (upper half of Fig. 6). The thin section represented by Fig. 6 was cut from a black arrowhead mottled with light reddish brown. The black portion (upper half) contains much less opaque matter than the light-colored portion (lower half), but in the lower half the opaque matter is iron-stained and reflects out more light, even while absorbing the shorter wavelengths; hence this portion appears light-colored and reddish brown.

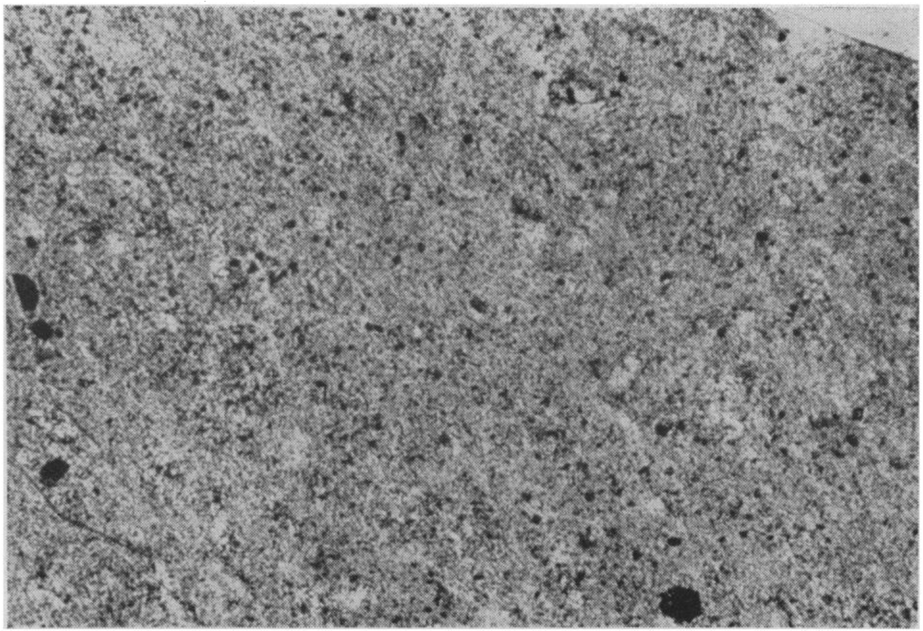
The absorption of light by color centers may be a secondary cause of color in a few flints. The color of most, however, is attributable to the refraction and reflection of light along intergranular surfaces and to the pigmenting effects of a few included impurities.

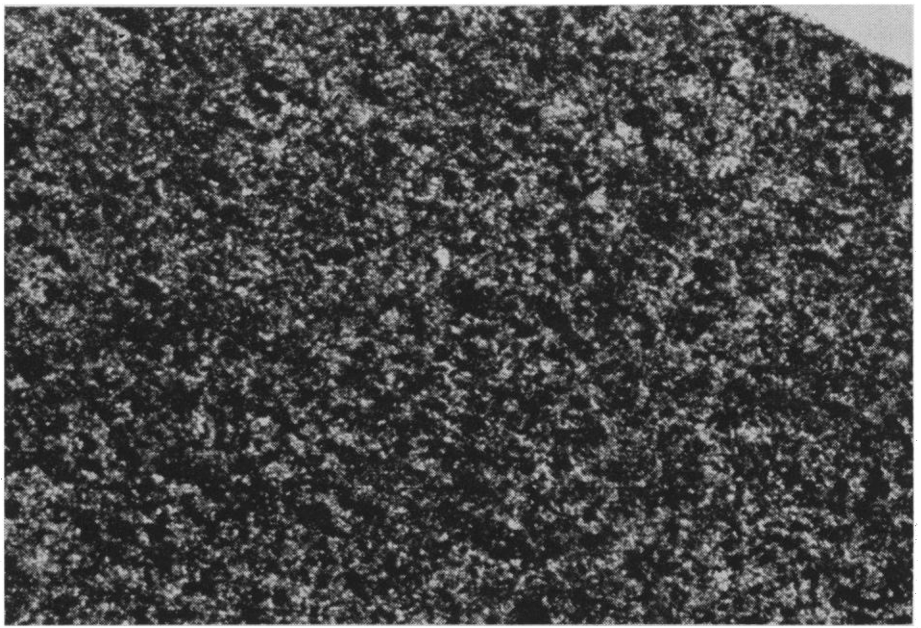
The Patination Process

Obsidian is volcanic glass. Patination in obsidian is essentially a single process, hydration, the rate of which is controlled by the rate of diffusion of water into the glass. For this reason the patination rate is strongly influenced by temperature.

