

## Some aspects of the patination of flint

R. Rottländer

Ever and again the thickness of patination was regarded as a guide for the time elapsed since the manufacture of the artifacts. Repeatedly this opinion was questioned, but no detailed study was carried out up now.

In our laboratory in Tübingen we investigated some aspects of flint patination in order to understand better the processes involved.

Firstly three different states of surfaces have to be discerned:

- Desert varnish, - White patination, which is faint blueish in thin layers, - and a glossy or shiny surface, in German 'Glanzpatina'. Desert varnish consists in the deposition of material on the stone surface and is well understood.

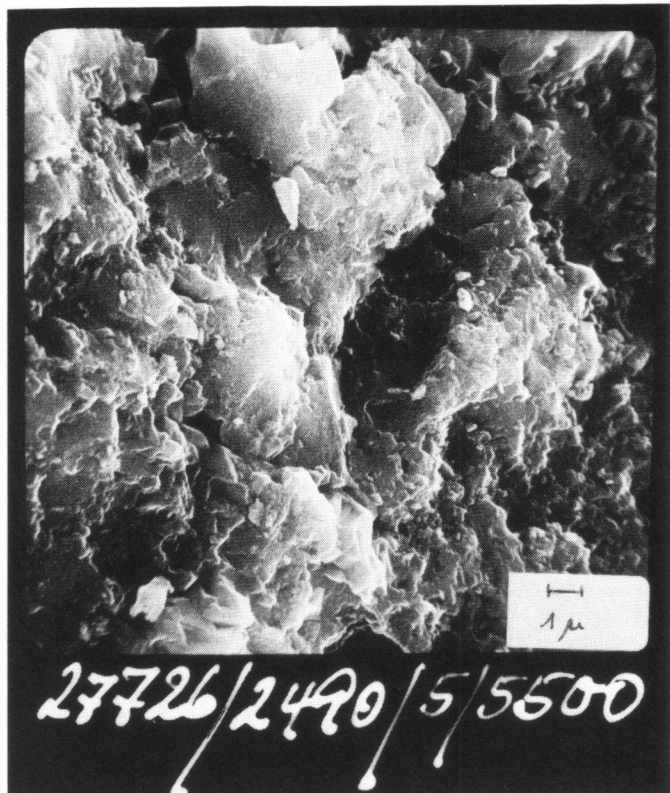


Fig. 1

Grey Flint: The scales with a diameter of about 4 - 6  $\mu$  consist of smaller grains, of about 0.8 - 1  $\mu$ .

There is no need to go into discussion here. The white patination is the commonly well known phenomenon on all sorts of silices and consists in a leaching out of material, leaving very small holes and thus causing an enlarged refraction of light. These holes partly can be refilled by humus and iron compounds, mostly resulting in brown colours.

The glossy surface is due to the removal of very small prominences of the surface and filling out of the fissures. All that must not be mixed up with the red colours which are seen on certain flints after heat treatment. It should be born in mind that after heat treatment a white patina or glossy surface can be developed and further that a white patination can be covered by a glossy surface. In order to understand the changes that occur to flints we have to deal with the inner structure of flints. Optical magnification of thin sections tell us that there are small particles with a nearly uniform optical behavior under crossed nicols. Magnifications of 5000 times with the scanning electron microscope reveal that there are flat particles arranged together like the scales of a fish. These scales again are built up by grains of nearly the same orienta-

tion and size. Even higher magnifications together with other experiments eventually show piles of plates to be present building up the grains. Between the boundaries of the grains there are small pores containing the impurities of the flint. It should be mentioned that the plates are hold together by SiOH - groups and a monolayer of water.



Fig. 2

Brown Flint of Courtenay, Paris basin, with irregular scale-size and kristalline parts.

