Orientation Partial Digest Geochemistry Over Navan Zn-Pb Mine , Ireland.

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Summary

A nine-step sequential leach was used to identify which, if any, partial digestion would indicate the presence of deeply buried mineralisation at Navan. Partial digest techniques appear to detect mineralisation which is not apparent using conventional (total digest) techniques.

Geological Setting

The stratabound Navan deposit (90+ million tonnes) lies within Lower Carboniferous (Mississippian) limestones in Central Ireland approximately 50 km north-west of Dublin.

The orebody is hosted by bioclastic/oolitic grainstones, sandy calcarenites and micrites of the Navan Group. The deposit is overlain by shaley bioclasitc calcarenites, calcsiltites, shales and sandstones. The ore is composed of fine-grained sphalerite, galena, minor pyrite/ marcasite and barite lenses (Ashton J. et al 2003).
Soils are residual fluvisols and podsols within a flat or slightly undulating terrain. No changes in regolith along the traverse are apparent. Samples were collected over land reserved for pasture which produces feed for domestic animals. The site is considered uncontaminated by mining activity.

Sample Locations

Twelve samples (A to L) of <1-mm soils were screened along a single line traverse which passes directly over buried mineralisation (Figure 1). The Tara orebody is located 400 m to 450 m below this traverse.

Analyses

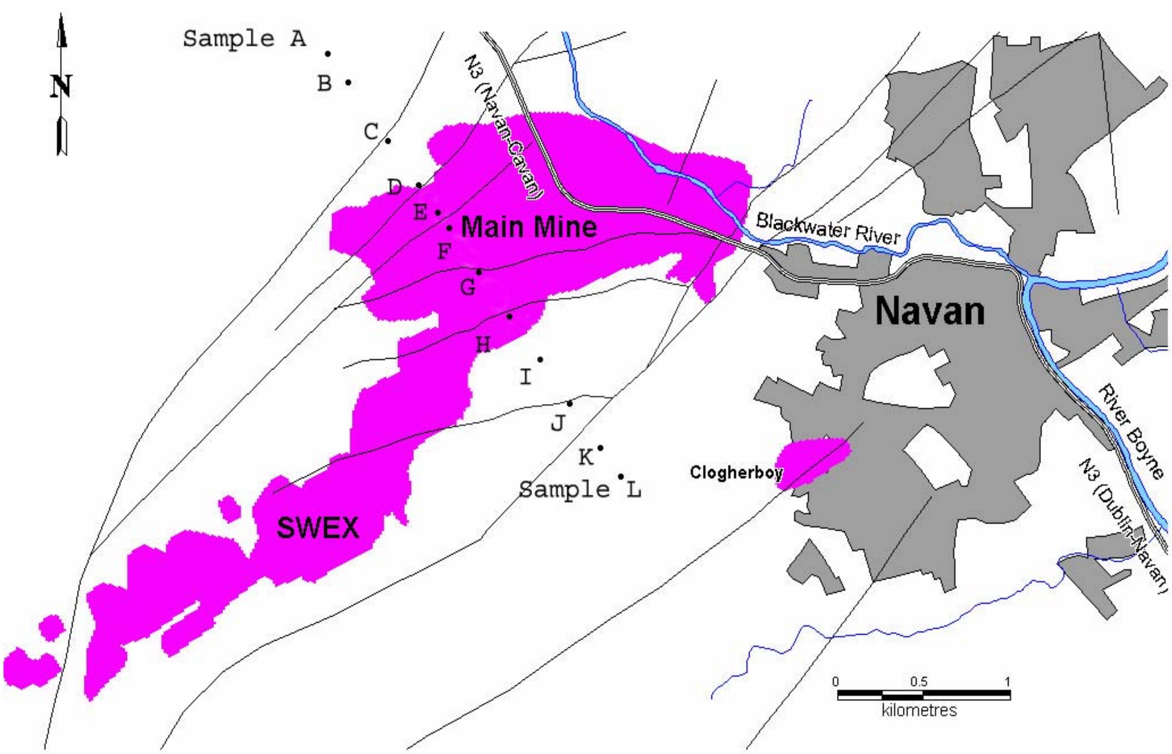
All analyses were carried out at Genalysis Laboratory in Perth, Australia. Reagents were all AR grade or better. Blank values for reagents and de-ionised water used were all below detection limit. Analyses for zinc, cadmium and lead were carried out on a Varian Spectra 55 Atomic Absorption Spectrometer. Sulphur was read on a Perkin Elmer Optima 3300 ICP-OES.

