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Energy dispersive spectrophotometric and X-ray diffraction observations in IUDs

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Abstract

This paper describes preliminary observations of the surface deposits on Lippes Loop, Dalkon Shield, and Saf-T-Coil IUDs removed after periods of time up to 15 years. Rosettes of euhedral rhombic crystals with a columnar prismatic habit were observed on a Lippes Loop that had been *in situ* for 15 years. All mineral deposits were found to be calcium salts, but the degree of crystallization varied significantly, from almost totally amorphous to the perfect euhedral crystal form. The microenvironment alone or in combination with cyclic changes in the biochemical milieu surrounding the IUD may influence the deposition of specific mineral species.

Introduction

Although the literature contains a modest number of articles on the structural changes observed on the surface of IUDs after variable usage, only a few reports have concomitantly examined surface deposits by energy dispersive spectrometry (EDS) and/or X-ray diffraction (XRD) [1,2]. Existing data confirm that the major component of surface deposits is calcium precipitated along with a variety of anions in the form of salts [3]. Calcium carbonate has been referred to in particular [4].

Our interest in this subject began with the observation of rosettes of euhedral rhombic crystals with a columnar prismatic habit on the surface of a Lippes Loop that had been *in situ* 15 years [1,2]. The appearance of these rosettes was so striking that we decided to determine the exact mineralogic species on the surface of a small group of used IUDs that were being studied by SEM to evaluate changes in surface morphology. This paper describes our preliminary observations.

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Materials and methods

Types of IUDs

Table 1 shows the type of IUD, the length of time *in situ*, the nature of the examinations performed, and the mineralogic findings in those specimens with

Table 1 Types of IUDs and clinical status

IUD number	*IUD type*	*IUD status*	*EDS/XRD*	*Minerals*
1	Lippes Loop 1	Used 15 years	EDS/XRD	Apatite
2	Cu-7	Control	EDS	N/A
3	Lippes Loop 2	Control	EDS	N/A
4	Dalkon Shield 1	Used 4 months	EDS	Not enough material
5	Dalkon Shield 2	Used 15 months	EDS	Not enough material
6	Saf-T-Coil	Used 8 years	EDS/XRD	Calcite
7	Cu-7	Used 4 years	EDS/XRD	Calcite
8	Dalkon Shield 3	Control	EDS	N/A

sufficient surface material for XRD as well as EDS. The IUD numbers correspond to the sequential order of IUD examinations recorded in a prior presentation [2]. A detailed description of sample preparation has already been provided [1].

EDS

Specimens for EDS were mounted on aluminum stubs and coated in a vacuum evaporator with spectrographic grade carbon. Analysis was done with a Kevex 7000 ux solid state spectrometer mounted on a JEOL JXA 50A scanning microprobe. Some of the material had previously been coated with gold and palladium for SEM observation; these contaminating X-ray lines were seen in some of the EDS spectrums.

XRD

Specimens for powder camera X-ray diffraction were ground and placed in 0.3 mm quartz capillary tubes, which were then mounted in a Debye-Scherrer 114.59 mm powder camera. This camera was placed on a Phillips water-cooled X-ray generator set at 35 kV and 15 mA. A nickel filtered copper tube producing K alpha radiation was used. The resulting film and diffraction patterns were measured on a Phillips film strip reader and the lattice spacing was matched with the JCPD (Joint Committee on Powder Diffraction) card index.

Results

General comments

Although the basic elemental analyses varied at different areas on a given IUD or among types of IUDs, all mineral deposits were calcium salts. The degree of crystallization varied significantly, however.

