American Mineralogist, Volume 86, pages 1519–1524, 2001

From mastodon ivory to gemstone: The origin of turquoise color in odontolite

INA REICHE,[1,*] COLETTE VIGNAUD,[1,2] BERNARD CHAMPAGNON,[3] GÉRARD PANCZER,[3] CHRISTIAN BROUDER,[4] GUILLAUME MORIN,[4] VICENTE ARMANDO SOLÉ,[5] LAURENT CHARLET,[6] AND MICHEL MENU[1]

[1]Centre de Recherche et de Restauration des Musées de France (C2RMF)—Musée du Louvre, UMR 171 CNRS, 6, Rue des Pyramides, 75041 Paris cedex 1, France
[2]Laboratoire de Physique des Liquides et Electrochimie, UPR 15 CNRS, case 133, 4, Pl. Jussieu, 75252 Paris cedex 05, France
[3]Laboratoire de Physico-Chimie des Matériaux Luminescents, UMR 5620 CNRS, Université Claude Bernard Lyon 1, Bât. 205, 69622 Villeurbanne cedex, France
[4]Laboratoire de Minéralogie Cristallographie, UMR 7590 CNRS-UPMC-Paris-IPGP, case 115, 4, Pl. Jussieu, 75252 Paris cedex 05, France
[5]European Synchrotron Radiation Facility, BP 220, 38043 Grenoble cedex, France
[6]Groupe de Géochimie Environnementale—LGIT, Université Joseph Fourier Grenoble, BP53, 38041 Grenoble cedex 09, France

ABSTRACT

Heat-induced color changes of fossilized Miocene mastodon ivory (13–16 Ma) have been known at least since the Middle Ages. Cistercian monks are believed to have created odontolite, a turquoise-blue "gemstone," by heating mastodon ivory found in Miocene geological layers next to the Pyrrenean chain, France, to use it for the decoration of medieval art objects. This material has been the object of investigations of famous European naturalists and gemmologists, among them Réaumur (1683–1757). Although vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$] is the commonly accepted coloring phase supposed to appear when heating fossilized mastodon ivory, our previous spectroscopic studies using PIXE/PIGE and TEM-EDX demonstrated that the chemical composition of collection odontolite and heated mastodon ivory corresponds to well-crystallized fluorapatite [$Ca_5(PO_4)_3F$] containing trace amounts of Fe (230–890 ppm), Mn (220–650 ppm), Ba (160–620 ppm), Pb (40–140 ppm), and U (80–210 ppm). No vivianite has been detected.

To provide new insights into the physico-chemical mechanism of the color transformation of fossilized ivory, we used the combination of UV/visible/near-IR reflectance spectroscopy, time-resolved laser-induced luminescence spectroscopy (TRLIF), and X-ray absorption near-edge structure (XANES).

Contrary to what had formerly been described as the color origin in odontolite, our study has conclusively identified traces of Mn^{5+} by UV/visible/near-IR reflectance spectroscopy, TRLIF, and XANES inside the fluorapatite. Thus, odontolite owes its turquoise-blue color to Mn^{5+} ions in a distorted tetrahedral environment of four O^{2-} ions. XANES also demonstrated oxidation of disordered octahedral Mn^{2+} ions to tetrahedral Mn^{5+} species in apatite during the heat process. So we give the first evidence of the real color origin in odontolite.