

## The Gloss Patination of Flint Artifacts

Calvin D. Howard

### ABSTRACT

*Gloss patina is a natural post-depositional surface alteration frequently present on flint artifacts. Features of this patina include reduced surface topography, smoothness, and a pronounced luster. Gloss patina is distinct from stain patina, desilication (white) patina, and the dark glossy patina known as desert varnish. Glossy river patina has similar features but is produced by abrasion accelerated dissolution whereas gloss patina is primarily a result of soil solution related chemical processes. Artifact adsorption of amorphous silica from its depositional environment can produce gloss patina but advanced examples of gloss patina have surface topography reduction, smoothness, luster and thickness strongly indicating dissolution and concomitant re-precipitation of artifact surface silica.*

**Keywords:** artifacts; patina; silica; dissolution; adsorption

Gloss patina is a common post-depositional alteration of the surfaces of flint artifacts. Researchers have referred to this phenomenon by a number of terms including glossy sheen (Kelly & Hurst 1956), glazing (Honea 1964), glossy patina (Rottlander 1975), gloss patina (Howard 1994; Stapert 1976), soil sheen (Vaughan 1985), and simply sheen (Levi Sala 1986). Herein the term gloss patina is maintained. This patina should not be confused with the dark glazed surface condition present on many artifacts from the American Southwest, which is commonly referred to as desert varnish. Although glossy, desert varnish is very dark, due primarily to its iron and manganese oxide content (Engel and Sharp 1958; Hayden 1976; Potter and Rossman 1979), clay, and organic material (Dorn et. al. 1992; Whitley and Dorn 1993), which are essentially absent from the clear gloss patina addressed here. Gloss patina is also distinct from desilication (white) patina (Rottlander 1975; Van Nest 1985) and stain patina (Howard 1994). In fact, all three of these natural surface modifications can be present on the same artifact. Gloss patina on artifacts may be present in various stages of development ranging from initial incipient stages difficult to detect, to advanced stages obvious to the unaided eye. Regardless of the stage of develop-

ment, the entire surface of the artifact is usually uniformly affected (Levi Sala 1986:230; Stapert 1976:12; Vaughan 1985:30). Artifacts with advanced gloss patina have a true glossy luster and feel pleasantly smooth to the touch. Virtually all flint artifacts that have been exposed to soil water solutions for extended periods have some stage of gloss patina (Vaughan 1985:42). The probable genesis of this phenomenon can be placed into two primary categories: (1) adsorption of dissolved silica from soil solutions in the artifact's *in situ* environment; (2) dissolution and re-precipitation of siliceous constituents of the artifact surfaces.

### THE ADSORPTION THEORY

Due to their study of patinated Archaic artifacts from coastal Georgia, Kelly and Hurst (1956) attributed the glossy sheen to a thin coating of goethite. Their microscopic examination of the flint material indicated that the aged surfaces contained "thousands of disseminated specks of iron oxide in variable states of hydration" (Kelly and Hurst 1956:194). Although iron oxides are frequently associated with silica deposition on artifacts from soil solutions, oxidation of artifact surface constituent ferric material would not produce a transparent coating of the nature or appearance of gloss pa-

---

Calvin Howard, P.O. Box 9168, Springfield, IL. 62791

*Plains Anthropologist*, Vol. 47, No. 182, pp. 283-287, 2002.

tina. Since some artifacts with gloss patina have a macroscopic depth of transparent material (Rottlander 1976:56), it is obvious that more is involved than merely a reflective surface resulting from extremely fine microtopography. The appreciable luster and depth of transparent material on such artifacts indicates a layer of silica relatively free of iron oxides.