Lippes Loop (IUD #1, Table 1)

The rosettes of crystals were a unique finding not duplicated elsewhere in this study or previously described by others in the contraceptive literature. Elemental analysis of these crystals revealed the characteristic X-ray lines of calcium and

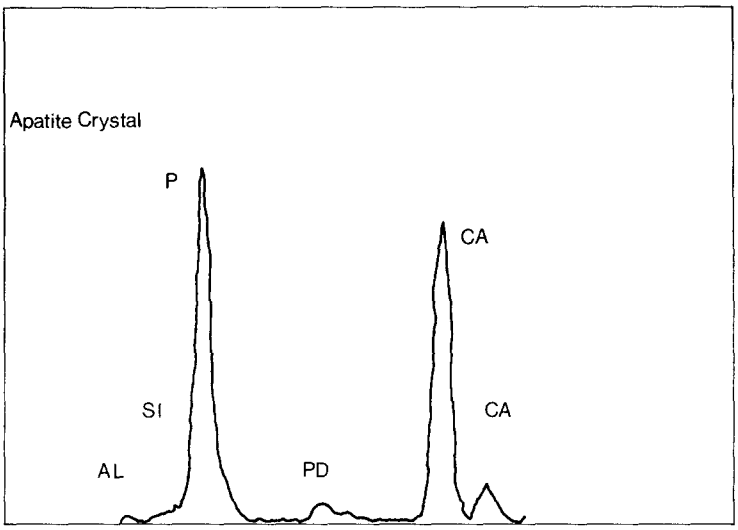

Figure 1 LL-1, energy dispersive spectrophotometric analysis of crystal rosettes

phosphorus (Figure 1). Since the ratio of their weight percent was approximately 1.67 Ca : 1P (in the presence of a crystalline habit), we presumed that these rosettes were of the calcium apatite mineral group $Ca_5(PO_4)_3(F_1Cl_1OH)$. To confirm this hypothesis, we removed several rosettes for XRD analysis. Calculation of the lattice spacings from the diffraction pattern confirmed our earlier impressions. Figure 2 is a film exposure of this diffraction pattern.

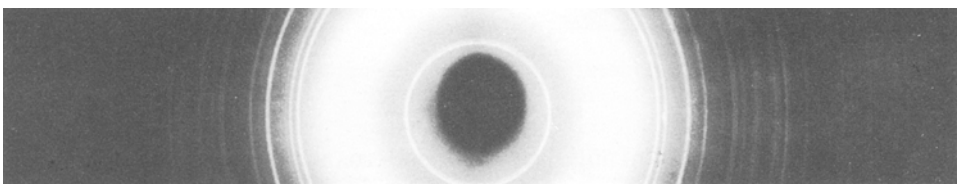

Figure 2 LL-1, powder camera XRD of crystal rosettes; apatite (JCPDS, 1974)

Other areas of this IUD and its strings looked like mud-cracked plaque and EDS analysis showed a similar spectrum but with a smaller weight percent of calcium and phosphorus. Gold/palladium X-ray lines from the SEM coating, however, overlap parts of the spectrum. XRD of these latter areas revealed weak diffraction lines indicating the plaque on the string and parts of the IUD was not well crystallized, compared with the crystalline rosettes.

Copper devices (IUDs #2 and #7, Table 1)

Tests of the Cu-7, which had been *in situ* 4 years (IUD #7), were similar to those of the Lippes Loop. Calcium was the predominant element, along with small

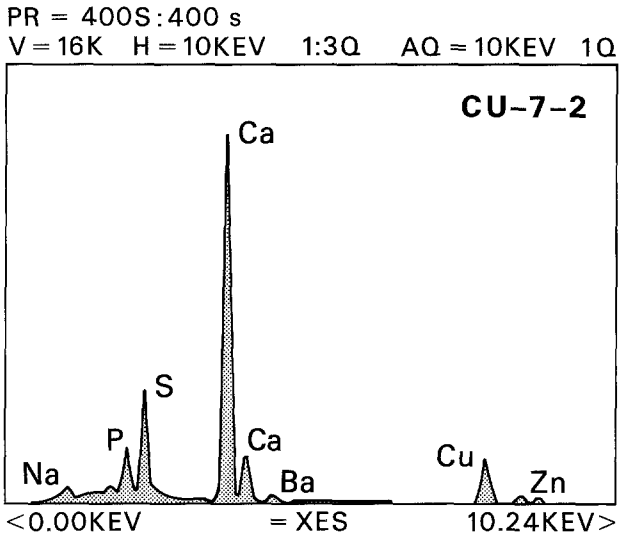

Figure 3 Cu-7-2, energy dispersive spectrophotometric analysis of 'crust' on copper coil and IUD surface

