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Blue Iron Rust

A Review on the Formation and Stability of Vivianite

FO: Eschenz
Amt für Archäologie des Kantons Thurgau,
www.archäologie@tg.ch
Photo: K. Wüst

Iron and Steel in Art: Corrosion, Colourants, Conservation,

Archteype Press London [forthcoming]:

Chapter 6: Iron phosphates

Iron (II) phosphate: $Fe^{2+}_3(PO_4)_2 \times 8H_2O$:

vivianite

Iron (III) phosphate: $Fe^{3+}PO_4 \times 2H_2O$:

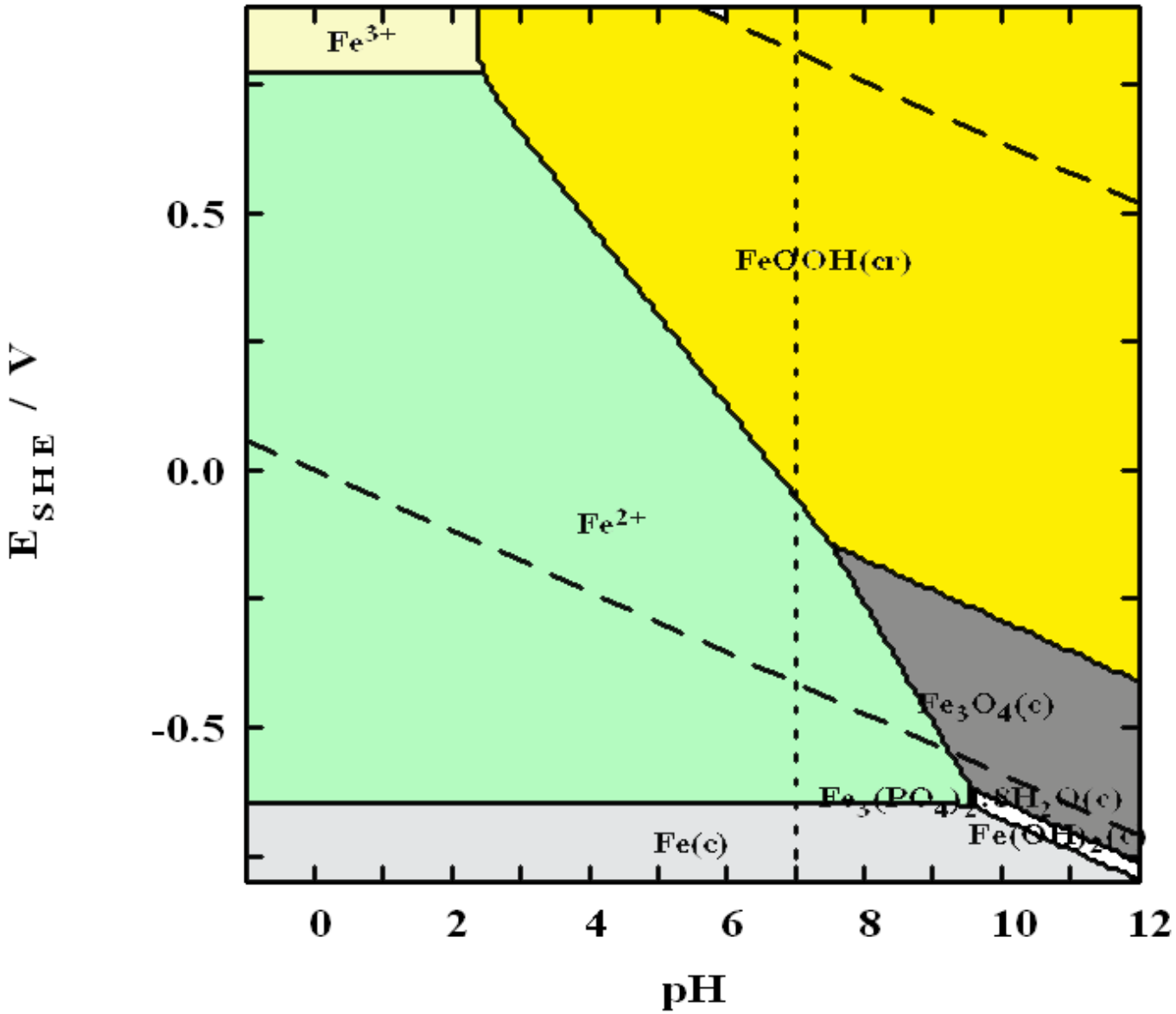
(meta-)strengite

Iron (II,III) phosphate:

