CHAPTER 9

FURTHER ASPECTS AND COMPARISONS OF THE NITRITE AND HYDROXYLAMINE FOSSIL PREPARATION METHODS

Three methods have been developed, optimized and validated, namely the use of hydrogen peroxide, nitrites and hydroxylamine. The chemistry of all the methods developed is not always similar, thus different experimental approaches had to be considered for the optimization and validation of each method.

9.1 Comparative qualitative analysis of the hydroxylamine and nitrite method for the removal of manganese oxides from fossil bones

A comparative investigation was performed to compare and contrast the use of hydroxylamine and nitrites for the removal of manganese oxide coatings from fossil bones. The hydroxylamine has been shown to remove these surface oxide coatings with great efficiency and the rate of removal is also kinetically efficient.

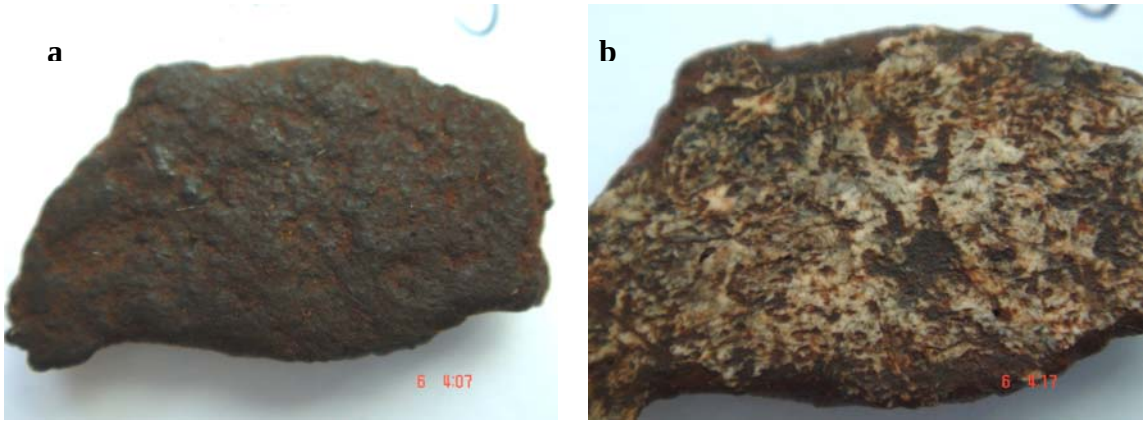

Figure 9.1 Fossil bone fragment possessing a thick manganese oxide coating that is obscuring the surface **a,** before application of the hydroxylamine method **b,** after the manganese oxide coated fossil bone fragment was treated in a 0.14 mol L^{-1} solution of hydroxylamine at pH: 3.75.

The nitrite method shows efficient removal of manganese oxide fossil bone coatings and does not cause any dissolution of the bone matrix or surface layer.