amounts of phosphorus, sulfur, and copper (Figure 3). The barium and perhaps part of the sulfur peaks appeared to emanate from the IUD *per se*. XRD analysis of the encrustation surrounding the copper wire confirmed the presence of calcite

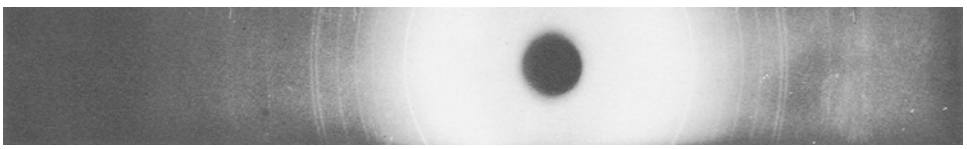

Figure 4 Cu-7-2, powder camera XRD of 'crust' on copper coil and IUD surface; calcite (JCPDS, 1974)

[(calcium carbonate; $CaCO_3$) (Figure 4)]. Based on the EDS examination (Figure 3) it is possible that small quantities of calcium sulfate ($CaSO_4$) and calcium phosphate ($Ca(PO_4)_3$ (F_1Cl_1OH) were also present, but their quantities precluded detection by the XRD technique.

Dalkon Shields (IUDs #4 and #5, Table 1)

The two devices studied represent relatively short-term use (4 and 15 months, respectively). As such, the quantity of surface deposits was less than that of other IUDs. Analysis of clean areas of the strings revealed only sulfur with trace amounts

of chlorine and potassium* (Figure 5), while analysis of encrusted areas, mainly around IUD/knot connection, showed an intense calcium line along with phosphorus (Figure 6). Once again, the sparse amount of material precluded XRD

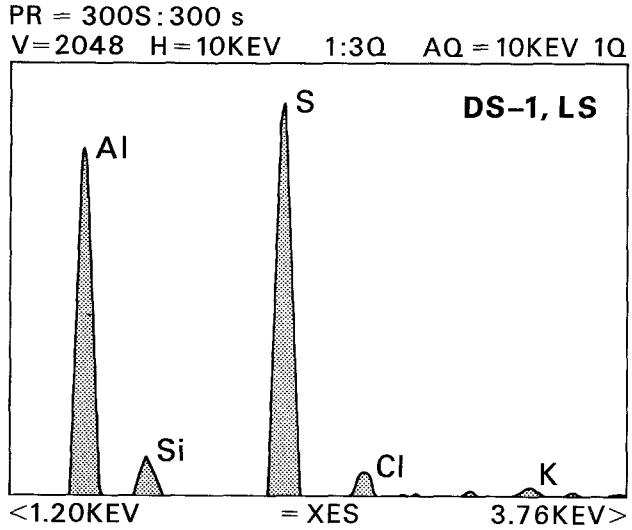

Figure 5 DS-1, lower string, energy dispersive spectrophotometric analysis of lower string on long axis