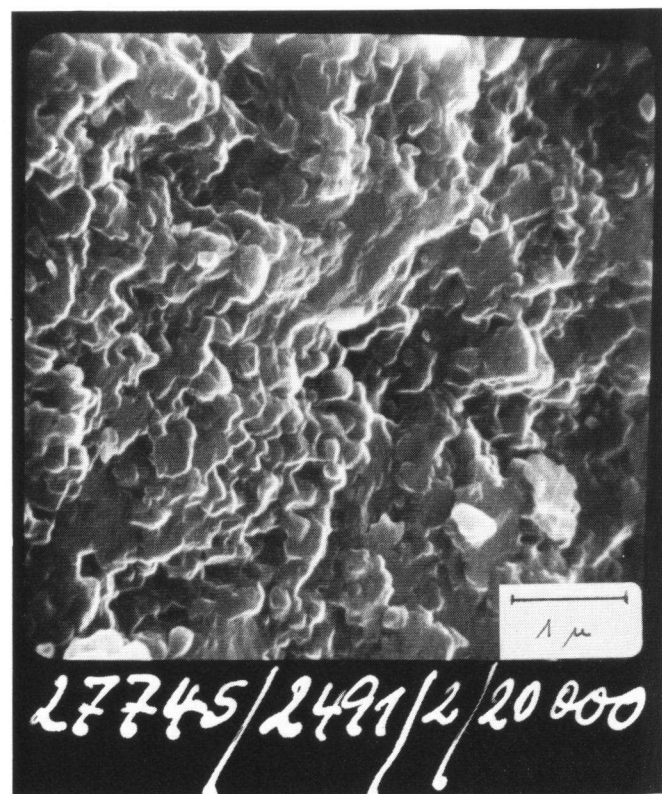


Fig. 3 Light jasper, Baden, with grains of 0.1 - 0.2  $\mu$  diameter.

The different sorts of silices may be discerned by their inner structure. Flint of Courtenay, France, is partly crystalline (Fig. 2). Jasper has the finest grains and scales of all and is easily detected by that. Hornstein on the other hand has the most coarse grains and the scales vary fairly in size. Besides that well defined quartz crystals are visible in most cases. The scales of the flints of the cretaceous chalk deposits have a medium size and are more regular. The inner holes of the flints are connected together and act like a sponge. Thus water can penetrate in surprisingly high amounts. Within 1000 years one liter of water is able to pass through a surface of 10 square cm of a northern flint, and for an Egyptian flint we found an amount four times as large as that of the other flint.

Let us turn first of all to the heat treatment, recently again in discussion. If the dark flint of the f.i. Lägerdorf chalk deposits is heated, its surface is turning white and it cracks. Rapid heating causes a small crash, but even very slow heating cannot avoid the thoroughly cracking of the material. By this property the flint in its narrow sense can be distinguished from other sorts of flint or chert.

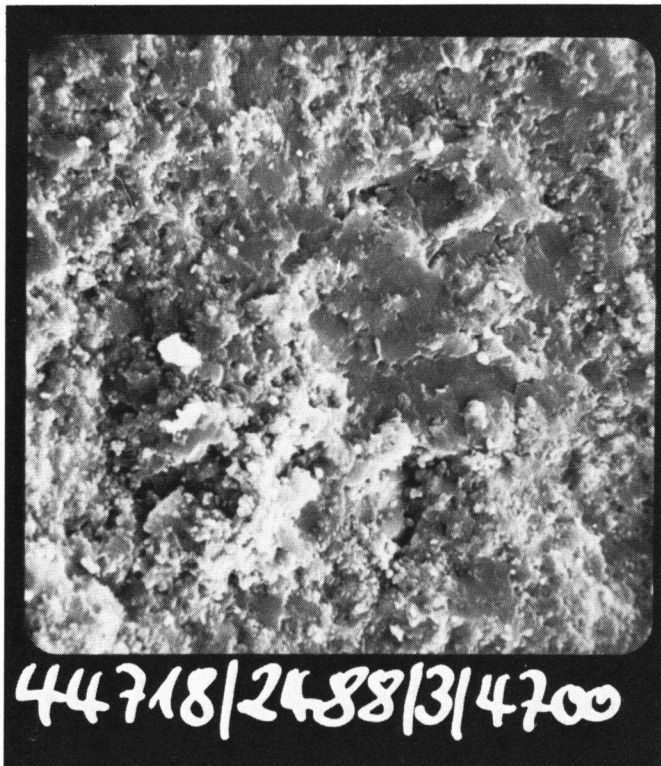


Fig. 4  
Hornstone, upper Jurassic : Malm  $\bar{\zeta}$  (Upper Danube).  
After Heating vitrification took place in larger areas.