Zeuner (Heizer & Cook 1960:315) attributed gloss patina to the deposition of soil colloidal silica onto artifacts. Because he envisioned it as an addition to, rather than a modification of, artifact surfaces, he did not consider it to be an actual patina. Honea (1964:16) referred to gloss patina as a glazing resulting from gradual coating of artifacts exposed to colloidal silica saturated environments. He did however allow for the possibility that the silica forming the glaze could be from "within the artifacts" (Honea 1964:15), which, of course, would not be the result of an adsorption process. Although Shepherd attributed gloss patina to the partial dissolution of artifact surfaces, he included the possibility that, under certain circumstances, evaporation of silica-rich soil solutions could result in silica adsorption on cold flint surfaces (Shepherd 1972:121). Rottlander (1976:56) credited soil dynamics involving the oxidation of silico-organic complexes for the precipitation of silicic acid gels onto artifacts that sometimes resulted in opal layers as great as ten micrometers thick.

### THE DISSOLUTION THEORY

Although they attributed the glossy sheen on Georgia flint artifacts to goethite, Kelly and Hurst (1956:194) did, however, credit chemical activity for the smoothness of the artifact surfaces. Matson (Heizer & Cook 1960:317) credited chemical reaction resulting from the unsatisfied bonds of freshly fractured stone for dissolution of artifact surfaces. Shepherd (1972:121) envisioned partial solution of artifact surfaces as the cause of high gloss present in low areas that could not be the result of friction. He compared the process to electrolytic polishing of metals and termed it solution-gloss. He also considered the possibility that the luster of affected artifacts could be due to the filling of surface porosity with silica from soil solutions (Shepherd 1972:116). Rottlander (1975:109; 1976:56) attributed glossy surfaces on artifacts to

weakly acting solvents preferentially dissolving prominent portions of the surfaces due to their higher potential energy and transferring the dissolved silica to areas of low energy levels. Stapert (1976:12) describes gloss patina as a uniform sheen caused by smoothness of artifact surfaces as a result of chemical processes in the soil. He considered the general smoothness to be a separate phenomenon from the rounding of ridges and edges of artifacts affected by the chemical processes (Stapert 1976:14). It is doubtful that these two conditions are caused by totally different chemical processes. Dissolution of artifact surfaces would naturally produce both general overall smoothness and rounding of prominent features. Adsorption of amorphous silica onto artifacts from soil solutions and stream waters rich with dissolved silica certainly must occur in nature, considering the many stages of silicic materials (Chadwick & Graham 2000:E59; Drees et al. 1989:943) and the effect upon silica precipitation by soil solution pH and ionic solute content (Chadwick & Graham 2000:E59; Siever 1962:135). Experiments by McKeague and Cline (1963), however, indicated that silicate minerals have a low capacity for adsorption of silica from solution. It is therefore questionable that adsorption alone would produce the more advanced examples of gloss patina with its appreciably reduced surface topography and remarkable smoothness. To markedly reduce flake-scar ridges and produce rounded edge surfaces would require a thickness of amorphous silica deposits that is obviously not present on many artifacts having gloss patina with these morphological attributes. Silica deposition of such a magnitude would require exposure to water solutions greatly and consistently above normal ambient silica saturation levels without periodic silica content reduction sufficient to trigger desorption. Such a scenario would only occur in the vicinity of silica-rich hot springs or geysers, certainly not in the vast majority of archaeological deposits. Thus, adsorption remains a questionable process to explain the total features of artifacts having classic examples of gloss patina.

Experimental evidence supports surface dissolution as a major factor in the natural process of gloss patination. Rottlander (1975:108; 1976:56) was able to produce glossy surfaces on flint flakes

during experiments involving their exposure to humic acids from peat in water. Dissolution was indicated by an appreciable increase in silica concentration of the aqueous solution and a 0.3% decrease in the weight of the flakes. All forms of quartz contained in flint artifacts- crystalline, microcrystalline, cryptocrystalline, and amorphous silica- are subject to dissolution processes when exposed to water or soil solutions for extended periods (Churchman 2000; Drees et. al 1989; Krauskopf and Bird 1967; Luedtke 1992; Siever 1962; Williams et. al. 1985). Obviously, flint artifacts are subject to alteration by these natural chemical processes.

