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NOTE

A METHOD FOR CHEMICAL REDUCTION AND REMOVAL OF FERRIC IRON APPLIED TO VERTEBRATE FOSSILS

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INTRODUCTION

Removal of fossil bone from calcareous matrix using dilute organic acids (especially acetic or formic acid) is now an established technique. Where there is a high level of ferruginous matter (e.g., as a ferric cementing agent within the matrix), limited success has been achieved following the application of 5% thioglycollic acid, mixed with 0.9% calcium orthophosphate in deionized water (Howie, 1974). Thioglycollic acid converts ferric to ferrous ions, which then form a water-soluble ferrous salt. This technique was found to be useful in combination with mechanical preparation of ironstone nodules containing cranial skeletons of hybodont sharks from the Wealden of Sussex, England (Maisey, 1983). Thioglycollic acid preparation nevertheless has several disadvantages (see Discussion).

An alternative means of achieving the same ends, but without the use of acids, is presented here. This technique was originally developed by mineralogists in order to remove ferruginous crusts from crystal specimens. It was first outlined by Waller (1980) and was refined slightly by King (1983), whose procedures we have adopted. To our knowledge, the process (which, following King, we refer to as "The Waller Method") has not previously been applied to the preparation of vertebrate fossils. This technique was presented by us in the Poster Session at the 48th Annual Meeting of the Society of Vertebrate Paleontology held in Drumheller, Alberta, where it attracted much interest. In view of this, we submit the salient details of the technique and report on the results of our experiments.

THE WALLER METHOD

This technique takes advantage of the fact that ferrous hydroxide ($Fe(OH)_2$) is more soluble than ferric oxide (Fe_2O_3), over a wide pH range. Iron is first reduced from the ferric to a ferrous state using sodium dithionite, and the ferrous hydroxide is then dissolved in a neutral solution containing a sequestering or chelating agent, which enhances the solubility of the ferrous ions.

The active solution contains three sodium salts. A stock solution is first prepared, comprising 71 g of sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, which sequesters ferrous ions) and 8.5 g of sodium bicarbonate ($NaHCO_3$, which acts as a buffer to maintain the pH near an optimal value of 7.3) per liter of distilled water. This stock solution may be stored indefinitely. The third salt, sodium dithionite ($Na_2S_2O_4$, which reduces ferric to ferrous iron), is added when the solution is required, in the ratio of 1 g per 50 ml of solution. Sodium dithionite oxidizes readily and must therefore be added only when needed.

The reducing solution is poured into a suitable plastic or glass container and the specimens to be cleaned are immersed. A batch of 12–18 small specimens or 2–4 larger ones can be treated in a single bath of 2–3 liters. The container should be covered, but not air-tight, and placed in a fume hood or well ventilated area (the redox reaction produces hydrogen sulfide). The solution should be stirred gently and continuously with a magnetic stirrer to enhance dissolution and penetration. It is important to keep the container covered during the reducing process, as sodium dithionite readily oxidizes on exposure to the atmosphere. Draping a thin plastic wrap over the solution (directly in contact with the surface) minimizes aerial exposure while allowing the escape of gaseous hydrogen sulfide. The solution remains active for about 12 hours at room temperature, after which time the specimens are washed in distilled water for another 12–24 hours before air-drying. If a crust of iron remains, or if greater penetration is required, the specimens can be transferred to a fresh reducing solution prior to washing.

There is a tendency for the sodium citrate to chelate calcium as well as ferrous ions, rendering the limestone matrix porous and chalky. King (1983) thus recommended that the Waller Method should not be used on calcite or aragonite mineral specimens, but in the case of vertebrate fossils embedded in limestone the removal of calcium can be advantageous because it softens the matrix and facilitates fine mechanical preparation. The accompanying illustrations show the "before" and "after" appearance of a small *Dastilbe crandalli* (Teleostei, Gonorynchiformes) specimen that is typical of many we have prepared from the Lower Cretaceous (Aptian) Araripina limestone from Brazil (Fig. 1). The results of experimentation on fossil insects in this matrix were disappointing, however, as original chitinous material was readily dissolved.

Best results were obtained by cleaning specimens of *Dastilbe* that were left embedded in their limestone matrix. Acid preparation alone was generally unsatisfactory for these particular specimens, primarily because the presence of complex iron phosphates (in permineralized muscle tissues) surrounding the bone prevented its complete exposure. The Waller Method gave better resolution of skeletal morphology in this material than either "free-standing" or "transfer" acid preparation (see Rixon, 1976 for details). Some problems were encountered with embedding plastics following treatment with the Waller Method, primarily because increased matrix porosity permitted excessive penetration by the plastic. Har-