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**REPLACEMENT OF IRON SULPHIDES BY OXIDES  
IN THE DINOSAUR BONE FROM THE LANCE FM.  
(WYOMING, USA) - PRELIMINARY STUDY.**

**Abstract:**

A unique aggregate of framboidal pyrite and iron oxides was found in the vascular canals of dinosaur bone from the Lance Fm. and was studied using SEM/EDS. Various types of pyrite, massive and framboidal, and their subsequent oxidation and replacement by iron oxides are described. The proposed sequence of events is as follows: 1: formation of pyrite framboids and framboidal aggregates; 2: infilling of the interstices between pyrite crystals by massive pyrite; 3: oxidation of former sulphides.

**Keywords:** dinosaur bones, pyrite, iron oxides, framboids, replacement

INTRODUCTION

Pyritized organic remains are common in the sedimentary record. Pyrite and iron oxides generally fill open voids, and can replace organic matrix or “soft parts”. Pyrite can adopt various forms, from massive to aggregated, euhedra, or framboids. Excellent descriptions of the mechanisms for fossil pyritization were given, for example, by Canfield and Raiswell (1991) and Raiswell et al. (1993). Infilling by iron oxides are quite common, although detailed studies are rare (Pfretzschner 2001a,b). Pawlicki and Nowogrodzka-Zagorska (1998) and recently Schweitzer et al. (2005) suggested that small mineral structures could be exceptionally preserved blood which stirred an especially hot discussion on the possible implications. Schweitzer and Horny (1999) presented iron and oxygen-rich microstructures in the bone tissues of *Tyrannosaurus rex* but rejected the structures as framboids due to their composition of iron oxides. This paper documents various stages of framboidal pyrite replacement by oxides in dinosaur bone.

SAMPLING AND METHODS OF INVESTIGATIONS

Four to five cm size fragments of large dinosaur long bones most likely from Hadrosaur or Triceratops were collected from the dark shales of the Lance Formation near the town of Lance Creek Wyoming. Several small (0.2-0.7 mm) pieces, were fractured from the bone, mounted and carbon coated for analysis. Equipment used was a field-emission SEM (HITACHI S-4700), equipped with YAG (BSE) detector and EDS analyzer (NORAN Vantage).

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## RESULTS

This study revealed the common occurrence of iron oxides in the vascular canals. The presence of iron sulphides was extremely rare but can help to understand the diagenetic processes that occurred in the bone. The internal voids were filled with large 250x100  $\mu\text{m}$  iron (hydroxy)oxides and subordinate pyrite microcrystals (Fig. 1a). Massive iron oxides surround the embedded pyrite framboid's (Fig.1b) and scattered uniform pyrite microcrystals (Fig.1c, e). The embedded framboid in figure 1b is irregular in outline suggesting replacement by a massive iron oxide. The pyrite 1-2  $\mu\text{m}$  crystals are octahedral with the smaller size typical of framboid microcrystals.

Fig.1c shows various typical microstructures. Visible in the left side of figure 1c, uniform pyrite microcrystals and imprints are embedded in the iron oxides. The smaller pyrite sub-crystals in fig 1e are also observed in the massive iron oxides. Figure 1d is a magnified view of the framboid's interstitial iron oxide network. Some secondary iron oxide microcrystals are preserved, whereas others are partly or totally dissolved or dislodged. Dissolution, leaving intact outer shells, is especially active in the cores of the microcrystals (Fig.1f) with several small pyrite microcrystals remaining in the iron oxide network (Fig.1d). Irregular barite aggregates are visible in the massive iron oxides on the right side of fig 1c. Note that the latter are locally highly dissolved. Barite is a relatively common iron oxide in all dinosaur bones examined from this location. Pyrite crystals analyzed under EDS were found to have a generally stoichiometric  $\text{FeS}_2$  composition. The EDS analyses of iron oxides show the range of various Fe:O ratios which can be comparable with  $\text{Fe}_2\text{O}_3$  (lighter in BSE image) and  $\text{FeOOH}$  (darker) compositions.

## DISCUSSION AND CONCLUSIONS

Pyritization of biogenic remains and the occurrence of isolated iron oxides in fossils is common (e.g. Canfield, Raiswell 1991; Sawlowicz 2000; in dinosaur bones, Hubert et al. 1996) whereas the co-occurrence of both iron minerals is relatively rare. This unique aggregate of framboidal pyrite, iron oxides and their subsequent oxidation, has allowed us to trace the formation of various types of iron oxide replacement. No massive pyrite was preserved, only massive iron oxides. We suggest based on the similar co-occurrences in many ore deposits, that the pyrite preceded the iron oxides. The proposed sequence of events is as follows: 1/ formation of pyrite framboids and framboidal aggregates; 2/ infilling of the interstices between pyrite crystals by massive pyrite, with partial replacement of the former framboidal pyrite; 3/ oxidation of former sulphides: a/ replacement of massive pyrite, followed by b/ replacement and/or dissolution of framboidal pyrite microcrystals.

