

COMPARATIVE ANALYSIS OF ODONTOLITE, FOSSIL IVORY AND BLUE FLUORAPATITE BY PIXE/PIGE AND TEM

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INTRODUCTION

Odontolite, heated fossil ivory from Rajégats and Malartic, Gers, France and blue fluorapatite present the same blue coloration, the origin of which still remains uncertain.

Odontolite was used during the Middle Ages for the decoration of art objects replacing mineral turquoise. Generally, one assumes that it consists of heated fossil ivory. In nature, blue coloured fluorapatite is also found.

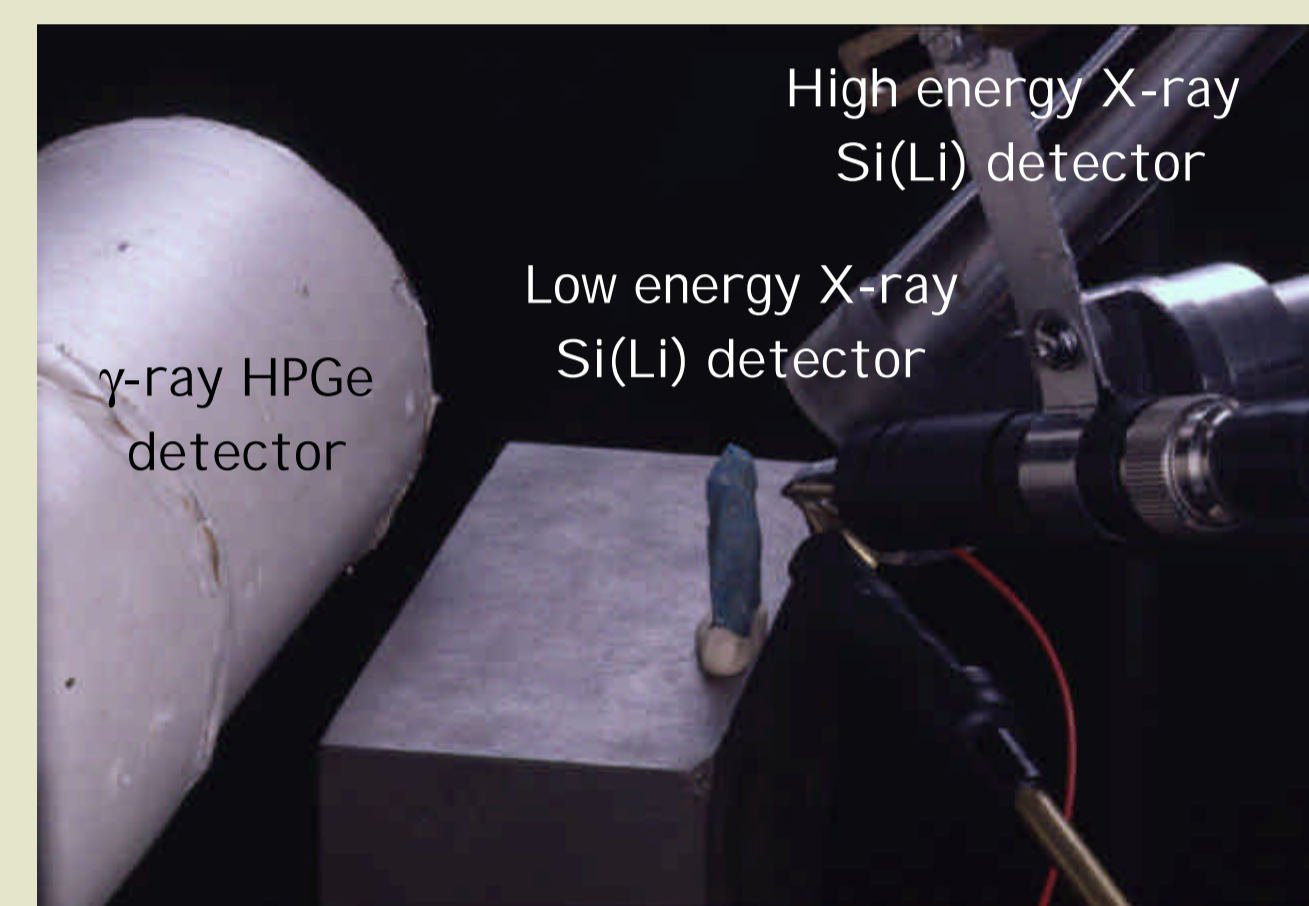
Comparative trace elemental analysis and micro-mapping by external PIXE/PIGE is undertaken. Transmission Electron Microscopy provides complementary structural and morphological information.

