

Cooperative Research Centre for Landscape Environments and Mineral Exploration



# MINERAL HOSTS FOR GOLD AND TRACE ELEMENTS IN THE REGOLITH, BODDINGTON AND MT PERCY GOLD DEPOSITS, WESTERN AUSTRALIA

Maïté Le Gleuher

# CRC LEME OPEN FILE REPORT 198

February 2008

(CRC LEME Restricted Report 196R 2003, 2nd Impression 2008)

CRCLEM







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#### ABSTRACT

Mineral-trace element associations have been investigated in the regolith developed on mineralised rocks, at the Boddington Cu-Au deposit and Mt Percy gold deposit, Western Australia. A detailed characterisation of the mineralogy and geochemistry has been achieved using *in situ* microanalyses on regolith materials. The use of Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) for the *in situ* quantification of trace elements in clays and other regolith minerals has been assessed, and a method to process the data was developed.

#### Boddington

#### Mineralogy

The weathering profiles consist of a saprock, saprolite, clay zone, bauxitic horizon, duricrust and a layer of loose pisoliths. The saprock is composed of abundant muscovite and quartz, epidote, chlorite, titanite and ilmenite. Chlorite-vermiculite and a biotite-chlorite interstratified mineral have been identified in the clay fraction. The Cu and Fe-sulphides are often partially dissolved or oxidised. The saprolite consists largely of microcrystalline kaolinite and quartz, with minor goethite, high charge corrensite, biotite-vermiculite interstatified mineral and vermiculite. Iron sulphides are replaced by goethite and hematite. In the overlying clay zone, kaolinite is replaced by microcrystalline gibbsitic and goethitic plasmas. The duricrust typically comprises a fragmental duricrust overlain by a pisolitic duricrust, characterised by the *in situ* induration of plasmic domains. Angular concretions, nodules and pisoliths contain abundant hematite, goethite and gibbsite, and are set in a soft gibbsitic matrix. Anatase-rich domains resulting from the weathering of ilmenite and titanite are scattered in the duricrust and the loose pisolitic material. Maghemite is occasionally present in the fragmental duricrust, and becomes more abundant in the loose pisolith along with boehmite and corundum.

#### Trace element-mineral associations

New data about natural concentrations of trace elements in regolith minerals are reported. In the saprolite, trace elements are concentrated in minerals of marginal abundance such as corrensite, vermiculite and Fe oxides. The trace elements directly related to the Cu-Au mineralisation (Cu, Au, As, Pb, Bi, Mo and W) released by the dissolution of the sulphides are incorporated in goethite and hematite, with a preference for the former. Corrensite and vermiculite contain large amounts of Cu. Tungsten, Bi and Mo are also hosted by anatase. Trace elements related to the nature of the host rock are either residual in primary minerals or in their alteration products. Manganese, originally contained in chlorite, is retained in vermiculite.

In the duricrust, Co, Zn, As and Mo are concentrated in goethite in the cutans and matrix of the nodules. Tungsten occurs as residual scheelite, in the matrix goethite and in anatase. Gold is present as microparticles scattered in the Al-Fe microplasmas. Copper, Zn, Ni, Co and Mn are also concentrated in goethite in the loose pisolith cortex.

Kaolinite and gibbsite do not scavenge any significant amounts of trace elements.

#### **Mt Percy**

#### Mineralogy

The regolith is over 60 m thick, and comprises a saprolite, a clay upper saprolite, a mottled and plasmic clay zone, a lateritic duricrust and gravel layer, and a top loamy soil containing

pedogenic carbonates. The saprolite is composed of fuchsite, quartz, sulphide relicts replaced by Fe oxides, minor rutile and Cr-spinels. The clay saprolite is characterised by the replacement of fuchsite by kaolinite and the development of kaolinitic and goethitic rich microcrystalline plasmas. In the vicinity of the sulphide relicts, the plasmas and quartz grains are dissolved and replaced by alunite. The overlying mottled and plasmic clay zone is strongly ferruginised in places, and cutans consisting of kaolinite, gibbsite and goethite fill cracks and voids.

#### Trace element-mineral associations

The trace elements used as pathfinders have multiple hosts. Antimony and W are hosted in rutile and in Fe oxides replacing the sulphides. Arsenic is strongly concentrated in goethite. Copper and Zn are contained in goethite in the saprolite and mottled and plasmic clay zone. Alunite hosts copper in the clay saprolite, and Zn is present in Cr-Zn spinels. The trace elements related to the parent-rock such as Ni, Co and Mn are concentrated in goethite replacing the sulphides, in vermiculite and fuchsite in the lower saprolite. Higher up in the profile, Ni, Co and Mn are held by goethite in the ferruginised rock and cutans.

The elements associated with the fuchsitic-carbonate alteration such as Ba, K and Rb are located in fuchsite in the saprolite. In the clay saprolite, alunite hosts Ba and kaolinite contains Rb.

#### **Implications for exploration**

The *in situ* mineralogical and chemical studies of the Boddington and Mt Percy regolith material have provided data of relevance for Au and mineral exploration. It has shown that targeting individual minerals and mineralogical phases provide a potential tool to enhance geochemical anomaly detection. Kaolinite and gibbsite do not scavenge any significant amounts of trace elements and should therefore be disregarded as a sampling medium. The importance of the clay fraction ( $<2 \mu m$ ) in kaolinite-dominated samples has been demonstrated. Phyllosilicates such as interstratified minerals and vermiculite provide the potential to trap large quantities of trace elements. Goethite is the ideal target for analysis as it has a high capacity to scavenge pathfinder elements. Tungsten and Sb are mainly hosted by resistant minerals and are not reliable indicators of mineralisation.

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# PREFACE

CRC LEME-Normandy Mining Limited (now Newmont Australia) Project has its principal objective to establish case-by-case relationships between mineral and trace element abundance and to develop new exploration methods based on mineral host for significant elements. This is part of the larger research theme which integrates the hydromorphic, mechanical and biogenic processes that control the distribution and dispersion of elements within the regolith in order to make exploration geochemistry more predictive, particularly in areas of cover. The project has investigated the element-mineral associations at three deposits in a variety of geological and geomorphological environments. This report presents results from Boddington and Mt Percy deposits. The Boddington Au deposit is located in the southwest of the Archaean Yilgarn Craton in the Saddleback Greenstone Belt, 120 km southeast of Perth. The climate is Mediterranean with hot dry summers and mild wet winters. The Mt Percy Au deposit is located at the northern end of the Kalgoorlie goldfield, about 2 km from the Kalgoorlie township and is hosted in the Archaean Norseman-Wiluna Greenstone Belt.

A combination of mineralogical and chemical microanalyses, with emphasis on in situ analyses, has been performed to locate trace elements in regolith material. Laser Ablation Inductively Coupled Plasma Mass Spectrometry has been intensively used, and has been shown to be valuable tool for the determination of trace elements in clays and ferruginous materials. Bulk sampling has to take into account the varying ability of different minerals to host elements which may be indicators of mineralisation. Targeting individual minerals and mineralogical phases for chemical analyses enhances anomalies, and reveals some which remain undetected in the bulk samples.

At Boddington, kaolinite and gibbsite do not scavenge any significant amounts of trace elements. Gold concentrations are highest in the ferruginous material in the bauxitic zone. The importance of the clay fraction ( $<2 \mu m$ ) in kaolinite-dominated samples has been demonstrated. The clay fraction should be investigated to determine the presence of phyllosilicates such as interstratified minerals and vermiculite, which are able to trap large quantities of trace elements such as Cu.

Goethite is the ideal target for analysis as it has a high capacity to scavenge Au, As, Bi, W, Mo, Zn, Mn, V, Cr and Zr. The preferential analysis of goethite should increase anomaly contrast.

At Mt Percy, gold is enriched close to the surface in the lateritic duricrust and calcrete. Gold is strongly depleted (<100 ppb Au) in the underlying horizons, the mottled and plasmic clay. However, the data obtained in this study provide insight for the sampling and analysis of the Au-depleted material. Gold is concentrated in goethite rich cutans precipitated along cracks and voids. High levels of As (up to 0.1%) are also present in the goethitic cutans.

Gold is associated with quartz crystals in the alunite-rich zone. Alunite is not a direct indicator of mineralisation, but its chemical composition is useful. Barium and Cu substitutions in the alunite crystals indicate the presence of porphyries and associated mineralisation.

Kaolinite is not a sink for trace elements and its abundance dilutes anomalous values of the bulk samples. Porphyries can be located by examining rutile in the surface horizons of regolith, as rutile hosted by wall rocks and porphyries generally have distinct isotopic signatures.

R. R. Anand and R. A. Eggleton, Project Leaders Project Leaders

# **1. INTRODUCTION**

The overall objective of this project was to investigate the association between regolith minerals and trace elements. Apart from a few resistates, most minerals are destabilised under surface conditions. As a result, minor and trace elements may be released in the environment and trapped in various mineral phases. Identifying secondary mineral hosts is of key importance as the geochemical dispersion of gold, base elements and their pathfinders is partly controlled by the availability of these receptors in the regolith. Once the location of trace elements has been established, directions for exploration sampling and geochemical prospecting can be suggested.

Three sites were selected to investigate the mineralogy and geochemistry of various regolith materials. The element-mineral associations observed in the lateritic profiles in the Boddington and Mt Percy gold deposits are discussed in this report, and a companion report investigates the regolith at the Scuddles Cu-Zn sulphide deposit (Le Gleuher, 2003).

Earlier works examining geochemical dispersion patterns in their regolith-landform context at Boddington (Anand, 1994; 2001) and Mt Percy (Butt, 1991) provide the reference framework for this study.

The associations between trace elements and minerals can be partially derived using statistical analyses of bulk geochemical data backed up with a relatively simple qualitative study of the mineralogy of the regolith. Selective sampling such as size-fractions or chemical selective extraction improves the result. In this study the physical location of the trace elements in the regolith minerals was directly determined using *in situ* optical and electron optical techniques. A combination of conventional, bulk and micro-analytical techniques covering a wide range of observation scales (X-ray diffraction, Scanning and Transmission Electron Microscopies) have been used to characterise the mineralogy and trace element distribution. As most trace elements concentrations lie beyond the detection capability of the electron microprobe, *in situ* Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) analyses have been performed on different types of weathered materials. The application of this technique to the study of regolith materials, including processing and interpretation of the data has been assessed and developed.

# 2. METHODS OF INVESTIGATION

# 2.1. Analytical methods

# 2. 1. 1. Bulk sample analysis

X-ray diffraction analyses of crushed and unoriented bulk samples were performed on a Siemens 5005D diffractometer operating at 40 mA and 40 kV using Co K $\alpha$  radiation, with a counting time of 1 second per 0.02° 2 $\theta$ . Slower scans were run on handpicked or micro-drilled microsamples mounted on a low-background quartz plate. The clay fraction was prepared and analysed following the procedures described by Moore and Reynolds (1997). Three scans were collected from each sample after treatment with MgCl<sub>2</sub>, ethylene glycol saturation and heating at 350°C.

The bulk samples have been analysed for Al, Fe, Mg, Ca, K, Na, Mn, Co, Cu, Pb, Zn, Ni, Bi, In, Mo and Sb (Normandy Mining Ltd data).

# 2. 1. 2. In situ analysis

Thin sections of selected samples were investigated by optical microscopy. Electron microprobe analyses were performed on polished thin sections and single grains mounted in an epoxy resin, using a JEOL 6400 SEM equipped with a LINK analytical EDAX system (Energy Dispersive X-ray analysis). Observations in backscattered electron imaging mode (BSE) provide additional information about the microfabric of the rock fragment, clay and accessory mineral mineralogy and distribution of the phases.

Transmission electron microscopy (TEM) and analytical electron microscopy (AEM) were used to refine the mineralogy and chemical composition of individual microcrystals. Images and chemical analyses were obtained with a Philips EM430 TEM and a Philips CM300 TEM operating at 300 kV, both equipped with an energy dispersive X-ray (EDS) detector.

The *in situ* determination of trace elements was carried out using a quadrupole inductively coupled plasma spectrometer (Plasmaquad PQ2) coupled to an excimer laser (Argon Fluoride 193n). The following section is dedicated to the analysis of regolith samples with this relatively new technique.

# **2. 2. Laser Ablation Inductively Coupled Plasma Mass Spectrometry analysis of regolith** material

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is an extremely powerful analytical technique for *in situ* analysis of solids. It has the potential to determine almost all elements at the part-per million level in 1 minute, with a spatial resolution of around  $20 \ \mu m$ .

# 2. 2. 1. Description of the technique and equipment

The technique can be summarised into three steps:

- 1. Ablation of solid samples using pulses from a laser and formation of microparticles.
- 2. Transport of the released material by a gas flow to the plasma where the atoms are ionised.
- 3. The ions are sorted by mass and detected in the mass spectrometer.

The analyses were performed using a quadrupole inductively coupled plasma spectrometer instrument (Plasmaquad PQ2) coupled to an excimer laser (Argon Fluoride 193 nm; supplied by Resonetics and based on a Lambda Physik LPX12Oi laser). The instrumental set up is as shown in Figure 1. The laser is deflected on to the sample cell by a mirror. The sample sits in a "Perspex" ablation cell on a holder which can be moved in the X and Y directions. Ablation occurs under a controlled atmosphere of argon and helium, and the ablated material is then carried out of the cell in an argon gas stream to the ICP via a pulse-smoothing manifold.

The size of the probe -i.e. the diameter of the ablation pit -i is controlled by inserting an aperture in the light path. The sample can be observed on a screen at a range of low magnifications.



Figure 1. Laser ablation inductively coupled mass spectrometry analytical set up. Inserts show the ablated sample and the ICP-MS responses of selected isotopes in the NIST SRM 612 standard.

# 2. 2. 2. Samples

The *in situ* LA-ICP-MS analyses were carried out on conventional polished thin sections, and polished stubs containing single grains or chips mounted in epoxy resin. Thin sections with a thickness greater than 30  $\mu$ m have also been prepared to avoid ablating the glass. Polished surfaces are required for the preliminary mineralogical and chemical characterisation and "mapping" of the samples (light optical microscopy, SEM). These samples were directly fitted in a custom-built ablation cell where they could be ablated without any further preparation.

# 2. 2. 3. Data acquisition and sampling protocol

Standards and samples were ablated using pulse rates of 5 Hz and beam energies of 100 mJ/pulse. In these conditions the average drill rate is about 0.5  $\mu$ m/s. Pits with a surface diameter of 29  $\mu$ m were ablated over 60 s incorporating 74 to 114 mass spectrum sweeps during routine analyses. In order to increase the response a 50  $\mu$ m probe was used when analysing for gold and silver, and the total analysis time was also 60 s with 97 sweeps. In some cases pre-ablation of the surface with a larger probe (65 or 200  $\mu$ m) was carried out to clean up the site.

A typical analytical sequence comprises:

- Acquisition of a "blank" signal (*i.e.* laser off) to obtain the background intensity;
- Analysis of 2 calibration standards;
- Ten analyses of samples;
- Analysis of 2 calibration standards and
- Acquisition of a "blank" signal.

Alternatively the plasma gas blank was acquired at the beginning of each sample analysis over 60 s. Data were collected in time-resolved mode to monitor possible inter-element fractionation and compositional heterogeneity. Figure 2A shows an example of LA-ICP-MS responses obtained on the NIST SRM 612 (standard) for a selection of trace elements. Backgrounds were counted for about 60 s prior to ablation and the laser was switched off after 120 s. The analyses were conducted in two modes: the samples were either scanned along a transect or ablated in depth (depth profiling).

# 2. 2. 4. Data reduction

The data reduction method is based on Longerich et al (1996).

All data reduction is carried out off-line using spreadsheet programs and for each isotope involves:

- Calculation of the background intensity mean;
- Calculation of the analyte intensity mean;
- Subtraction of the background and
- Concentration calculation (developed below).

#### Concentration calculation

In ICP-MS analysis it is not possible to calibrate results directly by comparing the raw count data for an analyte (sample) between standards and samples. The number of ions arriving to the detector depends partially on the amount of material removed during ablation. The behaviour of minerals with respect to ablation varies greatly. Under similar analytical conditions it depends mainly on the nature of the sample. The only two ways to get quantitative analyses are to normalise the intensities of the observed peaks to the weight of the sample or alternatively to an internal standard. The second option is routinely used as the first option is not easily feasible as not all the ablated material reaches the plasma or collector. When the ratio of the analyte peak relative to that of an internal standard I <sub>unknown</sub> / I <sub>Int STD</sub> is calculated, the concentration of the analyte can be calculated from the same ratio obtained from a calibration standard (external standard). Since it is not possible to spike solid minerals with any other substance, the two choices are:

1. to use an element contained in the mineral, which has been accurately analysed by another technique (electron microprobe),

2. to use the known elemental stoichiometry when crystalline materials are analysed.

The concentrations C of each isotope (C(analyte)<sub>SAM</sub>) in the sample are calculated from the count rates for each isotope using the equation (1)

 $C(analyte)_{SAM} = I (analyte)_{SAM} / S (1)$ 

**S**: normalised sensitivity determined on the calibration standard (CAL) corrected for the volume (mass) of sample ablated.



Figure 2. Time-resolved spectra of selected isotopes obtained on: A. NIST SRM 612 reference glass standard. B. Heterogeneous material. C. Iron oxides. D. Saprolite clays. E. LA-ICP-MS responses of Sn, In, Sb Bi and Pb produced by microchips of tin polishing plate encrusted in the sample.

 $S = I (analyte)_{CAL} / C(analyte)_{CAL} * (IIS_{SAM} / IIS_{CAL} * CIS_{CAL} / CIS_{SAM})$ 

I (analyte)<sub>CAL</sub>: intensity (count rate) of the analyte in the calibration standard  $C(analyte)_{CAL}$ : concentration of the analyte in the calibration material IIS<sub>SAM</sub>: intensity of the internal standard (Al, Si, Mn etc...) in the sample. IIS<sub>CAL</sub>: intensity of the internal standard in the calibration material CIS<sub>CAL</sub>: concentration of the internal standard in the calibration material CIS<sub>SAM</sub>: concentration of the internal standard in the sample

For calibration material - or external standard - (CAL) the synthetic glasses NIST SRM 610, NIST SRM 612 and NIST SRM 616, and the Basalt Glass USGS BCR-2G have been used. A combination of 2 of these standards was chosen for better monitoring of the data. The trace element concentrations used for the NIST SRM 610 and SRM 612 are listed in Appendix 1.

The sensitivity (S) is subject to a mass dependent drift with time. The sensitivity ratios of the analyte and internal standard are corrected using a linear interpolation between the calibration samples analysed prior and after each batch of analyses (about 10 analyses). When the blanks are collected at the beginning and at the end of a batch of analyses, a drift correction on the background intensity is applied.

The limit of detection is different for each analysis as the amount of material ablated is usually different for each analysis. The conventional standard deviation of the blank  $(3\sigma)$  approach is usually used.

# 2. 3. LA-ICP-MS analysis of regolith materials

# 2. 3. 1. Introduction

The regolith samples are structurally and compositionally heterogeneous. A method has been developed to accommodate the few problems introduced by this heterogeneity.

Very few applications of LA-ICP-MS for analysing soils, clays and sediments have been reported. Most of these few studies are assessing the methods and therefore, report analyses of known materials such as standard reference soils and sediments (Durrant, 1999). For analyses, samples were usually pressed into pellets without binder, or fused mixtures of soils and diluent (*e.g.* Baker *et al*, 1998; Motelica-Heino *et al.*, 1998).

Pioneer studies conducted by Hale *et al.* (1984) tested the use of laser ablation as a means of introducing iron and manganese coatings on stream sediments into an ICP-MS. Radford and Burton (1999) performed *in situ* analyses of polished slabs of pisolithic laterite. However it seems that there is no previous report of *in situ* analysis of undisturbed regolith material (or soils or sediments) reporting quantitative measurements.

# 2. 3. 2. Homogeneous and heterogeneous regolith materials

A regolith sample is an assemblage of minerals of various sizes usually randomly distributed. The size of the minerals crystals is usually much smaller than the probe size (29 and 50  $\mu$ m). A typical signal produced when analysing regolith samples is shown on Figure 2B. The total

signal reflects the chemical signature of successive discs of material with a diameter of 29  $\mu$ m (or 50  $\mu$ m) and a thickness of 0.5 to 1  $\mu$ m. For each time slice (usually 1s), the segment of signal represents the bulk composition of the material of the disc. The size of the crystals in the regolith is usually much smaller than the laser probe size (29 and 50  $\mu$ m) except for a few residual fresh minerals. For example, the mineral grains of a kaolinitic plasma are typically less than 2  $\mu$ m in size. If the spatial resolution is quite poor laterally, it is excellent in depth (0.5 to 1  $\mu$ m).

Two main types of regolith material have been recognised (Figure 3):

1. The ablated volume consists of a homogeneous assemblage of small crystal (A). The assemblage can be mono-mineralic or poly-mineralic. A microcrystalline plasma composed of kaolinite and goethite is an example of such material.

2. The ablated volume is heterogeneous and presents mineralogical variations (B).



Figure 3. Types of regolith material

# 2. 3. 3. Nature of the ablated material

The mineralogy and chemical compositions of the selected sites in thin sections is carefully characterised and mapped with SEM-EDAX before ablation. The SEM observation of the pits after ablation is useful in order to confirm the location of the analyses, and to assess the degree of homogeneity of ablated material. Inspection of the bottom and walls of the pit shown on Figure 4 indicates than the ablated sample, which seemed mono-mineralic on surface, is however composed of several phases at depth.

Visual inspection of the time resolved spectra, combined with a detailed knowledge of the mineralogy of the sample, provides a reasonably good idea of the nature of the ablated material. For this purpose, a few major element isotopes are systematically measured to serve as "navigators". It is then usually possible to pick the time slice where a mineralogical change has occurred. For example, a drop in the silica signal will illustrate the transition from kaolinite to gibbsite. As mentioned above the high spatial resolution in depth allows the detection of minute grains less than 1  $\mu$ m in size on the spectra.

# 2. 3. 4. Data acquisition

Samples can be scanned and ablated along a transect, or drilled in depth. Isotopes of majors elements likely to be present in the ablated volume are systematically analysed for several

purposes: 1) to serve as "navigators" *i.e.* to enable the identification of mineralogy of the ablated volume; 2) to enable the determination of the internal standard concentration.

# 2. 3. 5. Data processing

#### *Qualitative results*

Observation of the isotopic responses allows a rapid assessment of some of the trace element associations and therefore the identification of the host-minerals. Trace element profiles often appear noisy due to fine scale mineralogical variations and analytical noises. The fine amplitude spikes have not been taken into account, as they cannot be safely discriminated from instrumental noises. Sharp spikes are also ignored whereas top rounded ones have been considered as real features of the spectra indicating the presence of a minute particle.

#### Quantitative results

In order to achieve a quantitative analysis it is necessary to select an internal standard present in the sample and in the external standard (NIST glasses). The determination of the concentration standard is easily addressed when analysing a large individual crystal of a thin section (microprobe analysis or stoichiometry). It is however more difficult to obtain a value for an internal standard concentration when the material is not a single crystal. In this case a stoichiometric value, normalised to 100 wt% oxide or element, has been determined as follow:

- The concentrations of the isotopes are calculated according to Longerich's procedure using an arbitrary but possible CIS<sub>SAM</sub> value based on the mineralogy;
- The concentrations of the most abundant isotopes in the phase are summed up;
- The value of CIS<sub>SAM</sub> is adjusted to obtain a total of 100 wt. oxide or 100% element and
- The element concentrations and ratios such as Si/Al are checked to insure that they are in agreement with the stoichiometry of the assemblage. If it is not the case, overlooked phases or substitutions in some of the phases might account for the discrepancies.

The different methods, which have been used depending on the regolith type, are described below. Silica, Al or Mg were chosen as internal standards.

#### Type A: homogeneous regolith samples

The signals produced by homogeneous samples are typically flat, similar to the ones obtained when ablating massive iron oxides (Figure 2C). The chemical composition of the assemblage is analysed by SEM-EDAX throughout the site to check for any possible spatial variation.

A mono-mineralic sample is treated like a single crystal. There is little or no chemical variation, therefore the normalised EDAX value (to 100 wt% or 100 % element) of a chosen element is used as the internal standard concentration.

For a poly-mineralic sample two methods are used: the  $CIS_{SAM}$  value is either the normalised value of a window SEM-EDAX analysis, or a stoichiometric normalised value when the proportions of the different phases vary in the ablated volume.

#### Type B: heterogeneous regoliths

The signals shown in Figure 2D are produced by the ablation of a volume of saprolite consisting of vermiculite and kaolinite. The variations in depth of the responses obtained for a combination of major diagnostic elements (e.g. K+, Si, Al, Fe) are used to decompose the signals into slices, each slice representing a single or group of minerals. Only phases large enough to be ablated during at least ten time slices are considered for quantitative results. An

internal standard is chosen for each slice if necessary. The concentration of the internal standard is either an EDAX determined value or a stoichiometric value.

In the case of more complex mixture, the  $CIS_{SAM}$  is also a stoichiometric value. The value obtained for each isotope is the concentration of this isotope in a volume of material containing x%Al<sub>2</sub>O<sub>3</sub>, y% SiO<sub>2</sub> and z%Fe<sub>2</sub>O<sub>3</sub> for example.

# 2. 3. 6. Interferences and contamination

Problems are either inherent to the technique or due to the nature of the sample. Polyatomic ion and oxide interferences are in the first category. The most relevant atomic interferences for this study are interferences with Ar atoms of the plasma such as  ${}^{40}\text{Ar} + {}^{23}\text{Na} = {}^{63}\text{Cu}$  and  ${}^{40}\text{Ar} + {}^{28}\text{Si} = {}^{68}\text{Zn}$ . Isotopes  ${}^{65}\text{Cu}$  and  ${}^{66}\text{Zn}$  are therefore analysed. Other examples are interferences with silver and gold such as  ${}^{91}\text{Zr}^{16}\text{O} = {}^{107}\text{Ag}$ ,  ${}^{93}\text{Nb}^{16}\text{O} = {}^{109}\text{Ag}$  and  ${}^{181}\text{Ta}^{16}\text{O} = {}^{197}\text{Au}$ . It is necessary to analyse for the isotopes that can create interferences in order to discriminate between artefacts and true responses for the isotopes of interest.

Tin contamination and associated isotopes have been a major problem in the analyses of the samples. During the polishing of the thin sections, tin grains frequently set in or between crystals. Unfortunately the material of the plate certified "pure tin" also introduces anomalous concentrations of indium, bismuth, antimony and lead.

A careful inspection of the spectra is usually enough to discriminate between true trends and contamination. For this reason tin has been generally analysed but not quantified. Figure 2E shows Sn, Bi, In, Pb and Sb responses produced by such grains scattered in a mixture of clays and iron oxides. Tin pollution is more likely to be present when scanning the sample surface. In this case, the track to be analysed is cleaned by a rapid and larger scan (65  $\mu$ m) prior to ablation. Depth profiles are more useful because most of the spectrum under the top slices can still be used.

