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Appendix 1. Sampling and methods of analysis

1.1 Radiometric survey details

1.2 Sampling

1.3 Sample processing

1.4 Analytical methods

1.5 Quality control and safety

Field surveying and sampling of the Mary Kathleen mine site was conducted in July 1998, August and October 1999 (dry season). Gamma-ray data as well as, stream sediment, soil, wall rock, waste rock, mineral efflorescence, iron rich precipitates, tailings, vegetation and water samples were collected (Appendix 2).

1.1 Radiometric survey details

A portable GR-320 Spectrometer with a 512 channel spectrometer and a sodium-iodide detector and a Scintrex- BGS-1SL scintillometer were used for geophysical surveys. Specifications of the GR-320 Spectrometer include 256/512 channel operation, automatic spectrum stabilisation, exposure rate mode for environmental data (μR/hr, nSv/hr) and assay mode for geophysical data (concentrations in %K and ppm of U and Th). Four channels total gamma rays of all energies from K^{40} (potassium), Bi^{214} (uranium series), Tl^{208} (thorium series), total count cps, concentrations in %K and ppm of U and Th are logged. Both environmental and assay data were recorded (Appendix 3). Surface gamma ray point readings were taken for 60 seconds. Gamma ray traverses were conducted at a speed of approximately 0.16 m/s and a height of 1m over dry ground. GPS positions were recorded using a Garmin 12XL Personal Navigator. Limitations of the portable GR-320 spectrometer occur with high uranium concentrations (U >150ppm), at that stage geophysical assay data become unreliable.

It is important to note when comparing terrestrial gamma radiation (U, Th) the radiation does not emit from the parent nuclei but from the decay products mentioned above – and calculations of U and Th abundances derived from gamma ray measurements involved the assumption of secular equilibrium. Hence, the term 'equivalent', actual geochemical concentrations (ppm) of U and Th in Mary Kathleen samples are much larger. The larger difference between 'equivalent uranium' values and geochemical uranium concentrations is due to the escape of radon gas.

1.2 Sampling.

Location	**Prefix**	**No. of samples**	**Description**
Open pit wall	MKPW	7	rock chip (R.C.)
Waste rock piles	MKWD	24	rock chip
Pit, tailings dam	MKE	50	efflorescences & Iron rich pptte
Mine site & surrounds	MKS	45	top soil
Cameron Ck & waste pile	MKSS	55	stream sediment/drainage sediment
Mine site & surrounds	MKO	22	stream sediment
Tailings dam	MKT	3	tailings sediment
Mine site & surrounds	MKV	25	vegetation
Corella Dam, open pit, Cameron Ck	MKW	21	water

Sampling across the site was restricted to locations that provided reasonably safe access and where Department of Mines personnel (Mt Isa branch) and the manager of the cattle station permitted. The main sample types collected include dry soil, stream sediment, waste rock, pit wall, vegetation, mineral efflorescences, wet tailings sludge, and water.

The main equipment used for dry and wet sediment sampling included 1.05m long spade and a trowel. Such equipment was deemed appropriate for sampling tailings, soils, stream sediments, efflorescences and rock at this site. The nature of the sample material, for example mostly dry surficial sediment and approximately 10 wet seepage sludge also influenced the choice of sampling equipment. The major determining factor concerning the location of sample sites was the promixity to key landforms (discussed in Chapter One) of the Mary Kathleen mine site.

Where conditions permitted (e.g. degree of compaction of soil, bedrock), the spade was used to remove soil and sludge. In areas where the bedrock was close to the surface, small amounts of sample were accessible (mineral efflorescences) or under 2kg of sample was required the hand trowel was used. As a direct result of the lengths of these pieces of equipment, soil sampling was restricted to approximately the top one metre of the soil profile.

Approximately 100 to 2000 grams of dry sample (where permitted) were collected at each location. Each sample was individually contained in cloth (> 1 kg) or paper bags (100 - 1000 g) and labelled accordingly. Plastic bags were not utilised as the seal may have inhibited air drying processes. Each sample bag was labelled with MK (Mary Kathleen), characters to indicate sample type (WD= waste dump), and a one or two three-digit number (eg. MKWD34).

