DEVELOPMENT AND VALIDATION OF NON-INVASIVE CHEMICAL METHODS FOR CLEANING OF PALAEONTOLOGICAL SPECIMENS

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By

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DECLARATION

I declare that this Thesis is my own unaided work. It is being submitted for the degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in this or any other University.

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Stephen Pole

_____day of _____, 2008

Abstract

The dolomitic cave deposits of southern Africa hold arguably the most abundant hominid and fauna fossil record in the world. However, as a result of various mineral processes occurring, these fossils are often covered in a brown/black deposit. This layer is a mixture of manganese and iron oxides from mineral dissolution of the dolomite in cave environment in which all the specimens are found. This covering presents a particularly complex problem as it obscures fine surface details (e.g. cut marks and carnivore tooth marks) on the bone that are of particular interest in the fields of palaeontology and palaeo-anthropology. Being able to identify and distinguish between different modifying agents is important for interpreting how the bones were transported into the cave.

The deposit of manganese oxides was successfully removed from the bone using hydrogen peroxide, nitrites, chromium(III) and hydroxylamine without visibly altering the bone composition and structure, leaving all surface markings unaltered from their original state. It has been established that the above reagents can be used to reduce the manganese oxides resulting in Mn^{2+} as the main product of the reactions.

The concentration of reagents, reaction time and other conditions were optimised. The hydrogen peroxide method has been applied in the cleaning of over seven thousand manganese oxide coated fossil bones and teeth from the early hominid site of Coopers D situated in the Cradle of Humankind. A flow through system was also constructed and used for the mass cleaning of fossils using the hydrogen peroxide method and the hydrogen peroxide was continually replaced to maintain the $[H^+]$ and remove the

Mn^{2+} formed, and thus drive the Mn^{4+} reduction reaction. Validation and analysis of cleaning methods included pH, time, Mn^{2+} concentration as well as the Mn: Fe ratio determination. Although the chromium method was proved successful in removing the fossil bone coatings, the kinetics for this surface reaction were extremely slow. Qualitative validation of all these methods was performed by gravimetric analysis and through the use of scanning electron microscopy and proved that the manganese oxide removal does not damage bone matrix. Characterisation of the mixed oxide coatings was performed using powder X-ray diffraction, X-ray fluorescence mapping, Raman spectroscopy and Infrared spectroscopy. These chemical procedures of selectively removing the dark manganese oxide coating from fossils to expose surface modifications, is a breakthrough for the fields of palaeontology and archaeology and sub-disciplines concerned with fossil bones.

DEDICATION

To my mom, dad,

And close friends.

Your support and love has inspired me!

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LIST OF SYMBOLS AND ABREVIASIONS

SD Standard deviation

SEM Scanning electron microscopy

ICP-OES Inductively coupled plasma optical emission spectroscopy

XRF X-ray fluorescence

XRD X-ray diffraction

EXAFS Extended X-ray Absorption Fine Structure

AAS Atomic absorption spectroscopy

MPD Micro probe detector

EPA Environmental protection agency

IR Infrared

EPMA Electron probe mapping analysis

FB Fossil bone

CB Cow bone

HA Hydroxylamine

N Nitrite

DFOB desferrioxamine B

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