All samples were heated to 121 ^{0}C for four hours to satisfy Australian quarantine requirements.

Sequential Digest Scheme.

The sequential digest procedure was selected to identify the most effective partial digest technique.
The technique removes metal ions from specific sites within the soil matrix using the same samples starting with the softest digest, i.e. water and ending with a total digest, i.e. four acid. If no anomalous response is detected then one can infer that no ions are present or that the ions present are below the detection limit of the analytical system.

Figure 1. Plan projection of Tara ore-body and location of samples.



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The sequential digest scheme used here is similar to those by Tessier et al. (1979) and Hall et al. (1996). It differs from others by the addition of extra steps at the 'soft' end of the procedure.

1. *H_2O. 4 hrs.* Water soluble component.
2. *0.01M $Ca(NO_3)_2$. 4 hrs.* Weak cation exchangeable.
3. *1M $MgCl_2$. 4 hrs*. Strong cation exchangeable.
4. *0.03M HNO_3. 4 hrs*. Protonateable adsorption sites. If carbonates are present the final solution pH should be adjusted to pH 1.75.
5. *0.0027M (0.1%) EDTA. 4 hrs*. Non-specific strongly adsorbed. Acetic acid added to give a final pH value to 4.
6. *0.1M $Na_4P_2O_7$. 4 hrs*. Organics and some oxy-anions. The solution pH should not fall below 9.5. The solution should be centrifuged in closed vessels for 1 hour to remove suspended Fe and Mn oxides.
7. *0.25M $NH_2OH.HCl$ in 0.25M HCl. 4 hrs. 60 deg C.* Amorphous Fe and Mn oxides. If oxide soil matrix species are intergrown then dissolution may not be complete.
8. *1M $NH_2OH.HCl$ in 25% acetic acid. 4 hrs. 90 deg C.* Crystalline Fe and Mn oxides.
9. *HF-$HClO_4$-HNO_3-HCl.* – A four - acid 'total' digest. Silicates and some refractory minerals.

Points to note:-

- The scheme needs to be flexible to accommodate specific metals. For example, the cation used in the exchangeable phase should have a similar hydrated ionic radius to the targeted metal to enhance exchangeable efficiency. Cations can be the same for both the weak and strongly exchangeable extractions.
- The optimum pH for the extraction of different elements using weak acid alone (protonateable sites) may vary with the element.
- A 0.1M $NH_2OH.HCl$ in 0.015M HNO_3 digest can be included between stages 6 and 7 if predominantly exposed amorphous Mn oxides are targeted.
- If residues are observed after the four acid digest then fusion of these is recommended.

Twelve samples (A to L inclusive) were selected to represent a simplified traverse across a central buried mineralized zone. The solutions were read for Zn only and results are shown in Figure 2. On all profiles samples start with "A" on the left and finish with "L" on the right hand side of the profile. Results shown are for individual extractions and are not aggregated with previous softer digests.

