INTRODUCTION

Fossilized mastodon ivory from Southern France turns blue upon heating, and this property has been known since the Middle Ages (Astre 1949). This turquoise-blue ivory was used to decorate reliquary objects such as bronze crosses (Fig. 1). The famous French naturalist Réaumur reported in 1715 on the existence of a small industry in Southern France that extracted turquoise (Réaumur 1715). He thought that fossilized ivory transformed into the mineral turquoise by heating. His hypothesis, however, was based solely on resemblance with precious turquoise. The mineral turquoise is a Cu-Al phosphate having the formula \(\text{[CuAl}_6\text{(OH)}_8\text{(PO}_4\text{)}_4\cdot8\text{H}_2\text{O]}\). In 1823, Fischer recognized that odontolite and turquoise are different mineral species (Fischer 1823). He could not explain the color formation in odontolite, however. Until the present work, the origin of the color in odontolite has remained the subject of controversy. Several hypotheses have been proposed, mostly invoking inclusions of vivianite, a blue-colored Fe-phosphate having the chemical formula \(\text{[Fe}_3\text{(PO}_4\text{)}_2\cdot8\text{H}_2\text{O]}\), or Cu salts in bone or ivory (Réaumur 1715; Fischer 1823; Lapparent 1899; Franchet 1933; Webster 1986).

Odontolite was identified by us (Reiche et al. 2000a) as relatively well-crystallized fluorapatite containing traces 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 inapatite during the heat process. So we give the first evidence of the real color origin in odontolite.

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

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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 \(\text{[Fe}_3\text{(PO}_4\text{)}_2\cdot8\text{H}_2\text{O]}\) 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 \(\text{[Ca}_5\text{(PO}_4\text{)}_3\text{F]}\) 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.

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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 inapatite during the heat process. So we give the first evidence of the real color origin in odontolite.