ELEMENTAL ANALYSES BY PIXE/PIGE :

EXPERIMENTAL SET-UP AT AGLAE :

3 MeV protons are extracted to He atmosphere, through a 0.1 μm Si_3N_4 exit foil. Spectra are obtained with a dose of 0,12 μC and a current of 0.5 nA.

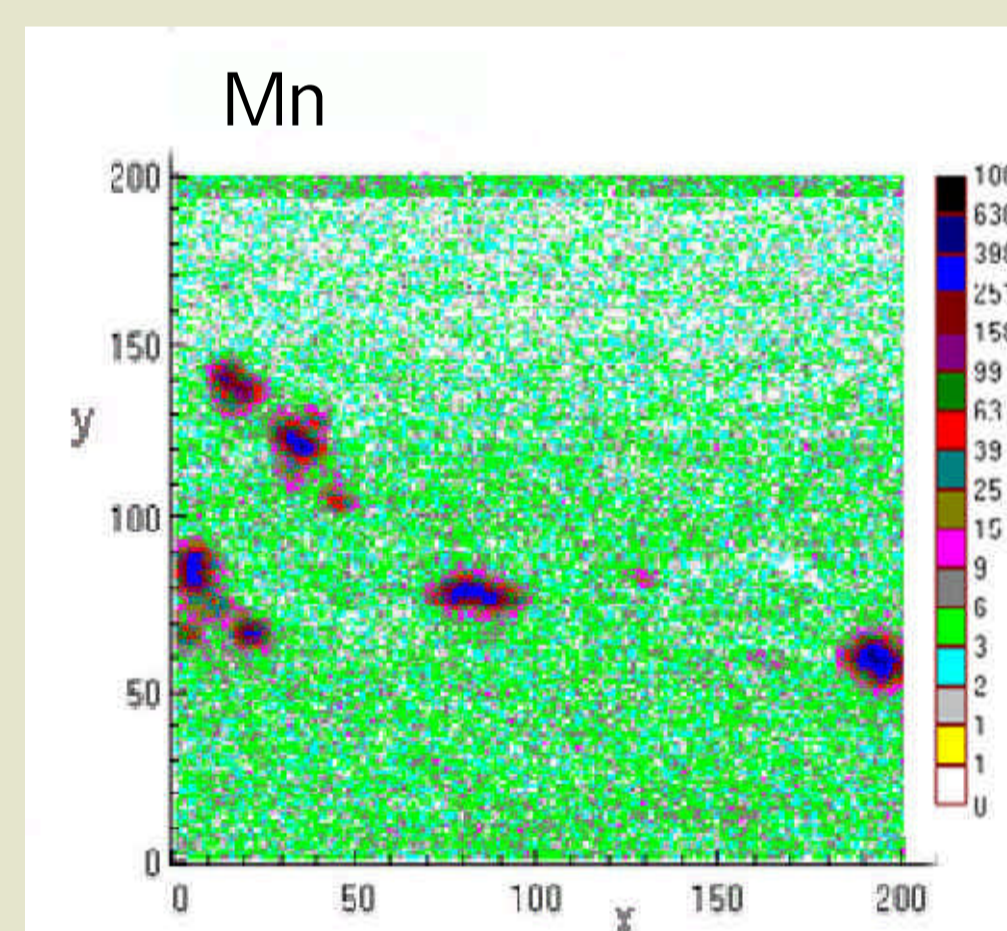
Micro-mapping is performed on a 2x2 mm surface with a beam diameter of ca. 100 μm . The current is of about 1 nA. One cycle takes of about 90 min.