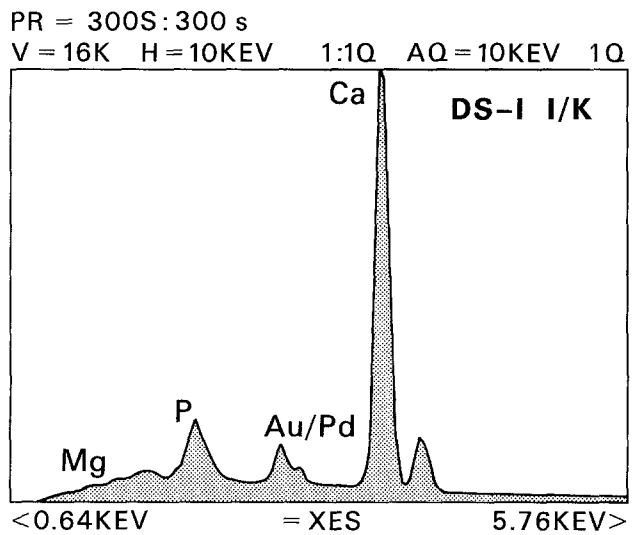

Figure 6 DS-1, IUD/knot, energy dispersive spectrophotometric analysis of 'crust' on IUD/knot connection area

* Aluminum and silicon are contaminating lines from the specimen stub and silicon artifacts.

analysis, but interpolation of other XRD analyses in this report would suggest the presence of calcite and apatite mineralization products.

Analysis of the distal-most portion of the lower aspect of the vaginal string of both devices showed calcium X-ray lines on both the IUDs studied, but more seemed apparent on the 15 month *in situ* IUD (Figures 7a and 7b). The calcium may precipitate in the form of sulfur, potassium, and possibly carbon salts. Similar analysis of the upper ends of the strings of these two IUDs revealed calcium again, but only in the IUD that had been *in situ* for 15 months.

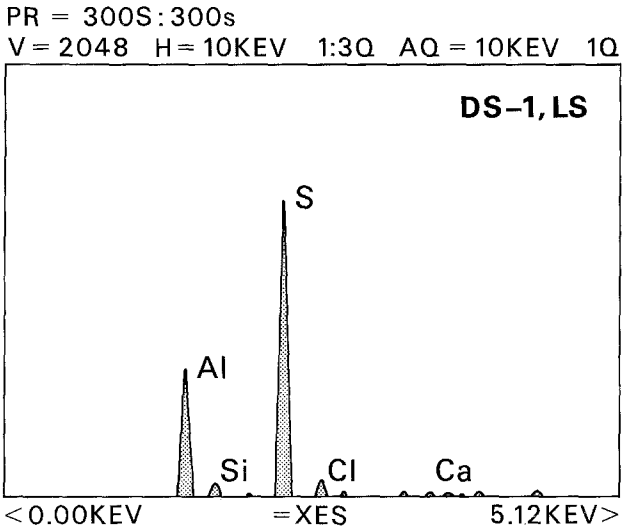

Figure 7a DS-1, lower string, energy dispersive spectrophotometric analysis of cross-section of lower string

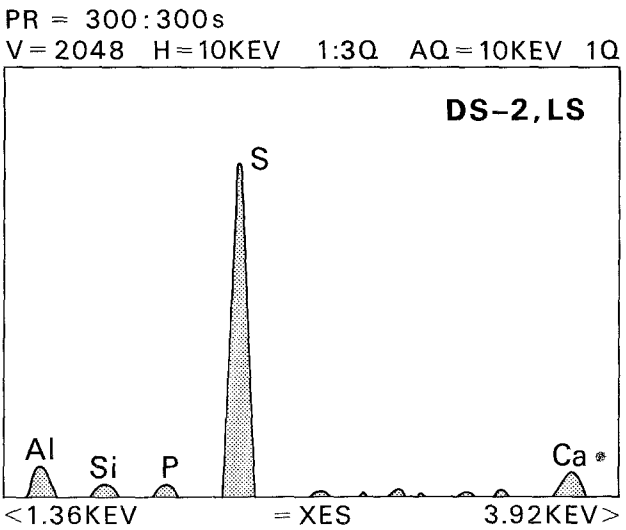

Figure 7b DS-2, lower string, energy dispersive spectrophotometric analysis of cross-section of lower string

Saf-T-Coil (IUD #6 Table 1)