# 3. THE BODDINGTON GOLD DEPOSIT

# 3. 1. Regional setting of the Boddington gold mine

# 3. 1. 1. Geological setting

The Boddington gold deposit is located in the southwest of the Archaean Yilgarn Craton in the Saddleback Greenstone Belt, 120 km southeast of Perth, Western Australia. The belt is 5 to 10 km wide and 35 km long, and is subdivided into the Marradong, Wells and Hotham Formations. These Formations include mafic to felsic volcanic rocks (mainly andesites with minor dacites and rhyolites), pyroclastic rocks and metasediments (Figure 4). Zircon U-Pb geochronology dated the felsic volcanic rocks at 2670 to 2650 Ma (Wilde and Pidgeon, 1986), indicating that they erupted approximately at the same time as the volcanics of the Eastern Goldfields Province of Western Australia. The volcanic sequence is intruded by Proterozoic dolerite dykes. The igneous rocks have been metamorphosed to greenshist facies.



Figure 4. Schematic geological map of the Saddleback greenstone belt (after Wilde and Low, 1980).

A porphyry-style Cu-Mo-Au-Bi-W mineralisation characterises the Boddington deposit. The primary ore is hosted within hydrothermally altered felsic to intermediate volcanic rocks and intrusions of the Wells Formation. Potassic alteration consisting of biotite-silica is present within all generations of diorite intrusions. A subsequent hydrothermal event led to the replacement of biotite by actinolite. A later phyllic alteration episode (quartz-sericite) takes place along zones of intense deformation. The primary mineralisation is synchronous with the emplacement of dioritic intrusions.

Gold is associated with molybdenum and copper in the approximate ratio of 1:10:1000 and occurs in the actinolite±quartz±clinozoite±biotite±titanite±sulphide veins.

The discovery of the Boddington deposit was the result of mapping and geochemical prospecting programmes carried out initially by the Western Australia Geological Survey (Wilde, 1976, Davy, 1979). Subsequent exploration programmes by Reynolds Australia Mines Pty. Ltd. led to the discovery of the gold mineralisation in 1980 (El-Ansary, 1980). The mine, currently on care and maintenance, was operated by Worsley Alumina Ltd on behalf of a joint venture which comprises Normandy Mining Ltd, Acacia Resources Ltd (Now Anglo Gold Ltd) and Newcrest Mining Ltd. Gold production exceeded 200 000 ounces in year 2000.

# 3. 1. 2. Climate, vegetation and topography

The climate is Mediterranean with hot dry summers and mild wet winters. The average annual rainfall at the mine site, for the 1983-2000 period, was 746 mm with the highest falls occuring from May to September. Evaporation is very high from November to February with a yearly average reaching 1587 mm for the same period (Worsley Alumina Pty Ltd data, 2001). The area is mainly covered by forests of eucalypts.

The Saddleback area is an eroded plateau 300-350 m above sea level covered by bauxitic laterite. The plateau is deeply cut by the valleys of the Hotham River and tributaries. Mounts Wells (547 m) at the North of the belt and Mount Saddleback (575 m) at the South are the two prominent features of the area.

# 3. 2. The lateritic profile

# 3. 2. 1. Description of the regolith units

The volcanic rocks of the Saddleback Belt have been extensively lateritised. Figure 5 shows a schematic representation of the weathering profiles along a toposequence. Overlying the fresh rock are the following units (Anand, 1994, 2001):

- The saprock, a greyish-green unit, comprises slightly weathered rocks and fresh rock fragments.
- The saprolite is a thick unit composed of olive-yellow clays where the original rock fabric is preserved.
- The clay zone is multicoloured with patches of white kaolinitic clays and reddish ferruginised areas. The thickness of the saprolite and clay zone combined varies from 30 to 100 m.

- The bauxite, about 4 m thick, is a friable, porous yellow-brown to red-brown material with local ferruginised patches, and is mainly composed of gibbsite, hematite and goethite.
- The duricrust is subdivided into 2 main units on the basis of the dimensions of the cemented material. The fragmental duricrust consists of angular concretions, that range in size from a few mm to more than 3 cm, set into a gibbsite-goethite rich matrix. It is gradually or abruptly merging into a pisolitic-nodular duricrust. The pisoliths and nodules, up to 25 mm in diameter, are rich in hematite and maghemite, and are cemented by a gibbsitic matrix. The duricrust is absent in the low areas and the bauxite is capped by a layer of packed loose pisoliths. Upslope erosion has stripped the surface material and exposed the fragmental duricrust.
- The soil is composed of lateritic gravels in a sandy and silty matrix.



Figure 5. Distribution of the regolith units along a toposequence (After Anand, 1994).

# 3. 2.2. Sampling

Anand (1994) has described the mineralogy and geochemistry of the regoliths developed from felsic andesites and dolerites. A selection of 36 specimens taken from 4 drill cuttings through felsic andesite has been studied: WBC15, WBC21, WBC26 and WBC25). Table 1 lists the position of the samples, as well as their regolith type and colour on the Munsell Soil Color Chart.

The selected samples illustrate the different types of weathered materials and/or have noticeable metal anomalies. The sets of samples from WBC15 and WBC21 represent "complete" weathering profiles whereas only clay and fresh specimens from the drill cuttings WBC26 and WBC25 were chosen.

	Drill cu	tting: WBC 1	5	Drill cutting: WBC 21						
Samples	Dept h (m)	Material type	Colour (dry powder)	Sample s	Dept h (m)	Material type	Colour (dry powder)			
07-0402	0.25	Loose pisoliths	5YR 4/4	07-0412	0.70	Loose pisoliths	5YR 3/3			
07-0403	2.00	Pisolitic duricrust	2.5YR 4/6	07-0414	3.30	Loose pisoliths	2.5YR 3/4			
07-0404	3.50	Bauxite	2.5YR 5/6	07-0415	4.00	Pisolitic duricrust	2.5YR 4/6			
07-0405	5.00	Clay zone	5YR 6/4	07-0416	5.50	Fragment al duricrust	2.5YR 5/6			
07-0406	8.00	Clay zone	2.5YR 5/6	07-0417	7.30	Bauxite	5YR 7/4			
07-0407	10.00	Clay zone	2.5YR 7/3	07-0418	8.30	Clay zone	2.5YR 8/3			
07-0408	12.50	Saprolite	7.5YR 7/6	07-0419	13.00	Clay zone	2.5YR 7/4			
07-0409	19.00	Saprolite	5YR 7/4	07-0420	19.00	Saprolite	7.5YR 7/4			
07-0410	26.50	Saprolite	7.5YR 8/3	07-0421	26.00	Saprolite	10YR 7/6			
07-0411	30.00	Bedrock	5Y 6/1	07-0422	33.00	Bedrock	5Y 7/1			

Table 1. Sampling: location and regolith types

	Drill cut	tting: WBC	26	Drill cutting: WBC 25							
Sampl es	Depth (m)	Material type	Colour (dry powder)	Sample s	Dept h (m)	Material type	Colour (dry powder)				
07- 0423	1.00	Clay zone	5YR 4/4	07-0433	1.50	Fragmental duricrust	10R 4/4				
07- 0424	4.00	Clay zone	5YR 4/6	07-0434	15.00	Clay zone	2.5Y 8/2				
07- 0425	7.00	Clay zone	7.5YR 8/2	07-0435	34.00	Saprolite	7.5YR 6/4				
07- 0426	9.50	Clay zone	10YR 5/6	07-0436	45.00	Saprolite	2.5Y 7/4				
07- 0427	17.00	Saprolit e	2.5YR 8/3	07-0438	53.50	Saprolite					
07- 0428	27.00	Saprolit e	2.5Y 7/2	07-0437	50.00	Bedrock	2.5Y 6/1				
07- 0429	32.50	Saprolit e	10YR 8/3								
07- 0430	42.00	Saprolit e	5Y 7/2								
07- 0431	51.50	Saprock	2.5Y 6/6								
07- 0432	53.50	Bedrock	2.5Y 6/2								

#### 3. 2. 3. Bulk mineralogy of the regolith units

This section gives a general overview of the mineralogy of the regolith units. A detailed mineralogical description of the samples is given in section 3. 3. The mineralogy of the different regolith units is similar in the four drill cuttings. The intensity and nature of the hydrothermal events affecting the original rock control local mineralogical variations. The fresh rock mainly contains quartz, muscovite, plagioclase, and lesser kaolinite, chlorite and epidote. Kaolinite and quartz are the dominant minerals in the clayey horizons (saprolite and clay zone). Upward through the profile the major change is the replacement of kaolinite by gibbsite associated with iron oxides, namely goethite, hematite and maghemite. Residual quartz is present throughout the profiles and its distribution and abundance strongly depend on the distribution of the hydrothermal quarzt veins. Part of the quartz in the upper units is allochtonous.

#### 3. 2. 4. Chemical composition of the bulk samples

The trends described below refer to the set of 36 samples described above. The chemical composition of the selected samples is given in Tables 2 and 3.

#### Major elements

The behaviour of the major elements is characteristic of lateritic weathering (Figure 6). The transition from saprock to lower saprolite is accompanied by an almost total loss of Na<sub>2</sub>O, CaO and MgO as plagioclase, epidote and chlorite are weathered. The behaviour of  $K_2O$  is controlled by the presence of muscovite mica, which still persists in small amounts in the bauxite zone. Alumina is relatively enriched upwards and is most concentrated in the bauxite zone and the duricrust, where it occurs mainly as gibbsite and in goethite. Iron is fairly constant through the saprolite and becomes enriched in the clay zone. The concentration variations observed in the clay zone are related to variable degrees of ferruginisation.

The pisolitic duricrust and the loose pisoliths contain the highest concentrations of Fe which is present as goethite, hematite and maghemite. Silica shows an overall decrease upwards through the profile as silicates are being dissolved. The slight increase of the silica content in the surficial levels of the two "complete" profiles (WBC15 and WBC21) is due to the presence of transported sandy material. The density of the quartz veining is responsible for the local variations of the silica in the saprolite and clay zone. Titanium is relatively enriched from the middle saprolite and upward where it is released by the weathering of ilmenite, titanite and mica and subsequently precipitates as anatase.

#### Minor and trace elements

Figure 6 shows the distribution of selected elements in profile WBC21. Copper, Mn, Zn, Ni and Co are concentrated in the lower saprolite, and are leached upwards the profile. There is a slight increase of Mn, Zn and Ni contents in the upper part of the profile. Chromium, V, Zr, Mo, As and Pb, are concentrated up the profile in the clay zone and overlying horizons. Chromium, V, and As are strongly depleted in the fragmental duricrust and bauxite relative to the clay zone and pisolitic duricrust. Iron displays a very similar spatial distribution, which suggests that Cr, V and As are associated with iron oxides.

There is a general increase of W, Bi and Sn levels up through the profile with the highest values in the fragmental duricrust. However, these elements are relatively depleted in the pisolitic duricrust and loose pisoliths. Gold increases in abundance from the saprolite to the bauxitic zone where it reaches a maximum value of 9000 ppb. Gold is drastically depleted in the overlying lateritic duricrust and loose pisoliths.

Anand (1994) carried out a detailed investigation of the major and trace element distribution on a large set of samples. Element-mineral associations were derived by applying statistical calculations on the data set. The trends described above refer to a much smaller batch of samples. It is therefore important to summarise the trends observed in these samples by Anand (1994):

• Vanadium, Cr, As, Bi, Sn, Ga, W, Zr, Nb, Mo, and Pb and tend to be progressively concentrated upwards through the profile. They are either associated with iron oxides and gibbsite (Ga), or are present as residual primary minerals (zircon, cassiterite and scheelite).

 Mn, Zn, Co, Ni and Cu decrease in abundance up the profile. There is a slight increase in Mn, Zn, Ni and Co concentrations at the surface, attributed to pedogenic processes. Their similar behaviour in the saprolite indicates that they are released during the weathering of primary minerals and leached out of the profile.

 Table 2. Chemical composition of the selected samples: major oxides (%), Anand (1994).

 (-: below detection limit)

Sample	depth(m)	Local m	nine grid	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	LOI	TOTAL
WBC15		east'a	north'a										
07-0402	0.25	9949	11649	10.9	45.3	31.5	0.1	0.1	0.1	0.1	3.3	9.7	101.1
07-0403	2.00	9949	11649	1.7	47.9	24.3	0.0	0.0	0.0	-	3.2	23.5	100.7
07-0404	3.50	9949	11649	8.1	47.2	15.0	0.0	0.0	0.0	0.1	2.3	26.1	98.9
07-0405	5.00	9949	11649	34.9	33.2	19.3	0.1	0.0	0.1	0.7	2.2	13.2	103.7
07-0406	8.00	9949	11649	37.2	31.7	15.2	0.1	0.0	0.1	0.7	2.3	12.7	100.0
07-0407	10.00	9949	11649	34.9	31.2	18.7	0.0	0.0	0.1	0.1	1.2	13.5	99.8
07-0408	12.50	9949	11649	17.5	48.0	8.2	0.0	0.0	0.1	0.1	1.7	24.1	99.7
07-0409	19.00	9949	11649	51.8	29.1	6.2	0.1	0.0	0.1	0.1	0.9	11.4	99.7
07-0410	26.50	9949	11649	62.0	22.1	4.7	0.5	0.1	0.1	0.6	0.8	8.1	99.1
07-0411	30.00	9949	11649	57.7	13.4	8.5	3.7	6.5	2.3	1.4	0.5	1.9	95.9
WBC21													
07-0412	0.70	10098	12780	5.8	46.7	35.2	0.0	0.1	0.0	0.1	2.8	9.4	100.0
07-0414	3.30	10098	12780	1.5	49.9	36.0	0.0	0.0	0.0	-	2.6	10.6	100.7
07-0415	4.00	10098	12780	1.7	45.2	30.9	0.0	0.0	0.0	-	3.9	18.2	99.9
07-0416	5.50	10098	12780	3.2	50.6	16.2	0.1	0.0	0.0	0.4	2.6	27.1	100.2
07-0417	7.30	10098	12780	4.5	49.3	17.3	0.0	0.0	0.0	0.2	2.6	26.6	100.5
07-0418	8.30	10098	12780	12.4	26.6	43.5	0.1	0.0	0.0	0.3	1.9	15.8	100.6
07-0419	13.00	10098	12780	37.4	36.8	11.4	0.1	0.0	0.1	0.4	1.7	14.5	102.4
07-0420	19.00	10098	12780	51.3	32.7	7.5	0.1	0.0	0.1	0.2	1.1	12.1	105.1
07-0421	26.00	10098	12780	55.8	25.7	7.1	1.1	0.2	0.3	1.2	0.9	9.4	101.8
07-0422	33.00	10098	12780	61.2	17.5	4.9	2.3	6.3	3.9	1.4	0.7	0.9	99.0
WBC26													
07-0423	1.00	9550	11098	29.3	28.2	28.5	0.1	0.1	0.1	0.2	3.6	11.7	101.6
07-0424	4.00	9550	11098	36.6	19.1	30.9	0.1	0.0	0.1	0.1	4.1	9.0	99.9
07-0425	7.00	9550	11098	66.1	19.7	5.2	0.1	0.0	0.1	0.1	2.2	7.6	101.0
07-0426	9.50	9550	11098	65.2	8.1	23.9	0.0	0.0	0.0	0.1	0.3	5.8	103.4
07-0427	17.00	9550	11098	71.2	21.7	1.6	0.2	0.0	0.0	0.9	0.7	7.0	103.4
07-0428	27.00	9550	11098	62.5	8.8	1.4	0.1	0.0	0.0	0.7	0.3	6.1	79.9
07-0429	32.50	9550	11098	70.2	17.3	3.9	0.2	0.0	0.1	0.7	0.6	6.5	99.4
07-0430	42.00	9550	11098	67.6	17.7	4.3	1.1	0.9	0.4	1.0	0.7	5.5	99.3
07-0431	51.50	9550	11098	72.7	15.7	6.4	1.2	0.5	0.3	1.5	0.5	5.0	103.8
07-0432	53.50	9550	11098	69.7	17.0	4.9	1.4	3.0	1.8	2.8	0.5	2.5	103.7
WDQ5				-	-	-							
WBC5	1 50	0700	10000	7.0	20.0	22.0	0.0	0.0	0.0		2.4	10.7	100.0
07-0433	1.50	9799	10900	7.9	38.9	32.0	0.0	0.0	0.0	-	2.4	10.7	100.0
07.0435	15.00	9/99	10900	65.U	23.2	1.4	0.1	0.0	0.0	0.6	0.8	7.9	102.0
07-0435	34.00	9799	10900	0.00	22.3	5.1	0.5	0.0	0.0	0.8	0.8	7.9	102.9
07.0430	45.00	9/99	10900	62.2	21.0	0.0 5 4	1.1	0.1	0.1	1.3	0.7	1.5	100.0
07.0438	53.5 E0.00	9799	10900	62.7	<u> </u>	5.4 6.4	1.2	0.3	0.3	1.1	0.7	0.9	103.7
07-0437	JU.UC	9799	10400	03.1	C.11	0.1	1.0	4.4	3.Z	∠.4	0.6	1.0	100.5



Figure 6. WBC21—Vertical distribution of selected major and trace elements.

Sample	Mn	Cr	V	Cu	Pb	Zn	Ni	Со	As	Sb	Bi	Мо	Ag	Sn	Ge	Ga	W	Ba	Zr	Nb	Au
WDC15	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	aqq
07.0402	110	100	E12	0	10	40	14	- 1	25	.2	10	22	-0.1	FD	-0	02	50	/1	700	20	40
07-0402	20	400	140	9	19	49	10	<4	30	<2	25	33 25	<0.1	0/	<2	03 72	0Z 05	41	564	20	460
07-0403		3400	283	19	1	12	<4	<4	47	<2	25	- 35 - 14	<0.1	04 72	<2	50	43	20	107	24	400 560
07-0404	<15	340 400	203	76	<2	25	<4 /Q	<4 Q	40 70	<2	25	14	<0.1	55	< <u>_</u>	53	43 70	152	497	15	3060
07-0405	<15	385	253	106	~2	20	58	7	63	<2	17	13	<0.1	70	4	58	50	157	506	24	1700
07-0400	<15	435	235	84	<2	53	30	/ <a< td=""><td>61</td><td>&lt;2</td><td>17</td><td>15</td><td>&lt;0.1</td><td>70 41</td><td>-4</td><td>34</td><td>20</td><td>31</td><td>348</td><td>12</td><td>1270</td></a<>	61	<2	17	15	<0.1	70 41	-4	34	20	31	348	12	1270
07-0407	<15	325	203	107	<2	35	40	<4	28	<2	7	21	<0.1	38	<2	42	20	27	210	12	1270
07-0409	<15	97	121	107	14	113	65	<4	13	<2	5	9	<0.1	20	<2	24	6	56	170	10	300
07-0410	227	62	86	566	5	98	31	10	<2	<2	3	2	<0.1	11	<2	23	12	104	170	7	10
07-0411	865	53	73	2730	3	109	72	28	2	<2	9	2	<0.1	33	<2	15	43	138	124	5	1190
WBC21	000	00	70	2700	Ŭ	107	72	20		12	,			00	12	10	10	100	121	Ŭ	1170
07-0412	85	354	678	14	20	39	17	<4	206	2	7	46	0.5	9	<2	83	13	36	596	20	110
07-0414	84	391	699	<2	18	32	<4	<4	204	2	11	38	< 0.1	7	<2	87	7	25	470	16	20
07-0415	99	334	626	16	7	18	<4	<4	123	4	9	41	0.5	17	<2	93	31	25	532	26	50
07-0416	<15	286	361	58	<2	12	<4	<4	89	4	14	34	<0.1	25	<2	68	41	109	454	20	250
07-0417	<15	490	369	66	<2	11	<4	<4	109	<2	13	15	<0.1	18	<2	80	17	75	462	22	9100
07-0418	<15	734	744	83	6	13	19	<4	183	5	13	19	<0.1	18	<2	83	14	148	689	12	7030
07-0419	17	246	193	204	4	26	77	7	48	<2	10	39	<0.1	12	<2	38	15	231	301	12	3750
07-0420	<15	140	149	288	3	13	57	<4	31	<2	2	21	<0.1	3	<2	31	5	116	142	11	4360
07-0421	1788	182	126	674	<2	54	139	127	62	<2	9	56	<0.1	12	<2	24	11	638	181	8	1530
07-0422	516	126	91	92	4	52	91	18	44	<2	<2	8	<0.1	46	<2	20	10	284	120	3	930
WBC26																					
07-0423	306	232	562	316	14	24	87	19	43	<2	5	33	0.5	23	<2	51	15	67	472	16	220
07-0424	301	156	514	587	20	19	58	14	33	2	2	44	<0.1	14	<2	30	17	48	309	18	540
07-0425	82	100	266	372	7	22	53	7	20	<2	5	26	<0.1	27	5	26	19	54	241	17	2990
07-0426	<15	<20	71	3310	9	116	114	15	94	<2	23	87	<0.1	65	<2	10	27	46	48	4	12000
07-0427	23	87	89	311	8	17	12	<4	9	<2	<2	8	<0.1	18	<2	22	15	439	192	5	490
07-0428	50	<20	106	125193	5	11	14	8	4	<2	20	4	233	50	<2	<4	55	624	65	<2	5150
07-0429	37	59	123	4400	5	49	29	<4	7	<2	2	12	2.5	13	<2	18	18	198	65	6	870
07-0430	328	74	94	6020	7	118	44	11	<2	<2	<2	5	<0.1	25	<2	22	61	241	157	4	330
07-0431	234	<20	72	3500	<2	119	50	12	7	<2	<2	7	9	26	<2	17	8	232	73	<2	240
07-0432	305	<20	72	4850	8	71	35	13	2	<2	<2	8	9	15	<2	20	<4	577	37	<2	290
WBC25																					
07-0433	34	251	699	308	14	8	<4	<4	78	<2	8	88	0.5	35	<2	78	57	19	420	17	1010
07-0434	<15	<20	75	387	<2	17	15	<4	9	<2	7	12	<0.1	15	<2	29	38	195	148	8	1280
07-0435	107	<20	90	3970	<2	36	27	8	11	<2	3	9	<0.1	21	<2	24	9	214	156	3	490
07-0436	255	116	83	6740	4	104	52	11	44	<2	10	10	<0.1	17	<2	26	14	225	132	3	1630
07-0437	413	55	66	2570	<2	118	41	17	<2	<2	<2	3	0.5	24	<2	19	<4	283	109	<2	450
07-0438	235	65	85	2630	3	96	38	14	5	<2	<2	7	3.5	10	<2	23	44	176	84	5	520
07-0437	413	55	66	2570	<2	118	41	17	<2	<2	<2	3	0.5	24	<2	19	<4	283	109	<2	450

Table 3. Chemical composition of the regolith units, WBC15, WBC21, WBC25 and WBC26: trace elements, Anand (1994).

#### 3. 3. In situ mineralogy and chemistry of the regolith units

#### 3. 3. 1. Fresh rock and saprock

The fresh rock is grey to light brownish grey and displays a weak foliation, but the overall texture is granoblastic. The samples show a wide range of mineralogy and textures resulting from the nature of the original volcanic rock itself, metamorphism and various hydrothermal events. Examples of common mineralogical assemblages observed in the saprock are shown on Figure 7.

The mineralogical investigation has shown that even the freshest samples have undergone incipient weathering. The disappearance of sulphides has been taken as the criteria to differentiate saprock from saprolite samples.

The chemical composition of the saprock minerals is given in Table 4. The saprock samples contain muscovite (often referred in this context as sericite in the literature) with about 2% MgO and FeO. Quartz is abundant and is present as equidimentional grains in the groundmass and in veins. Plagioclase albite is a major component of the groundmass of some samples where it occurs as micrometric (10 to  $30 \mu m$ ) xenoblasts. Actinolite-hornblende is not ubiquitous but represents as much as 15% of the whole rock in one of the samples. The chlorite is a ferro-magnesian trioctahedral chlorite. Epidote grains are enclosed in quartz or form large crystals in veins (Figure 7A). Titanite (sphene) grains are relatively abundant in the groundmass and occurs mainly as isolated small grains about 10  $\mu m$  in size intergrown with or enclosed in quartz or epidote (Figure 7A). Titanite granules (about 1 to 3  $\mu m$ ) are also observed between minerals (Figure 7C). Biotite is rarely observed fresh, and has a Mg/Fe<sup>2+</sup> ratio of 1.3 with total iron concentration assumed as FeO. Large skeletal grains of ilmenite are surrounded by titanite (Figure 7B).

#### The clay fraction

#### Interstratified biotite/vermiculite clay mineral

The X-ray diffraction analyses of the clay fraction (2  $\mu$ m) and the microprobe analyses indicate the presence of a randomly interstratified mica/vermiculite mineral. Figure 8 shows the characteristic collapse of the vermiculite component after heating the sample at 350°C, producing a shift of the 001 peak from 12.3 Å to about 10.3 Å. The 001 basal spacing of the mica/vermiculite indicates a mixture of about 60% of mica layers and 40% of vermiculite layers (Moore and Reynolds, 1997). The reaction biotite—biotite/vermiculite proceeds with a loss of potassium. Only the interstratified minerals situated in the vicinity of sulphides contain high levels of copper (up to 1.90 % CuO). The SEM micrograph (Figure 11F) shows the location of two biotite/vermiculite (bio/ver) grains which have been analysed. The micro-environment of these crystals suggests two sources for the copper: 1) The copper released during the dissolution of the adjacent sulphide has been trapped in the interlayer of the vermiculite and sulphide veinlets are synchronous, and are due to the same hydrothermal fluid.

#### Interstratified chlorite/vermiculite clay mineral

Chlorite is partially replaced by a randomly oriented high-charge chlorite-vermiculite interstratified mineral with a high proportion of chlorite layers. The X-ray diffraction data of the clay fraction ( $<2 \mu m$ ) show that heating the sample at 350°C creates a peak at 12.3 Å which result from the collapse of the vermiculite member (Figure 8). No expansion of the structure is observed with ethylene-glycolation. This reaction chlorite  $\rightarrow$  chlorite/vermiculite involves a loss of Mg due to dissolution of the brucitic layer of the chlorite.

#### Kaolinite

A small amount of kaolinite is detected in XRD patterns of the clay fraction (Figure 8). Scanning electron microscopy observations suggest that kaolinite results from the incipient alteration of vermiculite layers. The analysis of a mixture of vermiculite and kaolinite indicates that the reaction vermiculite layers—kaolinite-vermiculite proceeds with a loss of Mg and Fe which has precipitated as goethite.