MAJOR ELEMENT

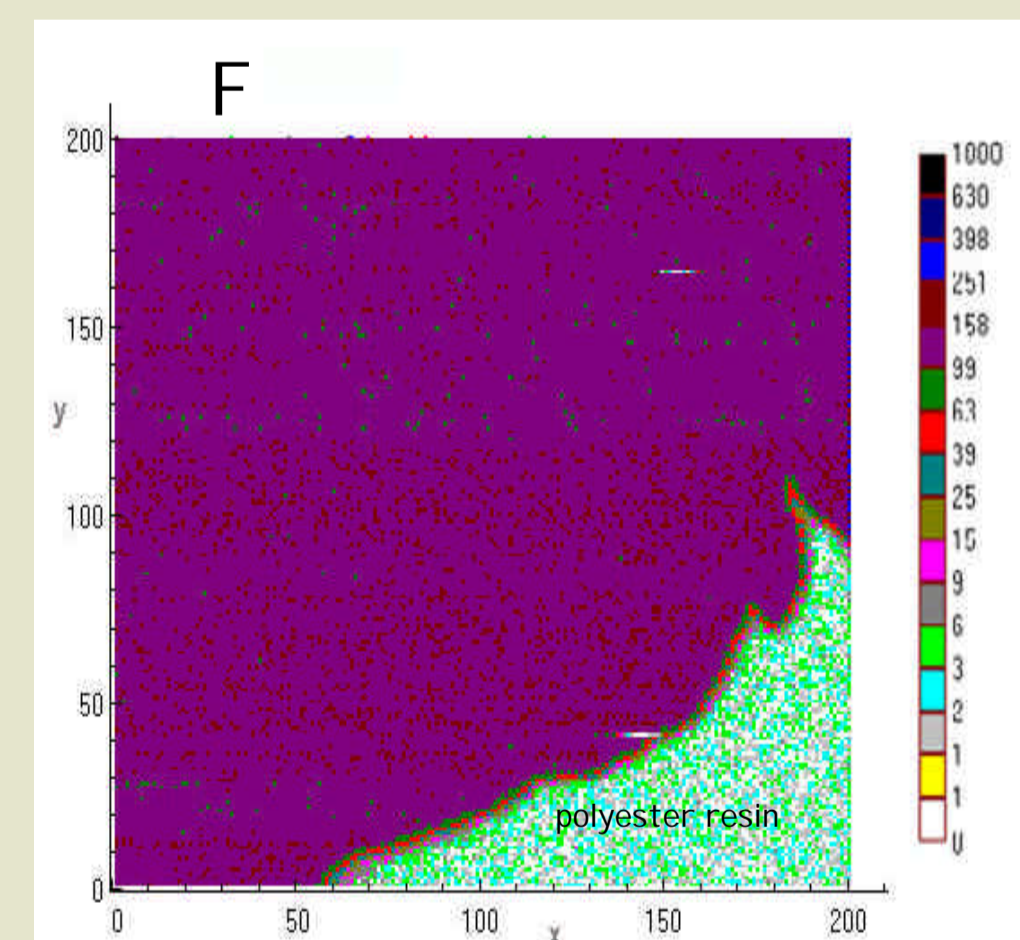
Four odontolites, 3 fossil mastodon ivory fragments and one blue geological fluorapatite are analysed. The three studied apatite species present the **same major element composition** : 36.5 ± 2.5 wt% of Ca, 17.0 ± 2.5 wt% of P and 4.0 ± 1.0 wt% of F.

ELEMENTAL MAPS BY MICRO-PIXE/PIGE :



In 700°C/20h HEATED FOSSIL IVORY from Rajégats (Gers, France), Mn oxides are present as stable inclusions after heat process. Analogous inclusions are observed in odontolite 3.

F is distributed homogeneously in all examined samples (example odontolite 1).



TRACE ELEMENT CONTENT :

All specimens contain traces of Mn (95 - 43 700 ppm), Fe (60 - 3 330 ppm), Sr (390 - 1 800 ppm), Ba (125 - 14 240 ppm), Y (11 - 2 830 ppm), Pb (41 - 206 ppm) and U (45 - 220 ppm).

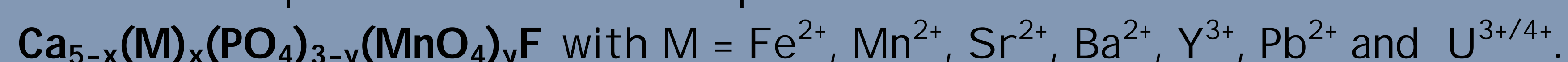
Copper traces are only present in two odontolites and one fossil ivory (12-100 ppm).

CONCLUSION

Odontolite, some heated fossil ivory and blue fluorapatite provide very similar composition and crystallisation.