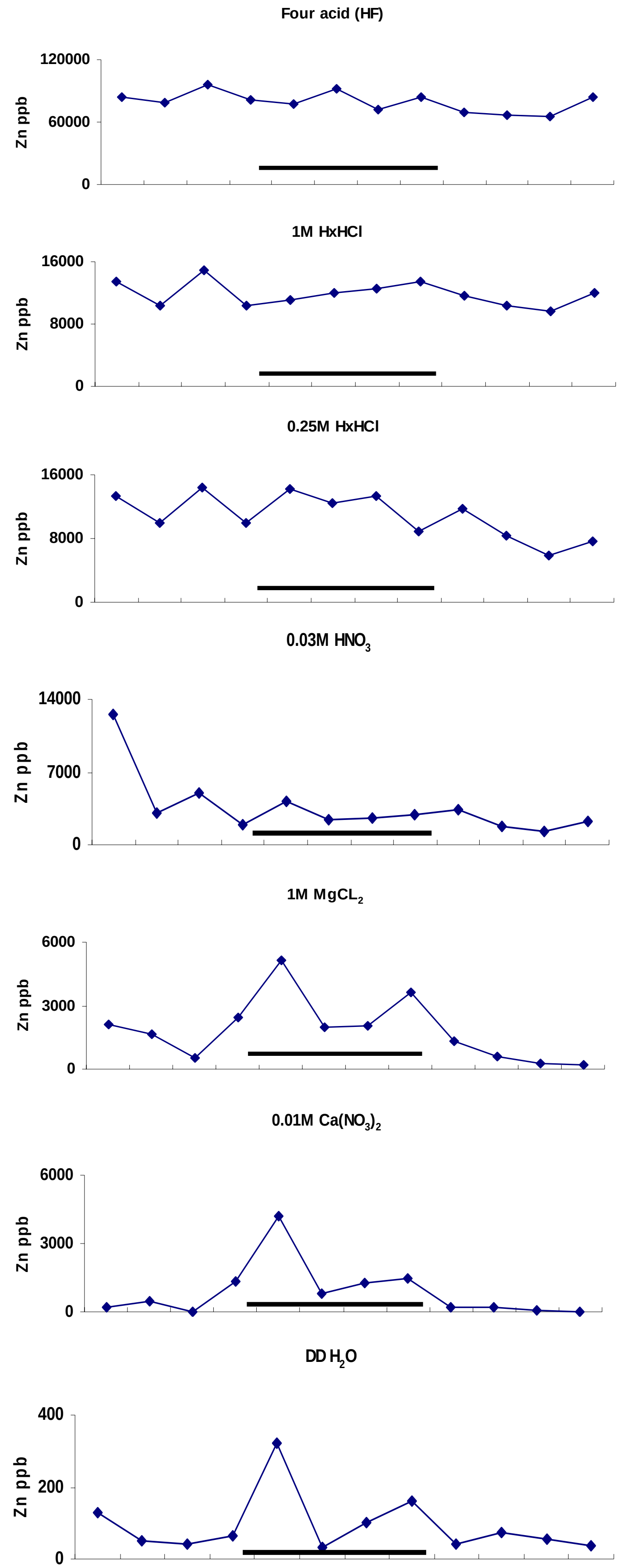

Figure. 2. Sequential digest results. Solid bar denotes surface projection of buried orebody.

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Variable Reagent Concentration Tests

To determine the effect of reagent concentration on the anomaly profile, the 12 orientation samples were digested under different concentrations of the same reagent. Three reagents utilized: the cation exchange salt ($Ca(NO_3)_2$), a general non specific complexing agent (EDTA), and a protonating reagent (HNO3). The 12 samples were grouped into those over mineralization i.e. the anomalous group, and those over background. The average zinc assay of the anomalous group was divided by the average response of the background group to establish an overall anomaly contrast ratio. The anomalous samples were E, F, G and H. The remaining eight were considered background samples. Anomaly contrast results are shown in Figure 3.

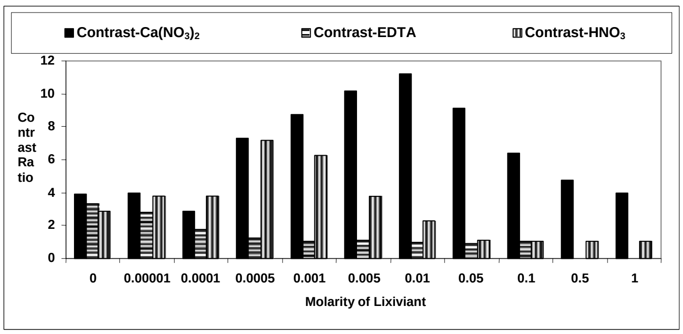

Figure 3. Anomaly to background ratios for 12 key samples.