metavivianite

FO: Ulm, Neue Straße (MA)
Photo: N. Ebinger-Rist

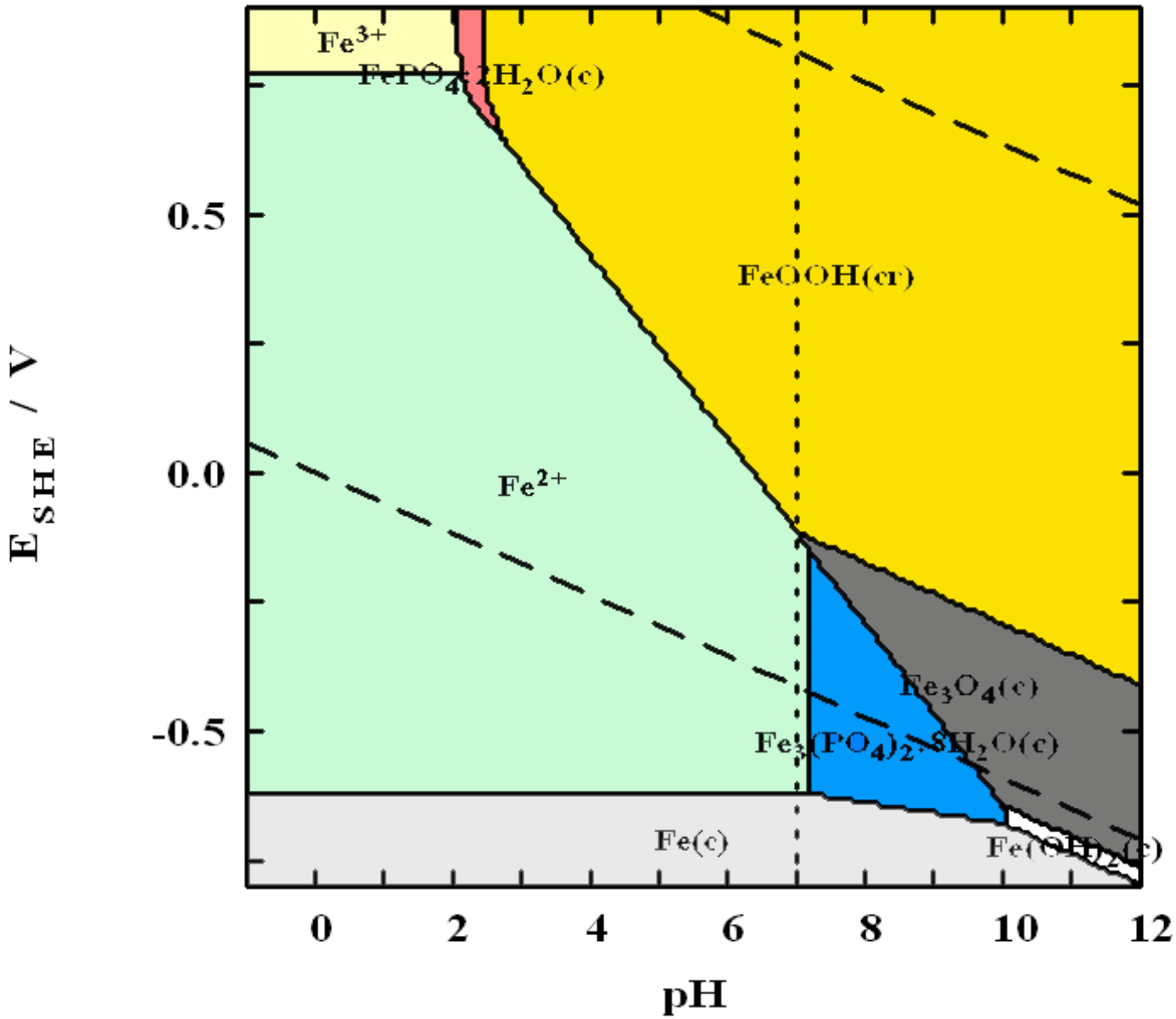
$[Fe^{3+}]_{TOT}$= 1.00 µM $[PO_4^{3-}]_{TOT}$= 1.00 µM