Water was sampled by filling two standard water sample bottles at each of the eight sample sites. The water bottle (250ml) for metal analysis was filtered in the field using 0.45 micron filters attached to plastic syringes. Water bottles (1 L) for major cations and anions were not filtered.

Other information recorded in a field note book included the site description, sample description, sample number, date sampled, GPS location and if relevant, the relative location to other significant sites and any other pertinent information.

All samples once collected were taken from the field and stored in the sample bags at James Cook University (Cairns) geology rock shed. All samples were kept at ambient temperature at all times. Soil, tailings, stream sediment, vegetation and mineral efflorescence samples can be considered air dried. Samples were not frozen or chilled in an attempt to prevent water loss from the mineral phases present in the samples.

1.3 Sample Processing

Sieving for soil and stream sediment samples was performed by hand, wearing disposable gloves, a face mask and sitting outiside for safety reasons. Homogenised samples were sieved in a non-reactive nest of sieves: approximatley half of the field sample was tipped directly from the field sample bag onto the 2 mm sieve and dry sieved. Stream sediment samples sieved to 2mm were then also sieved to 63 μm. Soil samples were sieved to less than 2 mm and stream sediment samples sieved to two size fractions, 2 mm to 63 μm and less than 63 μm.

Air dried and sieved sampled were then transferred into cleaned and dried screw-top plastic phials. Both the phial and the lid were labelled with the relevant sample details as well as indicating A or B for 2mm – 63um and < 63 um fraction samples respectively. Samples were then stored in these phials until they were ready to be crushed using the Rocklabs ring mill.

Washed and ashed vegetation samples were dissolved using a HNO_3-H_2O_2 microwave digestion (following US EPA method 3050) and the solutions were submitted for geochemical analysis (minimum detection limits included in Appendix 4).

Pitwall, waste rock, tailings, sieved soil and stream sediment samples were pulverised in a chrome-steel ring mill for 2 minutes. Crushing of the air-dried samples was undertaken in order to ensure that all components in each sample were uniform in size and of homogenous nature. Further geochemical analysis is made easier by the sample being in powdered form due to the increased ease of dissolving the sample into solution. Each sample was crushed individually using a ring mill. A chromium-steel ring mill was used to crush each of the samples. Crushing of clean quartz sand was undertaken between soil samples in order to remove any remaining sample from the mill. The crushed samples were then stored in labeled plastic phials for further geochemical analysis.

Polished thin sections of pit wall samples were prepared at the University of New England by Dr Paul Ashley.

Thirty five soil samples were measured for conductivity and pH with pH and conductivity meters (Appendix 4). Samples were prepared by mixing 5 g sample with 25 ml distilled water, left to settle for 24 hours and then measured (White, 1997). Selected 5.00 grams (± 0.01 grams) of crushed (2mm-63µm and <63µm) sample was weighed out into clean plastic screw-top phials. Each phial was labeled with "pH" and "EC" and the sample number that corresponded to the selected sample. After weighing 5.00 grams of material, the weight of the sample was recorded on the phial. The lid was screwed tightly onto the sample+liquid mix and then shaken by hand for sixty seconds in order to form a suspension mixture. The phials were shaken for a further one minute and allowed to settle for twenty-four hours in a secure location (AAC). Following the twenty-four hour settling period the pH and the EC was measured for each sample. The pH of each sample was tested using a pH Checkmite 10 pH meter. The reading of the pH Checkmite 10 was to 2 decimal places. The pH reading of each sample was recorded along side the sample name (Appendix 4). EC was measured using a hand held EC meter and measurements were recorded in µS/cm (micro siemens/cm) and recorded next to the sample name (Appendix 4).

Mineral efflorescence samples were dry crushed with a mortar and pestle for XRD analysis, with vigorous cleaning and drying between samples. Crushed samples (usually < 50g) were stored in small plastic bags and labeled accordingly.