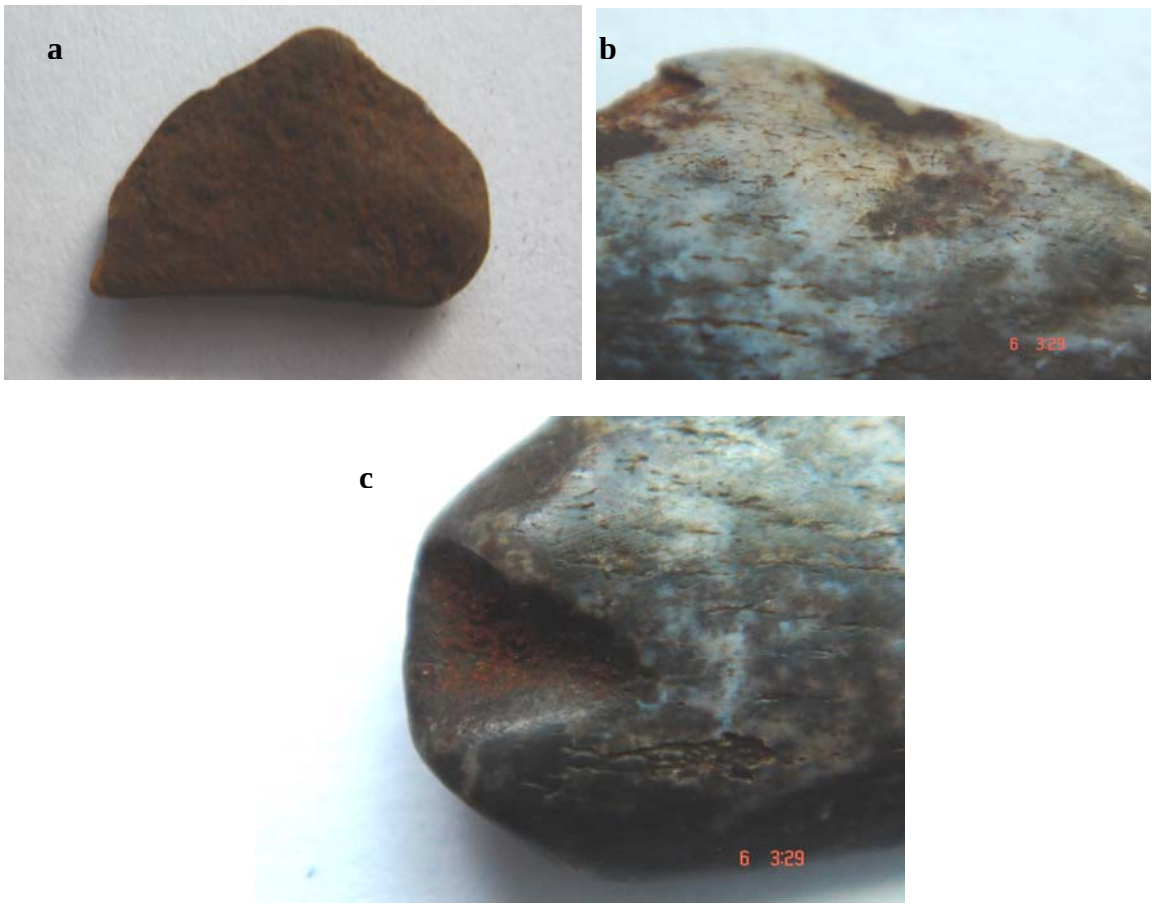

Figure 9.2 Fossil bone fragment possessing a thick manganese oxide coating **a,** Before application of the nitrite solution **b,** after removal of manganese oxide coating from a

fossil bone fragment using 1.8 mol L^{-1} nitrite solution at initial pH: 3.54. **c,** extensive surface detail is revealed previously obscured beneath the manganese coating.

From figs. 9.2a, b, and c, it is observed that the adequate removal of the manganese oxide coating is achieved with no macroscopically visible evidence of damage being incurred to the bone surface. Fossil bone topography and surface features are now clearly visible; the pores on the surface of the bone can also be seen without any magnification.

9.2 Elemental evolution trends for the optimized and validated hydroxylamine and nitrite methods

The elemental evolution trends for the use of nitrites and hydroxylamine to reduce manganese oxide coatings on the surface of fossil bones were compared. The elements of interest that were common to all the manganese oxide coatings were: Iron, manganese and calcium.

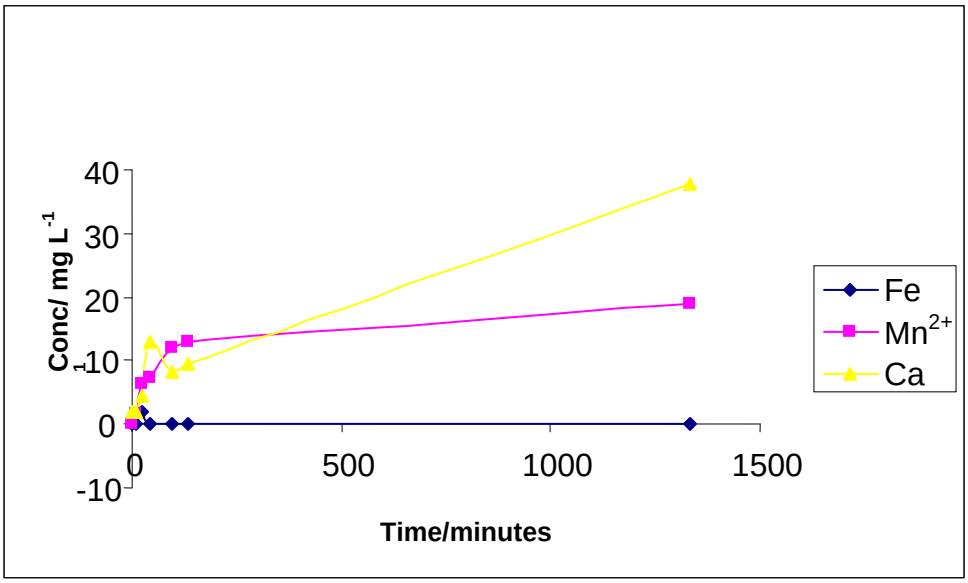

Figure 9.3 Comparative analyses of Ca, Mn, and Fe evolution trends for the nitrite method under optimized conditions, applied to manganese oxide coated fossil bones.

The rate of calcium evolution as compared to that of manganese and iron is greater after a short time interval, thereafter the rate of the calcium evolution increase is even greater with respect to the other elements. This steep increase could be due to the formation of nitrates reaching a critical level in the solution, and thus indirectly resulting in a greater rate of dissolution of calcium. It is important to note, however, that the overall mass loss of calcium in particular relative to the total mass of the bone, is negligible.