Heating of brown sorts of flint or of the Hornstein, a silice of the upper Jurassic chalk deposits, results in a generally improved mechanical behavior and a red colour. The transition in colour occurs at about 280° C. The improved mechanical properties are due to a certain vitrification fritting the scales of the silices together. Most probably this is effected by aqueous solutions under very high pressure which are formed during the heating process. It must be mentioned here again that all sorts of flint contain up to 1.2% of water which is released but successively with the increasing temperature, going finally up to 900° C. It might be the same content of water which makes cracking the true flint, for it has the biggest amount of water and the smallest pores.

The red artifacts of Hornstein are a very common feature in the south-west German mesolithic industries. For instance in the Beuronien A deposit of the Jägerhaushöhle this makes up to 60%, while it decreases to about 25% in the Beuronian B layers. Other sites are well comparable. Having explained the effects of heat treatment its clear

that the formation of patina is not influenced by preceding tempering. On the other hand the gloss produced by heat must not be confused with the glossy patination produced in the soil by chemical acting.

Since  $\text{SiO}_2$  is an acid anhydride it obviously can be resolved by strong alkalinic solutions. But strong alkaline soils are very rare in humid climates. Laboratory experiments demonstrated that in spite of a pH-value above 9 ground marble in aqueous suspension is not able to make a white patina. But after addition of sodium ions patination starts without an essential change in the pH-value. Again in laboratory experiments we found that patination by alkaline, sodium ions containing solutions runs much faster than by potassium ions containing solutions of the same concentration and pH-value. Ammonium by itself is not able to produce a white patination. That shows the complexity of patina formation in the soil/or the fast patination in dung hills. But commonly soils are not as much alkaline rather than neutral or sour. There was no explanation why patina occurs in these soils. The view that rain or running water should cause the patination, as suggested by Gehrke, was rightly not accepted by the archaeologists. So there must exist some agent working in none alkaline medium. From the early mesolithic site of Duvensee we have two pieces of flint fitting together, which were being worked at the same time. One of both pieces was found in the gyttja layer and was not patinated. The other piece was found in the carex peat and was thoroughly patinated. Its specific gravity was reduced to 2.49. Normal flint has a specific weight of 2.56g/cm<sup>3</sup>. From that follows, that patination occurs in the total absence of alkali ions but in presence of organic material.

Since years it is known that catechol, i.e. o-dihydroxybenzene, forms a water soluble complex with silicic acid in slightly alkaline solutions. We tried to form the complex with stepwise falling amounts of ammonia. Even without any ammonia the complex is formed and a pH-value of

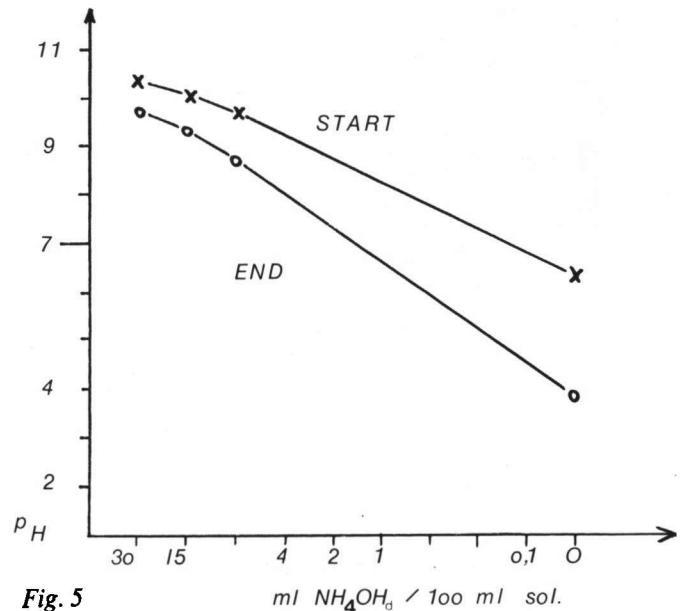


Fig. 5  
Quartz powder reacts with o-dihydroxybenzene even if ammonia is absent. Reaction time : 3 months.