The Saf-T-Coil was heavily encrusted with a blood-stained, whitish, irregular coating. EDS analysis of the plate-like encrustation on the string showed calcium

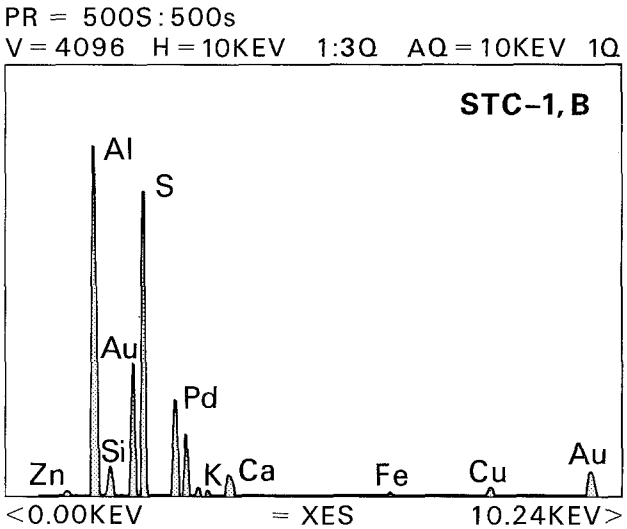

Figure 8 STC-1, string B, energy dispersive spectrophotometric analysis of cross-section of end of string

and phosphorus, with a highly intense sulfur line (Figure 8). The composition of the underlying string may have contributed to the intensity of the sulfur line. XRD and resulting lattice calculation were consistent with the mineral species calcite (calcium carbonate $CaCO_3$). Note in the powder camera exposure of this material,

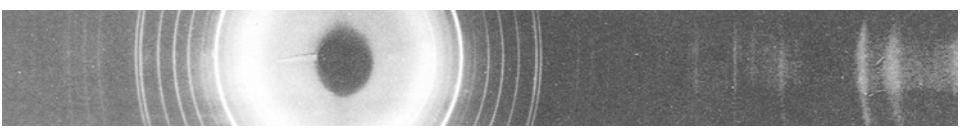

Figure 9 STC-1, IUD powder camera XRD of 'crust' on IUD surface; calcite (JCPDS, 1974)

taken off the IUD surface (Figure 9) the more highly crystallized state of the encrustation is apparent as sharp, well-exposed diffraction lines vis-à-vis that shown on the Cu-7 (Figure 3).

Controls

All control IUD analyses revealed similar findings. These included the presence of barium sulfate ($BaSO_4$) on the body of the IUD and sulfur on the string (Figures 10 and 11). Copper was detected on the copper-bearing IUDs.

Discussion

These preliminary experiments document the presence of calcium salt on all specimens examined. However, the specific mineral species found on different