Flint, on the other hand, is mainly silica, which is only slightly susceptible to hydration. Patination in flint proceeds by the interaction of at least three different processes operating, for the most part, on impurities in the flint: (i) oxidation and hydration, (ii) dissolution and leaching, and (iii) chemical and mechanical disaggregation.

Flints which are pure silica, or which contain only chemically stable impurities, cannot patinate, regardless of grain size or texture. To this class belong many of the light gray, trans-





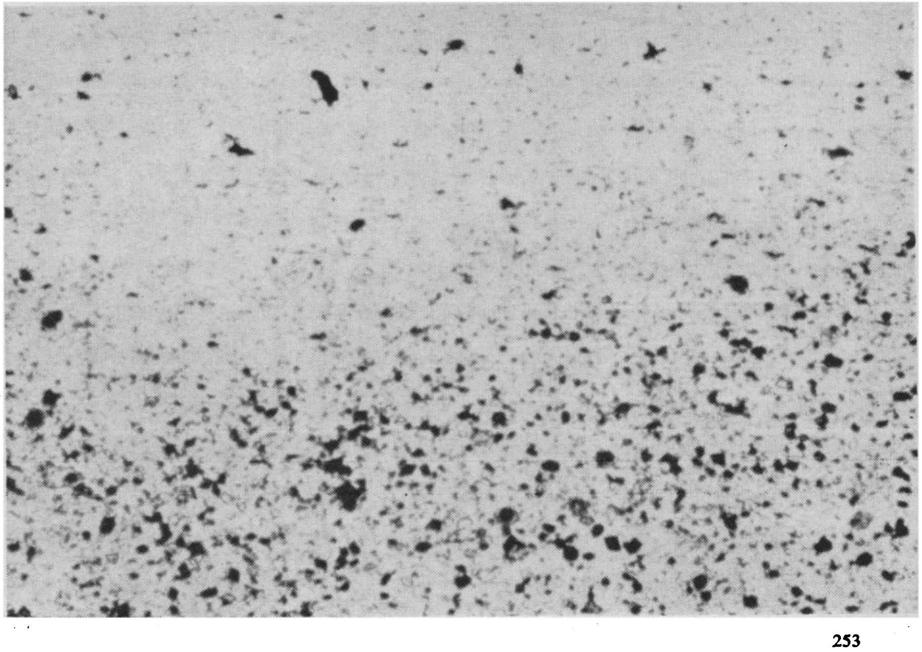


Fig. 4 (top). Photomicrograph of light gray flint, in thin section (transmitted light; × 147). Fig. 5 (middle). Photomicrograph of moderate gray flint, in thin section (transmitted light; × 147). Fig. 6 (bottom). Photomicrograph of black flint (upper half), mottled by pale reddish brown flint (lower half), in thin section (transmitted light; × 175).