Figure 7. SEM micrographs (backscattered electron images) of the saprock minerals. A, B and C. Silicate mineral assemblages. D. Large sulphide grain with pyritic core surrounded by Cu-sulphides. E. Alteration of Cu-sulphides into cuprite and Cu. F. Partial dissolution of Cu-sulphides. bio/ver : biotite/vermiculite.

Analysis	Mineralogy	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	K <sub>2</sub> O	CuO	Na <sub>2</sub> 0	Total Oxides
1	Epidote	38.1		26.4	9.2			23.8				97.5
2	Epidote	38.4		26.5	9.7			23.6				98.2
3	Epidote	38.4		26.6	9.2			23.9				98.1
4	Epidote	39.1		26.0	9.7			24.0				98.8
5	Epidote	39.3		29.4	6.5			24.2				99.4
6	Epidote	38.3		28.2	7.8			23.6		1.0		98.9
7	Chlorite	26.3		20.7		22.9	16.9					86.8
8	Biotite	37.4	1.2	17.2		16.5	12.6		9.7			94.6
9	Biotite/ vermiculite	37.2	1.0	17.1		14.8	11.6		7.8	1.2		90.7
10	Biotite/ vermiculite	36.2	1.0	16.6		15.4	12.3		8.9			90.4
11	Vermiculite/ biotite	39.4	0.9	17.1		15.3	12.7	1.0	2.3			88.7
12	Biotite/ vermiculite	37.3	1.0	17.2		15.4	12.7		5.9			89.5
13	Vermiculite/ biotite	41.3	0.9	16.1		16.5	9.9	1.2	2.0			87.9
14	Biotite/ vermiculite	37.6	1.0	17.0		15.9	13.0		8.7	1.7		94.9
15	Biotite/ vermiculite	36.7	0.9	16.0		16.2	12.7		7.5	1.6		91.6
16	Biotite/ vermiculite	37.0	1.0	16.4		16.2	12.8		7.6	1.9		92.9
17	Kaolinite/ vermiculite	42.2		29.9		4.1	2.2					78.4
18	Muscovite	45.9	0.6	30.2		2.4	1.9		10.1			91.1
19	Muscovite	47.6	0.6	33.4		2.1	1.5		10.4			95.6
20	Muscovite	49.7		29.9		1.6	1.7		9.3		2.0	94.2
21	Plagioclase	63.0		23.7				4.6			8.7	100
22	Plagioclase	67.5		20.6				2.0			9.8	99.9
23	Plagioclase	64.6		21.4	0.8			2.4			10.7	99.9
24	Ttitanite	30.7	38.6	1.8				28.7				99.8
25	Ttitanite	30.5	39.0	1.4				28.6				99.5
26	Ttitanite	31.1	36.9	2.1				28.2				98.3
27	Ttitanite	27.1	40.5	1.5	5.3			24.5				98.9
28	Ttitanite	30.8	38.7	1.6				28.5				99.6

Table 4. Electron microprobe analyses (%) of the saprock silicate minerals.

Mineral	Formula
Arsenopyrite	FeAsS
Bismuthinite	$Bi_2S_3$
Chalcopyrite	CuFeS <sub>2</sub>
Cubanite	$CuFe_2S_3$
Mackinawite and	(Fe,Ni) <sub>9</sub>
pentlandite	S <sub>8</sub>
Molybdenite	MoS <sub>2</sub>
Pyrite	FeS <sub>2</sub>
Durrhotito	Fe <sub>7</sub> S <sub>8</sub> -
Fyrmotite	FeS
Spharolito	(Zn,
Spharente	Fe)S
Violarite	Ni <sub>2</sub> FeS <sub>4</sub>

Table 5. Mineralogy of the Boddington gold deposit sulphides (From Symons et al., 1990)



Figure 8. X-ray diffraction patterns of the clay fractions separated from the saprock (A), middle saprolite (B) and upper saprolite (C). Ch= Chlorite; Co= Corrensite; M= Mica; K= Kaolinite; E= Epidote;

Go= Goethite; Gi= Gibbsite.

Vermiculite *sensu stricto* and smectites are not present in the saprock. However, the identification of vermiculite layers in the interstratified clays of the freshest samples is important as vermiculite has a high ability to adsorp and retain exchangeable cations and anions. Vermiculite has the largest cation-exchange capacity (CEC) of the clay minerals with values ranging from 100 to 200 meq/100 g depending on the method used (Douglas, 1989). The two types of interstratified minerals biotite/vermiculite and chlorite/vermiculite have been reported as being hydrothermal or supergene alteration products (Anand and Gilkes, 1984, Proust et al., 1986, Banfield and Eggleton, 1988, Dudoignon *et al*, 1988, Aspandiar and Eggleton, 2002).

# Sulphides

All the sulphides containing copper, iron, molybdenum, bismuth, arsenic, nickel, zinc and gold, listed in Table 5, have been reported in the fresh ore (from D. Gilbert, unpublished data, 1984, in Symons *et al*, 1990). In the samples investigated in this study, the dominant Cu-sulphides are anilite ( $Cu_7S_4$ )-djurleite ( $Cu_{31}S_{16}$ )-digenite ( $Cu_9S_5$ ) with no or little iron.

The sulphides occur as single and clusters of grains and as dendrites. Large variegated grains present a pyritic core surrounded by Cu-sulphides (Figure 7D). Although most of the sulphides are unaltered in the saprock, two types of alteration have been observed. Massive Cu-sulphides are partially replaced by native copper associated with cuprite, and some Cu-sulphide grains are being dissolved (Figure 7E and 7F). Vermiculite layers located nearby trap the Cu released during their dissolution.

# 3. 3. 2. Saprolite

The saprock is gradually replaced by a softer, but coherent material, which mainly retains the overall parent-rock fabric. The color becomes more yellow and reddish-brown. The major alteration processes are the intense weathering of the primary high temperature minerals and the ferruginisation of the material. The variety of the mineralogy of the fresh rock leads to the development of several supergene alteration facies in the saprolite. Kaolinite and quartz are the main and ubiquitous components of this horizon. Small amount of gibbsite has also been detected in the clay fraction of a sample from the middle saprolite.

# Muscovite

Muscovite is intenssely weathered into kaolinite and has almost completely disappeared at the top of the saprolite. The SEM micrographs in Figure 9 show the partial pseudomorphic replacement of large fans of muscovite by packs of kaolinite layers. In the more reddish material, mica has almost completely disappeared. Goethite invades kaolinite pseudomorphs along cleavages and contours of the initial mica crystals (Figure 10), and numerous goethite granules are scattered in the material. Goethite contains high levels of phosphorous up to 2% P<sub>2</sub>O<sub>5</sub> (Table 6)

# Interstratified clays

X-ray diffraction analysis of the clay fraction from the middle saprolite show that the two types of interstratified clays observed in the saprock i.e. chlorite/vermiculite and biotite/vermiculite are altered into vermiculite, kaolinite and goethite (Figure 8). The chemistry of altered biotite/vermiculite booklets indicates that they consist of a complex mixture of packs of layers of biotite/vermiculite, vermiculite *sensu stricto*, kaolinite and probably goethite (Table 6). The

vermiculite-rich product contains substantial amounts of copper (up to 1.30% Cu) when located in the vicinity of Cu-bearing sulphides. A few of these pseudomorphs are replaced by a microcrystalline plasma composed of kaolinite and goethite which locally erases the original fabric (Figure 10).

The interstatified minerals have not been detected in the upper saprolite indicating that their vermiculite members have been completely altered into kaolinite and goethite (Figure 8). Gradual changes leading to the formation of the clay zone are apparent in this sample including bleaching (deferruginisation) of areas associated with a loss of fabric. In the leached areas, clusters of kaolinite fans and muscovite booklets co-exist with large areas of microscrystalline kaolinitic plasma containing isolated clay remnants. The plasmatic kaolinite does not contain any iron (Table 6).

#### Kaolinite

Two types of kaolinite co-exist in this horizon: a pseudomorphic kaolinite (devoid of iron) resulting from the alteration of muscovite and interstratitied minerals, and a microcrystalline kaolinite associated with goethite. Copper is detected in the goethite-rich plasmas (up to 1.40% CuO) suggesting that it is hosted by the iron oxyhydroxides.

#### Goethite and hematite

Goethite occurs as a weathering product of the interstratified minerals and in the microcrystalline plasma, in association with kaolinite.

#### Cu-sulphides

Some hand-specimens display veins of quartz associated with steel grey bothryoidal tenorite enclosed in massive apple-green malachite. Figure 11A shows the centripetal replacement of tenorite by malachite which displays two habits: a massive form usually found in contact with the Cu oxide, and a peripheral fibrous type. Sheaves of fibrous malachite replace (epigenise) adjacent clay booklets. Figure 11B shows biotite/vermiculite layers replaced by malachite along cleavages. Kaolinite booklets located between malachite fibers contain appreciable amounts of CuO (up to 3.10% of CuO) and no iron. This copper is either in the kaolinite structure or exists as malachite microdomains.

# Fe-sulphides

In the middle saprolite, Fe-sulphides (Fe-Cu sulphides or grain containing Cu-sulphide and pyrite) are completely pseudomorphed by mixtures of goethite and hematite that have rhythmically precipitated (Figure 12). The product contains excess silica which cannot be allocated to clays, and phosphorous is present in all the analyses with an average of  $1.80\% P_2O_5$  (Table 6). Copper is abundant with an average value of 2.1% (Fe<sub>2</sub>O<sub>3</sub>/CuO=33).

The microscrystalline plasma composed of kaolinite and goethite (k-g) which surrounds the sulphide relict is Cu-rich. Analyses of this type of plasma elsewhere in the material show a strong correlation between the Cu content and iron content (i.e. goethite content), and the distance from a weathered Cu-bearing sulphide. These observations suggest that copper is associated with goethite in the plasmas, and that Cu migrates short distances before being trapped by another phase.

#### Titanite

Titanite grains are completely pseudomorphed by microcrystalline kaolinite associated with Ti and P-rich phases (Figure 13 A). The scattered granules are anatase, and Ca and Ce-rich
phosphates. Similar grains are distributed around the saprolite minerals (Figure 13B); they probably result from the alteration of titanite beads similar to the ones observed in the saprock. The weathering of titanite proceeds through a dissolution stage followed by the synchronous precipitation of: 1) aluminium and silica as kaolinite; 2) titanium as anatase; 3) calcium and rare earths as phosphates. Phosphorous is supplied by the circulating solutions.

# Ti-Fe grains

Numerous Ti-Fe grains are scattered in the saprolite (Figure 13C). They could result from the alteration of ragged ilmenite grains, or anatase grains (from the weathering of titanite) with iron absorbed on surface (Anand and Gilkes, 1984).

The two types of Ti-rich granules can be traced up to the *in situ* loose pisolith horizon, and therefore understanding their origin and distribution is valuable for the interpretation of geochemical data obtained by LA-ICP-MS.



Figure 9. SEM micrographs (backscattered electron images). A-B: Pseudomorphosis of muscovite booklets into mica-kaolinite intergrades and kaolinite. m-k = mica-kaolinite intergrade; k = kaolinite; qtz = quartz.



Figure 10. SEM micrographs (backscattered electron images). A. Partial alteration of muscovite booklets into kaolinite. B. Alteration of interstratified mica/vermiculite booklet into kaolinite. m-k = mica-kaolinite intergrade; k = kaolinite; k-g = kaolinite + goethite; qtz = quartz; k-m/v = kaolinite + mica/vermiculite interstrified clay.



Figure 11. SEM micrograph (backscattered electron images). Alteration of the Cu-sulphides in the saprolite. A. Replacement of tenorite by malachite. B. Fibrous malachite replacing layers of biotite/vermiculite (b/v).



Figure 12. SEM micrograph (backscattered electron image). Sulphide replaced by colloform goethite and hematite.

k = kaolinite; v-k = vermiculite-kaolinite; k-g = kaolinite + goethite; g-h = goethite + hematite



Figure 13. SEM micrographs (backscattered electron images). A. Alteration of titanite into kaolinite, anatase and phosphates.

B. Anatase grains scattered in the saprolite. C. Ti-Fe granules scattered in microcrystalline plasma.

k = kaolinite; p = phosphates; an = anatase; qtz = quartz; m-k = mica-kaolinite.

Analysis	Mineralogy	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	K <sub>2</sub> O	CuO	P <sub>2</sub> O <sub>5</sub>	Total Oxides
1	Muscovite	45.6	0.5	29.7	2.2	1.9		10.3			90.2
2	Muscovite	45.4	0.6	29.5	2.2	2.1		10.7			90.4
3	Muscovite	47.1		31.5	2.0	1.8		9.9			92.3
4	Muscovite	47.2		30.7	2.2	2.0		10.3			92.4
5	K-m	46.5		37.7	0.9	0.5		3.9			89.4
6	K-m	47.5		38.5	0.8	0.6		3.8			91.2
7	Chl/v +malachite	26.2		21.9	22.1	19.0			2.6		91.8
8	Chl/v +malachite	27.2		22.4	22.1	19.5			2.6		93.9
9	V/chl	31.6		26.4	15.5	11.8					85.2
10	V-k	34.0		27.2	3.7	2.7			1.0		68.6
11	V-k+Fe	34.7		19.7	23.9	13.8	1.2		1.3		94.4
12	V-k+Fe	36.9		19.4	23.9	16.6	0.6		1.3		98.7
13	K-v+Fe	41.3		32.9	15.7	1.3			0.8	0.4	92.4
14	K-v+Fe	47.3		37.7	8.5	1.0			0.6		95.0
15	K-v+Fe	34.5		24.2	23.5	4.4			0.8		87.3
16	K-v+Fe	44.6		36.0	11.8	1.0					93.5
17	K-v+Fe	47.5		38.0	10.0	1.0			0.5		96.9
18	K-m/v+ Fe	42.1		31.9	15.0	0.9		3.9	0.7		94.4
19	K-m/v+ Fe	40.6		32.0	19.6	0.4		1.9			94.5
20	K-m/v+ Fe	47.1		38.1	8.9			0.5			94.7
21	K + g	23.9		18.5	37.9				1.4	0.8	82.5
22	K + g	26.9		20.2	37.8				1.4		86.2
23	K+ g	31.3		23.5	37.1				1.1	0.8	93.9
24	K + g	44.5		35.5	10.8						90.7
25	K+ g	47.8		38.2	8.4						94.3
26	K + g	17.8	0.5	22.2	34.4					2.2	77.1
27	Kaolinite	39.7		32.3	0.7						72.6
28	Kaolinite	40.2		32.6	1.3						74.0
29	Kaolinite	40.0		32.6	1.3						74.0
30	Kaolinite	45.3		37.1	0.6						82.9
31	Kaolinite	44.2		35.5	0.6						80.3
32	Kaolinite	44.0		35.5	0.5						80.0
36	Kaolinite	46.2		38.1	0.4						84.7
37	Kaolinite	46.6		38.7	0.6			0.9			86.8
38	Kaolinite	43.3		35.9	0.3						79.6
33	Kaolinitic plasma	31.7		25.2							57.0
34	Kaolinitic plasma	28.2		21.9							50.1
35	Kaolinitic plasma	37.1		29.5							66.6
39	Kaolinite+malachite	45.2		38.0					1.2		84.4
40	Kaolinite+malachite	47.3		39.6					2.5		89.4
41	Kaolinite+malachite	42.5		35.0					3.2		80.6
42	Kaolinite+malachite	33.6		26.9					1.3		61.8
43	Gibbsite+goethite	0.3	0.9	13.8	52.3					3.7	71.0
44	Gibbsite + goethite	0.3	0.7	11.3	45.0					2.8	60.1
45	Gibbsite + goethite	0.2	l	50.9	3.2					0.6	54.9
46	Gibbsite	5.1	İ	56.5	0.4	l					62.0
47	Goethite+hematite	8.2	l	3.0	69.0		0.4	1	2.4	1.8	84.8
48	Goethite+hematite	8.0	İ	2.8	70.0	l			2.2	1.9	84.9
49	Goethite+hematite	8.6	l	2.7	71.5		0.4	1	2.3	1.8	87.3
50	Goethite+hematite	9.0	1	2.9	73.0		0.3		1.9	2.1	89.2
51	Goethite+hematite	6.6	1	2.3	67.7		-		2.0	1.4	80.0
52	Clays + malachite	10.1	1	9.2	1.1	0.7			52.8		73.9
53	Clays + malachite	5.7	1	5.5	0.9	0.4			58.5	l	71.0

Table 6. Electron microprobe analyses (%) of the clays and associated minerals in the saprolite.

Chl/v = chlorite-vermiculite; K-v+Fe - kaolinite-vermiculite + Fe oxides; K+g = kaolinite + goethite

#### 3. 3. 3. Clay zone

The clay zone is characterised by the development of areas where the original texture has been destroyed.

The material sampled at the middle of the clay zone largely consists of kaolinite, gibbsite and goethite with small amounts of quartz. The clay fraction contains kaolinite, chlorite and small amounts of mica. Towards the top of the clay zone, gibbsite becomes increasingly abundant. Chlorite is still detected in the clay fraction. The material consists of large areas of a microscrystalline plasma composed of gibbsite and goethite with relict kaolinite and ilmenite crystals (Figure 15C). Small clusters of mica-kaolinite booklets are still present at this depth. Small crystals of gibbsite, generally less than 3  $\mu$ m in size replace kaolinite, or appear to form directly from mica-kaolinite crystals (Figure 14A and 14B).

The original fabric of the rock is locally lost (Figure 14C) with the formation of bleached gibbsitic plasma (gp) and iron-impregnated plasma (fp). However the presence of ferruginised kaolinite crystals in places mimics the original fabric in the iron-rich plasma (Figure 14D). The chemical compositions of the minerals and of the plasma areas are listed in Table 7. Copper was not detected in the goethitic plasma; however no sulphide relict was observed nearby.

Ilmenite is intensively weathered into anatase in this horizon. Figures 15 A and B show globular ilmenite remnants formed during the progressive dissolution of the Ti-mineral, surrounded by anatase. The EDAX analyses indicate up to 2 wt.%  $Al_2O_3$  in anatase.



Figure 14. SEM micrographs (backscattered electron images). A. Clusters of mica crystals in gibbsitic microcristalline plasma. B. Formation of gibbsite. C. Development of gibbsitic (gp) and ferruginised (fp) plasmas. D. Ferruginisation of a kaolinite pseudomorph. k-m = kaolinite-mica intergrade.



Figure 15. SEM micrographs (backscattered electron images). A and B. Weathering of ilmenite in anatase. C. Mica relicts and weathered ilmenite in the kaolinitic regolith. k-m = kaolinite-mica intergrade.



Figure 16. SEM micrographs (backscattered electron images). A. Al-Fe-rich segregations in the gibbsitic plasma. B. Ferruginised kaolinite booklet in an iron-rich segregation.

Analysis	Mineralogy	SiO	TiO	ALO3	Fe <sub>2</sub> O <sub>2</sub>	ΜσΟ	K <sub>2</sub> O	Total
1 mary 515	Willier alogy	5102	1102	111200	10203	mgo	1120	Oxides
1	Mica	45.9	-	31.3	2.0	1.8	10.6	91.6
2	Mica	47.2	-	30.2	2.0	2.2	10.7	92.3
3	Mica	47.2	-	30.3	2.0	2.1	10.8	92.4
4	Mica	46.2	0.5	30.0	1.9	2.1	10.1	90.8
5	Mica	45.8	-	30.0	1.7	1.7	9.4	88.7
6	Mica	45.6	0.7	31.9	2.1	1.9	10.2	92.3
7	Mica	46.5	-	35.2	1.2	0.7	10.2	93.8
8	Mica	45.6	-	29.6	2.0	2.0	9.7	88.9
9	Kaolinite + mica	43.1	-	34.5	0.7	-	0.7	79.1
10	Kaolinite + mica	44.1	-	32.0	1.3	1.1	5.0	83.6
11	Kaolinite	43.9	-	36.1	0.6	-	-	80.5
12	Kaolinite fan	44.6	-	36.4	0.9	-	-	81.7
13	Kaolinite fan	42.1	-	34.8	0.7	-	-	77.5
14	Kaolinite	44.4	-	36.6	0.6	-	-	81.7
15	Kaolinite fan	44.1	-	36.6	0.6	-	-	81.3
16	Kaolinite pseu	44.6	-	37.8	0.6	-	-	83.0
17	Kaolinite lge book	40.1	-	33.6	0.9	-	-	74.7
18	Kaolinite+Fe/oxides	38.7	-	35.2	10.0	-	-	83.8
19	Kaolinite + Fe/oxides	41.9	-	37.5	8.0	-	-	87.5
20	Gibbsite	0.8	-	61.2		-	-	62.0
21	Gibbsite	0.5	-	59.1	-	-	-	59.5
22	Gibbsite		-	57.7	0.6	-	-	58.2
23	Gibbsite		-	62.9	-	-	-	62.9
24	Plasma	9.5	3.2	35.2	2.8	-	-	50.8
25	Plasma	0.9	-	11.7	67.3	-	-	79.8
26	Plasma	1.4	-	13.4	64.7	-	-	79.5
27	Weathered ilmenite	-	79.7	2.1	3.7	-	-	85.5
28	Weathered ilmenite	-	81.3	2.2	3.7	-	-	87.2
29	Weathered ilmenite	-	76.5	2.4	5.3	-	-	84.2
30	Weathered ilmenite	-	71.7	1.7	5.8	-	-	79.1
31	Weathered ilmenite	-	61.6	2.2	7.7	-	-	71.4
32	Weathered ilmenite	-	75.0	1.5	4.1	-	-	80.5
33	Weathered ilmenite	-	77.3	1.4	4.1	-	-	82.9

Table 7. Microprobe analyses of the clay zone minerals (wt% oxides). (- : below detection limit)

Table 8. Microprobe analyses of the bauxitic plasmas (wt% oxides).

Analysis	Mineralogy	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O3	Fe <sub>2</sub> O <sub>3</sub>	MgO	Cr <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Total Oxides
1	Fe-Al plasma	-	-	3.4	73.4	-	-	-	76.8
2	Fe-Al plasma	-	0.68	14.2	59.8	1.6	-	-	76.3
3	Fe-Al plasma	6.7	1.61	23.3	47.9	-	-	-	79.4
4	M-k + gibbsite	23.7	3.32	38.6	3.6	-	0.8	4.6	74.6
5	Ferruginised kaolinite	-	0.64	13.2	58.6	-	-	-	72.4
6	Gibbsite + kaolinite	8.3	3.13	43.3	5.2	-	-	-	60.0
7	gibbsite	0.7	-	60.1	1.3	-	-	-	62.1
8	gibbsite	-	62.54	-	1.5	-	-	-	64.0

M-k = mica-kaolinite

# 3. 3.4. Bauxite zone

The bauxite is composed of gibbsite associated with variable amounts of goethite and hematite. The abundance of quartz has decreased drastically, and small amounts of kaolinite have also been detected in the clay fraction.

The process of differentiation of the plasma intensifies. Subspherical to spherical ferruginous concentrations with hazy contours develop in the gibbsitic plasma observed at the top of the clay zone (Figure 16A). The original fabric can still be recognised in the iron-concentrations. Figure 16B shows a few large ferruginised kaolinite booklets surrounded by Fe-Al microcrystalline plasma. The plasma contains aluminium ranging from 3 to 15% Al<sub>2</sub>O<sub>3</sub> (Table 8), and is locally enriched in chromium (up to 1.60%  $Cr_2O_3$ ).

# 3. 3. 5. Duricrust

The duricrust is characterised by the *in situ* induration of plasmic domains. Two types of duricrust have been recognised according to their morphologies (Anand, 1994): (i) fragmental, (ii) pisolitic. The fragmental duricrust is composed of angular reddish concretions up to a few centimeters in size set in a porous yellowish gibbsitic matrix. The fragments are indurated domains of ferruginised plasma of gibbsite, hematite and goethite. In the pisolitic duricrust the concretions become strongly indurated and form well-defined nodules and pisoliths with cortex (Figure 17A). The size of the nodules ranges from a few millimeters to a few centimeters. Small grains of quartz are ubiquitous and their distribution reflects the primary veining system.

The core is essentially aluminous but iron-rich compared with the cortex and matrix, with up to 35 % Fe<sub>2</sub>O<sub>3</sub>. It consists of a relatively homogeneous assemblage of fine-grained gibbsite and hematite, and maghemite may also be present. Higher magnification observations reveal a complex arrangement with circumvoluted gibbsite-rich areas engulfed in more ferruginous plasma (Figure 17B). Later gibbsite filled veins cross cut the whole material.

Scattered Ti-rich domains are abundant, and occur as two different types. The first is represented by ill-defined rounded spots of submicrometric to micrometric size, which besides Ti, might also contain Al and Fe (Figure 17C). The second type forms larger areas with sharper contours (Figure 17D) and differs by its chemical composition which is titano-ferric with small amounts of Mn and no Al (Table 9). The presence of Mn indicates that the latter are relict weathered ilmenite grains. The former are plasmatic domains *sensu stricto* with abundant anatase. Anatase has formed *in situ* from the weathering of titanite, and possibly also by microtransfers of titanium through the plasma, indicated by the extreme dissemination of the grains.

Cracks filled with gibbsite or gibbsite/goethite cross the core, and some of them disappear at the core/cortex boundaries. The cortex is less dark in colour, more porous, less ferruginous, and shows varying degrees of differentiation. Some nodules are surrounded by cutans with hazy contours resulting from the reorganisation of the enclosing plasma. The cortex of others display a complex banding which is usually considered a further stage in the evolution of the nodule (e.g. Nahon, 1991). The layers are distinguished by their Al/Fe ratio as enhanced by the backscattered electron images (Figure 17A). Ti-rich specks are abundant.

Optically nodules and pisoliths are set in a tan coloured and more friable matrix. It consists of a fine-grained plasma of gibbsite and goethite with scattered ferruginous concentrations and Tirich domains (Figure 17A).



Figure 16. SEM micrographs (backscattered electron images) of the bauxitic material. A. Al-Fe-rich segregations in the gibbsitic plasma. B. Ferruginised kaolinite booklet in an iron-rich segregation.



Figure 17. SEM micrographs (backscattered electron images). A. Al-Fe nodules set in an Alrich matrix. B. Close up of the core. C. Ti-rich domains in the core. D. Ilmenite relict in the core.

# 3. 3. 6. Loose pisoliths and nodules

The loose pisoliths and nodules display a dark reddish-brown to black core surrounded by a usually thin reddish-brown cortex (Figure 18A). They are rounded or more irregularly shaped, and their size ranges from 2 to 20 mm in diameter, and are highly magnetic. Compound nodules enclose numerous small pisoliths set in a light-brown matrix.



Figure 18. SEM micrographs (backscattered electron images). A. Section across a pisolith showing the iron-rich core surrounded by a simple cortex. B. Weathered ilmenite. C. Marbled texture of the core.