Atoms at the surface of solids exist in different environments than the atoms within the bulk structure. This difference increases the surface reactivity of the solid when in contact with aqueous solutions (Robarge 1999:196; Sparks 1999:182). This increased reactivity at the solid/solution interface results from solution-induced structural and electronic modification of the first few atomic layers of the solid, and difference between the physical properties of the first few monolayers of water on the solid and the properties of the surrounding bulk solution (Churchman 2000:F55; Scheidegger & Sparks 1996:824; Sparks 1999:182). Thus the silica/water solution interface is reactive and contributes to dissolution and re-precipitation of secondary silica phases (Luedtke 1992:99; Robarge 1999:204). Lithic artifacts are modified by these chemical processes, which can convert their surface silica structures to secondary amorphous silica phases with only minimal transfer of material from the surface to the aqueous solvent.

The surfaces of silica materials naturally have molecular-scale steps, undulations, and microcracks (Robarge 1999:198; Scheidegger & Sparks 1996:824; Sparks 1999:180). Penetration of these physical features and the crystal lattice structure by water molecules causes disruption of chemical bonds and material modification through a sequence of hydration, hydrolysis, dissolution, and transfer of silica molecules (Churchman 2000:F55; Robarge 1999:204). The surfaces of flaked flint incur various forms of minute damage as a result of flake detachment. This damage includes microcracks and dislocation of material, which result in surface stresses that provide addi-

tional energy to the chemical dissolution process (Robarge 1999:198). Because of their greater surface-to-volume ratio, the protruding portions of flake-scar surface topography have the greatest interfacial free energy. This energy is also available to the dissolution process. Thus, initially the solubility of the flake scar surface is greatest and exposure to the elements results in a natural process toward development of a smooth surface. If the rate of silica modification exceeds the rate of molecular transfer to the aqueous solution, re-precipitation of an amorphous silica (opal) onto the artifact surface occurs. Such a combination of dissolution and re-precipitation may be responsible for the smooth and lustrous features common to artifacts having gloss patina.

#### GLOSS PATINA COMPARED TO RIVER PATINA

Many artifacts having brilliant patinas do not have macroscopically thick layers of glossy material. Artifacts with river patina (Howard 1999a) have intensely brilliant luster without appreciable build up of transparent layers of amorphous silica. Since evidence suggests that river patina is the result of abrasion-accelerated dissolution (Howard 1999a), it is apparent that the abrasion, and the continuous exchange of water solvent, would prevent artifact retention of the modified surface silica. Thus, the brilliant luster of artifacts having river patina is primarily due to reduction of surface microtopography and the presence of a highly reflective submicron layer of amorphous silica, which may be the active area of the dissolution process (Howard 1999a:295). However, in the case of artifacts with gloss patina acquired in soils by pedological process, the artifact surfaces and silica dissolution products were not subjected to the abrasion, or the extent of solvent exchange, typical of artifacts long exposed to flowing water. Therefore, more of the modified surface of the artifact, and the associated silica dissolution products, were retained and various depths of patina produced.

#### GLOSS PATINA ON ARTIFACTS FROM ARID REGIONS

Remarkable examples of gloss patina exist on artifacts from the eastern Sahara Desert (C. Vance Haynes, personal communication 1999). Although

the luster on these Neolithic artifacts appears comparable to that of artifacts having river patina, it was not associated with stream waters because no significant stream flow has occurred in the region for millennia. However, they may have been associated with desert playas wherein water briefly collected as the result of occasional rains. Artifacts buried in such an environment and exposed to periodic wetting, however infrequent, are subject to the same natural processes of dissolution previously described. Although wetting of the artifact is limited, the dissolution process may be highly active because solutions in arid regions often contain alkaline materials and other solutes that can increase the solubility of silica. Thus, artifacts in arid regions are subjected to occasional wetting by these highly chemically-active solutions that enter pores of the material and form films on their surfaces.

Water within and upon stones in natural environments may be in three equilibrium states: a monomolecular layer adsorbed (chemically & physically) on surfaces, liquid-droplet, and capillary (Karyakin et al. 1975:176; Van Nest 1985:336).

The monomolecular water is the most chemically reactive and reacts with silica to produce SiOH groups (Karyakin et al. 1975:178). Capillary water is the least reactive but its presence in the pores of silicious materials can contribute to surface alteration (Churchman 2000:F55) and may be involved in patina formation (Van Nest 1985:336).