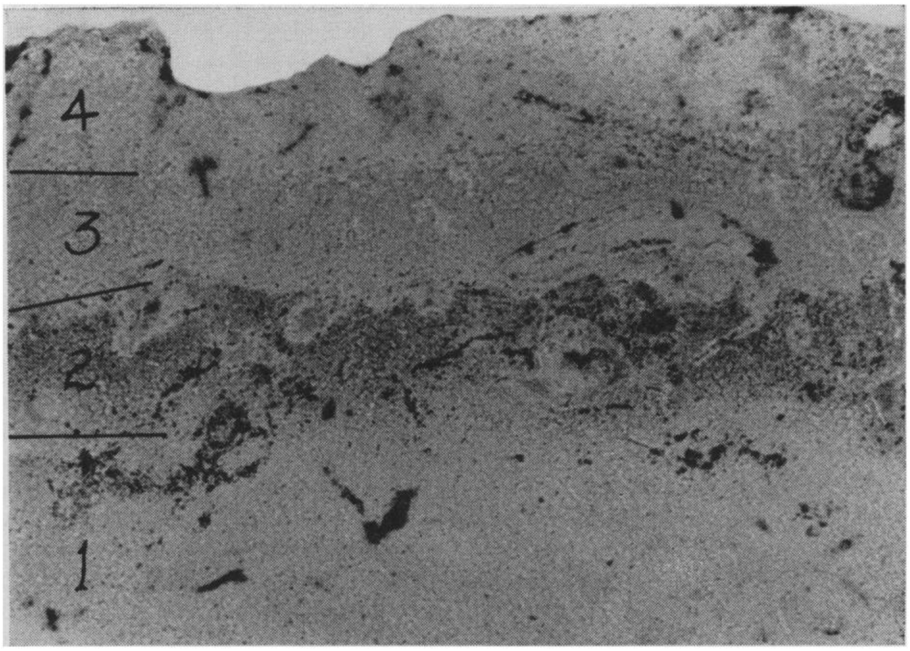


Fig. 7. Photomicrograph of a thin section, showing the characteristic development of the chalky white patina (see text). [Transmitted light; × 96]

lucent flints and the dark flints which owe their color to organic matter.

The flints which contain chemically unstable impurities are all susceptible to patination, but the rate varies greatly, depending on what is the predominant mechanism by which water and other weathering agents penetrate.

For the very fine grained, even-textured flints whose unstable impurities are thinly dispersed, the principal mechanism is diffusion along intergranular boundaries. Flints of this class are most useful for chronometric purposes, because their patination is controlled by only a few variables, foremost of which are (i) mean temperature and (ii) composition, as in the case of obsidian.

Most flints have grains of various sizes, an uneven texture, and inhomogeneously distributed impurities, and their patination is influenced by several factors in addition to temperature and composition. When a new surface is formed on one of these flints, any exposed carbonates begin to slowly dissolve and leach. As they are removed, new surfaces are exposed, the flint becomes more porous, and quartz crystallites are somewhat loosened. Where the weathering agents gain access to inclusions of iron sulfide, the ensuing oxidation and hydration cause local volume changes and create dilute acids which, in turn, attack some of the clays. The iron oxides hydrate and disperse along grain boundaries and in voids. The aggregate effect of the various oxidation, hydration, and dissolution processes is a loosening of quartz crystallites and a greatly increased porosity. This over-all textural change, which greatly increases the reflectivity of the specimen, is seen as a chalky white patina. Where iron oxide or other pigment is dispersed near the surface, the whiteness is correspondingly modified to cream, pink, brown, and so on.

Figure 7 illustrates the characteristic development of a chalky white patina. The core (zone *1*) shows relatively little change. The boundary between zones *1* and *2* is the depth to which patination has progressed. In zone *2* the ferruginous masses have been attacked and partly dispersed. In zone *3* dispersal is pronounced and leaching of ferruginous and calcareous matter is perceptible. In zone *4* leaching is pronounced and the flint is quite porous. The whiteness of the patina is largely due to textural changes and to the increase in reflectivity occasioned by dispersal of the opaque matter, and partly to leaching of carbonates and reddish brown pigment. The formation of the chalky white patina is favored by the high impurity content of clay and carbonate minerals.

Where the water in contact with a ferruginous flint is acidic, a large part of the iron in the patinating layer may be dissolved and leached away from the flint or, instead, may be dispersed along intergranular spaces and only slightly concentrated at the flint's surface. In the first case a chalky white patina develops; in the second case, a brown goethitic rind develops, as shown in Fig. 8. Different sets of local conditions can produce one or the other type of patina from the