D. Ti-rich domain in a core.

The core is composed of a very heterogeneous Al-Fe microcrystalline plasma with an Fe<sub>2</sub>O<sub>3</sub> content ranging from 6.5 to 82 % (Table 10). The plasma consists of intricate areas or of fine marbling with various Al, Fe and Ti contents (Figures 18B and D). Silica is often detected (up to 2.4% SiO<sub>2</sub>) and is probably adsorbed onto goethite crystals. The cores contain hematite, goethite, maghemite, gibbsite, boehmite, corundum and quartz. Ti-rich domains are numerous, and are differentiated by their aspect and chemistry. They either form dendritic patches composed of Ti, Fe and Mn, or occur as specks and small rounded areas (<10  $\mu$ m) without Mn and consist of anatase microparticles finely intermixed with Al-Fe plasma. As discussed above, the former type results from the weathering of ilmenite whereas anatase grains come from titanite alteration.

The cortex – or cutans - is usually thin and simple, and present hazy boundaries with the core (Figure 18A). Gibbsite and goethite are more abundant than in the core. Rare clusters of

muscovite booklets and quartz grains have also been observed. The mica is slightly ferruginised and can show sign of alteration into kaolinite. Titanium rich minute particles are disseminated in the microcrystalline plasma. Silica content is slightly higher than in the core plasma (4% SiO<sub>2</sub>).

Analys is	Mineralogy	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	MnO	Total Oxides
1	Core-cutan	1.0		75.4	17.6	-	-	94.0
2	Core	0.8	1.3	63.2	30.0	-	-	95.3
3	Core	0.6	1.2	64.1	28.0	I	-	93.9
4	Al-matrix	3.7	3.9	60.8	4.5	-	-	72.9
5	Vein filling	2.5		79.5	4.6	-	-	86.6
6	Ti -rich domain	0.7	64.7	8.5	14.3	0.8	-	89.0
7	Ti-rich domain	-	1.1	55.4	40.1	-	-	96.6
8	Ti-rich domain	-	83.5	7.5	7.8	-	-	98.8
9	Ti-domain (weathered ilmenite)	-	54.7	-	38.2	-	2.4	95.3

Table 9. Microprobe analyses of the duricrust nodules and matrix (%). (- : below detection limit)

Table 10. Electron microprobe (EDAX) analyses (%) of the microcrystalline plasmas in the loose pisoliths.

(- : below detection limit)

Analysis	Mineralog	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	$V_2O_5$	Mn	K <sub>2</sub> O	Mg	Total Ovider
	<u>y</u>		44 7	7.0	10.1	0 70	0		U	Oxides
1	Core	-	41.7	7.0	40.4	0.72	1.4	-	-	91.7
2	Core	-	55.1	-	41.34	-	3.6	-	-	100.0
3	Core	-	54.1	-	41.3	-	3.4	-	-	98.8
	Core	-	57.5	1.4	39.6	-	1.4	-	-	100.0
4	Core	-	87.6	2.1	6.2	-	-	-	-	95.9
5	Core	-	82.9	2.7	14.3	-	-	-	-	100.0
6	Core	-	38.9	8.7	49.7	-	-	-	-	97.2
5	Core	1.4	0.9	64.3	8.5	-	-	-	-	75.0
7	Core	1.3	-	68.4	6.6	-	-	-	-	76.3
8	Core	1.2	2.9	44.6	46.1	-	-	-	-	94.7
9	Core	0.7	2.35	38.93	45.2	-	-	-	-	87.2
10	Core	2.5	2.14	44.9	36.6	-	-	-	-	86.0
11	Core	1.9	6.03	36.8	42.5	-	-	-	-	87.2
12	Core	0.8	2.0	41.7	47.8	-	-	-	-	92.3
13	Core	-	1.5	17.3	74.6	-	-	-	-	93.5
14	Core	-	-	17.0	79.5	-	-	-	-	96.5
15	Core	-	-	14.8	82.6	-	-	-	-	97.4
16	Core	0.8	2.4	37.3	53.7	-	-	-	-	94.2
17	Core	0.5	2.8	59.2	35.6	-	-	-	-	98.0
18	Cutan	4.0	2.4	62.0	10.7	-	-	-	-	79.0
19	Cutan	45.8	0.7	31.2	5.6	-	-	10.6	2.2	96.0
20	Cutan	45.0	-	35.1	4.2	-	-	8.6	2.5	95.3

# **3. 4. Determination of trace elements in regolith material by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)**

# 3. 4. 1. Introduction

A total of 97 LA-ICP-MS analyses have been performed. The selection of the material was based on the mineralogical characterisation of the regolith units. Samples of saprolite, clay zone, pisolitic duricrust and loose pisoliths were analysed:

- Saprolite: 07-0436 (middle saprolite, WBC25) and 07-0420 (upper saprolite, WBC21);
- Clay zone: 07-0419 (middle horizon, WBC21);
- Duricrust: 07-0433 and
- Loose pisoliths: 07-0402.

The general description of the technique and the data reduction method are described in the first section of the report. The data acquisition and reduction procedure for each regolith unit is detailed in Appendix 2. The mineralogy and chemical composition of the regolith material is documented in Section 3. 3.

# 3. 4. 2. Saprolite

Thirty LA-ICP-MS analyses were performed on clay and iron oxide areas of the saprolite. The location of the analyses in the sulphide relicts and adjacent clays and in clays booklets in the saprolite are shown on Figure 19. When viewed with the SEM, the pits made in the clays with the 29  $\mu$ m spot are very clean. The larger pits have been produced by the 50  $\mu$ m probe when analysing for gold. The calculated concentrations are given in Tables 11, 12 and 13.



Figure 19. A. Location of LA-ICP-MS analyses in a sulphide relict and clays. B. Ablation pits in large booklets of vermiculite-kaolinite intergrades associated with goethite (v-k-g).

# Hematite and goethite in sulphide pseudomorphs

LA-ICP-MS spectra show low amplitude compositional variations, which are attributed to the fine rhythmic mineralogical layering, i.e. the relative abundance of goethite and hematite in the alternating bands of the sulphide pseudomorphs. (Figure 20A). The goethite–hematite layers contain abundant copper and arsenic (up to 2.6% Cu and 0.3% As). Vanadium, Cr, Zr, Ti, Mn and Zn contents are high, respectively to 689 ppm, 585 ppm, 148 ppm, 1158 ppm, 247 ppm and 114 ppm. The iron oxides contain high levels of Bi (to 232 ppm), Mo (to 177 ppm), Pb (to 127 ppm) and W (to 61ppm). Small concentrations of Sb are also detected (up to 8 ppm Sb). About 1 ppm of Ag is present in the iron oxides. Gold has been detected in three sites with a concentration of 80, 130 and 140 ppb (Table 12). The broad peak observed on one of the time-resolved spectra suggests that gold occurs in this sample as a particle about 0.5  $\mu$ m wide (Figure 20B).

#### Vermiculite, kaolinite and associated goethite

Vermiculite, kaolinite and goethite have been analysed in the vicinity of a sulphide pseudomorph and further away from it in order to capture element migration patterns. The vermiculite-kaolinite intergrades give two types of responses depending on the layer interstratification pattern. A regular and fine interstratification produces roughly constant spectra (Figure 20C), whereas interstratifications of thick packs of layers give a differentiated signal (Figure 20D). In the later case, the distribution of Mg and silicon indicates that the material can be roughly divided in depth into three units. The Mg-rich and Mg-poor slices are respectively diagnostic of vermiculite-rich and kaolinite-rich clays. In addition, the mineralogical study shows that the kaolinitic clay resulting from the weathering of the vermiculite contains goethite. The surface and the bottom of the pit are mainly composed of kaolinite and goethite, whereas vermiculite is abundant in the medium part. The pack of vermiculitic layers is about 10  $\mu$ m thick (ablation speed: 0.5  $\mu$ m /sec).

#### Zn and Mn

Zinc and Mn are abundant in the vermiculitic clay with values up to 985 ppm Zn and 1533 ppm Mn. The concentrations calculated on sliced signals indicate that the ratios  $Mg_{total}/Mg_{sliced}$ ,  $Zn_{total}/Zn_{sliced}$ ,  $Mn_{total}/Mn_{sliced}$  are remarkably constant ranging from 1.60 to 1.70. The same silica concentration (internal standard) has been used to calculate the concentrations in the total clay and in the slices because the reaction vermiculite  $\rightarrow$  vermiculite + kaolinite + goethite roughly maintains the silica level. The kaolinite-goethite slices (Mg lower) are relatively depleted in Zn and Mn. However, Zn and Mn contents increase with the goethite abundance, indicating that the iron oxide is trapping these elements. Figure 21 illustrates the strong correlation between Zn and Mn contents in the intergrade clays and the Mg content i.e. the vermiculite abundance.

These observations suggest that: (i) Zn and Mn, along with Mg, occur as interlayer and/or octahedral cations in the vermiculite structure; (ii) Mg, Zn and Mn are released into the microenvironment during the alteration of vermiculite but are not incorporated into kaolinite; (iii) Zinc, Mn and Mg have the same primary host chlorite.

#### <u>Cu</u>

Copper concentration (up to 1.50% Cu), increases with the vermiculite content. Kaolinite-goethite assemblages also contain high Cu levels, which increase with the goethite content and closeness to the sulphide relict. Up to 4 % Cu is detected in a rim composed roughly of 50% kaolinite and 50% goethite along a sulphide relict, whereas microcrystalline kaolinitic plasmas which do not contain goethite are characterised by lower Cu contents (up to 670 ppm).

Vermiculite and goethite host Cu, the former in its interlayer and the latter either in its structure or absorbed on crystal surfaces. Once released by the dissolution of sulphides, Cu is trapped in the immediate environment by corrensite (vermiculite precursor) or vermiculite and goethite. Copper is remobilised by the weathering of vermiculite into kaolinite and goethite, and is subsequently partly retained in goethite.

#### Bi, W, Mo, Pb and As

Bismuth, W, Mo and As are concentrated in the kaolinite-goethite slices of the weathered vermiculite booklets located near the sulphide pseudomorphs (Figure 20E). These elements, not present in the vermiculite, are scavenged by goethite, and are extremely abundant in the rim of goethite-kaolinite microcrystalline plasma: Bi (337 ppm), W (97 ppm), Mo (210 ppm), Pb (188 ppm) and As (0.5%). A comparison with the lower concentrations obtained on colloform goethite-hematite indicates that goethite preferentially accumulates Bi, W, Mo, Pb, As and Cu. Kaolinite does not bear any of these elements.

#### Ti, V and Cr

Titanium, V and Cr are distributed evenly in the vermiculitic and kaolinitic clays (Figure 20E). Titanium contents are highly variable ranging from 65 to 3600 ppm. The distribution of Ti shows that high concentrations are always caused by "inclusions" i.e. grains of anatase scattered in the ablated volume. Vanadium and Cr levels are high respectively up to 120 ppm and 185 ppm respectively.

#### Zr and U

Zirconium and U are relatively depleted in the vermiculitic material (Figure 20E) and concentrated in goethite-rich material (Figure 20E).

#### Au and Ag

Neither Ag nor Au were detected in the clays but are enriched in the goethite associated with them. Goethite contains higher Ag (690 ppb) and Au (270 ppb) levels than the goethite-hematite mixture. (These high values are lowered by the presence of kaolinite).

#### Muscovie-kaolinite intergrades and kaolinite

The mica-kaolinite intergrades are relatively poor in all isotopes. However, it contains abundant Ba (0.2%), V (220 ppm), Cr (110 ppm) and Ti (520 ppm), and Mn is also present (48 ppm). Barium, and V display similar spatial distributions and are probably contained in the mica structure (Figure 20F). The antagonist Cr distribution at the beginning of the ablation suggests that this element also exist as micro-inclusions (Figure 20F). Kaolinite resulting from the weathering of the intergrades contains similar V and Cr levels (Figure 22A). Vandium, Cr, U, Th, Bi, Mo and W are associated with anatase grains scattered in the plasma.

#### Anatase

Anatase grains result from weathering of abundant titanite and ilmenite. The grain shown on Figure 22B is about 10  $\mu$ m in size. The isotopic data show that titanium is associated with Zr, U, Th, Bi, W, Mo, and V. Zirconium, W, U and Th are commonly present in titanite, and are likely to be residual in the alteration product. Similarly V is present in ilmenite.

#### 3. 4. 3. Clay zone

Eleven LA-ICP-MS analyses were performed on the clay zone minerals. The analyses were mostly unsuccessful. Nine out of eleven ablations went through the sample after only a few seconds. The signals are similar to the ones obtained on kaolinite shown on Figure 22C. The short <sup>29</sup>Si response is also abnormally low. The spectra would represent the signature of a sample about 5  $\mu$ m thick under the ablation conditions (5Hz, 100mJ/pulse). The material - which is about 30  $\mu$ m thick - has been pulverised after a very short time under these conditions. Similar patterns have been obtained when ablating very hydrated clays such as hisingerite while experimenting on a variety of different materials for this project. The water content and the crystallinity of the mineralogical phases probably affect the ablation. The only two readable analyses were obtained on large booklets of kaolinite resulting from the weathering of muscovite (Figures 22 E and F). It is likely that this type of kaolinite is "better crystallised" than plasmatic microcrystalline kaolinite. Ablating thicker samples or sawn blocks might solve the problem. Experimental work is still needed to further define the ideal ablation conditions for different types of regolith material.

The kaolinite is similar to the kaolinite from the saprolite (Figure 22D). It contains high levels of V (100 ppm) and Cr (170 ppm), about 10 ppm Mo, and 0.3% Ti present as microgranules. Vanadium, Zr and Mo are associated with the Ti grains.



Figure 20. LA-ICP-MS time resolved spectra of selected isotopes in saprolite minerals. A and B. Hematite and goethite in a sulphide relict. C. Finely layered vermiculite-kaolinite intergrades. D and E. Vermiculite-kaolinite intergrades; the signals are decomposed into 3 slices. F. Muscovite-kaolinite intergrades.

Analyses	Mineralogy	<sup>26</sup> Mg	<sup>29</sup> Si	<sup>49</sup> Ti	<sup>51</sup> V	<sup>52</sup> Cr	<sup>55</sup> Mn	<sup>65</sup> Cu	<sup>66</sup> Zn	<sup>75</sup> As
0436-1 (a)	V + K + G	5.23	40.14	419	123	62	888	11746	614	314
0436-1 (b)	Vermiculite-rich	8.83	40.14	453	109	69	1483	15657	986	232
0436-1 (c)	K + G	0.67	40.14	302	107	40	147	6326	158	389
0436-2 (a)	K + V + G	1.12	45.29	384	131	58	200	6727	139	437
0436-2 (b)	Vermiculite-rich	3.86	45.29	349	110	69	601	7729	401	188
0436-2 (c)	K + G	0.15	45.29	377	123	56	50	5205	39	413
0436-3	K + G rim	0.26	28.32	1639	967	512	353	39855	186	4969
0436-4	Sulphide relict	0.17	9.54	1159	689	585	248	26477	114	3185
0436-5	Sulphide relict	0.11	8.19	969	589	443	248	23015	92	2523
0436-6	V + K + G	4.92	40.14	2391	88	185	517	7984	410	48
0436-7	V + K + G	1.87	38.37	106	54	82	205	4116	176	30
0438-8	V + K + G	2.32	38.37	133	57	78	256	4574	202	25
0436-10	V + K + G	1.77	38.37	167	56	77	195	3766	136	32
0436-11	K + G	0.78	48.08	104	55	57	135	2628	88	0
0436-12	K + G	0.55	48.08	3629	68	65	90	2037	75	15
0436-13	V + K + G	1.47	45.29	102	22	22	306	2640	128	3
0436-14	K + G	0.62	48.08	2136	60	40	150	1473	42	41
0436-15	V + K + G	1.89	38.37	741	48	36	441	5134	222	58
0436-16	V + K + G	6.22	40.14	259	82	122	1533	14490	965	29
0436-18	K + G	0.42	48.08	2639	177	94	88	5290	50	632
0436-19	K	0.15	54.64	566	54	62	15	678	21	34
0436-20	К	0.16	54.64	205	53	36	20	513	19	59
0436-21	V + K + G	1.72	38.37	65	50	91	199	2742	142	0
0436-22	V + K + G	1.53	38.37	1779	50	73	182	2479	107	0

Table 11. LA-ICP-MS analyses of the saprolite minerals. (Sample 07-0436). All data in ppm, except for Mg (% element) and Si (wt. % oxides). Internal standard: microprobe analyses and stoichiometric SiO<sub>2</sub> values normalised to 100%. V = vermiculite; K = kaolinite; G = goethite.

Analyses	Mineralogy	<sup>90</sup> Zr	<sup>95</sup> Mo	<sup>121</sup> Sb	<sup>138</sup> Ba	<sup>184</sup> W	<sup>208</sup> Pb	<sup>209</sup> Bi	<sup>238</sup> U
0436-1 (a)	V + K + G	34	15	1	3	9	12	18	1
0436-1 (b)	Vermiculite-rich	16	10	1	3	6	8	15	0
0436-1 (c)	K + G	57	19	1	3	11	15	25	1
0436-2 (a)	K + V + G	66	23	1	3	12	16	28	1
0436-2 (b)	Vermiculite-rich	31	12	1	3	6	8	12	1
0436-2 (c)	K + G	96	23	1	2	12	14	26	1
0436-3	K + G rim	247	210	14	36	97	188	337	13
0436-4	Sulphide relict	148	152	9	26	68	127	221	10
0436-5	Sulphide relict	136	125	6	22	59	93	169	9
0436-6	V + K + G	24	5	0	11	5	7	9	1
0436-7	V + K + G	13	2	0	2	1	3	3	0
0438-8	V + K + G	11	2	0	3	1	3	3	0
0436-10	V + K + G	16	4	0	6	1	3	4	0
0436-11	K + G	74	0	0	8	1	2	1	0
0436-12	K + G	58	5	0	5	13	9	9	1
0436-13	V + K + G	3	0	0	9	0	0	0	0
0436-14	K + G	137	2	0	526	102	5	6	1
0436-15	V + K + G	24	5	1	11	3	5	7	1
0436-16	V + K + G	29	2	0	2	1	3	3	0
0436-18	K + G	60	26	2	91	18	18	36	1
0436-19	K	26	1	0	45	1	3	2	1
0436-20	K	11	0	0	70	1	3	3	4
0436-21	V + K + G	10	0	0	2	0	2	0	0
0436-22	V + K + G	29	2	0	4	2	4	4	0

#### Table 12. LA-ICP-MS analyses of the saprolite (Sample 07-0436).

All data in ppm, except for Al and Si (wt. % oxides), Fe (% element) and Au and Ag (ppb). Internal standard: microprobe analyses and stoichiometric  $Al_2O_3$  values normalised to 100%. V = vermiculite; K = kaolinite; G = goethite.

Analyses	Mineralogy	<sup>27</sup> Al	<sup>29</sup> Si	<sup>49</sup> Ti	<sup>55</sup> Mn	<sup>57</sup> Fe	<sup>91</sup> Zr	<sup>93</sup> Nb	<sup>95</sup> Mo	<sup>98</sup> Mo
0436-40	Sulphide relict	2.9	8.2	949	245	58.9	161	2	177	174
0436-41	Sulphide relict	3.5	9.1	826	216	48.4	169	2	130	129
0436-43	Sulphide relict	3.3	9.5	1058	296	57.2	175	2	161	160
0436 42	K+G rim +sulphide	11 5	20.3	010	200	13.0	1/0	2	115	112
0430-42	relict	11.5	20.5	919	290	43.0	149	2	115	112
0436-45	Mica	31.9	46.7	3587	75	7.5	105	5	21	21
0436-46	V+K+G	20.0	37.5	2494	137	11.6	88	3	26	25
0436-47	V+K+G	20.0	37.9	705	1212	12.1	26	1	4	4
0436-48	V+K+G	20.0	36.6	479	822	8.8	104	1	4	4
0436-49	V+K+G	20.0	34.4	1328	391	11.9	64	1	25	24
0436-50	V+K+G	20.0	35.4	537	853	21.7	55	1	40	40

Analyses	Mineralogy	<sup>107</sup> Ag	<sup>109</sup> Ag	<sup>115</sup> In	<sup>181</sup> Ta	<sup>184</sup> W	<sup>197</sup> Au	<sup>209</sup> Bi
0436-40	Sulphide relict	1070	1040	7	0	61	80	232
0436-41	Sulphide relict	1020	1010	6	0	56	130	198
0436-43	Sulphide relict	920	920	7	0	65	140	213
0436-42	K + G rim + sulphide relict	690	690	6	0	53	270	168
0436-45	Mica	100	100	1	0	15	10	22
0436-46	V + K + G	130	110	1	0	17	20	31
0436-47	V + K + G	10	0	0	0	3	0	7
0436-48	V + K + G	80	80	1	0	3	10	6
0436-49	V + K + G	130	120	1	0	14	30	32
0436-50	V + K + G	200	200	2	0	20	90	57



Figure 21. Binary plot Mg versus Cu and Zn+Mn. v + k +g = vermiculite + kaolinite + goethite assemblage; k + g = kaolinite + goethite; h + g = hematite + goethite.

Table 13. LA-ICP-MS analyses of the upper saprolite minerals (Sample 07-0420). All data in ppm, except for Mg (% element) and Si (wt. % oxides). Internal standard: microprobe analyses and stoichiometric  $SiO_2$  values normalised to 100%.

Analyses	Mineralogy	<sup>26</sup> Mg	<sup>29</sup> Si	<sup>49</sup> Ti	<sup>51</sup> V	<sup>52</sup> Cr	<sup>55</sup> Mn	<sup>65</sup> Cu	<sup>66</sup> Zn	<sup>75</sup> As
0420-1	Mica-kaolinite	7683	52.0	527	225	114	49	21	7	1
0420-10	V+k+g	13478	38.4	96	65	83	208	4270	126	36
0420-3	Kaolinite	376	55.0	4261	84	196	0	67	9	3
0420-4	Kaolinite	370	55.0	7226	106	237	0	66	6	5
0420-5	Kaolinite	359	55.0	3657	80	184	0	64	9	9
0420-6	Kaolinite	221	55.0	557	33	89	0	41	5	2
0420-7	Kaolinite	349	55.0	7198	97	188	28	82	8	1
0420-8	Kaolinite	289	55.0	4280	83	186	1	69	6	10
0420-11	Kaolinite	303	55.0	2599	80	174	1	80	5	4
0420-13	Kaolinite	399	55.0	9926	134	286	1	85	7	15
0420-14	Kaolinite	305	55.0	5870	130	232	0	80	7	11
0420-15	Kaolinite	274	55.0	58	60	137	0	62	5	7
0420-16	Kaolinite	506	55.0	60	61	155	0	62	13	0
0420-17	Kaolinite	820	55.0	8461	136	246	2	88	9	4
0420-20	Kaolinite	463	55.0	9211	151	211	2	66	7	31
0420-21	Kaolinite	271	55.0	2488	70	156	0	42	8	9
0420-22	Kaolinite	335	55.0	2833	105	177	0	50	9	22
0420-2	Kaolinite	484	55.0	13343	150	257	1	49	8	15
0420-12	Kaolinite	364	55.0	20807	209	422	1	71	9	13
0420-23	Kaolinite	406	55.0	29869	460	524	0	77	10	100
0419-1	Kaolinite	327	55.0	3210	100	173	0	76	5	8

Analyses	<sup>90</sup> Zr	<sup>95</sup> Mo	<sup>121</sup> Sb	<sup>138</sup> Ba	<sup>140</sup> Ce	<sup>184</sup> W	<sup>208</sup> Pb	<sup>209</sup> Bi	<sup>232</sup> Th	<sup>238</sup> U
0420-1	8	1	1	2164	0	5	1	0	0	0
0420-10	28	5	0	5	0	2	5	5	0	0
0420-3	245	7	3	6	1	1	2	0	11	2
0420-4	252	13	5	6	2	2	3	0	11	3
0420-5	143	6	3	4	5	1	5	0	5	1
0420-6	23	1	0	2	0	0	1	0	2	0
0420-7	98	9	4	3	0	1	3	0	5	1
0420-8	42	8	3	3	0	1	3	0	3	1
0420-11	187	5	2	3	1	1	2	0	6	2
0420-13	316	15	7	13	28	2	21	1	12	3
0420-14	77	10	5	10	17	2	15	0	5	1
0420-15	7	0	0	2	0	0	2	0	0	0
0420-16	5	1	0	2	0	0	1	0	0	0
0420-17	221	13	6	99	10	6	12	1	8	2
0420-20	207	27	10	48	1	4	9	6	10	2
0420-21	179	6	3	2	1	0	2	0	4	1
0420-22	40	10	3	4	0	0	2	0	3	1
0420-25	57	10	4	3	0	1	3	1	3	1
0420-2	258	20	7	6	1	3	3	1	14	3
0420-12	260	35	15	6	2	5	6	1	17	5
0420-23	309	82	23	4	1	6	13	2	24	5
0419-1	57	10	4	3	0	1	3	1	3	1



Figure 22. A, B, C, and D. LA-ICP-MS time resolved spectra of selected isotopes in mineralogical assemblages of the saprolite and clay zone. A. Kaolinite in saprolite. B. Kaolinitic clay containing an anatase grain in saprolite; the end of the signal represents the ablation of the thin section glass. C. Kaolinite in clay zone. D. Large kaolinite crystals in clay zone. E and F. SEM micrographs (backscattered electron images) showing ablation pits in kaolinite booklets.

## 3. 4. 4. Pisolitic duricrust

Thirty-two LA-ICP-MS analyses were performed on clays and iron oxide areas of the pisolitic duricrust sample. Figure 23 shows the location of some analyses (depth profiles) performed in a nodule (core and cortex) and surrounding matrix. The calculated isotopic concentrations of the different phases are listed in Tables 14 and 15.



Figure 23. SEM micrograph (backscattered electron image) of Al-Fe nodules cemented by a more aluminous matrix in the pisolitic duricrust. The numbers indicate the location of the LA-ICP-MS analyses.

The mineralogical differences observed in the core, cortex and internodular matrix are reflected in their isotopic signatures.

#### Core

The core consists of a microcrystalline assemblage of gibbsite, hematite and goethite. The even isotopic responses for Al and Fe indicate that the plasma is fairly homogeneous (Figure 24A). High levels of Cr (up to 410 ppm), V (420 ppm), and Mo (up to 35 ppm) are present (Table 14). Titanium is abundant (up to 1.4 %) and occurs in the small domains observed with the SEM. High levels of W (up to 100 ppm) are associated with these Ti-rich areas.

#### Cortex

The cortex layers consist of gibbsite and goethite; hematite is not present. Goethite is associated with high levels of Cu (to 130 ppm), As (to 87 ppm), V (to 680 ppm), P (up to 280 pp) and Mo (to 96 ppm). Chromium concentrations, similar to those found in the core plasma, appear to be independent of the nature of the iron oxides. Tungsten and Ti show similar distributions in the core and cortex indicating that W is hosted in the Ti-rich phases observed with the SEM (Figure 24B).