With no clear indications when these stages occurred, the timing of boundary events can only be suggested. Pfretzschner (2001a) proposed two mechanisms, the first early stage involving dissolved ferrous ions reacting with sulphides released from the decaying bone. The second is sulphate reduction to sulphide by sulphate reducing bacteria (SRB). The latter process requires the presence of organic matter which would be easily metabolized by SRB. We suggest that pyrite framboids and

aggregates of framboidal pyrite were formed at this stage. The second mechanism proposed by Pfretzschner (2001a) is a precipitation of external ferrous sulphide as the result of rising pH values due to buffering by phosphates in the bone matrix. We would advocate the formation of massive pyrite by this process. Filling both cancellous bone and replacing the phosphatic bone by iron oxides is common in the Lance formation (ms in prep.). Pfretzschner (2001b) lists three different processes of iron oxide formation in bones, i.e.: 1/ redox-precipitation of ferric hydroxide; 2/ a pH-precipitation of ferrous and/or ferric hydroxides; 3/ oxidation pyrite. Although the two first mechanisms occur in other iron-oxide-rich bones, in the studied case, oxidation of pyrite seems to be most plausible. We suggest that the oxidation of former iron sulphides (see also Canfield and Raiswell 1991) took place during later diagenesis, when the reducing conditions related mainly to the decomposition of organic matter were no longer dominant and the influence of generally oxidized host rocks was predominant.

This study suggests the possibility that some of the iron-rich microstructures found in dinosaur bones may result from generally inorganic oxidation of former pyrite framboids.

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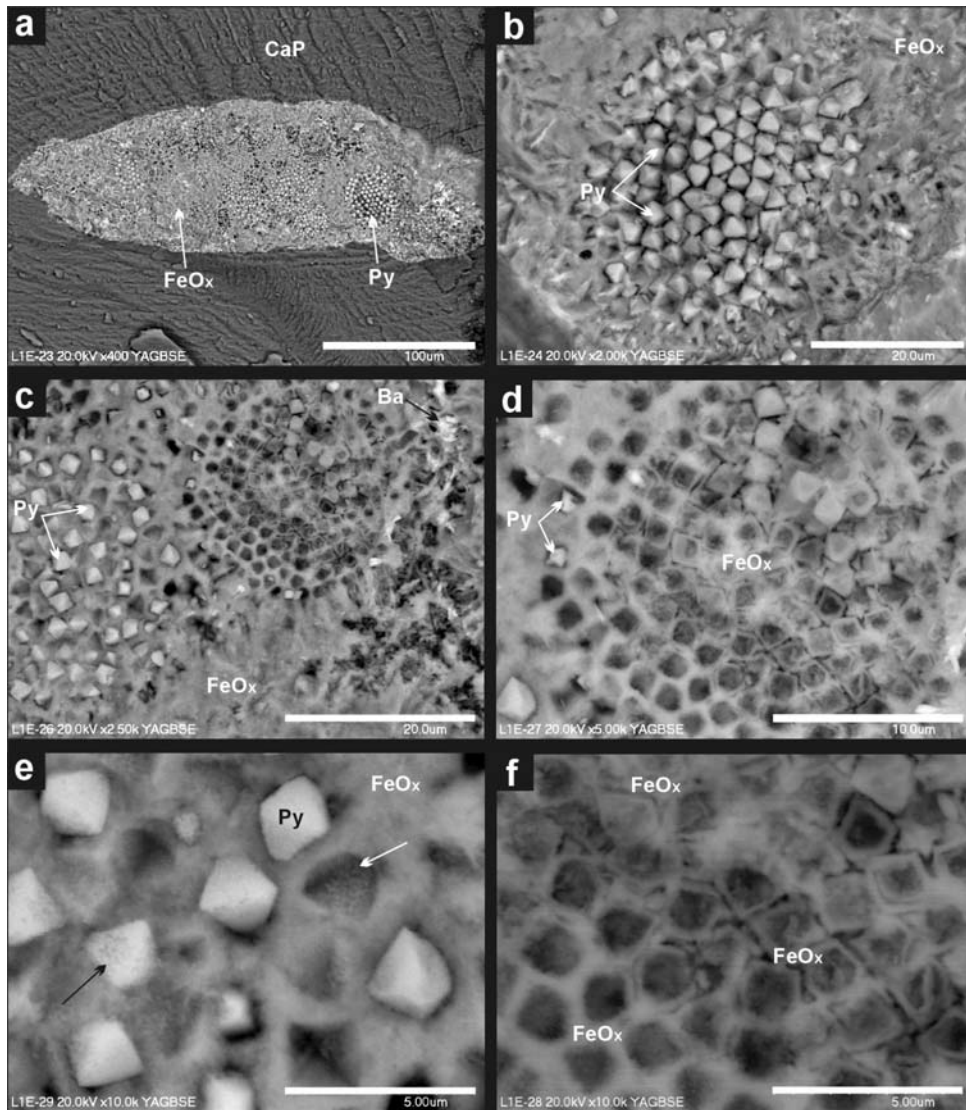


Fig. 1. SEM (BSE) images of the void (cross-section of the vascular canal) in the dinosaur bone, filled with framboidal pyrite and massive Fe (hydroxy)oxides: a/ a void filled completely with iron minerals (subsequent photos are magnifications of the various parts of this photograph); b/ irregular (partly destroyed?) framboid, built of regularly arranged pyrite octahedral microcrystals (light), embedded in the massive iron oxides (darker); c/ various microstructures of iron oxides (grey), with embedded pyrite microcrystals (light); d/ details of c photograph- note different stages of the dissolution of iron oxides octahedra; e/ details of the left part of c photograph - some pyrite crystals seem to be built of very fine microcrystals (left arrow), similar granular texture is also seen in the imprint after pyrite crystal (right arrow); f/ details of d photograph, interstitial network is typically composed of better crystallized iron oxides (lighter) than iron oxides octahedra and their remains (darker). Symbols: FeOx - Fe (hydroxy)oxides; Py - pyrite, CaP- Ca phosphate; Ba - barite.