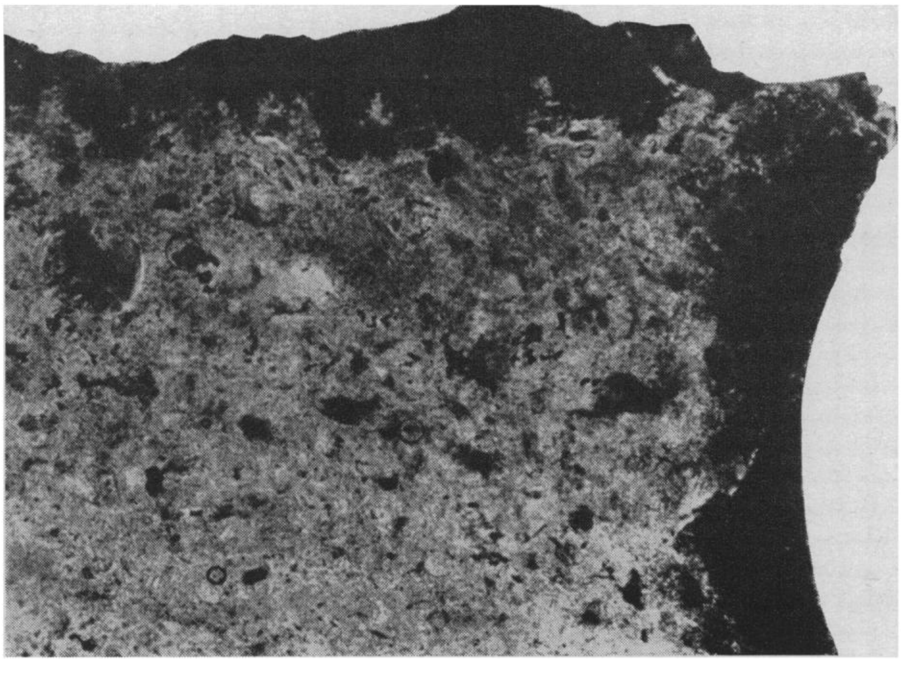


Fig. 8. Photomicrograph of a thin section, showing patina of the brown goethitic type. The patinating processes have caused the ferruginous matter (black areas), which was unevenly distributed originally and is still unevenly distributed in the core, to be dispersed along intergranular spaces in the patinating layer and concentrated on the exterior of the specimen to form a smooth brown goethitic rind. [Transmitted light; × 70]

same kind of flint. Where the flint is exposed to circulating acidic ground water, leaching of iron and development of the chalky patina is favored. Where the moisture involved in patination gains its acidity from chemical reactions within the flint, or where the flint reposes in stagnant phreatic water, the development of the brown goethitic patina is favored.

Texture and microstructure strongly affect patination, as illustrated in the flint shown in Fig. 9. This flint was formed by the silicification of a porous fossiliferous rock. Silica has replaced foraminiferal tests and other fossil fragments in the dark gray areas (Fig. 9, bottom) and has filled voids (the light gray, granular areas). The void-filling silica can be penetrated only through intergranular diffusion, and it contains no visible impurities; consequently it acts as a barrier to patinating agents and cannot, itself, develop a patina. On the right side, the impurity-laden flint in Fig. 9 has patinated normally. At the top, patination has proceeded normally down to the void-filling silica, which has a different texture and has acted as a barrier. The two outer zones of the typical chalky patina—the zone of pronounced leaching (zone *4* in Fig. 7), and the zone of homogenization of impurities (zone *3* in Fig. 7)—continue around the specimen from the right side to the top, as shown by the dashed lines, but the thickness of the next inner zone (zone *2* in Fig. 7) is much reduced. Continued patination of this specimen would thicken the patina on the right side by the inward migration of each zone boundary, but at the top only zone *4* would thicken, at the expense of zones *3* and *2*, without any over-all increase in the thickness of the patina.

Summary

All flints containing unstable impurities are susceptible to patination. The rate of patination varies with many factors: (i) the texture and microstructure of the flint; (ii) its permeability; (iii) the kind, proportion, and distribution of impurities; and (iv) environmental factors, such as temperature and soil chemistry. The thickness of the patina varies also with time.

Two contrasting types of patina can develop: a chalky white patina and a ferruginous brown patina. Both types are observable primarily as a color change, and study of these types is facilitated by a clear understanding of the causes of color in flint.

The color of most flints is the result of repeated refraction and reflection of light at numerous intergranular surfaces, whereby part of the light is internally absorbed and part is reflected back to the observer. The ratio of reflected to absorbed light governs the lightness of the color, or its value. The preferential absorption of certain wavelengths by natural pigments (such as iron oxide and hydrous iron oxide) disseminated through the flint determine the hue of the color.