#### Internodular matrix

The internodular matrix is generally more gibbsitic than the nodule cortex, i.e. is relatively depleted in goethite. Figure 24C shows some isotopic responses along a transect from the cortex of a nodule to the matrix. Copper, As, P and Mo trends are similar in the matrix and cortex, but the concentrations are

lower in the matrix. The isotopic spatial distributions also indicate that V is hosted by goethite, whereas Cr occurs independently. Cerium is abundant (170 ppm) and occurs as micrometric "inclusions" - probably of cerianite - in the gibbsitic plasma.

### Ti-rich domains

The two types of Ti-rich domains described in the mineralogical study present distinct isotopic signatures. They are present in the core, cortex and internodular matrix, and appear as scattered bright specks on the SEM micrograph (BSE) shown on Figure 23. The first type (Ti-Al-Fe) consists of anatase in an Al-Fe plasma and results from the weathering of titanite, whereas the second type is weathered ilmenite (Ti-Fe-Mn). The isotopic signatures of the two types of Ti-rich "inclusions" reflect their respective histories. Some elements are indicators of their origin and some are related to weathering processes.

The isotopic responses obtained on a Ti-Al-Fe domain, about 10  $\mu$ m thick, located in the cortex of a nodule, indicate that anatase hosts V, W, Bi and Ta, whereas Mo is associated with the goethite of the plasma (Figure 24D and E). The concentrations of these isotopes calculated on the Ti-rich slice to enhance the responses are high: 885 ppm V, 235 ppm W, 271 ppm Ta and 56 ppm Bi. High levels of Zr are also detected (>590 ppm). Tungsten, Zr and Ta, which are commonly found substituting for Ti in fresh titanite, are residual.

Ilmenite grains are replaced by a mixture of anatase and goethite during weathering. Figure 24F shows the isotopic responses obtained on weathered ilmenite in the internodular matrix. Residual elements inherited from ilmenite, and elements associated with goethite can be distinguished. Manganese (1.6 %), Mg (600 ppm) and Co (1.9 ppm) are residual in the cortex and internodular grains. The nature of the elements trapped by goethite depends on the location of the grains. The cortex grains contain very high levels of Zn (1070 ppm), Cu (226 ppm), As (120 ppm), Mo (106 ppm), W (540 ppm), Bi (104 ppm), and Pb (70 ppm) and V (1180 ppm). The internodular grains contain marginal concentrations of Zn, Cu, As,Pb and Bi (<30 ppm) and lower levels of Mo (59 ppm), W (65 ppm) and V (620 ppm). This chemical distinction, which has also been observed in the surrounding plasmas, results from element transfers during the differentiation of the weathered material into ferruginised and bleached domains.

# Gold and silver

Gold has been detected in the matrix, cortex and core. Figure 25A shows the responses of Au and other isotopes in the matrix plasma containing a Ti-rich domain on surface. The responses are very diluted because a 50  $\mu$ m probe was used to ablate the material. The Au distribution indicates that it is not absorbed on the surface of anatase in the Ti-rich grain but is located in the Al-Fe plasma. The response is very ragged with important intensity variations. The Au concentration in the ablated volume is 380 ppb whereas it reaches almost 1 ppm in the bottom of the pit. The comparison of Ta and Au spectra confirms that there is no Ta oxide interference (<sup>181</sup>Ta<sup>16</sup>O=<sup>197</sup>Au). Gold is likely to occur as individual particles in the plasma.

Similar levels (few hundreds ppb) of silver have been detected. However the comparison of  ${}^{93}$ Nb and  ${}^{109}$ Ag spectra strongly suggests oxide interference ( ${}^{93}$ Nb ${}^{16}$ O =  ${}^{109}$ Ag), and therefore the data have been disregarded (Figure 25B).

# Pollution

Figure 25C shows the isotopic responses obtained when ablating the material of the core along a transect. Tin, In, Sb, Pb, and Bi contamination is important. Tungsten, however is clearly associated with anatase, and therefore can be considered.



Figure 24. LA-ICP-MS time resolved spectra of selected isotopes in mineralogical assemblages in the pisolitic duricrust. A. Core. B. Cortex. C. Scan analysis from cortex to internodular matrix. D and E. Cortex of a pisolith with a Ti-rich domain at the surface of the pit. F. Ti-Fe-Mn speck in the matrix.

Table 14. LA-ICP-MS analyses of the pisolitic duricrust. (Sample 07-0433). All data in ppm, except for Au and Ag (ppb), Al and Si (wt % oxides), Ti and Fe (wt % elements). Internal standard: stoichiometric  $Al_2O_3$  values normalised to100%.

Analyses	Mineralogy	<sup>27</sup> Al	<sup>29</sup> Si	<sup>49</sup> Ti	<sup>55</sup> Mn	<sup>57</sup> Fe	<sup>91</sup> Zr	<sup>93</sup> Nb	<sup>98</sup> Mo	<sup>109</sup> Ag	<sup>181</sup> Ta	<sup>184</sup> W	<sup>197</sup> Au	<sup>209</sup> Bi
433-40	Core	59.0	7.3	1.53	4	21.9	224	17	19	30	1.24	74.04	0	4.74
433-41	Core	58.0	0.9	1.4	3	27.0	239	13	26	40	1.05	81.48	0	3.06
433-42	Cortex	71.0	2.0	1.6	16	16.9	222	17	50	40	1.34	75.72	90	10.24
433-43	Cortex	84.0	7.3	2.53	2	2.6	461	44	49	270	1.8	94.62	30	9.45
433-44	Cortex	70.0	4.5	5.04	22	12.2	419	74	114	170	4.22	113.14	100	11.94
433-45	Matrix	72.0	3.2	11.54	34	4.5	374	129	55	90	5.98	55.66	380	3.6
433-45 slice	Matrix	88.0	4.1	1.37	6	3.4	250	17	41	70	1.01	46.19	950	2.89
433-46	Matrix	59.0	4.8	4.41	1140	20.0	233	41	139	380	2.66	114.1	200	19.93
433-47	Matrix	73.0	5.6	2.86	18	11.6	226	33	110	110	2.11	114.53	80	7.06
433-48	Core	43.0	3.1	2.77	8	34.8	322	32	88	320	1.81	118.91	360	9.34
433-49	Core	56.0	5.7	3.8	6	22.9	559	44	70	360	3.13	137.88	330	8.79
433-50	Cortex	53.0	27.0	1.78	10	12.0	251	20	47	170	1.31	87.82	190	9.49
433-53	Core	34.0	4.9	22.52	3	17.6	598	151	86	150	7.37	183.86	120	20.61

Table 15. LA-ICP-MS analyses of the pisolitic duricrust (Sample 07-0433). All data in ppm, except for Al and Si (wt. % oxides), Fe and Ti (% element). Internal standard: stoichiometric  $Al_2O_3$  values normalised to100%.

Mineralogy	Analyses	<sup>24</sup> Mg	<sup>27</sup> Al	<sup>29</sup> Si	<sup>31</sup> P	<sup>47</sup> Ti	<sup>51</sup> V	<sup>53</sup> Cr	<sup>55</sup> Mn	<sup>57</sup> Fe	<sup>59</sup> C 0
Core	0433-1	37	67.0	1.1	50	0.83	363	355	2	21.0	1
Core	0433-2	35	70.0	1.7	75	0.87	425	411	2	18.9	1
Core	0433-3	33	61.0	0.9	94	1.46	352	348	1	25.5	1
Cortex	0433-4	17	77.0	0.9	277	0.82	682	321	0	14.7	0
Cortex	0433-5	31	85.0	2.6	233	1.75	319	276	4	6.4	1
Cortex	0433-6	27	89.0	2.2	270	1.55	242	249	5	4.5	0
Cortex	0433-11	59	78.0	4.1	279	2.79	534	239	532	9.1	0
Matrix slice	0433-14	185	86.0	7.7	145	1.13	237	236	7	3.2	0
Ti speck in cortex	0433-7	119	23.5	1.2	235	44.34	773	131	1	1.7	0
Ti-slice	433-7 (2)	124	11.1	0.6	219	53.08	885	91	1	1.3	0
Ti speck in cortex	0433-9	327	13.0	0.1	819	35.42	1184	515	16885	19.6	8
Ti speck in cortex	0433-10	307	12.0	0.2	787	33.92	1114	458	15492	20.4	8
Ti speck in matrix	0433-8	534	23.0	0.2	128	33.19	624	161	8433	15.5	17
Ti-slice	433-8 (2)	605	17.0	0.2	99	38.62	538	137	9480	14.2	19
Ti grain in matrix	0433-12	230	11.2	0.1	169	35.56	268	221	4170	22.2	9

Analyses	60 Ni	<sup>65</sup> Cu	<sup>66</sup> Zn	<sup>75</sup> As	<sup>98</sup> Mo	<sup>121</sup> Sb	<sup>137</sup> Ba	<sup>140</sup> Ce	<sup>181</sup> Ta	<sup>184</sup> W	<sup>208</sup> Pb	<sup>209</sup> Bi
0433-1	13	9	4	13	25	0	2	3	1	90	19	6
0433-2	27	6	3	17	35	0	2	4	1	89	18	10
0433-3	12	18	2	16	28		2	5	1	104	25	7
0433-4	5	114	2	88	54	1	1	1	0	69	15	12
0433-5	9	117	3	38	79	2	1	1	1	108	5	4
0433-6	9	72	6	33	66	0	1	25	1	97	4	5
0433-11	12	132	42	53	97	2	1	1	2	127	10	12
0433-14	6	81	26	15	30	1	12	174	1	59	0	11
0433-7	2	36	11	24	33	4	2	22	226	215	45	51
433-7 (2)	2	25	12	22	29	4	1	5	272	236	47	57
0433-9	5	205	1077	123	106	17	8	6	17	549	71	104
0433-10	2	226	904	110	106	17	7	6	19	461	71	101
0433-8	6	36	11	41	64	2	1	3	12	77	20	8
433-8 (2)	5	27	12	27	58	1	1	4	14	66	18	6
0433-12	7	20	17	33	25	1	0	1	6	60	20	10



Figure 25. LA-ICP-MS time resolved spectra of selected isotopes in mineralogical assemblages in the duricrust and loose pisoliths. A. Gold and other selected isotopes responses in the internodular matrix. B. Fake Ag anomaly in a Ti-rich speck in the cortex. C. Spectra (transect) showing contamination associated with Sn grains. D. Loose pisolith core. E. Loose pisolith cortex. F. Anatase grain in a loose pisolith cortex.

### 3. 4. 5. Loose pisoliths and nodules

A total of twenty-four LA-ICP-MS analyses performed on the core and cortex of loose pisoliths (Sample 07-0402) are presented. Figure 26 shows the location of some analyses (depths profiles and transects) performed in the core and cortex of two nodules. The calculated isotopic concentrations are shown in Tables 16 and 17. Tin concentrations are listed to show the enrichment due to pollution during the scan ablation (analysis 402-1).



Figure 26. SEM micrograph (backscattered electron images). A and B. Location of the LA-ICP-MS analyses (transects and depth profiles) in pisoliths. C. Detail of the core of pisolith B with pit 402-20.

#### The core

The microcrystalline core material produces homogeneous isotopic responses (Figure 25D). Compared with the core of the duricrust nodules, there is a pronounced enrichment in Mg, V, Cr, As, Mo, Ce and Pb with contents respectively up to 405 ppm, 1280 ppm, 660 ppm, 152 ppm, 81 ppm, 71 and 105 ppm. Copper, Co and Zn levels are very low. Tungsten is abundant (up to 101 ppm), and its spatial distribution indicates that it is associated with the Ti-rich marbling imaged with the SEM. The more gibbsitic plasma is relatively poor in trace elements, suggesting that the oxy-hydroxides are the hosts.

#### The cortex

Magnesium, K and Ba contents are higher in the cortex than in the core of the pisoliths. These elements are present in relict muscovite crystals which have been observed during the mineralogical study. Copper, Zn, Ni, Co and Mn are also enriched in the cortex. Vanadium, Cr, As, Mo and P show similar contents in both materials. Cerium is more abundant and is present as microparticles, probably of cerianite (Figure 25E). Compared with the duricrust nodules, the cortex of the loose pisoliths is extremenly depleted in Cu and enriched in Ce.

In core and cortex, there is no indication of trace element accumulation in Al-rich material, i.e. in gibbsite, boehmite and corundum.

#### Anatase

Some anatase grains located in the cortex are concentrated in Mn, Fe, and Co, and do not show any W enrichment. This element association indicates that they result from the alteration of ilmenite (Figure 25F).

### Gold and silver

Gold and silver contents are very low, with a maximum of 30 ppb Au and 40 ppb Ag in the core.

## Table 16. LA-ICP-MS analyses of loose pisolith core and cortex.

All elements in ppm except for Al, Si in wt % oxides and Ti, Fe (% element). Internal standard: stoichiometric Al (wt % oxide) normalised to 100%. All depth profilings except for analysis 402-1 (transect).

Analyses	Mineralogy	<sup>24</sup> Mg	<sup>27</sup> Al	<sup>29</sup> Si	<sup>31</sup> P	<sup>39</sup> K	<sup>47</sup> Ti	<sup>51</sup> V	<sup>53</sup> Cr	<sup>55</sup> Mn	<sup>57</sup> Fe	<sup>59</sup> Co	<sup>60</sup> Ni
402-11	Core	180	48.0	1.3	245		2.12	1284	658	30	32.88	1	15
402-15	Core	97	60.0	0.2	328		1.01	744	661	12	27.16		16
402-17	Core	260	40.0	0.6	261	92	0.88	1076	636	37	40.44	0	15
402-18	Core	405	41.0	0.6	303	150	1.85	762	533	34	38.29	0	14
402-20	Core	231	36.0	3.9	263	65	1.64	714	626	38	39.84	0	12
402-14	Core (Ti-grain)	200	29.0	0.9	145		24.68	703	540	443	20.89	2	9
402-1	Cortex (scan)	572	65.0	4.0	173		1.5	861	475	27	19.92	1	23
402-12	Cortex	1591	55.0	9.3	148	1762	3.57	1088	326	61	20.96	6	72
402-13	Cortex	1179	65.0	12.3	300	1188	2.21	540	343	53	12.67	3	46
402-16	Cortex	740	67.0	8.4	387	744	2.19	649	454	58	14.17	2	51
402-19	Cortex	641	66.0	7.4	525	1043	1.8	660	416	42	15.68	2	47
1	(* ((	75	Ō.	n .	117	110	101	127	1.40	101	104	300	

Analyses	<sup>65</sup> Cu	<sup>66</sup> Zn	<sup>75</sup> As	<sup>98</sup> Mo	<sup>115</sup> In	<sup>118</sup> Sn	<sup>121</sup> Sb	<sup>137</sup> Ba	<sup>140</sup> Ce	<sup>181</sup> Ta	<sup>184</sup> W	<sup>208</sup> Pb
402-11	1	1	153	81	3	119	5	9	71	1	101	105
402-15		5	77	35	2	77	2	4	22	1	45	42
402-17	7	1	64	53	2	89	6	10	44	1	63	56
402-18	9	3	83	45	2	125	5	14	33	2	72	72
402-20	10	4	67	39	2	124	4	14	36	2	59	68
402-14	2	5	90	96	2	177	6	9	48	4	135	84
402-1	31	28	66	45	6	1387	2	24	84	2	44	73
402-12	21	13	97	59	0	60	1	47	765	2	72	53
402-13	2	10	56	73	1	88	3	21	24	2	72	25
402-16	15	8	92	48	2	111	2	32	103	3	68	105
402-19	8	9	112	50	2	85	1	38	129	2	63	87

Table 17. LA-ICP-MS analyses of pisolith core and cortex.

All elements in ppm except for Al and Si (wt % oxides), Ti and Fe (% element) and Au (ppb). Internal standard: stoichiometric Al (wt % oxide) normalised to 100%.

A	Manada	27 • 1	2901	49 <b></b>	55 N.T	57	917	93 <b>N</b> TL	95n.r.	98ъ.r.	109	<sup>181</sup> T	184	<sup>197</sup> A	209 <b>n</b> •
Analyses	Mineralogy	AI	51	11	win	Fe	Zr	ND	NIO	NI0	Ag	a	W	u	BI
0402-40	Core	40.0	6.3	3.67	35	32.88	610	54	74	74	40	4	88	30	15
0402-41	Core	43.0	2.3	0.96	28	37.88	411	14	20	20	10	1	67	0	17
0402-43	Core	68.0	1.5	0.79	22	20.04	243	10	21	21	10	1	31	0	17
0402-44	Core	62.0	20.8	3	166	8.75	525	50	48	46	40	4	79	20	14
0402-46	Core	34.0	3.0	2.03	15	41.81	323	18	16	16	0	2	44	0	22

# 4. MYSTERY ZONE, MT PERCY, KALGOORLIE

# 4. 1. Regional setting of the Mt Percy gold deposits

## 4. 1. 1. Geological setting and mineralisation

The Mount Percy gold deposits are located at the northern end of the Kalgoorlie gold field, about 2 km from the Kalgoorlie township, and are hosted in the Archeaen Norseman-Wiluna Greenstone Belt. The Kargoorlie stratigraphic succession comprises a lower sequence of ultramafic to mafic volcanic rocks and concordant mafic sills 3.3 to 4.0 km thick, overlain by a 1 km thick volcano-sedimentary sequence. The Mount Percy gold deposits, located in the lower part of the sequence, consists of the Hannans Lake Serpentinite and associated porphyries, the Devon Consols Basalt, Kapai Slate and the ultramafic section of the Williamstown Dolerite (Figure 27). These units are crosscut by a series of north trending, steeply dipping dextral faults.

The Hannans Lake Serpentinite (300 to 700+ m thick) is a serpentinised komatiitic peridotite, with rare thin black interbeds of sulphidic mudstones. The serpentinite has been replaced by talc, chlorite and carbonate, and is altered to a green fuchsite-carbonate rock at the contact with the porphyries. The Devon Consols Basalt (60 to 200 m thick) consists of high magnesium basalt with a pillowed to massive structure and a variolitic texture. The basalts have been replaced by a carbonate-chlorite±sericite and minor epidote assemblage. The Kapai Slate is a 0.5 to over 10 m thick unit composed of sulphidic shales and cherts. The Williamstown dolerite intrudes the sequence to the east, and has a hornblendite base grading up into a pyroxene-rich gabbro. The lower part of the dolerite has been altered into talc and chlorite.

The Mt Percy gold deposits consist of two main mineralised zones parallel to the regional NNW strike: the Sir John-Union Club-Lucknow lodes in the Devon Consols Basalt, and the Mystery orebody to the west in the Hannan's Lake Serpentinite. Numerous porphyries intrude the serpentinite in the Mystery zone. They are roughly vertical, 20 to 100 m wide dykes that are composed of oligoclase, orthoclase and quartz phenocrysts in a quartzo feldspathic groundmass. Xenoliths of metasomatosed serpentinite occur on the margins of the porphyries.

In the Mystery orebody, gold mineralisation is preferentially hosted within the porphyries and contact alteration zones. Pyrite is the dominant sulphide with subordinate chalcopyrite and sphalerite. Gold occurs as micrometric particles around pyrite grains, coarse fracture filling in quartz-carbonate or fuchsite rich veins, or in alteration selvages of veins (Clout et al, 1998).

# 4. 1. 2. Climate, vegetation and topography

The climate is semi-arid, and has irregular average rainfall of 250 mm. Mt Percy is situated in a relatively high part of the landscape, in a region that has a total relief of only a few tens of metres. The elevation is probably due to the armouring effect of the lateritic duricrust, developed here most strongly over the Hanan's Lake Serpentinite

# 4. 2. The lateritic profile

# 4.2.1. Description of the regoliths units

The rocks in the Mount Percy area are intensely weathered. The regolith varies in depth from 50 to 70 m, and has been preserved *in situ* by a lateritic duricrust. Figure 28 shows the regolith stratigraphy along section 15850N, in the Mystery Zone. Four main regolith units have been recognised over fresh rock by Butt (1991):

- The saprolite is a greenish horizon about 40 to 50 meters thick, with a top soft clayrich horizon or clay saprolite.
- The mottled and plasmic clay zone is 1.5 to 5 metres thick, and consists of pale greengrey clays with diffuse or indurated reddish yellow iron oxide concentrations.
- The lateritic duricrust and gravel layer, 1 to 5m thick, covers much of the deposit. It is composed of nodules and pisoliths which display various degrees of cementation from strongly indurated duricrust to loose gravels. Local silification occurs in the duricrust developed over fuchsitic ultramafic rocks.
- The soil is a red-brown loam covering most of the area. It contains pedogenic carbonates and numerous duricrust nodules and pisoliths.

# 4. 2. 2 Sampling

Samples have been collected along section 15850N in the Mystery Zone (Butt, 1991). The location of the samples is shown on Figure 28. Three types of parent-rocks are present along this section: talc chlorite ultramafic rocks, fuschitic ultramafic rocks and carbonate- feldspar porphyries.

# 4. 2. 3. Bulk mineralogy and chemistry of the regoliths units

The chemical composition of the samples is listed in Tables 17 and 18. Butt (1991) discusses the distribution of major and trace elements in the regolith units in a study based on the geochemical analysis of about 550 regolith samples.

The fresh porphyries are rich in Si, Al, Na, Ba, Sr, REE, Hf, Ga, Pb, Nb, Ta, Th and W. Compared to the porphyries, the ultramafics are enriched in Mg, Ca, Cr, Co, Fe, Sc, Ni, Mn. The porphyries and fuchsitic ultramafic rocks contain an average Au content of 1000 ppb. According to Butt (1991), the present-day element distribution in the regolith results from the weathering under two very different climatic regimes: a humid and warm tropical climate during the Cretaceous to middle Miocene, followed by a dry climate since the Miocene.

# Element distribution in the regolith

Iron is concentrated towards the top of the regolith, that is in the mottled zone and lateritic duricrust. Silica abundance depends on the presence of porphyries and the degree of silicification of the weathered fuchsitic rock. Aluminium is concentrated higher in the profile with high values reflecting the location of porphyries.

Gold is mostly considered as secondary in the regolith, and is most abundant in the lateritic duricrust and pedogenic calcrete. The mottled and plasmic zones are relatively Au depleted (<100 ppb), with patchy enrichments due to unweathered quartz veins. The upper saprolite displays local Au concentrations in an alunite-rich zone. Butt (1991) noted that the elements generally considered associated with the Au mineralisation such as S, Sb, Ag, Te and W are not directly correlated with Au in the alteration zone and display distinctive dispersion patterns. The highest Sb levels are, for example, detected in the mottled zone which is strongly Au deficient.

Manganese, Co, Ni, Cu, and Zn display similar behaviour. They all tend to be leached from the top horizons and are concentrated downwards. However, there is no obvious association between these elements in the lower part of the profile. Butt (1991) observed that the Cu and Zn secondary enrichment partly coincides with the alunite zone in the clay saprolite.



Figure 27. Interpreted geology of the Mount Percy area (After Johnston et al., 1990).



Figure 28. Traverse 15850N, Mystery zone, showing the regolith stratigraphy and the samples location.

(After Butt, 1991).

Sample	Regolith type	SiO <sub>2</sub>	Al <sub>2</sub> O 3	Fe <sub>2</sub> O 3	TiO <sub>2</sub>	CaO	MgO	Na <sub>2</sub> O
Regolith de	veloped on fuchsite carl	bonate i	ultram	afic ro	cks			
MW0001	Calcareous soil	50.4	10.0	3.4	0.44	15.0 0	1.98	0.30
MW0531	Mottled clay	31.4	20.0	20.5	1.08	0.05	1.05	0.27
MW0545	Mottled clay	58.1	18.0	8.0	1.02	0.02	0.70	0.32
MW0565	Plasmic clay	62.5	16.0	10.1	0.71	0.01	0.22	0.22
MW0568	Plasmic clay	58.7 9	12.8	13.8	0.60	0.01	0.62	0.28
MW0780	Mottled clay	41.5	16.0	20.7	0.79	0.07	0.99	-
MW0794	Mottled clay	29.5	22.0	24.9	0.78	0.06	0.31	-
MW0766	Clay saprolite	78.6	12.0	0.8	0.56	0.03	0.39	-
MW1013	Clay saprolite	74.4	12.0	1.7	0.66	0.05	1.21	-
MW1022	Clay saprolite	70.4	13.0	4.6	0.70	0.05	1.09	-
MW1140	Clay saprolite	71.6	10.0	1.4	0.53	0.03	0.55	0.24
MW1294	Saprolite	53.4	8.1	17.8	0.38	0.05	0.42	0.16
MW1302	Saprolite	61	11.0	5.6	0.70	0.03	0.75	0.20
MW1471	Saprolite	66.5	13.0	2.7	0.53	0.03	0.97	-
MW1533	Saprolite	62.3	13.0	9.4	0.52	0.04	0.63	0.22
MW1545	Saprolite	63	11.0	5.8	0.56	0.04	1.28	1.42
MW1632	Saprolite	58.3	10.0	12.7	0.40	0.03	0.18	0.19
MW1711	Saprolite	53.3	10.0	15.9	0.50	0.04	1.01	0.15
Regolith de	veloped on porphyry							
MW0183	Lateritic gravels or duricrust	7.16	5.7	50.5	11.8 7	0.01	0.10	0.04
MW0399	Lateritic gravels or duricrust	21.9 2	20.5	29.4	2.61	0.01	0.24	0.39
MW0566	Plasmic clay	52.5 6	14.9	16.6	0.66	0.01	0.31	0.23
MW0576	Plasmic clay	22.8	23.0	20.5	3.89	0.02	0.11	0.35
MW0746	Plasmic clay	56.7	16.0	10.1	0.69	0.04	0.48	-
MW1120	Clay saprolite	71.2 1	14.1	4.0	0.61	0.01	0.47	0.35
MW1527	Saprolite	45.6	13.0	19.8	0.50	0.03	0.36	0.15
MW1734	Saprolite	65.5	16.0	5.2	0.76	0.02	0.82	2.15

Table 17. Chemical composition (%) of selected Mt Percy samples (Butt, 1991). (-: below detection limit)

Sample	As	Au	Ba	Br	Ce	Co	Cr	Cu	Mn	Nb	Ni	Pb	Rb	S	Sb	Sc	Та	V	W	Zn	Zr
	ppm	ppb	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Regolith deve	loped	on fuc	hsite c	arbon	ate ult	tramaf	ic rock	S													
MW0001	12	1060	496	14	14	12	270	57	126	2	174	6	30	0.14	1.8	10.2	-	110	3	22	104
MW0531	160	240	154	17	1	23	5350	105	50	1	496	11	108	0.13	25.4	60.7	-	771	22	57	89
MW0545	58	340	154	14	4	10	3660	24	35	3	205	1	61	0.12	11.0	30.2	-	564	13	17	94
MW0565	180	24	133	28	1	5	2430	41	4	1	114	5	33	0.29	11.0	22.4	-	300	10	6	67
MW0568	322	45	487	19	4	5	3910	53	17	1	59	7	86	0.16	11.0	30.7	-	349	11	12	61
MW0780	190	170	138	25	3	22	5700	122	57	1	500	14	96	0.16	81.8	64.5	-	830	16	77	66
MW0794	86	57	66	64	1	21	4540	108	75	1	418	9	12	0.21	15.0	62.8	-	390	1	12	70
MW0766	9	360	73	7	2	3	3460	1	5	1	129	1	35	0.02	13.0	24.9	-	339	6	3	44
MW1013	12	66	168	8	1	3	3710	7	7	3	157	1	124	0.15	18.0	33.2	-	609	15	13	47
MW1022	46	230	286	16	1	8	4610	23	22	1	343	3	113	0.32	30.7	39.7	-	514	22	68	46
MW1140	14	160	112	15	2	4	2750	17	24	1	297	11	34	0.60	15.0	24.4	-	182	13	13	38
MW1294	516	1370	302	14	7	36	3260	125	66	1	477	21	58	0.78	22.9	37.0	-	343	80	81	29
MW1302	98	130	133	14	1	5	4700	82	18	2	260	3	96	0.45	15.0	49.6	-	386	17	41	56
MW1471	42	260	255	13	4	4	3790	66	13	1	327	2	121	1.56	18.0	54.7	-	358	15	39	41
MW1533	160	1450	483	13	10	19	3260	121	48	1	412	22	69	0.61	22.3	67.1	-	345 1	10	53	90
MW1545	64	280	212	20	6	16	3230	79	54	1	397	5	69	0.47	12.0	36.8	-	311	20	48	58
MW1632	150	34	34	12	5	111	3120	199	231	1	1347	10	9	0.15	6.0	50.1	-	216	1	300	24
MW1711	41	15	214	9	25	454	3430	131	757	1	3665	2	139	0.11	15.0	57.5	-	307	35	463	31
Regolith deve	loped	on por	phyry																		
MW0183	78	350	298	4	10	70	636	28	168	15	71	13	3	0.08	13.0	17.6	2	4426	54	19	225
MW0399	394	380	120	24	8	30	1960	72	123	6	242	15	6	0.84	5.2	35.3	-	1309	13	54	143
MW0566	150	26	589	17	4	5	1380	51	13	3	89	10	45	0.18	10.0	16.7	-	476	25	13	125
MW0576	77	16	137	40	3	21	2510	52	130	8	253	19	3	1.44	6.1	42.9	1	1613	12	13	213
MW0746	170	39	1003	20	6	5	1100	48	8	3	80	6	66	0.25	27.1	28.6	-	262	28	13	172
MW1120	20	420	780	8	4	2	1680	24	12	4	64	5	58	0.15	8.5	23.3	-	175	40	16	146
MW1527	555	795	606	13	19	51	1530	278	205	2	682	23	40	0.14	24.7	67.3	-	455	20	100	105
MW1734	100	2090	1227	5	88	73	555	68	856	4	365	21	76	0.02	10.0	17.6	-	192	30	93	171

Table 18. Chemical composition of Mt Percy selected samples (Butt 1991). (-: below detection limit)

# 4. 3. In situ mineralogical and chemical composition of the regolith

# 4. 3. 1. Saprolite

The saprolite displays ferruginised light to dark brown areas and pale green patches composed of mica and quartz. The bulk sample contains 20% goethite, 29% quartz, and 51% muscovite. The mica is fuchsitic, with up to 1.6 %  $Cr_2O_3$ , and 2.4 % MgO, and high levels of iron (4.4 to 5.6 % FeO) due to the presence of goethite (Table 19).