Samples were initially dissolved in water (lixiviant molarity =0) and increasing strength of reagent added after an aliquot was extracted. The variance at molarity = zero reflects result reproducibilty of the water digest. Because of the limited solubility of EDTA no concentrations above 0.1 M were achieved for that reagent. The calcium nitrate extraction of around 0.01M appears to produce the greatest contrast.

Soil pH Over the Orebody

Lower pH directly above the orebody at surface suggests that it may be contributing hydrogen ions as well as base metal ions (Figure 4). This is consistent with observations by Smee (2003) and Govett (1984). Soil pH measurements may therefore produce an additional data set with which to rate future anomalies provided soils are not extremely acidic or extremely alkaline.

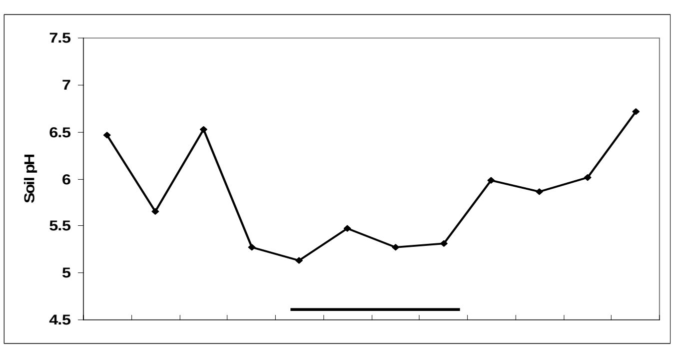

Figure 4. Soil pH (1:5). Solid bar denotes surface projection of buried orebody

Seasonal Variations

Samples were collected from the same location on a monthly basis. The "barren" sample was close to site C and the "ore" sample was close to site G in Figure 1. However, neither sample was considered close enough to reliably reproduce the results actually from sites C and G.

Variations during the season are evident in Figure 5. The ore and background samples are changing in a systematic fashion during the year. The contrast ratio is

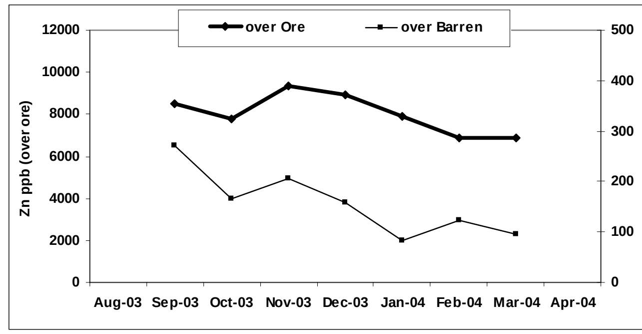

Figure 5. Monthly variation in Zn ppb on re-sampled sites over ore and background. 0.01M $Ca(NO_3)_2$ digest.

also changing (Figure 6). This has implications for sampling at any time of the year. It may require an additional data set that is created by normalising all assay results to an individual survey background.

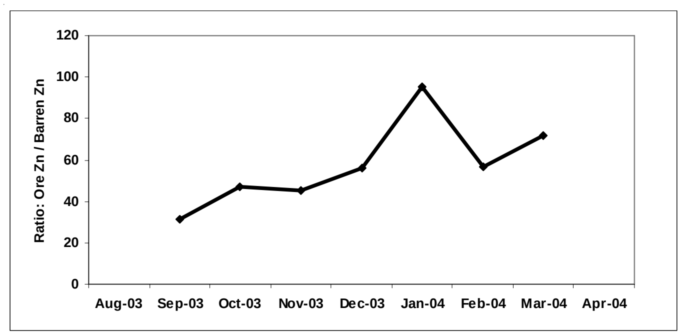

Figure 6. Monthly variation on re-sampled sites. Anomaly to Background Contrast Ratio

We speculate that solar radiation, air temperature and to a lesser extent vapour pressure and wind speed enhance evaporation of soil moisture and the subsequent accumulation of metal ions within the upper portion of the soil profile.

