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To cite this version:
D. Hukins, A. Cox, J. Harries. EXAFS CHARACTERISATION OF POORLY CRYSTALLINE DEPOSITS FROM BIOLOGICAL SYSTEMS IN THE PRESENCE OF HIGHLY CRYSTALLINE MINERAL. Journal de Physique Colloques, 1986, 47 (C8), pp.C8-1181-C8-1184. <10.1051/jphyscol:19868231>. <jpa-00226138>

HAL Id: jpa-00226138
https://hal.archives-ouvertes.fr/jpa-00226138
Submitted on 1 Jan 1986
EXAFS CHARACTERISATION OF POORLY CRYSTALLINE DEPOSITS FROM BIOLOGICAL SYSTEMS IN THE PRESENCE OF HIGHLY CRYSTALLINE MINERAL

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Abstract EXAFS can be used to characterise the phase of an amorphous calcified deposit mixed with a crystalline phase which does not contain calcium. In such a mixture, the amorphous phase may not be detectable by X-ray diffraction. This application of EXAFS is illustrated by the characterisation of the calcium phosphate deposited in association with struvite in encrusted urinary catheters.

1. Introduction

X-ray diffraction (XRD) is conventionally used for characterising mineral and other crystalline deposits; furthermore, it can be used to identify the components of a mixture provided they are present in sufficiently high concentrations [1]. However, XRD is relatively insensitive to the presence of an amorphous solid mixed with a crystalline phase [2]. In contrast, EXAFS spectra are well suited, for example, to the characterisation of amorphous phases which contain calcium when they are mixed with crystalline phases which do not - if spectra are recorded above the calcium K edge.

This type of application will be illustrated by the EXAFS characterisation of calcium phosphate deposited in encrusted urinary catheters [3]. Minerals deposited in the urinary tract have conventionally been identified by XRD [4]. However, this technique detects only the mineral struvite (NH₄MgPO₄·6H₂O) in catheter deposits [5], despite their invariably containing appreciable concentrations of calcium phosphate [3,6].

2. Methods

Model compounds were synthesised by the methods described elsewhere [3] and characterised by IR spectroscopy, XRD and atomic absorption spectroscopy (to determine Ca/P ratios). All samples were ground to a fine powder with acetone in an agate mortar.

Specimens for XRD were mounted in thin-walled capillary tubes. Diffraction patterns were recorded with a Debye-Scherrer camera using nickel-filtered, copper Kα radiation.

Specimens for EXAFS mode were sandwiched between strips of sellotape. Spectra were recorded in the transmission mode on beamline 7.1 at the Synchrotron Radiation Source, SERC Daresbury Laboratory [7]. All spectra were background subtracted and are presented as \( k^2 \chi(k) \) plotted against k [7]. Ab initio phase shifts from hydroxyapatite were used for calculation of their Fourier transforms [8].
X-Ray diffraction patterns of deposits from urinary catheters whose Bragg reflections can be attributed to (a) struvite and (b) hydroxyapatite by comparison with results from standard compounds [4].
Fig. 2 EXAFS spectra recorded above the calcium K edge, with the moduli of their Fourier transforms, for (a) a typical catheter deposit, (b) brushite, (c) an amorphous calcium phosphate, and (d) a poorly crystalline hydroxyapatite. All spectra are presented as $k^3 \chi(k)$ plotted against $k$. 
3. Results and Discussion

Fig. 1(a) shows a typical XRD pattern from a catheter deposit; the position and relative intensities of its Bragg reflections can be identified with those from the mineral struvite. Note that, in this pattern, the 040 reflection is less intense than the 211 and 022 reflections. One of our samples of deposit yielded the XRD pattern shown in Fig. 1(b) which is characteristic of poorly crystalline hydroxyapatite. Some XRD patterns from deposits closely resembled Fig. 1(a) except that the 040 reflections appeared more intense than the 211 and 022 reflections. This observation could be explained by the presence of poorly crystalline hydroxyapatite in the deposit, since its 211 reflection (d = 0.281 nm) is so close to the 040 reflection of struvite (d = 0.280 nm) that the two will overlap to give enhanced intensity in this region of the diffraction pattern. However, many XRD patterns showed no evidence for the presence of hydroxyapatite in the deposits despite their having molar Ca/Mg ratios, as measured by atomic absorption spectroscopy, of ~3.

The presence of calcium in the deposits was confirmed by the appearance of the absorption edge close to the expected position for calcium (K edge at 4.038 KeV). Fig. 2(a) shows a typical EXAFS spectrum recorded from a deposit above this edge. The spectrum is distinctly different from that of brushite (CaHPO$_4$$\cdot$2H$_2$O), Fig. 2(b), which has been proposed as the form of calcium phosphate present in encrusted catheters [6]. However, its appearance is intermediate between those of Figs. 2(c) and (d). Fig. 2(c) was recorded from an amorphous calcium phosphate which gradually converts into the poorly crystalline hydroxyapatite whose spectrum appears in Fig. 2(d). Thus the calcium phosphate in the catheter deposit appears to be an amorphous/very poorly crystalline phase related to hydroxyapatite. Conversion of amorphous calcium phosphate to hydroxyapatite is known to be inhibited by magnesium [9]. The high concentration of magnesium, as evidenced by the deposition of struvite, may inhibit this conversion in the catheter deposits.

This example illustrates the usefulness of EXAFS for characterising the phase of amorphous solid mixed with a crystalline solid when the conventional XRD technique for characterising the phases of the components of a mixture is unsuccessful.

Acknowledgements

We thank Drs A.P. Kennedy and T.M. Sutton for collaboration in work on the urinary catheters and the director and staff of Daresbury Laboratory (especially Dr S.S. Hasnain) for help with the EXAFS experiments. Further help was provided by Miss K.E. Davies, Dr D.S. Hickey, Dr C. Holt, Mr J.C. Irlam and Miss T. Westley. Financial support was provided by SERC and Bard Ltd.

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