Sulphide relicts are numerous and mainly occur as aggregated grains. The sulphides have been dissolved and partially to completely pseudomorphed by massive Fe oxides. Isolated crystals are occasionally euhedral (Figure 29). In places, the simultaneous replacement of adjacent grains creates rounded masses with a colloform texture.



Figure 29. SEM micrographs (backscattered electron images). A. Ferruginised saprolite with numerous sulphide relicts. B. Colloform iron oxides; C. Euhedral sulphide relicts.

The pseudomorphs consist of a mixture of goethite and hematite in various proportions as suggested by the range of their Fe contents (Table 19). Aluminium is more abundant in the goethite-rich product (i.e. the less ferric) whereas Si and S do not show any specific affinity. Nickel concentration ranges from nil to 4.5 % NiO and increases with the goethite content of the mixture. This fractionation is particularly obvious in the collomorph products consisting of hematite-rich and goethite rich alternating layers. The analysis of a hematitic band shows that it does not contain Ni, and its Al content is the lowest of all  $(0.5 \% \text{ Al}_2\text{O}_3)$ .

A vermiculitic type mineral contains Al as the main octahedral cation and Na<sup>+</sup> as the interlayer cation, whereas Mg is the main occupant of these sites in a vermiculite *sensu stricto*. Up to 1.70 % Cr<sub>2</sub>O<sub>3</sub> and 0.9 % NiO have been detected in these clays (Table 19), and both cations are probably located in octahedral sites. A few isolated grains of chromium-bearing spinel show high amounts of Zn (to 7.5% ZnO) and Al (to 12% Al<sub>2</sub>O<sub>3</sub>).

Mineralogy	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	Cr <sub>2</sub> O <sub>3</sub>	NiO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	ZnO	Total Oxides
Mica	49.1	0.3	23.5	5.6	2.0	0.5	-	9.2	-	-	-	90.0
Mica	47.6	0.4	26.1	4.4	2.4	0.6	-	10.5	-	-	-	92.0
Mica	48.7	0.4	26.3	4.5	2.2	0.4	-	10.1	-	-	-	92.6
Mica	49.3	0.3	27.2	4.5	2.3	0.7	-	9.9	-	-	-	94.3
Mica	47.7	-	25.9	4.6	2.3	0.9	-	10.5	-	-	-	91.8
Mica	47.8	0.5	25.0	5.1	2.5	1.6	-	10.4	-	-	-	92.8
Mica	47.8	-	25.9	4.4	2.4	0.7	-	10.6	-	-	-	91.8
Mica	47.0	-	25.7	4.9	2.4	0.6	-	10.2	-	-	-	90.8
Goethite-hematite	1.8	-	1.7	67.9	-	-	4.5	-	-	0.8	-	76.8
Goethite-hematite	2.1	-	2.8	69.9	-	-	4.1	-	-	1.2	-	80.0
Goethite-hematite	2.8	-	1.2	72.0	-	-	1.9	-	-	1.1	-	78.9
Goethite-hematite	2.7	-	2.4	72.6	-	-	2.0	-	-	0.7	-	80.4
Goethite-hematite	4.5	-	2.0	73.7	-	-	1.7	-	-	0.9	-	82.7
Goethite-hematite	2.3	-	1.5	75.8	-	-	0.9	-	-	1.1	-	81.6
Goethite-hematite	2.4	-	2.3	76.6	-	-	1.5	-	-	1.1	-	83.8
Hematite-goethite	2.5	-	0.9	80.2	-	-	0.8	-	-	0.7	-	85.0
Hematite-goethite	2.9	-	1.2	80.6	-	-	0.9	-	-	0.9	-	86.4
Hematite-goethite	2.2	-	0.6	86.4	-	-	-	-	-	-	-	89.6
Vermiculite	36.6	-	28.3	10.3	7.2	1.7	0.8	-	2.8	-	-	87.6
Vermiculite	35.4	-	26.9	10.8	6.5	1.3	0.8	-	2.7	-	-	84.3
Vermiculite	34.9	-	27.1	10.6	6.5	1.5	0.9	-	2.7	-	-	84.2
Zn-spinel	-	-	12.0	28.6	-	50.5	-	-	-	-	7.5	98.5

Table 19. Electron microprobe analyses (%) of the saprolite minerals. (-: below detection limit)

# 4. 3. 2. Clay saprolite

The saprolite merges upwards into a pale greenish softer and clay-rich material. The clay saprolite shows important variations in the degree of alteration of the mica. The amount of fuschite in one sample is as high as 40%, whereas kaolinite only represents 5 % of the bulk sample. Large clusters of mica booklets remain fresh or partially pseudomorphosed by kaolinite (Figure 30). During the replacement of the muscovite layers by kaolinite, iron is lost whereas Cr seems to remain (Table 20). A microcrystalline kaolinitic plasma eventually replaces the kaolinitic pseudomorphs.

Weathered sulphides are scattered throughout the clay saprolite. They define patchy networks of iron impregnations mimicking the original vein distribution of the sulphides. The iron oxides also enclose voids created by the dissolution of disseminated sulphides crystals. The surrounding microcrystalline plasma is iron-rich (with up to 50% Fe<sub>2</sub>O<sub>3</sub>, Table 20), and is composed of kaolinite and goethite.

In the vicinity of the sulphide relicts, the minerals of the clay saprolite display signs of destabilisation. Figure 31A shows a sharp reaction front between the clay saprolite composed of quartz and kaolinite and its alteration product. The kaolinitic plasma is progressively replaced by sulphate crystals. Different steps of the reaction are illustrated on Figure 31: growth of single

crystals and clusters of crystals, and islands of sulphates. The abrupt disappearance of quartz grains shows that they also have been dissolved.

The sulphate is an alunite with some  $Al^{3+}$ -Fe<sup>3+</sup> substitutions (up to 5% Fe2O3, Table 20). Silica has been predominantly washed out from the alteration site. The low SiO<sub>2</sub> levels in some analyses are either due to remaining kaolinite, to a residual siliceous phase resulting from the alteration of quartz, or is integrated in the sulphate structure. The replacement of the kaolinite by sulphates maintains the chromium at similar levels (up to 1.20% Cr<sub>2</sub>O<sub>3</sub>), suggesting that it might be accomodated in the alunite lattice. Chromium, like Si may replace the sulphate SO<sub>4</sub> complex as CrO<sub>4</sub><sup>2+</sup> and SiO<sub>4</sub><sup>2+</sup>. The reaction kaolinite-alunite requires the presence of K and S in the microenvironment. Sulfur might be provided by the late dissolution of sulphides in the porphyry, and K may be released by the alteration of residual mica in the saprolite, and minerals (feldspars, micas) in the porphyries.

# Rutile

Two populations of rutile have been recognised in the clay saprolite. Some rutiles contain as much as 4%  $Cr_2O_3$  and V (up to 1.4%  $V_2O_5$ ) are residual in the ultramafic rocks. The second type, enclosed in quartz crystals located in a partially weathered porphyry, contains V, but not Cr.

## 4. 3. 3. Mottled and plasmic clay zone

The clay saprolite is overlain by the mottled and plasmic clay horizon. This unit is composed of muscovite, kaolinite, quartz, goethite, hematite and minor gibbsite. The rock is strongly ferruginised in places. Iron oxides replace mica booklets and quartz grains. Two stages are illustrated in Figure 32. Iron oxides form a rim outlining the quartz crystals, and penetrate along the fuchsite cleavages. At a more advanced stage, quartz is dissolved and replaced by hematite and a few packs of mica layers remain.

Surprisingly, most of the mica layers are fresh (Table 21), or replaced by Fe oxides without an apparent intermediate kaolinitic stage. The Fe oxides are massive mixtures of goethite and hematite with up to 0.9% NiO and no Cr. The fabric of the original material is locally preserved, and they occasionally present a colloform texture with more hematitic layers around former quartz grains. The elements released by the dissolution of mica and quartz have been leached out, whereas Ni is likely to have been supplied by the Fe-rich fluids.

Another characteristic feature of this horizon is the development of cutans in cracks and voids. They consist of a cryptocrystalline mixture of kaolinite, goethite and gibbsite as indicated by the alumina excess in most analyses. The microcrystals have precipitated from solution along the walls of cracks and cavities. The successive layers are parallel to the walls of the fissure, and have slightly different proportions of clay and Fe oxy-hydroxides as shown on a BSE SEM micrograph (Figure 33A). Chromium is present (up to 1.1% Cr<sub>2</sub>O<sub>3</sub>), and V has been detected in one analysis (0.8% V<sub>2</sub>O<sub>5</sub>). The petrographic observations suggest that the cutan formation postdates the ferruginisation. A few mica and quartz relicts in the cutanic plasma and the hazy boundaries between cutans and encasing material suggest that the ferruginised material is progressively invaded by the crypto-plasma (Figure 33B). It is possible that the fluids carrying some of the elements mobilised by the dissolution of mica and quartz are responsible for the precipitation of these cutans thus explaining the presence of Cr.

Ferro-cutans forming in cavities show the characteristic colloform fabric consisting of alternating layers of different chemical compositions ( $\pm$  goethite).


Figure 30. SEM micrograph (backscattered electron images). A. Mica booklet replaced by kaolinite. B. Network of sulphide relicts.  $\mu$  k: microcrystalline kaolinite.



Figure 31. SEM micrographs (backscattered electron images). Replacement of the clay saprolite by alunite. A. Alteration front. B. Cubic crystals of alunite growing in kaolinitic plasma. C. Island of sulphates in kaolinitic plasma. D. Replacement of a kaolinite booklet by alunite.

Mineralogy	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MgO	Cr <sub>2</sub> O <sub>3</sub>	$V_2O_5$	K <sub>2</sub> O	SO <sub>3</sub>	Total Oxides
Mica	49.9	-	27.5	1.9	3.1	0.6	-	10.0	-	93.0
Mica-kaolinite	46.5	-	25.9	2.1	2.8	1.7	-	8.3	-	87.6
Mica-kaolinite	44.6	-	26.8	1.5	-	1.3	-	6.8	-	81.0
Mica-kaolinite	44.7	-	23.7	1.7	-	0.8	-	7.2	-	78.0
Mica-kaolinite	43.0	-	25.9	1.4	1.9	1.0	-	5.5	-	78.7
Mica-kaolinite	43.6	-	28.2	1.4	1.8	1.1	-	5.4	-	81.5
Kaolinite-mica	45.6	-	33.0	0.5	-	1.3	-	1.6	-	82.0
Kaolinite-mica	40.3	-	27.0	0.7	-	0.7	-	3.5	-	72.2
Kaolinite-mica	45.4	-	29.5	0.9	-	1.2	-	4.3	-	81.2
Kaolinite-mica	39.4	-	25.0	0.8	-	1.0	-	4.6	-	70.8
Kaolinite-mica	35.6	0.5	26.4	4.7	-	0.8	-	1.6	-	69.5
Kaolinite	43.4	-	34.7	2.7	-	1.0	-		-	81.8
Kaolinite	44.9	-	35.8	2.1	-	0.8	-		-	83.7
Kaolinite	42.4	-	32.2	1.3	-	1.1	-	0.9	-	77.9
Kaolinite	41.1	0.4	30.7	1.3		1.0	-	0.6	-	75.2
Kaolinite-goethite plasma	18.9	-	15.5	40.4	0.7	1.9	-	1.3	-	78.7
Kaolinite-goethite plasma	16.8	0.7	15.4	37.5	0.4	1.4	-	0.4	-	73.0
Kaolinite-goethite plasma	26.1	0.7	21.1	21.4	0.4	0.8	-	0.5	-	71.0
Kaolinite-goethite plasma	20.7	0.2	23.2	12.0	0.4	0.7	-	3.2	-	60.3
Kaolinite-goethite plasma	13.1	0.4	13.2	48.6	0.5	1.7	-	0.3	-	77.7
Kaolinite-goethite plasma	15.9	0.3	13.3	30.7	-	1.1	-	0.4	-	61.7
Kaolinite-goethite plasma	18.0	-	15.8	37.0	-	1.3	-	-	1.3	73.3
Kaolinite-goethite plasma	12.6	-	12.3	49.5	-	1.7	-	-	0.8	76.9
Kaolinite-goethite + jarosite	17.3	0.5	16.0	23.9	0.4	0.7	-	1.4	2.8	62.9
Kaolinite-goethite + jarosite	10.5	-	30.1	15.7		1.1	-	3.2	15.9	76.4
Kaolinite-goethite + jarosite	20.7	-	25.5	13.2	-	0.9	-	2.8	12.8	76.0
Kaolinite-goethite + jarosite	5.8	-	33.4	8.3	-	0.9	-	5.6	33.8	87.9
Sulphates	2.5	-	40.9	5.0	-	0.8	-	7.1	39.6	95.8
Sulphates	2.3	-	38.9	1.6	-	0.9	-	5.1	40.3	89.0
Sulphates	1.5	-	40.7	1.7	-	1.2	-	5.0	41.5	91.6
Sulphates	-	-	37.6	3.7	-	0.9	-	5.3	37.9	85.4
Sulphates	-	-	21.6	0.7	-	-	-	6.5	25.6	54.4
Sulphates	-	-	19.0	0.5	-	-	-	5.9	23.3	48.6
Ti-mineral	-	92.5	-	0.5	-	4.1	1.4	-	-	98.6
Ti-mineral	-	95.2	-	-	-	2.1	1.2	-	-	98.5
Ti-mineral	-	97.6	-	-	-	1.4	1.0	-	-	99.9
Ti-mineral in quartz grain	-	97.7	-	-	-	-	2.0	-	-	99.6

Table 20. Electron microprobe analyses (%) of the clay saprolite minerals. (-: below detection limit)



Figure 32. SEM micrographs (backscattered electron images). A. Mica and quartz partially replaced by Fe oxides. B. A more advanced stage of the ferruginisation with only a few residual packs of mica layers.



Figure 33. SEM micrograph (backscattered electron images). A and B. Cutans filling a fissure and replacing the ferruginised saprolite. Quartz and mica relicts are visible ( $\mathbf{R}$ ).

Mineralogy	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	Cr <sub>2</sub> O <sub>3</sub>	NiO	V <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	Total Ovides
Mica	45.4	0.6	23.5	8.0	26	0.5	-		10.1	90.7
Mica	47.8		27.9	6.5	2.0	0.0	_		11.0	96.2
Mica	47.0	0.6	27.3	7 1	2.0	1.0	_		10.8	95.8
Mica	46.1		26.2	7.1	2.0	0.7	_	_	10.0	92.2
Mica-kaolinite	34.5	-	20.2	28.8	17	0.7	_	_	77	94.2
Kaolinite-mica	14.0	_	12.0	62.9	0.4	11	-	_	1.0	91.2
Kaolinite-mica	15.3	-	9.8	56.6	0.7	1.1	-	-	1.0	85.2
Cutans	1 4	-	3.6	77.5	0.7	0.8	-	-	-	83.3
Cutans	1.2	-	5.5	73.5	0.6	1.0	-	-	-	81.9
Cutans	1.2	-	4.8	74.1	0.5	1.0	-	-	-	81.7
Cutans	1.4	-	3.2	78.0	0.0	0.7	0.5	-	-	83.8
Cutans	1.3	-	2.5	80.3		0.6	0.6	-	-	85.3
Cutans	1.0	-	2.7	77.9		0.6	0.6	-	-	82.8
Cutans	1.1	-	7.0	72.1		0.6	-	-	-	80.8
Cutans	0.9	-	6.8	72.2		0.7	-	-	-	80.6
Cutans	1.0	-	7.0	72.9		0.7	0.6	-	-	82.2
Cutans	0.9	-	6.7	73.6		0.6	-	-	-	81.7
Cutans	0.9	-	6.5	75.7		0.7	-	-	-	83.8
Cutans	0.8	-	6.4	73.1		0.7	-	-	-	80.9
Cutans	1.7	-	4.8	77.0			-	-	-	83.6
Cutans	1.9	-	6.4	69.6		0.6	-	-	-	78.5
Cutans	4.0	-	5.9	68.6	0.7	0.7	-	-	-	79.9
Cutans	4.2	-	6.2	68.8	0.6	0.6	-	0.8	-	81.2
Cutans	11.4	-	14.1	51.9	0.5	1.1	-	-	-	78.9
Cutans	10.5	-	13.5	52.2	0.6	1.0	-	-	-	77.8
Cutans	11.3		14.0		0.4	0.9				26.6
Cutans	13.6	0.6	15.8	52.7	0.5	0.9				84.0
Cutans	14.2		16.1	49.2	0.6	0.8				80.9
Cutans	12.2		14.8	52.9	0.5	0.9				81.3
Cutans	13.2		15.7	53.3	0.5	1.0				83.6
Cutans	11.4		14.9	58.4	0.6	1.2				86.4
Cutans	17.7		17.6	46.7		0.9				82.8
Cutans	19.7		19.0	50.0		0.9				89.5
Cutans	13.4		13.6	54.9		0.8				82.7
Cutans	13.5		10.5	53.5	0.6	0.9				78.9
Cutans	13.3		14.8	49.8	0.6	1.0				79.4
Cutans	13.2		14.5	53.8	0.6	0.9				83.0
Fe oxides	3.3		2.8	76.7			0.7			83.6
Fe oxides	1.6		1.2	82.4			0.9			86.0
Fe oxides	1.6		1.3	82.7						85.6
Fe oxides	1.7		2.4	76.4			0.6			81.0
Fe oxides	1.7		1.2	81.6			0.7			85.2
Fe oxides	1.6		1.1	79.9			0.8			83.4
Fe oxides	1.5		1.5	78.6			0.7			82.2
Fe oxides	7.3		4.6	70.7						82.6
Fe oxides	1.2		2.1	80.3			0.8			84.4
Fe oxides	1.4		1.6	82.5			0.9			86.4

 Table 21. Electron microprobe analyses (%) of the minerals in the mottled and plasmic clay zone. (-: below detection limit)

## 4. 4. Determination of trace elements in regolith material by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

# 4. 4. 1. Introduction

Laser ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) analyses have been performed on the mineralogical phases described in Section 4. 3 to locate trace elements with emphasis on pathfinders and Au. Samples from the saprolite (MW1711), clay saprolite (MW1140) and mottled and plasmic clay zone (MW780) were analysed. The procedure, including data acquisition and reduction, is detailed in Appendix 3.

## 4.4.2. Saprolite

Thirty two LA-ICP-MS analyses were performed on the saprolite minerals. Figure 34A shows the location and aspect of some ablation pits in the fuchsite and Fe oxides, and the calculated concentrations are listed in Tables 22A and 22B.



Figure 34. SEM micrographs (backscattered electron images). A. Location of LA-ICP-MS analyses in fuchsite and sulphide relicts in the saprolite. B. Ablation crater in fuchsite-kaolinite intergrades in the clay saprolite.

## Fuchsite (Cr-muscovite)

Fuchsite displays a very homogeneous isotopic signature, and contains a large variety of cations (Figure 37A). Chromium is the most abundant octahedral cation with an average concentration of 0.40%, followed by Ti (1760 ppm), Ni (778 ppm), V (557 ppm), Sc (37 ppm), Cu (26 ppm), W (21 ppm) and Sb (14 ppm). Rubidium (402 ppm) and Ba (185 ppm) substitute for K in the interlayer sites.

## Iron oxides in sulphide relicts

Quartz and fuchsite were also often ablated when probing sulphide pseudomorphs (Figure 37B). The isotopic concentrations, calculated on the material containing the smallest amount of fuchsite and quartz, show that the Fe oxides contain high levels of Ti (248 ppm), Cr (455 ppm), Ba (17 ppm) and V (128 ppm). They are rich in Ni (1.9%), Co (0.3%), Zn (0.24 %), Mn (0.15 %), Cu (0.19%), As (0.11%), Sc (106 ppm) and Ce (54 ppm). Up to 290 ppm P have been detected in one sulphide pseudomoph. Antimony and W contents vary from 10 to 25 ppm and up to 13 ppm Mo are present.

Three groups of isotopes can be distinguished from these data: (i) Ni-Co-Mn-Zn and probably Sc reflect the ultrabasic nature of the original rock; (ii) Ti-Cr-V-Ba are related to fuchsite; (iii) Cu-As are associated with the mineralisation. Although not abundant, chalcopyrite and arsenopyrite occur in the sulphide rich-zone. It is also possible that Cu was hosted by silicate minerals in the unweathered rocks.

## Rutile

Micrometric rutile grains contain high W and Sb concentrations (Figure 37C). The concentrations calculated on a slice containing 30% Ti are 139 ppm W and 103 ppm Sb (Ti/Sb and Ti/W about 300 and 220 respectively). Substitutions of Ti by Sb and W are common in rutile.

## 4. 4. 3. Clay saprolite

Forty-six LA-ICP-MS analyses were conducted on the clay saprolite (Sample MW1140). The calculated isotopic concentrations are listed in Tables 23A, 23B and 25.

## Fuchsite-kaolinite

Figure 34B shows an ablation crater in mica-kaolinite intergrades. The raised walls are produced by the pressure at the bottom of the pit generated during the ablation. The partial weathering of fuchsite into kaolinite-mica intergrades is characterised by an important loss of Ba (about 35 ppm), a slight lost of Rb and Ni, and an increase in Cr (up to 1%) and V (up to 900 ppm). Antimony and W concentrations,  $\leq 20$  ppm and  $\leq 30$  ppm respectively, increase to 110 ppm and 75 ppm when scattered Ti-rich grain are also ablated (Table 23).

## Kaolinite-goethite plasma

The isotopic responses obtained on the plasma show that the mixture is very homogeneous (Figure 37D). An increasing proportion of goethite correlates with a higher isotopic abundance indicating that goethite is the preferred host for the elements in the clay saprolite environment. However, compared with the Fe oxides in the sulphide relicts of the saprolite, the goethite shows the following trends:

- (i) It is strongly depleted in elements related to the ultrabasic nature of the parent-rock: Ni (up to 680 ppm), Co (about 20 ppm), Zn (up to 30 ppm) and Mn (up to 60 ppm).
- (ii) It contains similar concentrations of elements related to the mineralisation: Cu (up to 380 ppm) and As (up to 320 ppm).

Chromium (1.1 %) and V (2220 ppm) are concentrated in the microcrystalline plasma, whereas Rb (40 ppm) has been lost during the weathering of fuchsite into kaolinite. The high levels of Ba (up to 370 ppm) suggest that alunite is present in the microcrystalline plasma. Phosphorous is also abundant (1880 ppm).

Titanium is evenly distributed in the plasma, indicating that it occurs as scattered anatase microparticles resulting from the breakdown of the mica structure (Figure 37E). Zirconium is abundant (up to 180 ppm), and correlates with iron indicating that it is associated with goethite. Antimony and W levels are very high, up to 150 ppm and 460 ppm respectively, and are related to goethite abundance in the microcrystalline plasma.

## Sulphates

Figure 35 shows the location of some LA-ICP-MS analyses performed in an alunite-rich area, where locally the clay saprolite minerals are dissolved and replaced by alunite. The reaction is accompanied by major chemical changes resulting from the dissolution of the Fe oxides and clays (Figure 37F). The sulphates are enriched in Ba (up to 0.17%), P (up to 380 ppm), Sc (up to 160 ppm), and in a lesser way in Pb (up to 80 ppm). Vanadium, Ni, Ti, W and Sb are greatly impoverished, whereas Cr (6800 ppm) and Cu (340 ppm) levels are comparable to those observed in the plasma. The elements which cannot be accommodated in the aluminium sulphate lattice such as Ni and V are removed from the microenvironment. The large cations, Pb and Ba, substitute for K, Cu substitutes for Al in octahedral coordination, and P and Cr replace S.