The color changes produced during patination relate to changes in texture and impurity content occasioned by the attack of weathering agents on impurities in the flint. The creation of voids by the dissolution and leaching of carbonates, the loosening of quartz crystallites, and the dispersal of clays

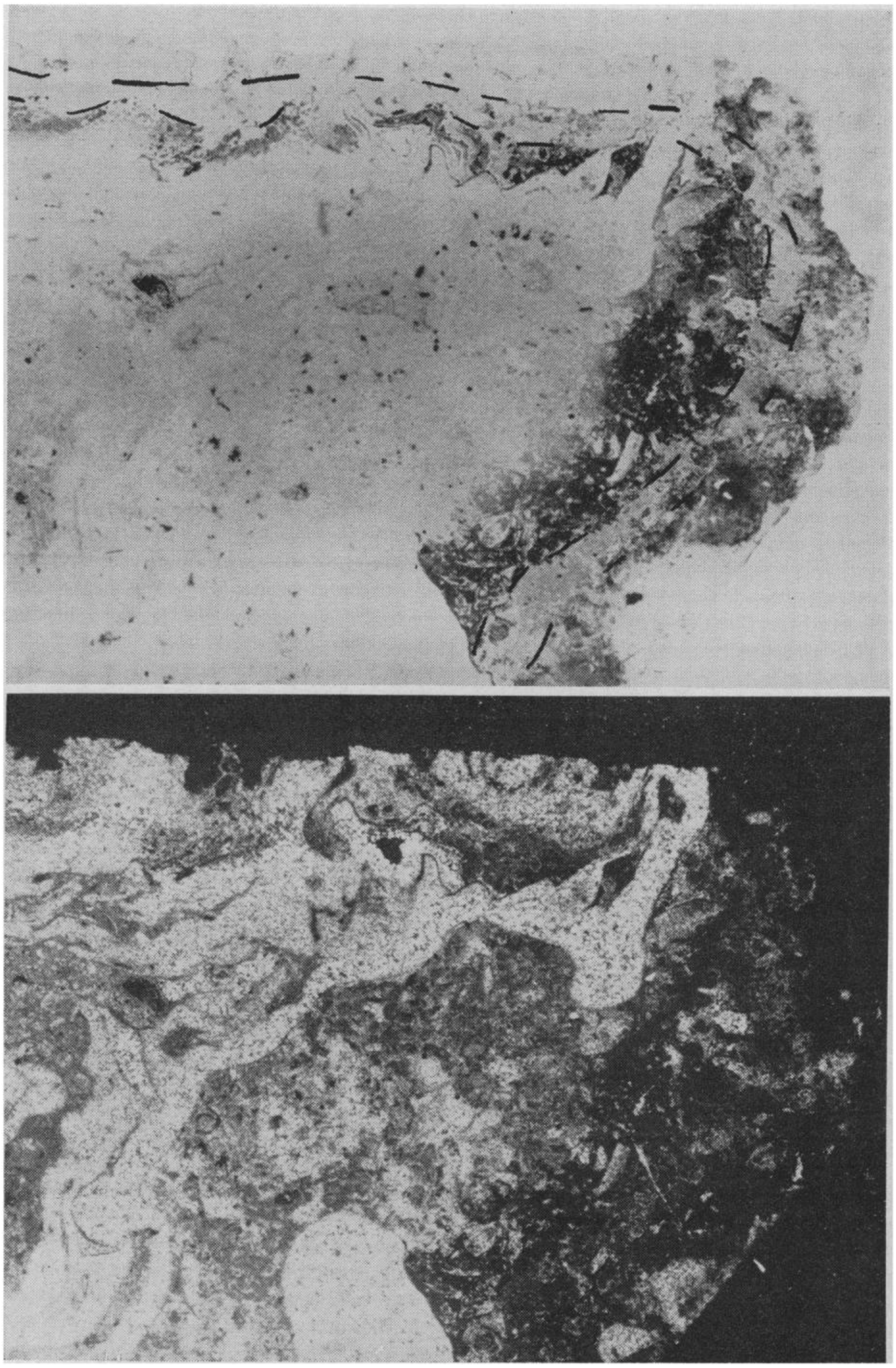


Fig. 9. Photomicrographs of a flint formed by the silicification of a porous fossiliferous rock (see text). [Top, plain light; bottom, polarized light; × 10]

all modify the reflectivity of the flint. Chemical changes involving the pigments, their dispersal along intergranular surfaces, or removal by leaching modify both reflectivity and capacity to preferentially absorb.