Since the monomolecular layer of water on artifacts is reactive with silica, it can serve as a catalyst for dissolution. Only low levels of soil moisture would be required to replenish and maintain this active layer; thus, the occasional and infrequent wetting typical of desert areas can produce dissolution of artifact surfaces. Since dissolution and precipitation are influenced by temperature and fluid solvent concentration (Williams & Crerar 1985:313), the extreme temperature cycling of desert regions, and the increase of solvent concentration due to evaporation during drying cycles, may create conditions conducive to dissolution of the surfaces of desert artifacts. Much of the time that moisture is present under these conditions, it may be sufficient for dissolution but inadequate for effective leaching and transfer of dissolution products. Such a low diffusion rate allows for re-

precipitation of the dissolved silica (Williams & Crerar 1985:312). As a result, the surfaces of desert artifacts may acquire a thickness of gloss patina that seems disproportional considering the moisture exposure visualized for an arid environment.

## DISCUSSION AND CONCLUSION

A condition of extremely specular bright spots sometimes exists at scattered locations on artifacts (Levi Sala 1986:231; Semenov 1964:11; Stapert 1976:38; Vaughan 1985:185). Evidence suggests that these brilliant spots may be the result of the flocculation of siliceous soil solutions and the precipitation of silica gel onto artifacts that subsequently dehydrates and solidifies (Howard 1999b). Artifacts with these bright spots frequently also have a general overall gloss patina. Since the two different conditions are present on the same artifact, it is reasonable to suspect that different natural pedological processes are responsible for their specific origins. If adsorption of precipitated soil solutes is the origin of bright spots, it is reasonable to suspect that the more general and less brilliant gloss patina is due to other natural processes. Thus comparison of these two conditions indirectly supports dissolution and re-precipitation as the origin of gloss patina.

If gloss patina was the result of the deposition of silica from soil solutions, it would seem that the soil surrounding the artifact would also be affected. That is, the soil would be firmly consolidated, or "cemented", such as duripan soil horizons, and the soil in direct contact with the artifact would be cemented to it. This is certainly not the case. Artifacts with gloss patina are found in a wide variety of soils, many of which are not firmly consolidated and are easily removed from the artifact. These factors also support dissolution over deposition as the probable cause of gloss patina. The information presented herein primarily supports artifact surface dissolution and concomitant re-precipitation of amorphous silica as the probable genesis of gloss patina. This chemical process appears far more compatible with the total features of artifacts having this patina – the combination or reduced surface topography, smoothness, and luster- than does the mere exposure of artifacts to deposition from silica-rich stream water or soil solutions.