t= 25°C

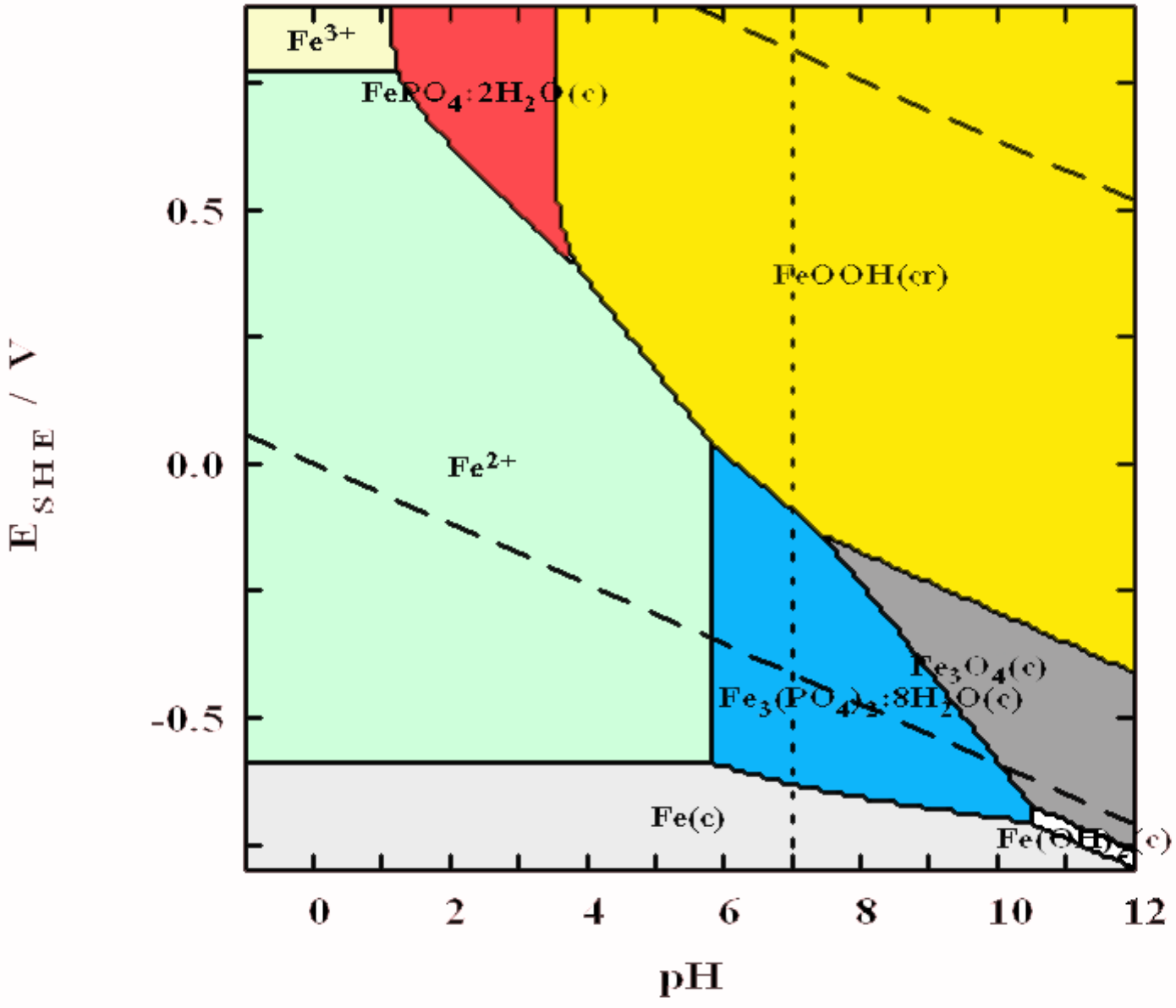
$[Fe^{3+}]_{TOT}$= 10.00 µM

$[PO_4^{3-}]_{TOT}$= 10.00 µM



t= 25°C

$[Fe^{3+}]_{TOT}$= 0.10 mM $[PO_4^{3-}]_{TOT}$= 0.10 mM

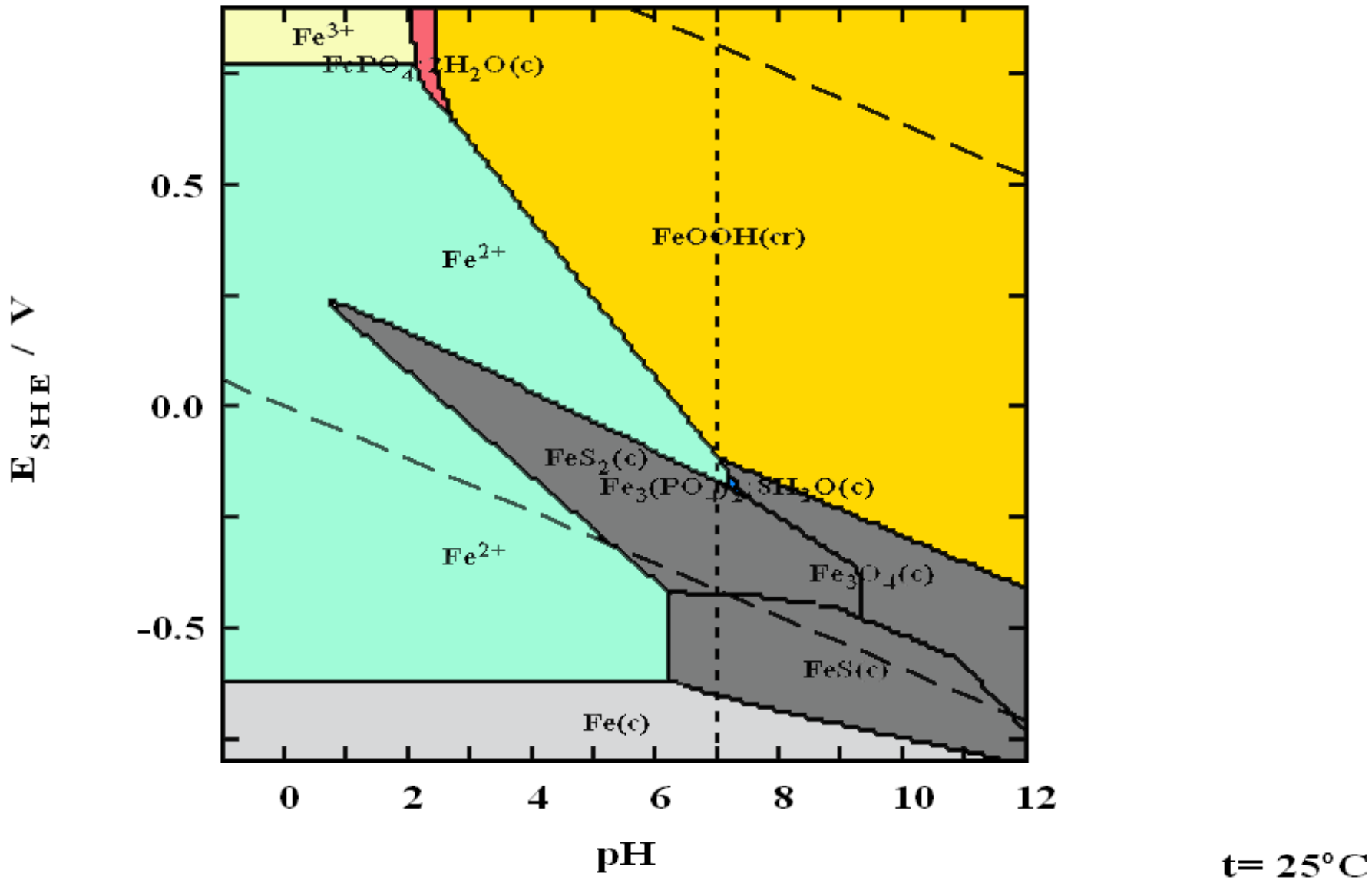


t= 25°C

$[SO_4^{2-}]_{TOT}$= 10.00 µM

$[Fe^{2+}]_{TOT}$= 10.00 µM

$[PO_4^{3-}]_{TOT}$= 10.00 µM



t= 25°C

Why does vivianite get blue ?

2 different sites for iron in the lattice, A and B.

By absorption of yellow light, electrons can jump from Fe^{2+} to a Fe^{3+} ion formed by oxidation:

$$Fe^{2+}_{A} + Fe^{3+}_{B} \rightarrow Fe^{3+}_{A} + Fe^{2+}_{B}$$

Oxidation of Vivianite

$$Fe^{2+}_{viv} + H_2O_{viv} \rightarrow Fe^{3+}_{viv} + OH^-_{viv} + e^- + H^+$$

