Speciation Analysis of Intra-cellular Metallic Implant Debris Using Synchrotron XRF-Imaging

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INTRODUCTION: Wear and corrosion debris generated from total hip replacements (THR) have been associated with adverse local tissue reactions (ALTR) or osteolysis, often leading to premature implant failure.[1] Metallic degradation products can be released from bearing surfaces and taper junctions made of CoCrMo or Ti6Al4V alloy. A better understanding of the chemical nature of particulates, metal ions, and their chemical alteration within tissue is a crucial step to improve implant longevity. It is the goal of this study to demonstrate the beneficial use of the synchrotron X-ray Fluorescence imaging (XRF) and spectroscopy to perform elemental speciation (distribution and valency state) analysis of intracellular metallic debris.

METHODS: Joint pseudo-capsule tissue retrieved from a THR patient during revision surgery was studied. This retrieved implant was a dual modular metal-on-metal THR with moderate bearing surface wear and severe fretting corrosion damage on the modular components made from CoCrMo alloy and Ti-alloy. Two serial, 5 µm sections of formalin-fixed, paraffin-embedded tissue were made. One section was stained with H&E to provide a histological overview of the tissue response. For the synchrotron analysis, the other section was placed on a plastic foil. The entire tissue was prescreened using a 30 µm step size scan. Sub-regions of the samples were then cut off and transferred to a 5×5 mm Si frame for high resolution scans to obtain intracellular elemental and chemical information. P/Ti/Co colocalized images were obtained using 300 nm step size scans (**Fig. 1 A_i** to **C_i)**. Single cells were then selected (white boxed area) and scanned at higher resolution using an 80 nm step size (**Fig. 1 A_ii** to **C_ii)**. Additionally, the X-ray absorption near edge structure (XANES) of intracellular debris were acquired at the Co, Cr, Mo, and Ti K-edge to determine the oxidation state of the metallic debris.

RESULTS: Histological evaluation of the tissue sample revealed the marked presence of debris-laden macrophages giving the cells a slate blue appearance. However, there were some areas near blood vessels, where the density of the debris within the macrophages caused the cells to appear black. The predominant intracellular metallic elements in these macrophages was revealed to be Cr by XRF imaging analysis. Elemental ratios of Cr/Co and Ti/V were determined for the entirety of 64 individual macrophage cells. The mean Cr/Co ratio was 29.66 ranging from 15.59~37.9, and the mean Ti/V ratio was 4.76 ranging from 4.46~5.51. Many submicron particulate debris were observed intracellularly in various shapes. The same elemental ratios were calculated for individual intracellular particles marked by color-coded ROIs in selected cells from three separate sub-regions. Within single particles the Cr/Co ratio ranged from 1.12-100.16, and the Ti/V ratio ranged from 2.21-6.68. Overall, two types of Cr XANES spectra were found which corresponded to Cr_2O_3 and $CrPO_4$, yet no metallic Cr was observed. $CrPO_4$ had higher Cr/Co ratios than Cr_2O_3 and was colocalized with calcium. Most of the Co-rich debris was confirmed to be Co^{2+} by comparison to Co standard XANES spectra, whilst a few particles showed spectra that most closely resembled that of Co in its alloy state. The Mo spectra were also taken from some Co and Cr-rich areas. It mainly occurred in its oxidation state and matched MoO_2. However, at a low Cr/Co ratio (<2:1), it occurred in its alloy state. The XANES of Ti-rich debris showed mainly a rutile-like structure, but the pre-edge peaks were somewhat distorted.

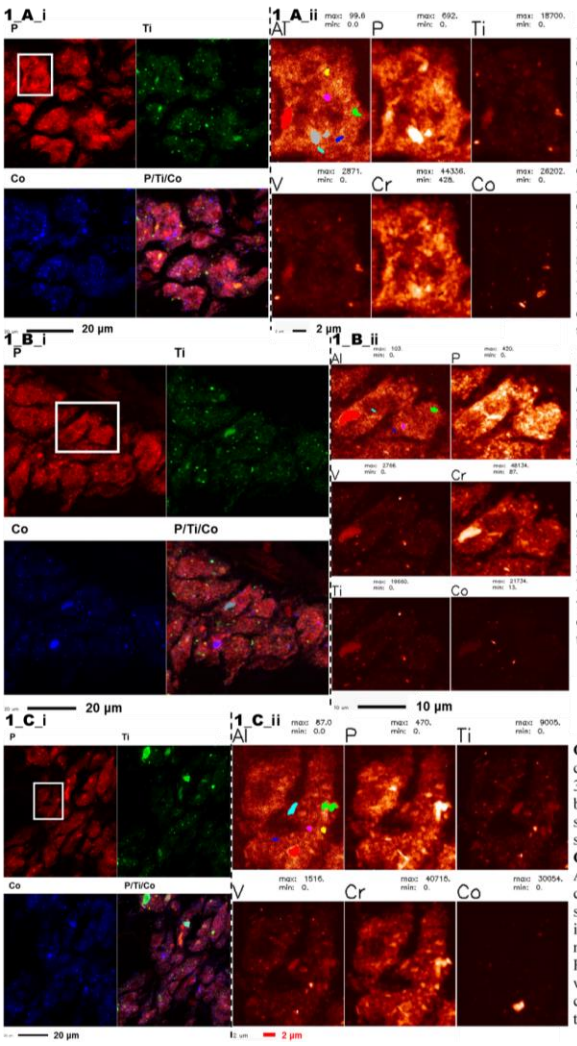

Fig 1: A_i) P/Ti/Co elemental composition mapping using 300 nm beam. The white boxed area is the selected sub-region_1, which was scanned using 80 nm beam. **A_ii)** The expanded view of Al/P/Ti/V/Cr/Co elemental composition mapping in sub-region_1. Selected intracellular debris are marked by color coded ROIs shown in the Al map, where XANES and ratio of content is measured. (refer to **Table 1**)

B_i) P/Ti/Co elemental composition mapping using 300 nm beam. The white boxed area is the selected sub-region_2, which was scanned using 80 nm beam. **B_ii)** The expanded view of Al/P/Ti/V/Cr/Co elemental composition mapping in sub-region_1. Selected intracellular debris are marked by color coded ROIs shown in the Al map, where XANES and ratio of content is measured. (refer to **Table 1**)

C_i) P/Ti/Co elemental composition mapping using 300 nm beam. The white boxed area is the selected sub-region_3, which was scanned using 80 nm beam. **C_ii)** The expanded view of Al/P/Ti/V/Cr/Co elemental composition mapping in sub-region_1. Selected intracellular debris are marked by color coded ROIs shown in the Al map, where XANES and ratio of content is measured. (refer to **Table 1**)

CONCLUSION/SIGNIFICANCE: Wear and corrosion are still a major cause of THR failure and revision surgery. There is still little knowledge on a threshold of critical particle or metal ion burden in terms of amount and type. Synchrotron XRF provides a detailed and accurate method to characterize intracellular wear debris and corrosion products, which will significantly improve the understanding of implant alloy degradation.