## REFERENCES CITED

- Chadwick, O. A. and R. C. Graham  
2000 Pedogenic Processes. In *Handbook of Soil Science*, edited by M. E. Sumner, pp. E41-E75. CRC Press LLC, Boca Raton.
- Churchman, G. J.  
2000 The Alteration and Formation of Soil Minerals by Weathering. In *Handbook of Soil Science*, edited by M. E. Sumner, pp. F3-F76. CRC Press LLC, Boca Raton.
- Dorn, R. I., P. B. Clarkson, M. F. Nobbs, L. L. Loendorf, and D. S. Whitley  
1992 New Approach to the Radiocarbon Dating of Rock Varnish, with Examples from Drylands. *Annals of the Association of American Geographers* 82:136-151.
- Drees, L. R., L. P. Wilding, N. E. Smceck, and A. L. Senkayi  
1989 Silica in Soils: Quartz and Disordered Silica Polymorphs. In *Minerals in Soil Environments*, edited by J. B. Dixon and S. B. Weed, pp. 913-965. Soil Science Society of America, Madison.
- Engel, C. G. and R. P. Sharp  
1958 Chemical Data on Desert Varnish. *Bulletin of the Geological Society of America* 69:487-518.
- Hayden, J. D.  
1976 Pre-Altithermal Archaeology in the Sierra Pinacate, Sonora, Mexico. *American Antiquity* 41:274-285.
- Heizer, R. F. and S. F. Cook (editors)  
1960 *The Application of Quantitative Methods in Archeology*. Viking Fund Publications in Anthropology 28, New York.
- Honea, K.  
1964 The Patination of Stone Artifacts. *Plains Anthropologist* 9:14-17.
- Howard, C. D.  
1994 Natural Indicators of Lithic Artifact Authenticity. *North American Archaeologist* 15:321-330.  
1999a River Patina on Flint Artifacts: Features and Genesis. *Plains Anthropologist* 44:293-295.  
1999b Amorphous Silica, Soil Solutions, and Archeological Flint Gloss. *North American Archaeologist* 20:209-215.
- Karyakin, A. V., Y. B. Kholina and N. V. Soboleva  
1975 The Interaction of Water with Silica. *Geochemistry International* 12:176-179.
- Kelly, A. R. and V. J. Hurst  
1956 Patination and Age Relationship in South Georgia Flint. *American Antiquity* 22:193-194.
- Krauskopf, K. B. and D. K. Bird  
1967 *Introduction to Geochemistry*. WCB/McGraw-Hill, Boston.
- Levi Sala, I.  
1986 Use Wear and Post-Depositional Surface Modification: A Word of Caution. *Journal of Archaeological Science* 13:229-244.
- Luedtke, B. E.  
1992 *Archaeologist's Guide to Chert and Flint*. University of California, Los Angeles.
- McKeague, J. A. and M. G. Cline  
1963 Silica in Soil Solutions II. The Absorption of Monosilicic Acid by Soil and by Other Substances. *Canadian Journal of Science* 43:83-96.
- Potter, R. M. and G. R. Rossman  
1979 Mineralogy of Manganese Dendrites and Coatings. *The American Mineralogist* 64:1219-1226.
- Robarge, W. P.  
1999 Precipitation/Dissolution Reactions in Soils. In *Soil Physical Chemistry*, edited by D. L. Sparks, pp. 193-238. CRC Press LLC, Boca Raton.
- Rottlander, R.  
1975 The Formation of Patina on Flint. *Archaeometry* 17:106-110.  
1976 Some Aspects of the Patination of Flint, Second International Symposium on Flint. *Staringia* 3:54-56.
- Scheidegger, A. M. and D. L. Sparks  
1996 A Critical Assessment of Sorption-Desorption Mechanisms at the Soil Mineral/Water Interface. *Soil Science* 161:813-831.
- Semenov, S. A.  
1964 *Prehistoric Technology*. Translated by M. Thompson. Adams and Dart, Bath, England.
- Shepherd, W.  
1972 *Flint: Its Origins, Properties and Uses*. Faber and Faber, London.
- Siever, R.  
1962 Silica Solubility, 0-220 Degree C, and the Diagenesis of Siliceous Sediments. *Journal of Geology* 70:127-150.
- Sparks, D. L.  
1999 Kinetics and Mechanisms of Chemical Reactions at the Soil Mineral/Water Interface. In *Soil Physical Chemistry*, edited by D. L. Sparks, pp. 135-191. CRC Press LLC, Boca Raton.
- Stapert, D.  
1976 Some Natural Surface Modifications on Flint in the Netherlands. *Palaeohistoria* 18:7-41.
- Van Nest, J.  
1985 Patination of Knife River Flint Artifacts. *Plains Anthropologist* 30:325-339.
- Vaughan, P. C.  
1985 *Use-Wear Analysis of Flaked Stone Tools*. University of Arizona Press, Tucson.
- Whitley, D. S. and R. I. Dorn  
1993 New Perspectives on the Clovis vs Pre-Clovis Controversy. *American Antiquity* 58:626-647.
- Williams, L. A., G. A. Parks, and D. A. Crerar  
1985 Silica Diagenesis, I. Solubility Controls. *Journal of Sedimentary Petrology* 55:301-311.
- Williams, L. A. and D. A. Crerar  
1985 Silica Diagenesis, II. General Mechanisms. *Journal of Sedimentary Petrology* 55:312-321.