Only subtle seasonal variations are evident with soil pH (Figure 7) although the trend hints of a hydrogen ion increase in sympathy with zinc.

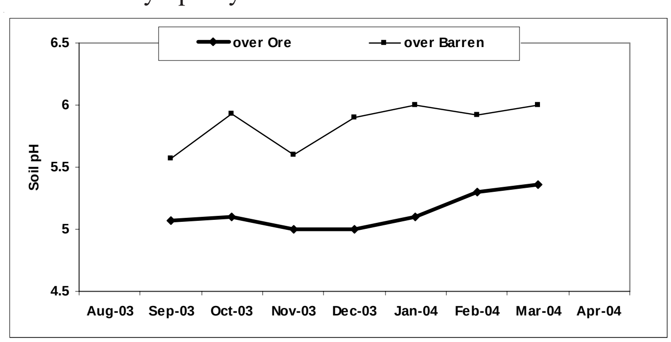

Fig. 7. Monthly variation in soil pH on re-sampling of sites over ore and background.

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Lead, Cadmium, Sulphur and Iron Analyses

The dissolution and oxidation of galena, sphalerite and pyrite/marcasite could lead to accumulations of lead, cadmium, iron and sulphur within the soil over the Tara orebody in a manner similar to zinc.

Analyses of the calcium nitrate digest are shown in Figure 8.

Iron, cadmium and possibly lead are slightly anomalous. A very low level broad feature is also apparent for sulphur. We speculate that if sulphur is present as a sulphate species then it may have dispersed laterally to form this feature.

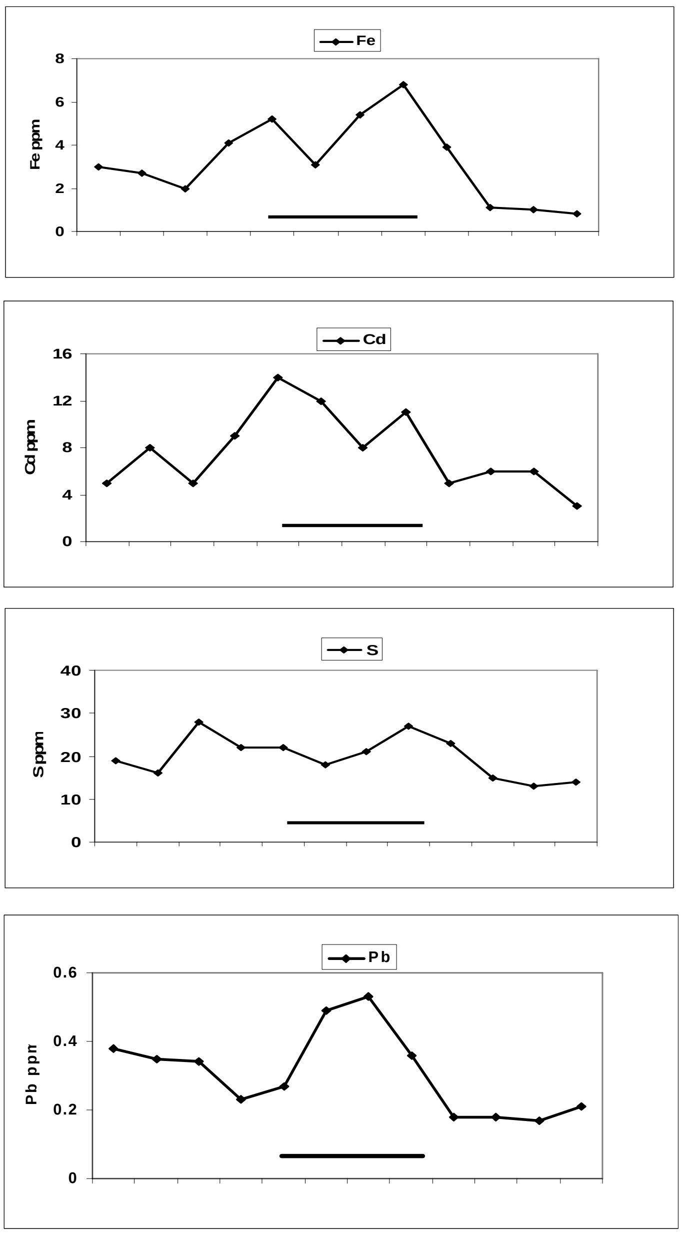

Fig 8. 0.01M $Ca(NO_3)_2$ digest. Fe, Cd, S and Pb. Solid bar represents the buried orebody projection of the orebody.