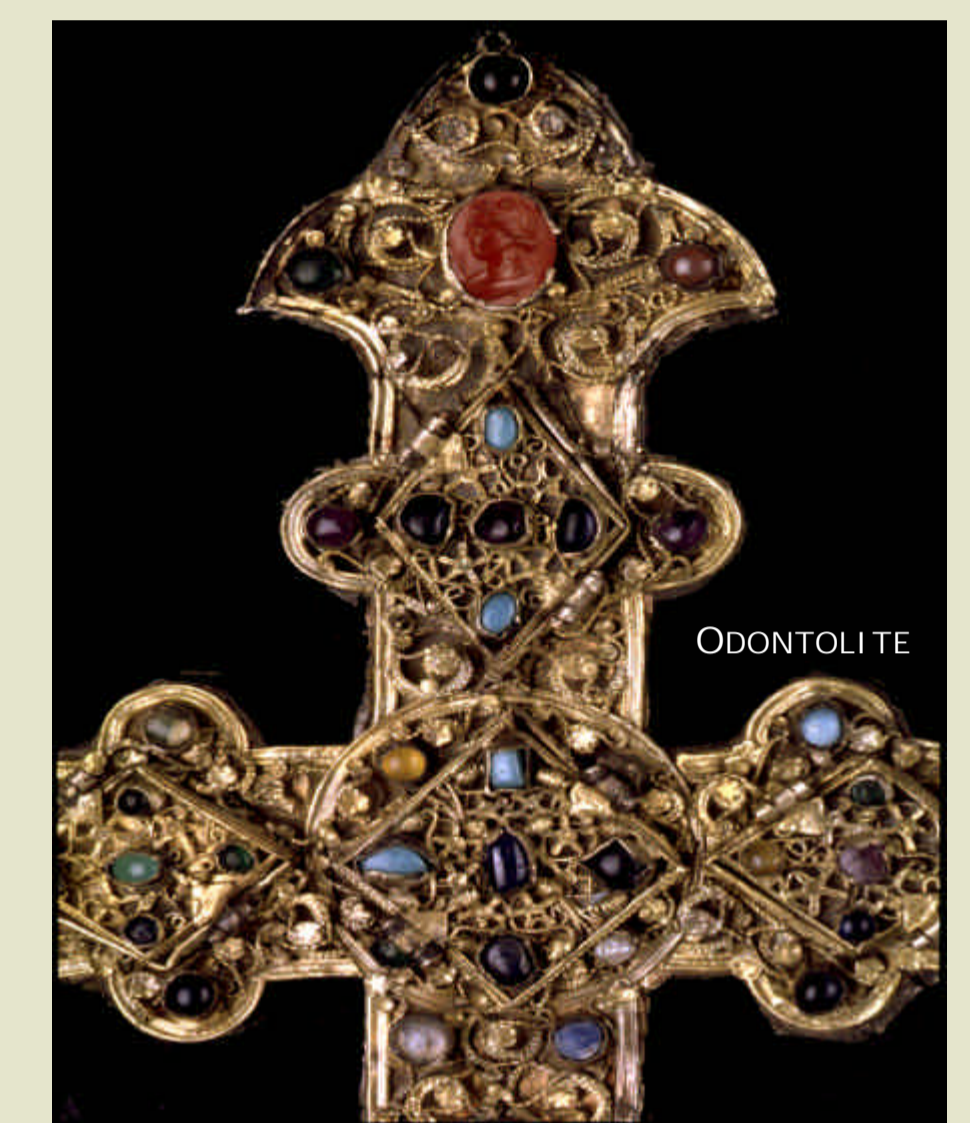
Trace element analysis suggests that the colour mechanism might be an intervalence charge transfer Mn^{5+} and O^{2-} with MnO_4^{3-} substituted at the PO_4^{3-} sites, already reported for blue fluorapatite.

Chemical composition of the three species is :



EXAMPLE OF ODONTOLITE ON AN ART OBJECT :

Religious bronze cross from the XIII century in the Cluny museum (Paris).



STRUCTURAL ANALYSIS BY TEM :

EXPERIMENTAL SET-UP FOR TEM :

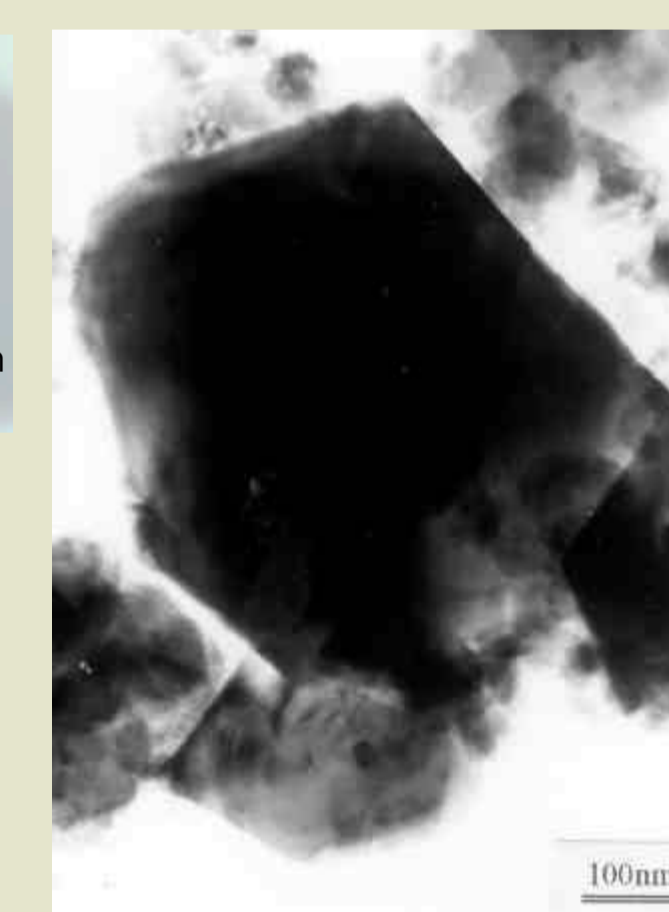
200 kV Jeol electron microscope equipped with a Link Isis x-ray analysis system.

