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A possible silver (Ag^+) hydrosulphide hydrate unstable intermediate in Ag_2S toning.

The frequent black (Ag_2S) toning of silver from river or seabed recoveries is well known: such environments are subject to a constant rain of dead animal and plant matter subsequently undergoing sulphide generating microbiological metabolism reacting with silver occasionally represented stoichiometrically as:

$$2Ag \ + \ H_2S \ \rightarrow \ H_2 \ + \ Ag_2S$$
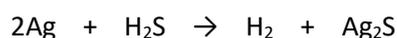
This is generally not seen with inland finds. Forgers, particularly during the 'grand tour' period and after were commonly unaware of this.

David Cummings[1] (sometime Chairman of the Ipswich and District Metal Detector Club) reports a curious reaction seen immediately after a local find. A number of mid-late 4c clipped siliquae from what appeared to be local glacial drift showed after cleaning the usual matte slightly darkened greyish look, except one recovered nearby from what appeared to be a soft impervious clay-like substance, presenting after cleaning an unusual white colour or tone. This placed in a plastic envelope and examined later after about half an hour had turned black. This apparently friable sulphide was removed electrolytically the two illustrations showing about half and full treatment:
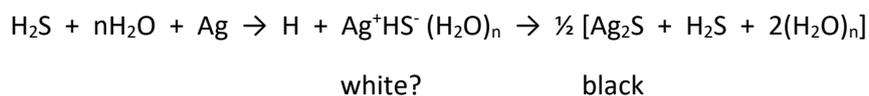

Valentinian II (probably) 'Urbs Roma' siliqua, clipped 13mm

Mint off flan (Rome or Siscia)

Cf Sear 20229-31   375-83 AD

Similar coins under Arcadius and Theodosius I

There appears to have been a long-time formation of an intermediate hydrosulphide stabilised by equilibrium with reagent and reaction products within a sealed environment disappearing on recovery, an unusual set of circumstances:

$$H_2S \ + \ nH_2O \ + \ Ag \ \rightarrow \ H \ + \ Ag^+HS^- (H_2O)_n \ \rightarrow \ \tfrac{1}{2} \, [Ag_2S \ + \ H_2S \ + \ 2(H_2O)_n]$$

white?   black

-the second stage occurring rapidly. Similar X^+ unstable compounds exist:

$Ag^+ HS^- Ag$ stabilised by unionised Ag adduct and $Na^+ HS^- (H_2O)_n$ where n is either 1 or 2 depending on sources.[2]

References

1) Cummings, D. R. F., 2021: Conversations with the author, INS meeting November, Ipswich.
2) Lowry, T. M. and Cavell, A. C., 1942: Intermediate Chemistry. London.