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HOLLANDITE-CORONADITE IN FOSSIL BONE

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ABSTRACT

Manganese is a widespread minor element in fossil bone. We have identified the manganese-containing mineral as a member of the hollandite group. Precipitation of the hollandite minerals is catalyzed by the presence of citric and butyric acid in bone.

INTRODUCTION

Manganese has been reported as a widespread minor element in fossil bone (Parker and Toots, 1970; Matter, Davidson, and Wyckoff, 1970), but the precise nature of the manganese-containing phase has not been reported. Manganese-rich bones are brown to black in color from black manganese compounds filling lacunae, tiny voids occupied by osteocyte cells in living bone (Fig. 1).

IDENTIFICATION

Electron microprobe examination of some manganese-rich fossil bones showed that lead and barium are associated with the manganese-bearing phase which fills the lacunae in fossil bone of Oligocene age from South Dakota and are not present in the apatite of the bone. We have noted from whole bone analysis that high lead is invariably associated with high manganese and usually manganese plus barium. We have obtained sufficient material for X-ray diffraction from a heavily impregnated bone from the lower Oligocene of the Shirley Basin, Wyoming. The pattern consists of lines attributable to apatite and hollandite-coronadite (Mouat, 1962). As Hewett (1971, p. 174) notes, hollandite and coronadite are not distinguishable by X-ray

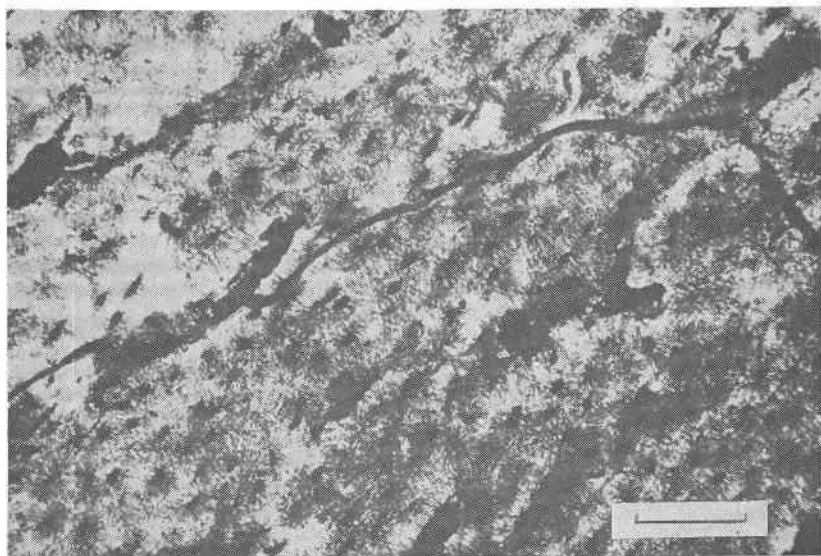


FIG. 1. Photomicrograph of fossil bone with lacunae and postmortal fracture filled with hollandite-coronadite; line is 100 μ m.

diffraction. Potassium occupies the Pb-Ba site in the mineral cryptomelane, but we detected no potassium in our samples. We do not suggest that all manganese in fossil bone is contained in hollandite-coronadite inasmuch as we have analyzed high manganese specimens which are free of lead and barium.

MODE OF DEPOSITION

Fossil bone is a particularly favorable substrate for minor element concentration during diagenesis of the enclosing sediments. Indeed, elements present in amounts up to several tenths of a per cent in the bone are normally not detectable in the surrounding sediment. In the case of manganese, barium, and lead, we believe we have an explanation. In both the Shirley Basin locality and a second locality near Orchard, Nebraska (Voorhies, 1969) the manganese-rich bones are confined to coarse grained channel deposits surrounded by less-permeable rocks. Presumably, ground water flow through these channels provided an adequate supply of minor element ions.

We suggest that the manganese is precipitated from solution by oxidation of Mn^{2+} to higher valence states. Such oxidation is catalyzed by both citric and butyric acids. Citrates account for about one per cent of bone (McClean and Urist, 1968) and butyric acid is a well-known product of oxidation of animal fats. The compounds catalyze the autooxidation of Mn^{2+} at pH 8.0 whereas autooxidation in the absence of catalysts requires a pH of 10.0 or above (Mulder, 1964). Thus, manganese precipitation seems accounted for at a reasonable pH for ground water. Bacteria of several species also oxidize manganese ions (Zajic, 1959, p. 162-163; Mouat, 1962), but their role in fossilization has not been evaluated.

According to Byström and Byström (1950, 1951) the hollandite-group structures are derivatives of the $\alpha-MnO_2$ structure, with the voids in the structure occupied by Ba, K, and Pb with suitable balancing in the valence state of the manganese. We suggest that the manganese precipitated as the $\alpha-MnO_2$ structure and provided traps to capture the Pb and Ba from the circulating ground water.

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LUNAR TRIDYMITE AND CRISTOBALITE

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ABSTRACT

Tridymite and cristobalite in lunar basalt 15085 are better than 99% SiO₂; they contain small percentages of TiO₂ (0.38, 0.28), Al₂O₃ (0.18, 0.34), K₂O (0.17, 0.26), and Na₂O (0.05, 0.05). The approximate equivalence of Al to K + Na indicates substitution of the type KAl = Si, the large cations being accommodated in lattice vacancies.

One of the mineralogical surprises in the Apollo 11 rocks returned to Earth was the rather frequent occurrence of tridymite and cristobalite as accessory minerals. This feature has been repeated in the rocks from later missions. Typically the tridymite occurs as thin platy crystals (appearing as narrow laths in thin sections), and the cristobalite as anhedral to subhedral grains (Figs. 1 and 2). The cristobalite shows a mosaic structure with a rectangular blocky appearance and low birefringence, attributed to inversion from the high-temperature form. The tridymite also shows patchy extinction attributable to inversion from the high-temperature form; it also has low birefringence (0.003 approx.) but somewhat higher than the cristobalite (0.001 approx.).

Rock 15085, a pyroxene-plagioclase basalt from the Mare Imbrium surface near the Apollo 15 landing site, contains well-developed tridymite (0.7 percent by weight) and cristobalite (0.4 percent). The comparatively coarse grain-size made these minerals particularly suitable for microprobe analysis, which was carried out with a view