3.8 arises by itself. That is fairly sour in terms of a soil. With respect to the fact that catechol does not appear frequently free in nature, we repeated the experiment with quartz-powder and gallic acid, obtaining equivalent results. From that it is apparent that water soluble compounds with the o-dihydroxy-benzene group are able to form complexes with silicic even in an environment not too sour. From the Speckberg site, which was inhabited from middle palaeolithic to urn field times repeatedly, we have Hornstein artifacts heavily patinated. They belong to late middle palaeolithic and early young palaeolithic



cultures. For some of them the specific gravity is as drastically reduced as to even  $1.6 \text{ g/cm}^3$ . They were found in a soil lessivé, a nearly complete leached out faint yellow sand with 93%  $\text{SiO}_2$ . This soil horizon had developed from limestone, but now had a pH - value of 5.0.

From the botanist we could learn that during the last glaciation the Speckberg hill was covered by a plant society called '*elynetum alpinum*'. That means that most of the plants were *carices* or sedges, plants shaped like gras. The roots of these plants have certain cell groups, called idioblasts. They all segregate more or less gallic acid, as we could prove in a series of samples. Moreover the roots contain up to 30% of tannin; (the amount being calculated from the dried material). By that the reason was found for the heavy patination of the flint-piece of the carex-peat of the site of Duvensee as well as for the Speckberg specimens. It seems to us that generally gallic acid, widely spread in plants, tannin and humic acid are the most effective agents for patination in none alkaline soils. Here I have to recover that humic acid, which is a collecting notion for a lot of partly not identified compounds, contains sufficiently o-dihydroxybenzene groups. In this connection compounds as labiatic acid, caffeic acid and protocatechuic acid even common in plants are of lower significance.

However, in their effects these compounds are not independent of the soil dynamics. They act in the A-horizon and are saturated in the B-horizon. If an artifact happens to be embedded in the B-horizon, it will not be patinated even if it is of an essential higher age than an artifact of an A-horizon, which may be patinated to a high degree. That explains why patination by itself is no reliable guide to the age of an implement. On the other hand it *can* be a guide under certain circumstances: If there are two mixed industries and if the history of soil development can be reconstructed and if it can be stated that the two industries once were separated in two different layers in different soil horizons, then the degree of patination is a reliable guide in separation even of the flakes. But these conditions have to be investigated separately for each site.



Fig. 6

Smoothed surface of a 'Glanzpatina' with holes etched in it by strong alkaline solution. (1 n NaOH, 48h at 80° C).

Last not least we have to deal with the glossy patination. It occurs, if the concentration of the chemical agents are too weak to penetrate into the holes and fissures of the flints. So they just remove the prominents of the flaked surfaces, because of their higher potential energy. Since the fissures and holes have a significantly lower potential energy than the normal surface, they act as pitfalls for silicic acid occurring free in solution. By this mechanism the surface is smoothed and polished. In our lab experiments we hardly could produce a glossy surface by slightly alkaline solutions, because they act too vigorously. But with a suspension of peat in water at a temperature of 50°C we obtained a glossy surface on freshly flaked flint within a three weeks time. It was accompanied with a weight loss of 0.3% as an average value.

In course of climatic changes, as for instance at the beginning of the holocene, soil dynamics change in a similar range. In certain cases that means that in spite of a higher production of organic material the organic material in the soil decreases due to the much higher degradation rate. Thus silico-organic complexes once formed are oxidised and the silicic acid has to be precipitated. This mechanism goes via silicious gels which can be transported at a certain degree. So this gel normally is deposited at existing solid  $\text{SiO}_2$ , that means at sand grains and artifacts. In some cases we have found an overcoat of opal  $10 \mu$  thick. More surprising than the formation of patina by organic compounds might be that even simple light is able to form a sort of dull gray patination. But this is understandable in the light of the fact that water is a constituent of the structure of flint. Light gives the energy to split off water even from a chemical bondage. It is well known that flint has to be wet in order to be of good technical properties. And it is as well known that flint which was a long time on the surface of the soil is not useful.

Finally I have to mention that some concentrated aqueous solutions of salts and organic compounds are able to be absorbed in the patinated parts of flints and to replace the iron in the two valent form present in the inner part of the flint. This mechanism has influences on the colour of the flint. The twovalent iron, once brought to the surface, is rapidly oxidised and trapped in this form, until it happens to be resolved by oxalic acid solutions or to be reduced by organic compounds in a gley. This explains why as a rule flint artifacts from fields treated with fertilizers show a brown surface. Ammonic salts are most capable of replacing iron ions of the inner parts of flints. I am conscious of the fact that a lot of work still has to be done in order to increase the material of well established observations and that this paper only can be a short outline.