Metavivianite

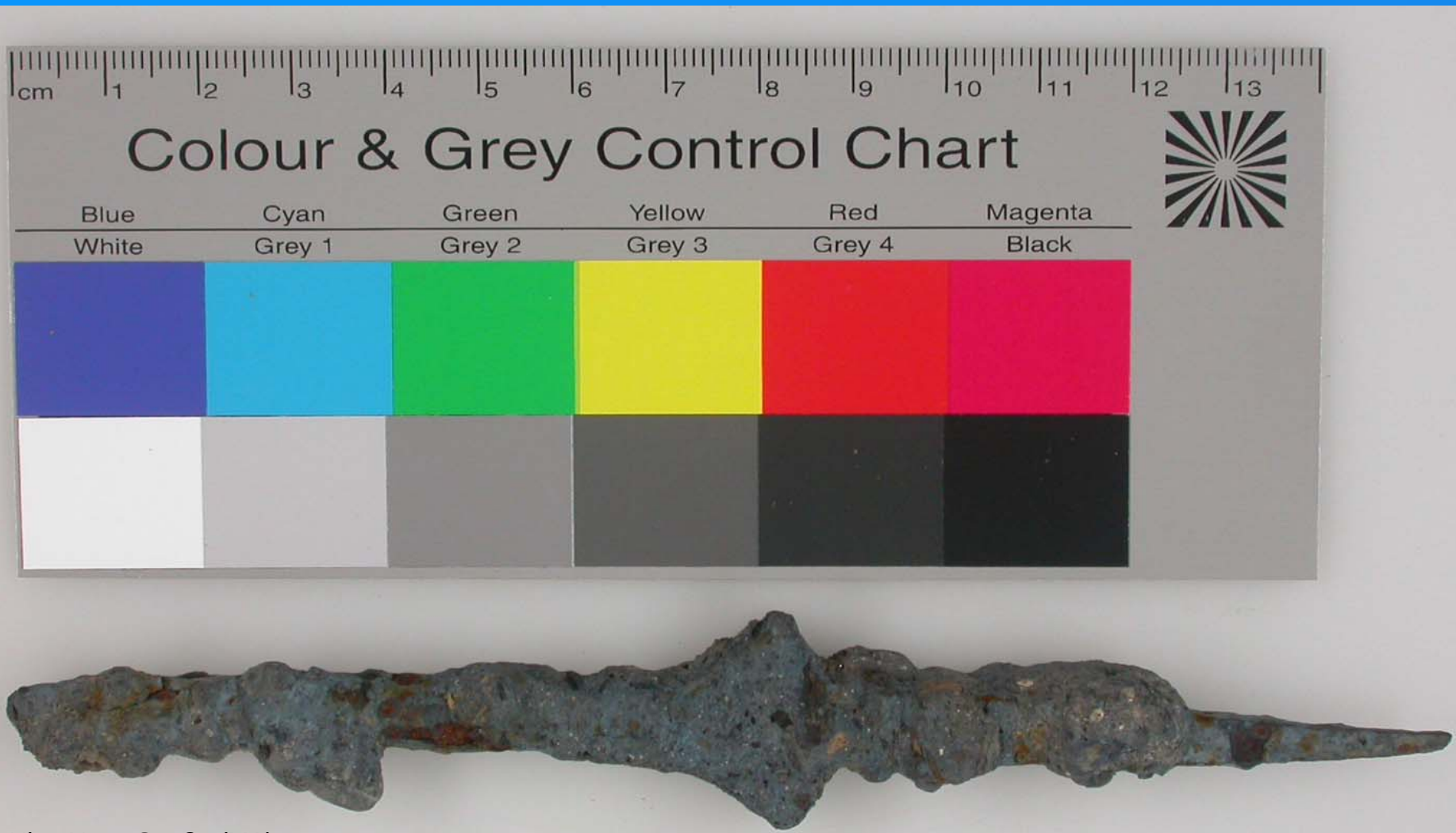
x= number of ox. Fe^{2+}

$$Fe^{2+}_{3-x}Fe^{3+}_{x}(PO_4)_2\,(OH)^-_x \cdot (8-x)H_2O$$

End product

$$Fe^{3+}_{3}(PO_4)_2\,(OH)^-_3 \cdot 5H_2O$$

yellow-brown, amorphous



FO: Ulm, Neue Straße (MA)
Photo: N. Ebinger-Rist

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- ***Kathrin Wüst, Liechtenstein***

Notes

- Foil 1: Roman iron band from a wet site in Switzerland
- Foil 3: Mediaeval key from Ulm
- Foil 4: (nearly) No phosphate phases with 10(-6). Fields colour coded (FeOOH field in ochre etc.) to help people unfamiliar with Pourbaix diagrams
- Foil 5-6: More phosphate, strengite and vivianite field show up
- Foil 7: A little sulphur and the vivianite field disappearsnearly totally. Resume: Vivianite only found with much phosphate and no sulphur!
- Foil 10: Object of unknown function, Ulm(MA), crack on the left, flaking: corrosion continues beneath!