Analysis of Rye Grass

Dr Kevin Tiller, CSIRO, Division of Soils, South Australia (pers.com. 1995) recommended the use of calcium nitrate to remove soluble and weakly adsorbed metal ions. Calcium nitrate and potassium nitrate solutions have been used in agricultural science to determine the levels of metal ions available in soils as plant nutrients.

The elevated concentration of ions detected by the calcium nitrate digest should therefore be available to the rye grass growing over the Tara orebody.

Very crude grab sampling of rye grass was conducted along an extended line in close proximity to the initial orientation line. The rye grass was quarantine heat treated on arrival in Australia to a temperature of 121 ^{0}C for four hours.

The samples were then digested in concentrated AR grade nitric and perchloric acid to a maximum hot plate temperature of 150 ^{0}C. This oxidative digest destroys plant tissue leaving virtually no residue. Zinc was subsequently measured on an AAS.

Although there is significant sample to sample variance there is an increase in the zinc concentration of grass over the buried ore-body (Figure 9).

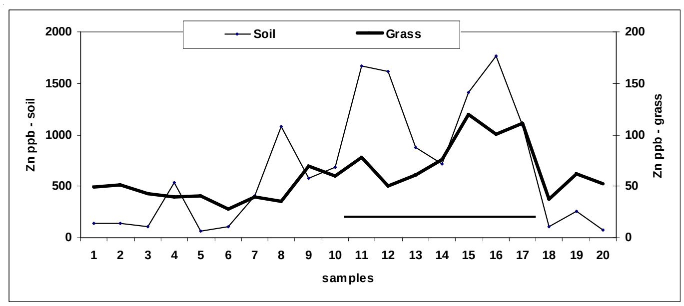

Figure 9. Analysis of soil and rye grass over buried mineralisation. Solid bar denotes surface projection of buried orebody. 0.01M $Ca(NO_3)_2$ digest on soil.

Conclusion. **WORK COMPETED TO DATE**

Partial digests have been successful in identifying buried mineralisation at Tara Mine not apparent in total digest geochemistry (Figure. 10).

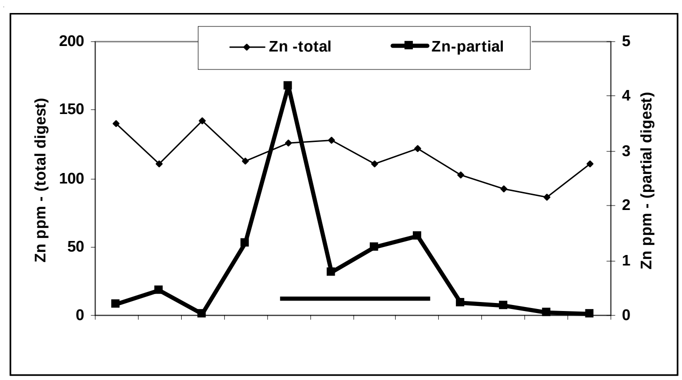

Figure 10. Total and partial digest Zn ppm.

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A weak calcium nitrate digest (0.01M $Ca(NO_3)_2$) appears to generate the best anomaly to background contrast for this specific site.

Zinc is strongly anomalous. Soil pH is also anomalous. Cadmium, iron and lead show low level anomalism. Additional work is required to confirm that sulphur is also anomalous.

Seasonal variations may necessitate the re-sampling of a single line that contains anomalous samples. This may be useful in normalising data between survey campaigns carried out over changing seasons.

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