1.4 Analytical methods

Pulverised soil, stream sediment, tailings, waste rock, mineral efflorescence and pit wall samples were submitted to Australian Laboratory Services (ALS), Townsville. Sample powders were subject to a hot mixed acid digest and analysed by inductively coupled plasma optical emission and mass spectrometry (techniques IC587 and MS587) for Cu, Pb, Zn, As, Ba, Ca, Fe, K, Mg, Mn, Na, Ni, P, S, Sr, V, Ce, La, U, Th and Y. That is, the samples were first acidified using 0.3ml of 20% HNO_3. They were then settled over night. 10ml of the clear solution was taken and subjected to ICP-AES analysis using a Varian Liberty Serries II. The measuring parameters were: RP Power – 1.2kw, viewing height – 10mm, plasma flow – 15l/min, aux flow – 1.5l/min and sample uptake rate – 1ml/minute. Selected powders were also submitted for total organic carbon (TOC) assays using a LECO furnace. The result is corrected to the original sample weight and expressed as TOC or $NonCO_3$ C.

Vegetation sample identifications were made by N.J. Beresford-Smith and the Queensland Herbarium (Appendix 6). Vegetation samples were analysed for Cu, Pb, Zn, As, Ba, Ca, Fe, K, Mg, Mn, Na, Ni, P, S, Sr, V, Ce, La, U, Th and Y by inductively coupled plasma mass spectrometry at ALS Townsville.

Water samples were analysed by the Australian Centre for Tropical Freshwater Research for major ionic composition, trace metals (Ag, Al, As, Ba, Be, Ca, Cd, Cl, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, U, Zn) and physical parameters (pH, conductivity, total hardness, total alkalinity, total dissolved solids). Temperature, pH, salinity, dissolved oxygen and conductivity were measured in the field using a Horiba water quality checker/U-10. Piper diagrams were generated using GW_CHART software version 1.1.2.0.

Soil, stream sediment and rock chip geochemical results are tabulated in Appendix 4. Water results are tabulated in Appendix 5. Vegetation results are tabulated in Appendix 6.

The mineral constituents in selected mineral efflorescences, soils and tailings were identified by X-ray diffraction (Siemens D5005, 40Kv, 30 mA) at the Advanced Analytical Centre (JCU Cairns). Bulk soil XRD analysis was used to assess an overall picture of the mineral phases present within the samples. Bulk soil XRD samples, approximately 500 milligrams of powdered sample was placed into a plastic cavity mount holder and levelled using the edge of a clean thin section glass slide. The plastic cavity mount holders were then labelled with the sample identification number. Samples were analysed one at a time in a run of twenty samples including a known XRD standard. Each sample was analysed from 3° to 70° 2θ for a period of one hour and 50 minutes. Each sample analysed, produced a unique XRD trace that was then interpreted using the software program "EVA" (Biulen – AKS).

Scanning electron microscope (SEM) photography of samples was undertaken at the Advanced Analytical Centre (JCU Cairns). Twenty samples were selected for SEM analysis based on geochemistry and XRD results. Each sample was mounted onto stubs and carbon coated. These samples were then analysed at 15KV using a JEOL SEM to determine the crystal habit, textural associations and major elemental constituents in each sample. Several photomicrographs were taken. Basic investigations of these samples under the SEM, EDS spectra for each sample were collected. EDS was used to determine the elemental compositions of various grains/ areas within each sample.

1.5 Quality control and safety

On collection, all samples were labelled, logged, stored in separate paper or cloth bags and covered in plastic to prevent cross contamination. All samples were re-homogenised prior to sub-sampling for analysis. Soil, stream sediment, waste rock and pit wall samples were pulverised in a chrome-steel ring mill for 2 minutes each with quartz cleaning between each sample. Duplicate samples, Cape Flattery silica sand and the geochemical reference material GXR-2 (Appendix 4) were submitted to ALS Townsville for quality control. Deviations from GXR-2 for the listed elements are <5% for all components. All remaining, non-hazardous samples have been archived at JCU (Appendix 7). The GR-320 Spectrometer did not require re-calibration between field trips and background checks were made daily.

A thermoluminescent dosemeter for gamma/X-radiation (Harshaw TLD 0110 card and 8814 holder) was worn for safety at all times. The dosemeter was issued monthly and read by the Queensland Radiation Monitoring Service. Accumulated dose over 12 months was zero "MDL" (Minimum Detectable Limit).

Minimum detection limits for all elements and all samples are listed in Appendix 4.