Attempts to correlate patina thickness with age, and thus to use flint patinae chronometrically, have proven unsatisfactory because other factors, whose importance in some cases exceeds that of age, have not been taken into account. The texture and microstructure of flint, its permeability, and the kind, proportion, and distribution of impurities can be evaluated by regular petrographic techniques. Environmental factors can be assumed constant for artifacts from the same types of soil in a given climatic region. Only after allowances have been made for these additional variables does the age-dependence of flint patination become clear.

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Infectious Nucleic Acids, a New Dimension in Virology

Their release from infected tissues and resistance to antibodies may explain some anomalous conditions.

Roger M. Herriott

In the last few years a new dimension in virology was discovered by finding that naked, or free viral nucleic acids are infectious (*1–12*) and that they are not affected by antisera which neutralize whole virus (*3, 5, 8*). Discovered first in plant viruses (*1*), the infective nature of viral nucleic acids was soon afterwards demonstrated for poliomyelitis (*2, 3*), eastern equine and West Nile encephalitis (*2, 4*), Semliki Forest encephalitis (*12*), foot-and-mouth disease (*10*), influenza (*5, 11*), a bacterial virus disease (*7*), and a viral-induced tumor disease (*6*), to mention some representative cases (*31*). Both ribose and deoxyribose - type nucleic acids are among the examples, so there is every reason to believe this is a general phenomenon. Only the efficiency of infection is lower in the nucleic acid preparations than in the case of intact viruses. In all cases the nucleic acid produced the usual disease with the release of whole virus particles.

This capacity of nucleic acid to breach the main defense mechanism of animals led me to several questions and to some speculation which may be worth examining in detail in order to determine the degree to which infective nucleic acids of viruses play an unrecognized role in natural diseases.

The questions which follow serve as the nucleus around which this article is organized.

1) If the viral nucleic acids are released from diseased tissues and if antibodies do not react with nucleic acids, what stops a viral infection?

2) Is the persistence of some infective agents for long periods in the blood of infected subjects—as in serum hepatitis or infectious anemia of horses—due to an infective nucleic acid?

3) Are infectious nucleic acids, either free or in an unreactive envelope, responsible for reports of infectivity in the presence of antibodies?

4) Can the long immunity imparted by infection with certain viral agents be attributed to the maintenance of a low-grade infection, perpetuated by infectious nucleic acid?

5) What will infectious nucleic acids do in an individual vaccinated with a "killed" virus preparation?

6) Since viral nucleic acids can infect hosts not infectible with whole virus, does the search for insect vectors and susceptible hosts which might serve as reservoirs or intermediate hosts need reinvestigation?

7) Do these properties account for the failure to find transmissible agents in human tumors?

While the answers to all or even most of these questions may not lie in the existence of free infectious nucleic acid, the phrasing of the questions deliberately focuses attention on the unusual properties of viral nucleic acids. Questions of a similar nature have been raised briefly by others (*14, 15*).

Viral Nucleic Acid in Infected Cells

Let us first consider the likelihood that free or naked nucleic acid may be present in infected cells and may be liberated to infect surrounding tissues. If there is evidence against such a possibility, it would suggest that the infectious nucleic acids are artificial products of the laboratory and play no part in natural diseases. In two instances in which this point has been examined, free viral nucleic acid has been found or implicated.

Phage-infected *Escherichia coli* have been studied most intensively. In this system, infection is initiated by injection of viral nucleic acid into the host cell (*16*). This is soon followed by synthesis of a "pool" of viral nucleic acid from which progeny virus is formed (*17*). This pool of nucleic acid is maintained essentially constant during intracellular phage formation. At lysis, presumably, the viral nucleic acid from the pool which had not been enclosed in the protein coat is released along with whole virus.

In the case of tissues infected with animal viruses, the evidence is more pertinent to the present discussion. Wecker (*18*) reported that cold phenol, which does not separate viral nucleic

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