## Rutile

Rutile grains are extremely rich in W (820 ppm) and Sb (780 ppm) with Ti/W and Ti/Sb ratios about 500 (Figure 38A).

## Gold and silver

Figure 38B shows Ag and Au LA-ICP-MS responses obtained on quartz crystals. Zirconium, Nb and Ta distributions indicate that Ag and Au signals do not result from oxide interferences (See Section 2). The ragged spectra suggest that these two precious elements occur as micrometric and submicrometric particles in the quartz veins. Gold and Ag distributions are not related. All the grains contain high Ag levels ranging from 600 to to 1400 ppb. Up to 450 ppb Au has been detected in a quartz grain.

#### 4. 4. 4. Mottled and plasmic clay

Thirty-nine sites, including cutans and ferruginised material, were analysed by LA-ICP-MS (Figure 36). Tables 24A, 24B and 26 show the calculated isotopic concentrations.

#### Oxides in the ferruginised rock

All the spectra are the responses of volumes of material comprising Fe oxides, fuchsite and/or quartz (Figures 38C and 38D). The highest Cr and Ti levels are found in the mica-rich material. The composition of the Fe-rich material shows that most Ti and part of Cr and Ba contained in the fuchsite are lost during the weathering of the mica, whereas V is retained. Compared with the fuchsite, the Fe oxides are enriched in Ni (0.44%), Co (120 ppm), Zn (360 ppm), Mn (220 ppm), Cu (141 ppm), As (370 ppm), and Sb (47 ppm). Phosphorous is also trapped by the Fe oxides (to 500 ppm).

Molybdenum levels are generally low (around 8 ppm), but one analysis indicates a very high content of 430 ppm. The <sup>95</sup>Mo, <sup>98</sup>Mo and <sup>82</sup>Se (<sup>82</sup>Se + <sup>16</sup>O) measurements confirm this value. The distributions of Mo and Fe are similar and homogeneous, excluding the presence of a Mo-bearing-mineral in the material.

These iron oxides contain lower levels of trace elements than the iron oxides pseudomorphing the sulphide relicts in saprolite, suggesting that the fluids circulating in the plasmic clay horizon are themselves depleted in these elements.

#### Cutans

The petrographic observations suggest that the ferruginised rock is progressively replaced by cutans. These cutans are characterised by a wide range of chemical compositions. The isotopic composition of the cutans reflects (i) the mineralogy of the cutans i. e. the proportions kaolinite/goethite; (ii) the nature of the fluids which led to the deposition of the microplasma in voids and cracks; (iii) the mineralogy and degree of ferruginisation of the mica-quartz rock.

The goethite-rich cutans (Fe >50 %) contains high levels of Cu (up to 740 ppm), As (up to 1140 ppm), Mo (up to 435 ppm) and Sb (up to 900 ppm). Nickel and Zn concentrations are comparable, and V concentrations vary from 410 ppm to 0.3% (Figures 38E and 38F). The more kaolinitic and gibbsitic cutans are comparatively depleted in these elements and enriched V, Ba and Pb. Unlike W the high levels of Sb in the goethite are not caused by the occurrence of scattered anatase grains as shown by the distribution of these two elements (Figure 38G).

#### Gold and silver

Four out of six analyses performed on cutans indicate more than 150 ppb of gold, with a top value of 400 ppb. There is no clear relationship between Au and the other measured isotopes (Figure 38H). Gold has a homogeneous spatial distribution, suggesting that it occurs as crypto-crystalline particles disseminated in the microcrystalline plasma. No significant amounts of Ag were detected in this sample.



Figure 35. SEM micrographs (backscattered electron images). Location of some LA-ICP-MS analyses in the clay saprolite material.



Figure 36. SEM micrographs (backscattered electron images). A, B, C, D. Location of some of the LA-ICP-MS analyses in the ferruginised rock and cutans.



Figure 37. LA-ICP-MS time resolved spectra of selected isotopes in mineralogical assemblages in Mt Percy saprolite and clay saprolite. A. Fuchsite in the saprolite. B. Goethite-hematite (sulphide relict) in the saprolite. C. Rutile crystal in the saprolite. D and E. Kaolinite-goethite plasma in the clay saprolite. F. Alunite in the clay saprolite.



Figure 38. LA-ICP-MS time resolved spectra of selected isotopes in mineralogical assemblages in Mt Percy clay saprolite and mottled and plasmic clay. A. Rutile and fuchsite in the clay saprolite. B. Gold and silver associated with quartz in the clay saprolite. C and D. Ferruginised material in the mottled and plasmic clay. E, F and G. Goethite-rich cutans in the mottled and plasmic clay. H. Gold in the goethite-rich plasma.

Table 22A. LA-ICP-MS analyses of the saprolite minerals (Sample MW-1711). All data in ppm, except for Al and Si in wt% oxides, and Mg in % element. Internal standard: Al stoichiometric values normalised to 100 wt% oxides.

Mineralogical assemblage	Analyses	<sup>24</sup> M g	<sup>27</sup> Al	<sup>29</sup> Si	<sup>31</sup> P	<sup>45</sup> Sc	<sup>49</sup> Ti	<sup>51</sup> V	<sup>53</sup> Cr	<sup>55</sup> Mn
Mica	1711-1	1	27.0	55.0	0	37	1730	550	4015	6
Mica	1711-2	1	27.0	54.9	0	37	1710	552	3902	5
Mica	1711-3	1	27.0	55.0	0	36	1684	543	3897	8
Mica	1711-4	1	27.0	55.5	0	38	1747	556	4133	6
Mica	1711-18	1	26.0	56.6	0	41	1852	567	4817	8
Mica	1711-31	1	26.0	55.9	0	37	1847	577	4559	7
Fe oxides (sulphide ghosts) + quartz	1711-13	0	2.0	6.2	184	107	249	129	455	1547
Fe oxides (sulphide ghosts)	1711-8	0	2.8	6.5	217	97	843	184	720	1695
Fe oxides (sulphide ghosts) + quartz	1711-12	0	4.4	23.7	191	157	479	171	926	2596
Fe oxides (sulphide ghosts) + quartz+ mica	1711-14	0	5.4	22.9	127	133	467	184	1477	2251
Fe oxides (sulphide ghosts) + mica	1711-5	0	7.8	16.3	189	95	12554	292	1678	1534
Quartz + Fe oxides (sulphide ghosts)	1711-10	0	4.2	26.2	109	108	480	156	1056	1680
Fe oxides (sulphide ghosts) + mica + quartz	1711-30	1	10.0	16.3	175	88	1074	257	3826	1660
Fe oxides (sulphide ghosts) + mica + quartz	1711-20	0	7.5	17.7	240	104	524	191	1594	2830
Fe oxides (sulphide ghosts) + mica + quartz	1711-22	0	7.8	22.9	290	101	937	220	2051	2960
Fe oxides (sulphide ghosts) + mica + quartz	1711-24	0	6.4	31.1	217	122	502	150	1138	3196
Fe oxides (sulphide ghosts) + mica + quartz	1711-23	0	11.0	32.9	240	93	772	255	2603	1946
Quartz + mica + Fe oxides (sulphide ghosts)	1711-16	0	6.4	37.2	164	64	522	243	1804	961
Fe oxides (sulphide ghosts) + mica + quartz	1711-25	0	8.8	38.3	293	86	1004	245	2079	2802
Mica + Fe oxides (sulphide ghosts)	1711-29	0	16.5	37.9	47	73	1419	382	6138	861
Fe oxides (sulphide ghosts) + mica + quartz	1711-21	0	18.0	43.5	59	81	1624	421	5623	2107
Fe oxides (sulphide ghosts) + mica	1711-7	1	19.5	43.5	29	47	1258	450	3068	1979
Mica + quartz + Fe oxides (sulphide ghosts)	1711-9	0	12.5	55.9	69	62	2769	301	4274	1573
Mica + Fe oxides (sulphide ghosts)+ quartz	1711-17	1	19.5	52.3	14	53	1380	496	4701	339
Fe oxides (sulphide ghosts) + quartz	1711-26	0	4.2	82.3	62	29	380	99	1060	904
Fe oxides (sulphide ghosts) + mica	1711-6	1	25.0	53.8	0	39	1572	542	3668	118
Mica + Fe oxides (sulphide ghosts)	1711-19	1	21.5	59.3	6	39	1549	517	4137	63
Mica + Fe oxides (sulphide ghosts)	1711-32	1	25.0	52.9	0	44	2417	566	5516	86
Quartz + Fe oxides	1711-11	0	0.3	91.9	0	11	41	12	48	232
Quartz	1711-28	0	2.7	92.5	0	16	232	66	758	261
Quartz + mica + Fe oxides (sulphide ghosts)	1711-15	0	12.0	77.4	0	27	3109	282	4043	34
Quartz	1711-27	0	2.3	92.8	0	10	168	51	678	159
Fe oxides + mica (sliced on Ti-grain)	1711-5 (2)	0	7.8	15.2	155	77	310000	279	1827	1401

Analysis	<sup>57</sup> Fe	<sup>59</sup> Co	<sup>60</sup> Ni	<sup>65</sup> Cu	<sup>66</sup> Zn	<sup>75</sup> As	<sup>85</sup> Rb	<sup>98</sup> Mo	<sup>115</sup> In	<sup>121</sup> Sb	<sup>137</sup> Ba	<sup>140</sup> Ce	<sup>184</sup> W	<sup>209</sup> Bi
1711-1	3	3	776	2	24	1	412	0	0	13	185	0	20	0
1711-2	3	3	776	2	24	1	396	0	0	14	168	0	18	0
1711-3	3	5	783	3	26	1	403	0	0	13	160	0	19	0
1711-4	3	3	793	2	24	1	399	0	0	14	201	1	21	0
1711-18	3	6	749	3	31	1	392	0	0	10	227	2	25	0
1711-31	3	4	794	2	27	0	416	0	0	10	172	0	25	0
1711-13	65	3023	19618	1940	2465	1095	8	12	1	21	17	54	10	1
1711-8	63	2195	14467	529	2557	810	23	13	0	40	32	59	30	1
1711-12	51	3598	25490	963	3898	650	37	13	56	38	60	117	13	3
1711-14	50	3377	24349	863	3120	658	56	12	0	24	82	47	12	0
1711-5	49	550	8105	436	1246	183	113	8	6	60	62	38	65	0
1711-10	49	3323	23376	1360	2809	715	48	11	6	22	65	45	12	1
1711-30	48	723	9624	593	1444	165	51	7	4	9	89	40	8	0
1711-20	47	1356	11374	275	2038	141	76	7	12	14	61	34	13	0
1711-22	45	1629	12718	277	2953	201	119	8	3	22	131	55	36	0
1711-24	43	1383	9740	270	1074	137	48	8	1	12	41	32	12	0
1711-23	39	1126	9658	295	1890	160	136	6	0	12	152	27	18	0
1711-16	38	450	6603	327	1422	178	86	8	1	15	139	38	17	0
1711-25	35	1095	8320	383	1466	290	120	5	1	66	137	38	25	47
1711-29	27	557	7093	348	1037	103	245	5	0	9	279	23	25	0
1711-21	21	607	5106	122	637	58	241	3	1	7	425	60	26	1
1711-7	20	431	5836	263	603	98	334	7	0	19	107	44	20	0
1711-9	16	455	4967	158	371	91	165	3	1	30	220	18	62	9
1711-17	13	233	3132	119	386	37	289	4	0	9	254	12	22	0
1711-26	9	268	2193	51	288	23	50	1	0	4	81	8	8	0
1711-6	7	72	1661	47	132	22	412	2	0	17	161	4	21	0
1711-19	6	33	1151	21	55	13	342	2	7	10	189	43	23	1
1711-32	6	55	1291	23	109	8	395	1	0	14	237	4	43	0
1711-11	5	326	2337	96	431	90	2	1	0	3	2	4	2	0
1711-28	3	104	970	21	130	12	32	1	0	5	64	2	7	0
1711-15	2	12	409	5	27	2	174	0	0	31	222	5	56	0
1711-27	2	44	413	13	43	5	30	0	0	2	53	1	3	0
1711-5 (2)	41	580	8019	418	1197	165	105	8	6	103	73	35	139	0

Table 22B. LA-ICP-MS analyses of the saprolite minerals (Sample MW-1711). All data in ppm except for Fe in % element. Internal standard: Al stoichiometric values normalised to 100 % wt oxides.

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Mineralogical assemblages	Analyses	<sup>24</sup> Mg	<sup>27</sup> Al	<sup>29</sup> Si	<sup>31</sup> P	<sup>45</sup> Sc	<sup>49</sup> Ti	<sup>51</sup> V	<sup>53</sup> Cr	<sup>55</sup> M n
Fuchsite-kaolinite+ quartz	1140-1	1.4	28.0	55.5		49	2003	819	10079	6
Fuchsite-kaolinite+ quartz	1140-2	1.1	26.0	50.0		40	35906	680	9755	3
Fuchsite-kaolinite+ quartz	1140-12	1.3	28.0	55.1		66	2287	913	5394	5
Fuchsite-kaolinite+ quartz	1140-36	1.4	28.0	57.2		47	1011	922	6658	4
Fuchsite-kaolinite+ quartz	1140-37	1.1	25.0	68.1		28	2669	598	5811	6
Fuchsite-kaolinite+ quartz	1140-38	0.9	23.5	71.9		31	1369	573	5698	5
Kaolinite + goethite plasma	1140-3	0.3	17.0	18.7	189	44	2907	2227	10960	60
Kaolinite + goethite plasma	1140-4	0.4	19.5	19.0	204	54	2756	2153	11310	56
Kaolinite + goethite plasma	1140-5	0.3	40.0	33.4	190	65	2958	855	8402	24
Kaolinite + goethite plasma	1140-6	0.3	40.0	41.1	232	56	2985	587	7923	20
Kaolinite + goethite plasma	1140-7	0.3	37.0	42.1	251	53	7739	657	8535	24
Kaolinite + goethite plasma	1140-8	0.3	34.0	44.8	222	55	3314	579	7509	23
Kaolinite + goethite plasma+ quartz	1140-9	0.4	14.0	72.1	94	23	2078	417	3941	15
Kaolinite + goethite plasma	1140-10	0.3	20.0	28.7	216	54	3482	1968	10492	60
Kaolinite+ sulphate + quartz (rim)	1140-15	0.6	44.0	47.9	104	66	3371	405	7935	12
Kaolinite+ sulphate + quartz (rim)	1140-16	0.3	23.0	73.5	26	34	5769	214	3848	7
Kaolinite+ sulphate + quartz (rim)	1140-17	0.5	45.0	45.9	174	65	3180	365	8325	13
Kaolinite+ sulphate + quartz (rim)	1140-18	0.3	29.0	62.9	119	46	4548	295	5416	11
Kaolinite+ sulphate + quartz (rim)	1140-19	0.3	23.0	71.7	49	39	2000	215	4024	12
Kaolinite+ sulphate + quartz (rim)	1140-20	0.2	10.8	87.8	12	18	606	110	1991	7
Kaolinite + quartz+ sulphate (?)	1140-34	0.5	23.0	74.8	22	38	2083	699	4847	2
Sulphate + kaolinite	1140-22	0.1	38.0	10.9	277	104	370	90	5796	3
Sulphate + kaolinite + Fe oxides	1140-31	0.1	37.0	18.2	192	78	688	148	5862	5
Sulphate + kaolinite + Fe oxides	1140-32	0.1	42.0	7.6	309	116	495	150	6542	3
Sulphate + kaolinite + Fe oxides	1140-33	0.2	29.0	19.2	105	54	2156	241	5285	9
Sulphate + kaolinite + Fe oxides	1140-35	0.3	43.0	30.8	139	70	2428	382	8078	11
Sulphate	1140-21	0.0	39.2	0.3	314	112	22	44	5613	1
Sulphate	1140-23	0.1	39.2	0.5	299	99	31	43	5996	1
Sulphate	1140-24	0.1	39.2	0.1	383	169	10	78	6856	1
Sulphate	1140-25	0.0	39.2	1.0	314	113	78	46	6087	1
Sulphate	1140-28	0.0	39.2	0.1	353	113	9	48	6536	1
Sulphate	1140-29	0.0	39.2	0.6	245	92	105	50	5188	1
Sulphate	1140-30	0.0	39.2	0.6	283	106	41	54	6585	1
Rutile	1140-13	0.4	11.0	19.3	7	29	397786	1169	6165	3

Table 23A. LA-ICP-MS analyses of the clay saprolite minerals (Sample MW-1140). All data in ppm, except for Al and Si in wt% oxides, and Mg in % element. Internal standard: Al stoichiometric values normalised to 100 % wt oxides.

Sample	<sup>57</sup> Fe	<sup>59</sup> Co	<sup>60</sup> Ni	<sup>65</sup> Cu	<sup>66</sup> Zn	<sup>75</sup> As	<sup>85</sup> Rb	<sup>98</sup> Mo	<sup>121</sup> Sb	<sup>137</sup> Ba	<sup>140</sup> Ce	<sup>184</sup> W	<sup>208</sup> Pb	<sup>209</sup> Bi
1140-1	1.6	9	431	18	7	7	312	0	16	42	0	21	3	0
1140-2	1.1	6	509	12	6	2	242	0	111	29	0	76	2	0
1140-12	2.0	9	461	16	14	7	265	0	20	35	0	25	4	0
1140-36	1.3	8	643	10	15	1	255	0	13	31	0	16	1	0
1140-37	1.5	6	594	12	7	5	212	0	17	22	0	29	2	0
1140-38	1.3	6	570	11	9	5	174	0	13	31	0	16	3	0
1140-3	43.9	24	362	377	32	324	40	9	146	35	4	334	15	3
1140-4	41.5	24	365	387	15	312	39	9	140	90	4	341	19	3
1140-5	18.0	20	530	247	10	137	67	4	58	375	2	156	36	1
1140-6	12.4	20	674	209	19	90	83	3	45	371	2	105	35	1
1140-7	13.1	18	685	212	26	96	68	3	62	309	2	123	35	1
1140-8	12.6	18	661	203	25	93	52	3	49	293	2	115	39	2
1140-9	8.6	10	370	87	10	63	35	2	43	78	1	70	13	1
1140-10	32.9	24	486	431	18	272	46	7	151	27	3	335	14	2
1140-15	4.5	14	655	131	15	43	174	1	18	421	1	43	16	0
1140-16	2.2	7	361	56	10	18	77	1	22	1574	1	34	19	0
1140-17	4.9	16	646	153	17	46	136	2	18	489	1	42	23	0
1140-18	3.7	10	495	91	14	31	91	1	20	296	1	42	15	0
1140-19	2.6	8	365	63	10	22	76	1	11	230	1	24	12	0
1140-20	0.5	4	325	15	22	4	25	0	4	69	1	8	11	0
1140-34	0.7	7	550	30	14	7	99	0	14	115	0	16	12	0
1140-22	1.7	13	86	245	4	37	7	0	3	1049	1	8	43	0
1140-31	2.5	13	148	211	3	40	18	1	6	931	1	16	30	0
1140-32	2.4	14	161	252	6	42	21	0	5	1159	1	14	59	0
1140-33	4.9	13	316	138	7	46	42	2	19	463	1	49	17	0
1140-35	6.4	16	535	195	12	61	81	2	23	660	1	58	19	0
1140-21	1.1	14	44	272	3	32	1	0	0	1172	1	1	42	0
1140-23	1.1	14	47	241	3	37	1	0	0	1207	1	1	49	0
1140-24	1.3	17	48	346	3	43	1	0	0	1776	2	1	81	0
1140-25	1.3	13	44	282	2	39	2	0	0	1174	1	2	43	0
1140-28	1.2	17	56	303	2	39	1	0	0	1232	1	1	52	0
1140-29	1.3	15	53	261	2	33	2	0	1	1095	1	2	39	0
1140-30	1.2	13	45	242	2	33	2	0	0	1023	1	2	46	0
1140-13	1.2	12	233	240	7	14	86	0	785	25	1	821	5	0

Table 23B. LA-ICP-MS analyses of the saprolite minerals (Sample MW-1711).All data in ppm, except for Fe in % element. Internal standard: Al stoichiometric values normalised to 100 wt% oxides.

Table 24A. LA-ICP-MS analyses of the minerals in the mottled and plasmic clay (Sample MW-780). All data in ppm, except for Al and Si in wt% oxides and Mg in % element. Internal standard: Al stoichiometric values normalised to 100 wt%

oxides.

Mineralogy	Analyses	<sup>24</sup> Mg	<sup>27</sup> Al	<sup>29</sup> Si	<sup>31</sup> P	<sup>39</sup> K	<sup>49</sup> Ti	<sup>51</sup> V	<sup>53</sup> Cr	<sup>55</sup> Mn
Fe-oxides + mica-kaolinite	780-6	0.2	5	6	336	1	363	546	2244	78
Fe-oxides + mica-kaolinite	780-9	0.3	7	10	391	2	503	607	3457	60
Fe-oxides + mica-kaolinite	780-11	0.3	6	22	392	2	482	591	3130	67
Fe-oxides + mica-kaolinite	780-12	0.3	6	8	422	1	398	603	2684	96
Fe-oxides + mica	780-25	0.2	5	10	1077	1	1648	726	3221	351
Fe-oxides + mica-kaolinite	780-14	0.3	7	11	500	2	2694	758	4252	89
Mica-kaolinite + Fe oxides	780-17	0.8	22	55	64	4	2916	536	5907	4
Mica-kaolinite + quartz + Fe oxides	780-18	0.9	14	59	72	5	3648	824	4597	5
Mica-kaolinite + Fe oxides	780-19	0.8	15	35	122	5	3853	1560	8535	36
Fe-oxides + mica-kaolinite	780-20	0.7	15	47	109	4	1762	1447	7599	24
Fe-oxides + mica-kaolinite	780-29	0.4	18	22	189	2	1480	1764	7567	71
Fe-oxides + mica-kaolinite	780-30	0.4	10	30	201	2	963	2192	6504	107
Quartz + Fe-oxides + mica- kaolinite	780-32	0.2	5	77	109	1	404	669	3099	40
Quartz + mica-kaolinite + Fe oxides	780-13	0.1	3	89	76	1	573	154	913	15
Quartz + Fe oxides + mica	780-32	0.2	5	77	109	1	404	669	3099	40
Quartz mainly	780-15	0.1	2	96	62	1	99	30	538	0
Cutans (goethite)	780-1	0.1	2	1	551	0	109	551	3505	44
Cutans (goethite)	780-2	0.1	2	2	504	0	100	460	2988	40
Cutans (goethite)	780-3	0.3	9	2	398	0	658	1550	5765	219
Cutans (goethite)	780-5	0.2	9	1	301	0	517	1409	5490	204
Cutans (goethite)	780-8	0.1	3	1	599	0	136	562	3585	42
Fe-oxides	780-21	0.1	2	2	429	0	282	410	2234	48
Fe oxides	780-31	0.1	4	3	518	0	62	837	3063	147
Fe-oxides + kaolinite	780-22	0.3	6	7	486	0	407	3097	4664	147
Fe-oxides + kaolinite	780-23	0.4	19	15	285	0	2037	2240	7055	136
Fe-oxides +kaolinite	780-24	0.4	19	14	318	0	1820	2596	7414	257
Fe-oxides + kaolinite	780-26	0.4	20	15	337	0	1786	2283	7103	280
Fe-oxides + kaolinite	780-27	0.3	21	16	252	0	1190	1547	7346	61
Fe-oxides + kaolinite	780-28	0.2	22	20	203	0	885	1493	6710	57

Analyses	<sup>57</sup> Fe	<sup>59</sup> Co	<sup>60</sup> Ni	<sup>65</sup> Cu	<sup>66</sup> Zn	<sup>75</sup> As	<sup>98</sup> Mo	<sup>121</sup> Sb	<sup>137</sup> Ba	<sup>140</sup> Ce	<sup>184</sup> W	<sup>208</sup> Pb
780-6	63	120	4456	142	363	370	9	48	63	2	23	6
780-9	59	101	4240	137	351	366	10	60	83	2	35	6
780-11	49	89	3491	159	201	351	9	45	64	1	45	7
780-12	60	107	4743	152	302	364	10	41	55	2	37	6
780-25	59	53	1382	200	335	309	54	156	33	5	15	28
780-14	55	100	3980	175	204	401	12	70	90	2	80	7
780-17	11	6	568	72	17	94	1	36	96	1	21	8
780-18	14	6	342	128	17	146	4	27	99	1	28	7
780-19	29	9	475	192	28	374	23	134	80	4	37	87
780-20	23	8	416	110	28	305	23	106	74	3	23	82
780-29	40	14	454	113	36	460	19	224	96	5	16	143
780-30	41	21	458	177	49	614	30	261	72	7	12	174
780-32	11	10	218	110	30	239	26	79	91	2	5	19
780-13	6	7	160	81	43	151	1	8	35	0	4	2
780-32	11	10	218	110	30	239	26	79	91	2	5	19
780-15	0	0	42	0	11	4	0	4	30	0	1	0
780-1	68	124	5507	122	371	328	10	68	0	1	40	4
780-2	68	120	5781	108	451	290	9	60	1	1	29	4
780-3	63	96	2005	482	287	1149	25	121	2	8	93	17
780-5	65	74	1617	546	171	1131	22	123	1	5	75	16
780-8	69	126	5699	143	375	348	10	79	0	2	51	6
780-21	68	126	5550	110	467	258	9	53	1	1	31	4
780-31	65	65	1373	165	388	249	38	193	9	5	2	11
780-22	61	36	571	741	137	1080	436	643	14	15	32	131
780-23	46	51	894	447	101	1006	329	902	78	11	21	83
780-24	46	62	941	481	109	932	121	436	70	11	13	78
780-26	45	52	887	383	91	837	73	166	104	10	12	63
780-27	43	23	508	205	46	539	23	148	92	6	11	74
780-28	40	16	433	141	35	441	18	178	83	5	11	85

Table 24B. LA-ICP-MS analyses of the minerals in the mottled and plasmic clay (Sample MW-780). All data in ppm, except for Fe in % element. Internal standard: Al stoichiometric values normalised to 100 wt% oxides.