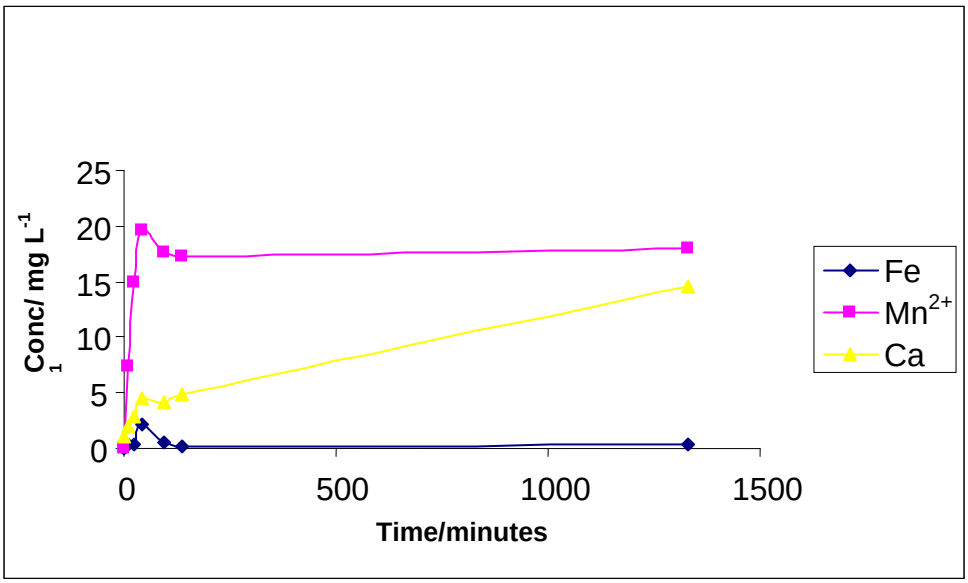

Figure 9.4 Comparative analyses of Ca, Mn, and Fe evolution trends for the hydroxylamine method under optimized conditions applied to manganese oxide coated fossil bones.

As previously seen for the nitrite method, the rate of calcium evolution follows a similar trend in that it increases throughout the treatment process at a steady rate. However, for the hydroxylamine method the rate of manganese evolution increases at a much greater rate up until an equilibrium state is reached, or all the manganese is removed from the coating via our proposed ligand dissolution reaction. Hydroxylamine is known to dissolve manganese in acidic conditions (Tan *et al*., 2005). As the pH of the solution approaches alkalinity, the ligand becomes less active and thus the rate of manganese removal stabilizes. A possible reason for the rate of the calcium evolution still increasing could be due to calcium having a higher affinity for the hydroxylamine and could be thus less dependent on pH unlike manganese dissolution (Mei and Yocum, 1991).

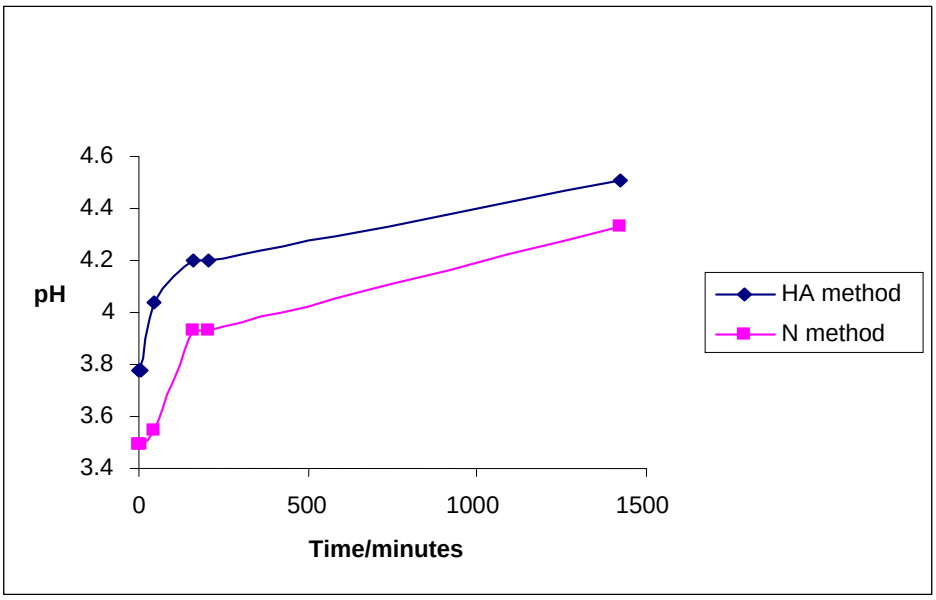

Figure 9.5 Relationship between pH and time for the hydroxylamine (HA) and nitrite (N) method using two fragments originating from the same manganese oxide coated fossil bone.

The pH change as each reaction proceeds follows a similar trend, as demonstrated by the curves almost following a parallel behaviour. One important aspect to notice is the pH value at which equilibrium is almost established for each cleaning method. The hydroxylamine method, takes approximately the same time to reach equilibrium if it is taken into account that the initial pH values for the two methods differ by the same magnitude, as the overall gap between each graph is approximately equal throughout the plot. This implies that when comparing the kinetics of the hydroxylamine and nitrite method, the pH value does not appear to play a significant role in the different rates of evolution of metals from the coatings, but rather the nature of the reagent itself.