Odontolite, heated fossil ivory and blue fluorapatite present **similar crystal sizes and morphologies**. Electron diffraction patterns only correspond to fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (JCPDS: 15-876).



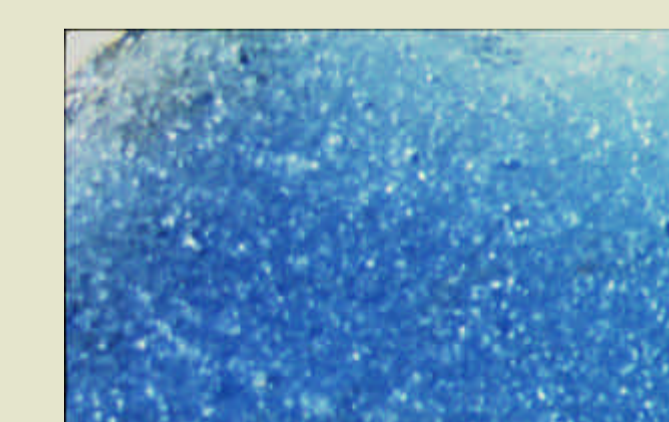
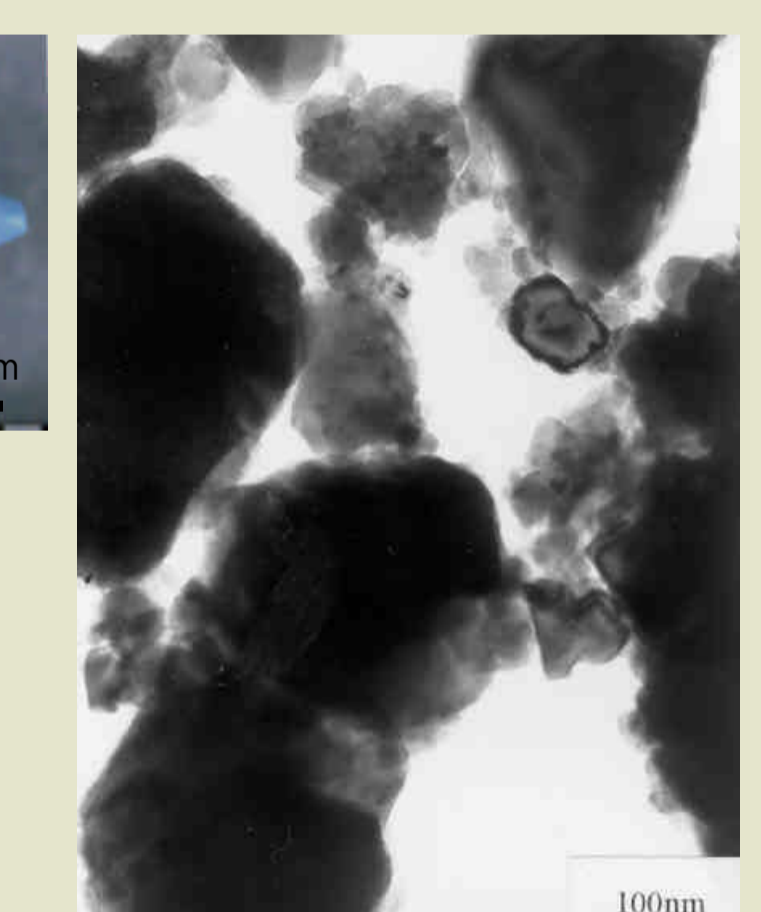
Optical and TEM image of 700°C/20h HEATED FOSSIL IVORY

Average crystal size : 500 nm.



Optical and TEM image of ODONTOLITE 1.

Average crystal size : 400 nm.



Optical and TEM image of BLUE FLUORAPATITE.

Average crystal size : 700 nm.