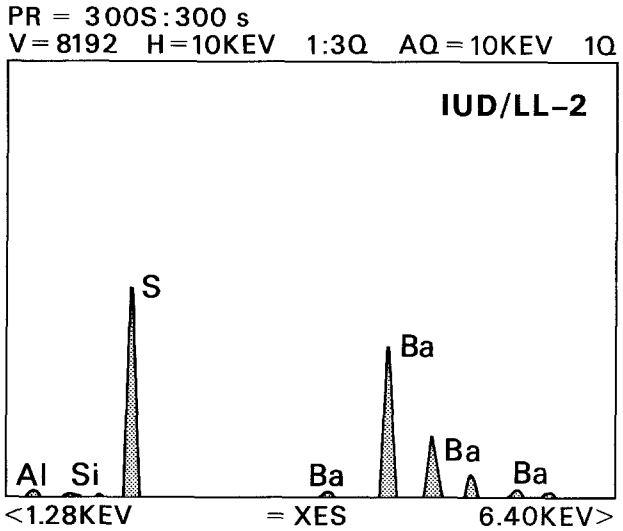

Figure 10 LL-2, IUD, energy dispersive spectrophotometric analysis of IUD body

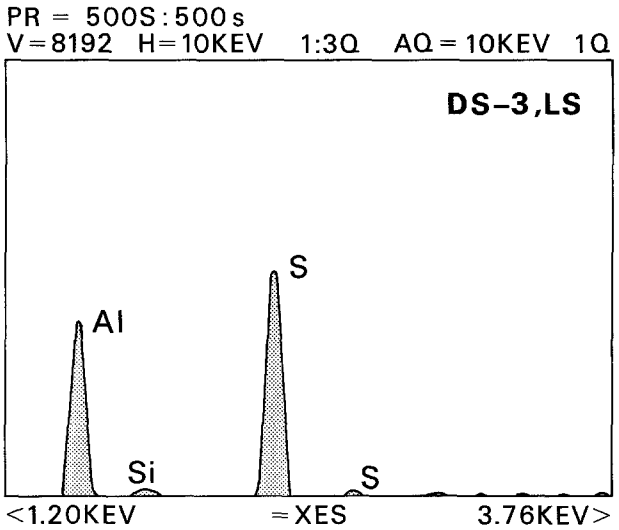

Figure 11 DS-3, lower string, energy dispersive spectrophotometric analysis of outer sheath of lower string long axis

portions of the same IUD or on any two IUDs varied considerably. The ratio of quantity of a specific salt to another salt varied almost continually. In other words, in some areas one salt predominated and in others salt types were mixed. These ratios varied from area to area on the same IUD as well as on different IUDs. This finding suggests that the microenvironment, or possibly a combination of the microenvironment and cyclic changes in the biochemical milieu surrounding the IUD, influence the deposition of specific mineral species.

The degree of crystallization observed on these IUDs ranged from the almost totally amorphous (Lippes Loop, mud-cracked plaque) to the perfect euhedral crystal form (the apatite mineral species on the Lippes Loop). Some specimens showed no microscopic crystalline development (STC-1, and Cu-7) but were shown to be cryptocrystalline upon XRD analysis, i.e. well-defined diffraction patterns.

Our experiments and a few others described in the literature [1–4] have been concerned with the nature of the elements that have precipitated onto IUD surfaces after their use. The exact cause of this precipitation and the factors influencing it are unclear. Also unclear is the composition substrate that coats the IUD or its strings prior to the deposition of elemental salts. Secretions of mucoproteins from the uterus, cervix, or vagina are a logical possibility, but the extent to which they act, and the presence or absence of specific cofactors, requires further study.

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Resumé

On décrit ici des observations préliminaires concernant les dépôts constatés à la surface de DIU de type Lippes Loop, Dalkon Shield et Saf-T-Coil; ces DIU ont été retirés et étudiés après une durée d'utilisation allant jusqu'à 15 ans. On a observé, sur un DIU resté en place pendant 15 ans, des rosettes de cristaux rhombo-édriques, disposés en colonnes prismatiques. Tous les dépôts de minéraux consistaient en des sels de calcium, mais le degré de cristallisation était très variable, réalisant des structures presque totalement amorphes ou au contraire des cristaux parfaitement euédriques. Il est possible que le micro-environnement influence à lui seul, ou avec les modifications cycliques du milieu biochimique entourant le DIU, le dépôt de minéraux spécifiques.

Resumen

Se describen las observaciones preliminares de depósitos en la superficie de los dispositivos intrauterinos Lippes Loop, Dalkon Shield y Saf-T-Coil, quitados despues de períodos de tiempo hasta de 15 años. En un DIU que estuvo *in situ* durante 15 años, se observaron rosetas de cristales rómbicos euhedrales con una relación prismática columnar. Todos los depósitos minerales fuerron sales de calcio, pero el grado de cristalización varió significativamente desde el casi completamente amorfo hasta el perfecto cristal euhedral. El microambiente solo o en combinación con los cambios cíclicos en el medio bioquímico que rodea al DIU, puede influir en la deposición de especies minerales específicas.