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|                          | <b>Experiment title:</b><br>An EXAFS study of bone meal treated Ni and Cd contaminated soil | <b>Experiment number:</b><br>ME-155 |
| <b>Beamline:</b><br>ID26 | <b>Date of experiment:</b><br>from: 30/5/01 to: 7/6/01                                      | <b>Date of report:</b><br>27/8/01   |
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**Names and affiliations of applicants** (\* indicates experimentalists):

**Dr. J.F.W. Mosselmans, CLRC Daresbury Laboratory \***

**Dr. E. Valsami-Jones, Natural History Museum \***

**Dr. P.F. Schofield, Natural History Museum \***

**Dr. L.M. Murphy, CLRC Daresbury Laboratory \***

**Dr M.E. Hodson, University of Reading**

## **Report:**

### **Introduction**

In order to advance the development of a cost-effective remediation treatment for metal contaminated soil we have been developing methods in which potentially toxic metals are fixed *in situ* by treatment with bone meal. The formation of metal phosphates in metal contaminated soil is increasingly recognised as a potentially cost-effective remediation technology. Phosphates are highly insoluble, thus it has been suggested that the conversion of metals in contaminated soil into metal phosphates renders the metal non bio- available. Bone meal is a cheap and widely available source of phosphate. Results from our laboratory chemical extraction experiments on metal contaminated soils indicate that bone meal additions reduce both the release and availability of the metals. Previous experiments using electron microprobe analysis and diffraction have indicated an association between the phosphorus and the metal, but failed to prove phosphate formation. In this experiment we examined a series of bone meal treated soils using X-ray absorption spectroscopy to look for metal phosphate phases after the treatment.

### **The experiment**

We were looking at soil from four different sites in the UK, three former mining areas {Parys mountain, PM, (2ppm Ni, 2317ppm Cu, 16ppm Cd) Leadhills, LH, (50ppm Ni, 83ppm Cu), Wanlockhead, WH, (25ppm Ni, 1668ppm Cu, 56ppm Cd )} and an industrial site (Lampton, LA, 36ppm Ni, 86ppm Cu). Unfortunately the soils also contained a range of other elements in particular Fe at between 5000-10000 ppm level. We recorded data at the Ni, Cu and Cd K-edges on bone meal-treated and untreated samples. As we were made aware before the experiment that the Fe concentration might render the experiment impossible, some more concentrated Cd samples from a sewage sludge treatment site, a mine spoil site and a synthetic sample: (Cd sorbed on Humic acid) were also examined. These were studied to determine the Cd speciation so remediation strategies could be developed. The strength of the Fe fluorescence signal meant that a photo-

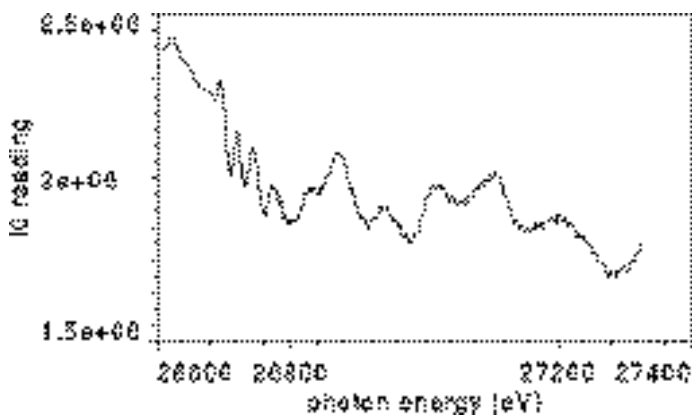
diode had to be used instead of the Silicon DRIFTS detector that would normally be used for dilute 3d elements samples on ID26.

## Results

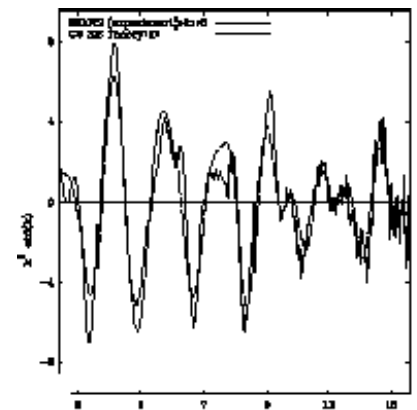
The use of a non-energy resolving detector with a very, very weak signal made the experiment very vulnerable to movement of the beam and changes in the background signal. Thus although we could obtain Ni XANES spectra and these showed some sign of changes between the treated and untreated samples in the LA case, the noise level was such that features in the individual spectra were at a similar level to random noise features which varied scan to scan. Hence the data must be treated with great care.

The Cu data was a little better and Cu EXAFS spectra were obtained for the samples with high Cu content (WH and PM). The LA Cu XANES showed a much larger white line for the treated sample suggesting some phase change on bone meal addition. The other Cu spectra were very similar for the treated and untreated samples. This implies that for the Cu in these soils phosphate formation does not occur on bone meal addition. The Cu EXAFS spectra showed mainly sulfur coordination, suggesting a stable sulfidic phase such as chalcopyrite or covellite is the principal Cu-bearing phase in these soils, explaining why no transformation occurs.

We could not obtain a very useful  $k$  range of Cd data for the soil samples (PM and WH), as the I0 signal was very unstable over the scan range, perhaps because of the undulator tuning. An I0 background is shown below on the left. This was not repeatable (i.e. it varied scan to scan), but a consistent oscillation with an amplitude of ca. 10-15 % was seen. For the dilute samples using a photodiode, this background did not normalise well, giving a spurious 'phantom EXAFS' signal that was as big as the real signal. However the XANES of the treated samples was similar to that of the untreated samples. The EXAFS suggested that in the WH sample the Cd was in a sphalerite phase.



The humic acid sample was also quite dilute and only a one shell fit could be achieved with 6 O atoms at 2.23 Å. The sewage sludge sample also fitted to 6 nearest neighbour O atoms



at 2.22 Å. Here however a second shell containing ca. 6 C atoms could be seen. This is thus either indicative of organic material ligating the Cd or possibly a Carbonate phase. The best data was obtained on the mine spoil sample. The EXAFS is shown above on the right. This has been fitted as a mixture of two phases; about 20 % of the Cd is in a sphalerite phase with 4 S neighbours at 2.51 Å and the 12 Zn atoms at 3.74 Å, while the remaining 80% is in a phase similar to that found in the sewage sludge with 6 O atoms at 2.22 Å and then ca. 6 C at 3.03 Å. Hence there is some correlation between the data showing two principal Cd bearing phases in all the samples: Cd in sphalerite, which does not seem reactive to bone meal, and Cd in a carbonate or organic phase which may do. We are planning further experiments definitively determine the C-containing phase by using a range of model compounds.

## Conclusions

The high concentration Cd samples gave reasonable data, but because of the background problems low concentrations samples yielded a very short data range. The 3d element work was even more problematic. The flux of the station is such that to studies of this kind should be possible. A hemi-sphere of diffracting multilayers between the sample and the detector, such that only the desired fluorescence X-rays reach the

detector, would make experiments on natural multi-element bearing samples feasible on ID 26. Such materials are very important to Molecular Environmental Science.