Mineralogy	Analyses	<sup>27</sup> Al	<sup>29</sup> Si	<sup>49</sup> Ti	<sup>55</sup> Mn	<sup>57</sup> Fe	<sup>77</sup> Se	<sup>82</sup> Se	<sup>91</sup> Zr	<sup>93</sup> Nb	<sup>98</sup> Mo	<sup>109</sup> Ag	<sup>115</sup> In	<sup>118</sup> Sn	<sup>181</sup> Ta	<sup>184</sup> W	<sup>197</sup> Au	<sup>209</sup> Bi
Goethite+kaolinite (Plasma)	1140-40	15.0	17.4	3375	55	46.4	9	8	188	1	9	60	1	8	0	466	40	2
Goethite+kaolinite (Plasma)	1140-43	18.5	20.3	3740	59	43.3	8	7	178	1	9	50	1	9	0	388	50	2
Kaolinite+goethite (Plasma)	1140-41	41.0	40.2	4231	16	12.6	2	0	110	2	3	30	1	81	0	98	110	1
Koalinite+goethite (Plasma)	1140-46	43.0	41.8	4846	14	10.0	2	0	74	2	3	50	1	2	0	84	120	0
Kaolinite+goethite+quartz	1140-48	44.0	51.9	3003	4	2.2	0		78	1	1	40	0	2	0	24	80	0
Kaolinite+quartz+goethite	1140-44	40.0	53.0	3509	5	3.3	1	0	48	1	1	110	0	1	0	35	120	0
Kaolinite+goethite+alunite	1140-42	39.0	35.9	5293	23	16.4	3	1	94	2	4	40	2	272	0	118	110	1
Kaolinite+goethite+alunite	1140-47	30.0	18.1	2623	11	9.8	2	1	59	1	2	30	1	1	0	65	80	0
Alunite	1140-45	40.0	0.5	28	1	1.4	4	4	3	0	0	0	1	0	0	1	0	0
Quartz	1140-49	0.5	97.0	2709	2	0.2	0		15	0	0	1380	0	0	0	14	450	0
Quartz	1140-50	1.4	96.1	1203	3	0.2			20	0	0	620	0	28	0	5	250	0
Quartz	1140-51	0.9	98.4	1361	4	0.2	0		27	0	0	1440	0	13	0	26	70	0
Quartz	1140-52	0.9	98.1	1250	4	0.2	0		30	0	0	620	0	20	0	9	70	0

Table 25. LA-ICP-MS analyses of the clay saprolite minerals (Sample MW-1140). All data in ppm, except for Al and Si in wt % oxides, Fe in % element, and Au and Ag in ppb. Internal standard: Al stoichiometric values normalised to 100 wt% oxides.

Table 26. LA-ICP-MS analyses of the mottled and plasmic clay minerals (Sample MW-780). All data in ppm, except for Al and Si in wt % oxides, Fe in % element, and Au and Ag in ppb. Internal standard: Al stoichiometric values normalised to 100 wt% oxides.

Mineralogy	Analyses	<sup>27</sup> Al	<sup>29</sup> Si	<sup>49</sup> Ti	<sup>55</sup> Mn	<sup>57</sup> Fe	<sup>91</sup> Zr	<sup>93</sup> Nb	<sup>98</sup> Mo	<sup>109</sup> Ag	<sup>181</sup> Ta	<sup>184</sup> W	<sup>197</sup> Au	<sup>209</sup> Bi
Cutans	780-40	21.0	20.9	1246	59	42	65	0	23	70	0	11	170	0
Cutans	780-41	20.5	23.0	956	55	40	55	0	18	40	0	11	180	0
Cutans	780-42	17.7	20.2	1197	71	44	64	0	22	50	0	14	170	0
Cutans	780-44	18.5	15.3	1903	269	47	89	1	85	50	0	12	100	0
Cutans	780-46	12.1	9.9	2938	43	55	90	4	23	130	0	16	410	0
Cutans	780-48	2.3	1.7	142	55	67	30	0	13	30	0	49	0	0
Ferruginised material	780-43	12.7	13.9	1266	143	52	67	0	46	60	0	13	90	0
Ferruginised material	780-45	3.9	30.8	297	210	46	23	0	69	70	0	8	10	0
Ferruginised material	780-47	6.4	9.8	489	225	60	37	0	431	110	0	32	30	0
Ferruginised material	780-50	4.6	3.0	329	126	65	36	0	15	60	0	57	20	0

# **5. DISCUSSION AND CONCLUSIONS ON ELEMENT-MINERAL ASSOCIATIONS IN THE BODDINGTON AND MT PERCY GOLD DEPOSITS**

## 5.1. General

A combination of mineralogical and chemical microanalyses, with emphasis on *in situ* analyses, has been performed to locate trace elements in regolith material. Laser Ablation Inductively Coupled Plasma Mass Spectrometry has been intensively used, and has been shown to be a valuable tool for the determination of trace elements in clays and ferruginous materials. This present study provides new data about the occurrence and levels of selected trace elements in a variety of minerals and mineralogical assemblages. The data also characterise the behaviour of some trace elements during mineral weathering.

## 5. 2. The Boddington gold deposit

## 5. 2. 1. Element-mineral associations

Tables 27 and 28 summarise the chemical data obtained during this work for the saprock, saprolite, fragmental duricrust and loose pisoliths horizons. They show the main mineralogical hosts and their trace element concentrations. It is important to note that LA-ICP-MS data are often obtained on mixtures of minerals, and therefore the concentration values for the pure mineralogical phases are lowered by the response of the surrounding material.

The data show that the trace elements generally have multiple hosts in each horizon.

#### Saprolite

Kaolinite is, with quartz, the main constituent of the saprolite, but hosts only small quantities of trace elements. Traces are concentrated in minerals of marginal abundance which remained undetected by X-ray diffraction analysis of the bulk samples: vermiculite, goethite, hematite and accessory minerals such as anatase.

In this horizon, the trace elements directly related to the Cu-Au mineralisation (Cu, As, Pb, Bi, Mo and W) have been solubilised by the dissolution of sulphides. Once released by the parent-minerals, they are either immobilised *in situ* in the goethite and hematite pseudomorphs, or are trapped by goethite after a localised migration. Tungsten, Bi and Mo are also hosted by anatase. They show a much stronger affinity for goethite than for hematite. Large amounts of Cu are incorporated in vermiculite, whereas As, Pb, Bi, Mo and W are not. Kaolinite contains only minor Cu. Copper oxides also account for a part of the copper in the lower saprolite.

Gold is preferentially associated with goethite (>270 ppb) in the vicinity of weathered sulphides indicating gold macrotransfers. This also shows that the conditions prevailing during the formation of the goethite are more favorable for the co-precipitation of gold than those leading to the formation of a goethite-hematite mixture. Silver displays the opposite trend, it is concentrated in the goethite-hematite bands.

The trace elements related to the nature of primary host-rock are either residual in unaltered minerals and in the weathering products of the primary minerals, or are mobilised and integrated into other phases. For example, Zr occurs in resistant zircon and in the weathering product of titanite, anatase. Manganese, originally contained in chlorite, is retained in its weathering product vermiculite.

Kaolinite is the most depleted mineral of all; it only retains a fraction of trace elements (such as Ba) contained in the parent-mineral, it does not seem to scavenge any elements present in the microenvironment.

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Element	Saprock	ррт	Saprolite	ppm
Р			Ca and Ce-phosphates	
			Goethite	16000
			Goethite-hematite	9000
Ti			Anatase	
	Titanite, ilmenite		Goethite-hematite	1158
	Biotite and muscovite	7000	Muscovite	3500
	<ul> <li>Biotite/vermiculite</li> </ul>	6000	Muscovite kaolinite?	5500
V			Goothita hamatita	680
V	_		Goetinie-nematite	089
	Ilmenite		Anatase	220
	_		Muscovite	220
			Vermiculite-kaolinite	130
Cr			Goethite-hematite	585
			Goethite	512
			Vermiculite-kaolinite	185
			Anatase	
			Muscovite-kaolinite	110
Mn			Vermiculite	1533
	Ilmenite		Goethite	352
			Goethite-hematite	296
Co				
NE				
				10000
Cu	Sulphides, cuprite,		Vermiculite	10000
	- native Cu.		Malachite, tenorite	
	Biotite/vermiculite	15400	Goethite-hematite	26000
			Goethite	40000
Zn			Vermiculite	985
			Goethite	185
			Goethite-hematite	114
As			Goethite	
			Goethite-hematite	3180
Zr			Zircon	
			Goethite	246
	Zircon		Goethite-hematite	174
	_		Mica	105
			anatase	
Mo			Goethite	210
			Goethite-hematite	177
	-		Anatase	1 / /
Δα			Goethite_hematite	1
лg			Goothite	700
CL			Coethite	/00
50			Goethite	14
			Goetnite-nematite	8
Ва	—		Muscovite-kaolinite	
Ta			Anatase	
W			Goethite	96
			Goethite-hematite	67
			Anatase	
Au			Goethite	270 ppb
			Goethite -hematite	140 ppb
Pb	_		Goethite	188
			Goethite-hematite	127
Bi			Goethite	337
			Goethite-hematite	
	1		Anatase	232
Се			Ce-phosphates	
Th			Anatase	
111			Goethite	
	-1		Goethite hemotite	
TT			A patago	
U			Anatase	
			Goetnite, goetnite-nematite	

Table 27. Location and concentrations of selected trace elements in Boddington regolith samples. —: not measured or no qualitative data available.

Element	Clay zone	ppm	Duricrust	ppm	Loose pisoliths	ррт
Р			Goethite	280	Goethite-hematite	525
Ti	Anatase			<885	Anatase	
V	Anatase	100	Hematite-goethite Goethite Anatase	420 680		1280
Cr	Kaolinit e	170	Hematite-goethite	410	Anatase	540 660
Mn			Anatase	16880	Anatase	443
Co			Anatase	19	Anatase Al-Fe plasma cortex	
Ni					Al-Fe plasma cortex	72
Cu			Goethite	130	Goethite-hematite	31
Zn					Goethite-hematite	28
As			Goethite	120	Goethite-hematite	153
Zr	Anatase		Anatase	590		
Мо	Anatase	9	Hematite-goethite Goethite	35 106	Goethite-hematite	81
Ag						
Sb			Goethite	16		
Ba				11	Muscovite	
Ce			Cerianite?		Cerianite?	
Та			Anatase	271		
W			Anatase Goethite	235 549	Anatase	101
Au			Al-Fe plasma (goethite?)	950ppb	Microparticles associated with Fe-Al plasma	
Pb			Goethite	71	Goethite-hematite	105
Bi			Anatase Goethite	50 104		

 Table 28. Location and concentrations of selected trace elements in Boddington regolith samples.

 —: not measured or no qualitative data available.

## Clay zone

The microprobe analyses and the few LA-ICP-MS analyses show that kaolinite is extremely poor in trace elements. Chromium is the only element found associated with this clay.

## Duricrust

The lateritic duricrust is depleted in Mn, Cu, Zn, Co and Ni compared with the saprolite, whereas V, Cr, As, Mo, W, Zr, Nb and Pb are concentrated. Gold contents are very low compared to the underlying horizons (Anand, 1994). These general trends, which characterise the whole horizon, are further accentuated at the macroscale as a result of the reorganisation of the weathered material into nodules cemented by a matrix.

Copper, Zn, As and Mo are concentrated in goethite in the cortex of the nodules, and Cu and Zn are enriched, in a lesser way, in goethite of the internodular matrix. The core of hematite, goethite and possibly maghemite is relatively depleted in these elements. These observations suggest that (i) hematite can only incorporate low levels of Cu, Zn, As, and Mo in its structure; (ii) or these elements were not available in the microenvironment at the time of hematite formation.

Gibbsite, like kaolinite, is extremely low in trace elements.

Some of the W accumulated in the duricrust is hosted by anatase resulting from the weathering of titanite. Tungsten, which commonly substitutes for Ti in titanite, is residual in anatase. Tantalum, also found in titanite, exhibits a similar behaviour. The W and Ta anomalies at the top of the weathering profiles are partially caused by the relative accumulation of anatase. Tungsten also occurs as residual scheelite (Anand, 1994), and is contained in goethite in the matrix along with Mo. The W-Ta association is a good indicator of the origin of anatase and might be used to differentiate anomalous and anatase-related W contents.

Anomalous Au levels have been detected in the core, cortex and internodular matrix of the nodules. Gold occurs as microparticles scattered in the Al-Fe microplasma.

## Loose pisoliths

The chemical differentiation between core and cortex is not as marked as is observed in the duricrust. The slight Cu, Zn, Ni, Co and Mn concentration in the cortex is related to a higher abundance of goethite. Relict micas are also common and are responsible for Ba, Mg, and K enrichment.

## 5. 2. 2. Mineral weathering reactions

The microscale behaviour of some trace elements during the weathering of minerals can be derived from these data.

## $Chlorite \rightarrow corrensite \rightarrow vermiculite \rightarrow kaolinite + goethite$

Interstratified minerals and vermiculite are major bearers of trace elements in Boddington saprock and saprolite and inherit the original chlorite trace elements. Moreover, they have the ability to trap Cu released by sulphide dissolution. The final alteration products, kaolinite and goethite, do not inherit the original chlorite trace elements (Zn and Mn), nor scavenge any Cu.

## $Muscovite \rightarrow kaolinite$

Barium substitutting for K in the mica layers is not preserved in kaolinite.

## *Goethite-hematite-maghemite*

Hematite and maghemite are dehydration products of goethite. Anand (1994) observed that hematite-maghemite-rich areas are low in As relative to the goethite-reach areas, suggesting that As is ejected during the transformation of goethite to maghemite. The LA-ICP-MS data indicate that goethite not only contains more As, but also more Cu, V, P, Mo, W, Pb, Bi. Zr, Zn and Mn than its alteration products.

## 5. 2. 3. Implications for exploration

The *in situ* mineralogical and chemical study of the Boddington regolith material has provided data of relevance for Au and mineral exploration. Bulk sampling has to take into account the varying ability of different minerals to host elements which may be indicators of mineralisation. Targeting individual minerals and mineralogical phases for chemical analysis enhances anomalies, and reveals some which remain undetected in the bulk samples.

Kaolinite and gibbsite do not scavenge any significant amounts of trace elements. Bleached kaolinitic horizons and non-ferruginous bauxite should therefore be disregarded as a sampling medium. At Boddington, Au concentrations are highest in the ferruginous material in the bauxitic zone. Therefore, the degree of ferruginisation of these types of material has to be considered.

The importance of the clay fraction (<2  $\mu$ m) in kaolinite-dominated samples has been demonstrated. The clay fraction should be investigated to determine the presence of phyllosilicates such as interstratified minerals and vermiculite, which are able to trap large quantities of trace elements such as Cu.

Goethite is the ideal target for analysis as it has a high capacity to scavenge pathfinder elements. Apart from Cu, goethite at Boddington fixes As, Bi, W, Mo, Zn, Mn, V, Cr, Zr and Au. Hematite is also responsible for the fixation of lower levels of trace elements of interest for Au exploration. The preferential analysis of goethite should increase anomaly contrast. This is easily achieved by performing *in situ* micronalyses on goethite-rich material such as cortex of nodules and pisoliths rather than cores, cementing matrix, and ferruginous mottles in clay horizons. Conventional chemical methods generally used for bulk samples could be performed on cortex mechanically separated from the core, and on ferruginous mottle material.

Anatase is concentrated upwards through the profile and introduces anomalies which are not directly related to the mineralisation minerals. Anatase resulting from the weathering of titanite is partially responsible for W, Ta, Bi concentration in the duricrust and loose pisolith horizons. The separation of Ti-minerals from the sample might correct false anomalies. However, the analysis of surface anatase brings valuable information about the parent-mineral (titanite and ilmenite) and by extension the nature of the parent-rock. The coexistence of the two populations would indicate either (i) a transport away from the source if only observed at the surface; (ii) or like in Boddington the partial overprinting of the parent-rock by later events.

# 5. 3. The Mt Percy gold deposit

## 5. 3. 1. Element-mineral associations

Table 29 presents an inventory of the location of some trace elements in the clay-rich horizons at Mt Percy.

Inter-element correlation data obtained by Butt (1991) are matched against the analytical results presented in this work, and commented upon. In most cases, the LA-ICP-MS data explain unresolved complex element behaviour observed at the profile scale.

## Elements associated with the mineralisation

Gold and silver occur as microparticles associated with quartz grains in the clay saprolite. Quartz has probably protected Au from dissolution. Gold is further concentrated in the cutans observed in the mottled and plasmic clay where it seems to be trapped by goethite.

Antimony is residual in rutile in the saprolite and clay saprolite (up to 780 ppm). It is also located in Fe oxides directly derived from the weathering of sulphides ( $\leq 40$  ppm) in the saprolite, and strongly concentrated in goethite in the clay saprolite (up to 150 ppm) and mottled and plasmic clay (up to 900 ppm). The Sb levels in the bulk samples (15 ppm in the saprolite and clay saprolite, 81 ppm in the mottled clay) have been lowered by the dominant minerals quartz and mica which are relatively depleted in this element (5 ppm and  $\leq 20$  ppm). Tungsten is more abundant and follows the same pattern except in the mottled clay. It is reasonable to assume that although the majority of Sb and W comes from the ultramafic rocks, a part is inherited from the sulphides, and that they have been concentrated in Fe oxides. The dual origin and location of Sb and W is responsible for the absence of close correlation between Au, W and Sb at the alteration profile scale reported by Butt (1991).

Arsenic is strongly concentrated in Fe oxides by a factor of 25 relative to the saprolite bulk sample. Copper and Zn, both present in the primary Au mineralisation in chalcopyrite and sphalerite, display patchy coincident or distinct concentrations in the regolith. They are both hosted by Fe oxides in the saprolite and mottled and plasmic clays. Copper is incorporated in alunite thus explaining the partial overlap of the alunite-rich zone and some Cu concentrations. Although some of the higher Zn values are also detected in the alunite zone, Zn is not hosted by alunite. Zinc concentration is partly controlled by the occurrence of a Cr-Zn-spinel which is resistant to alteration.

## Elements associated with the parent-rock

Nickel, Co and Mn are concentrated in the Fe oxides replacing the sulphides in the lower saprolite. These elements are released by the weathering of the parent ferromagnesium silicate minerals, and incorporated into the weathering products in Fe oxides and clays (Ni-Cr-vermiculite). Nickel shows a very strong affinity for goethite. Subsequent vertical migration of these elements is responsible for further accumulation at the bottom of the regolith. Higher in the profile, Ni, Co and Mn are held by Fe oxides in the ferruginised rock and cutans. Little Ni is incorporated into fuchsite during the fuchsite-carbonate alteration of the ultramafic rocks.

Chromium accumulation is mainly residual, and its distribution is controlled by the stability of the hosts during supergene alteration. In the fresh rock, Cr is held by zincochromite, and possibly a Cr-rich chlorite as suggested by the presence of a Cr-rich vermiculite in the saprolite, fuchsite and rutile. Kaolinite inherits Cr during the weathering of the mica. Absolute concentration of Cr also occurs deep in the profile where it is trapped by Fe oxides and by alunite in the clay saprolite. Porphyry rutile does not contain any Cr and therefore can be differentiated from rutile originally hosted in the ultramafic rocks.

Titanium, held in rutile, fuchsite and kaolinite, accumulates residually upwards through the profile. Vanadium is retained in fuchsite and rutile, and is enriched in the ferruginous mottles and cutans of the mottled and plasmic clay.

## Elements associated with the fuchsitic-carbonate alteration

Barium levels in the bulk sample and fresh fuchsite are similar (about 200 ppm) in the saprolite, indicating that Ba is exclusively hosted by the Cr-mica. Barium is also substituting for K in alunite in the clay saprolite. Some of the trends observed within the weathered material are in fact the expression of Ba occurence in alunite: (i) the presence of alunite coincides with Au enrichment in the clay saprolite (ii) the location of weathered primary Au mineralisation is indicated by Ba concentration along traverse 15850N (Butt, 1991).

Rubidium occurs in fuchsite and is partially transmitted to kaolinite during weathering. Alunite does not contain Rb, thus explaining the absence of correlation between K and Rb in the alunitic horizon observed by Butt (1991).

## 5. 3. 2. Implications for exploration

At Mt Percy, gold is enriched close to the surface in the lateritic duricrust and calcrete. Gold is strongly depleted (<100 ppb Au) in the underlying horizons, the mottled and plasmic clay. However, the data obtained in this study provide insight for the sampling and analysis of the Au-depleted material. Gold is concentrated in ferruginous mottles, with the highest Au contents

in the ferrocutans precipitated along cracks and voids. High levels of As are also present in the Fe oxides and especially in cutans (up to 0.1% As).

Gold is associated with quartz crystals in the alunite-rich zone. Alunite is not a direct indicator of mineralisation, but its chemical composition is useful. Barium and Cu substitutions in the alunite crystals indicate the presence of porphyries and associated mineralisation.

As emphasised in the Boddington study, W and Sb are not reliable indicators of mineralisation. These two elements are mainly hosted by resistant minerals such as rutile and are therefore relatively enriched upwards in the weathering profile.

Kaolinite is not a sink for trace elements and its abundance dilutes anomalous values of the bulk samples.

Porphyries can be located by examining rutile in the surface horizons of regolith, in the case of non- transported material, as rutile hosted by wall rocks and porphyries generally have distinct isotopic signatures.

	Saprolite	ррт	Clay zone	ppm	Mottled and plasmic zone	ppm
р			Goethite	1800	Goethite-hematite	500
-			Alunite	380		
S	Goethite-hematite	4700	Alunite Kaolinite-goethite ?	5000		
Ti	Rutile Fuchsite	1850	Rutile Kaolinite-goethite plasma	4000	Rutile-anatase Fuchsite-kaolinite Kaolinite	3800 2000
Sc	Goethite-hematite Fuchsite	160 40	Alunite	170	_	—
v	Fuchsite Goethite-hematite	570 120	Rutile Goethite Alunite	11000 2200 78	Goethite+kaolinite Goethite-hematite	3000 540
Cr	Cr-spinel Vermiculite Fuchsite Goethite-hematite	345000 11000 10000 450	Rutile Fuchsite Kaolinite-goethite cutans Alunite	28000 11000 12000 8000	Goethite-kaolinite Fuchsite-kaolinite	7000 8500
Mn	Goethite-hematite	1500	Goethite-hematite	60	Goethite-kaolinite	351
Co	Goethite-hematite	3000	Goethite-hematite	20	Goethite Goethite-hematite	126 120
Ni	Goethite Vermiculite Fuchsite	35000 7400 790	Kaolinite-goethite Rutile	670 230	Goethite-hematite Goethite	7000 5780
Cu	Goethite-hematite	1900	Goethite Alunite Rutile	380 340 240	Goethite	740
Zn	Cr-spinel hematite-goethite Fuchsite	60000 2400 30	Goethite	30	Goethite Goethite-hematite	460 360
As	Goethite-hematite	1100	Goethite	320	Goethite Goethite-hematite	1150 400
Rb	Fuchsite	410	Rutile Kaolinite	85 40	—	—
Мо	Goethite-hematite	100			Goethite Goethite-hematite	430 12
Ag	Particles (quartz)				Kaolinite-goethite cutans	130
Sb	Rutile Fuchsite Goethite-hematite	100 14 40	Rutile Goethite Fuchsite-kaolinite Alunite	780 150 20 1770	Goethite Goethite-hematite	900 60
Ba	Fuchsite	220			Kaolinite-fuchsite	100
Та					Kaolinite-goethite cutans	130 ppb
W	Rutile Goethite-hematite Fuchsite	140 40 25	Rutile Goethite Fuchsite-kaolinite	820 460 30	Goethite-hematite Goethite	80 90
Au					Goethite-kaolinite	410
Pb			Alunite Goethite	80 40	Goethite-hematite	170

 Table 29. Location and concentrations of selected trace elements in Mt Percy regolith samples.

 —: not measured or no qualitative data available.

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## 7. REFERENCES

Anand, R.R. 1994. Regolith-landform evolution and geochemical dispersion from the Boddington gold deposit, Western Australia. CSIRO Australia, Division of Exploration and Mining, Perth. Report 24R.CSIRO/AMIRA Project 240 and 240A: Laterite Geochemistry and Yilgarn Lateritic Environments.Reissued as CRCLEME Open File Report 3, 1998. 149p.

Anand, R.R. 2001. Evolution, classification and use of ferruginous regolith materials in gold exploration, Yilgarn Craton, Western Australia. Geochemistry: Exploration, Environment, and Analysis, 1, 221-236.

Anand, R.R., and Gilkes, R.J. 1984. Weathering of hornblende, plagioclase and chlorite in meta-dolerite, Australia. Geoderma, 34, 261-280.

Anand, R.R., and Gilkes, R.J. 1984. Weathering of ilmenite in a lateritic pallid zone. Clays and Clay Minerals, 32, 5, 363-374.

Aspandiar, M.F., and Eggleton, R.A. 2002. Weathering of chlorite: I. Reactions and products in microsystems controlled by the primary mineral. Clays and Clay Minerals, 50, 5, 685-698.

Baker, S.A., Bi,M., Aucelio, R.Q., Smith, B.W., and Winefordner, J.D. 1998. Analysis of soil and sediment samples by laser ablation inductivley coupled plasma spectrometry, J. Anal. At. Spectrom., 14, 19-26.

Banfield, J.F., Eggleton, R.A. 1988. Transmission electron microscope study of biotite weathering. Clays and Clay Minerals, 36, 47-60.

Butt, C.R.M. 1991.Dispersion of gold and associated elements in the lateritic regolith, Mystery zone, Mt Percy, Kalgoorlie, Western Australia.CSIRO Australia, Division of Exploration and Mining, Perth.Report 156R. Reissued as CRCLEME Open File Report 45, 1998.V.1, 60 p.

Butt, C.R.M. 1993.Geochemical background, Mt Percy, Kalgoorlie, Western Australia.CSIRO Australia, Division of Exploration and Mining, Perth.Report 389R. Reissued as CRCLEME Open File Report 54, 1998.V.1, 103 p.

Clout, J.M.F., Cleghorn, J.H. and Watt, R.D. 1998. Geology of Kalgoorlie Mining Associates leases, Kalgoorlie, in Bicentennial Gold 88, D.I. Groves, M.E. Barley, S.E. Ho and G.M.F. Hopkins (eds), 70-77.

Davy, R. 1979. Geochemical exploration, Saddleback Greenstone Belt. Geol.Surv.West.Aust., Rec.1979/8.

Douglas, L.A. 1989. Vermiculites. In: Minerals in Soil Environments, J.B.Dixon and S.B.Weed (Eds), Soil Science Society of America Book Series, 635-674.

Dudoignon, P., Beaufort, D., Meunier, A. 1988. Hydrothermal and supergene alterations in the granitic cupola of Montebras, Creuse, France. Clays and Clay Minerals, 36, 505-520.

Durrant, S. 1999. Laser ablation inductively coupled plasma mass spectrometry: achievements, problems, prospects. Journal of Analytical Atomic Spectrometry, 14, 1385-1403.

El-Ansary, M. 1980. Exploration for commodities other than bauxite in the Worsley Project area. Reynolds Australia Mines Pty. Ltd., unpublished report.

Hale, M., Thompson, M., and Wheatley, M. R. 1984. Laser ablation of stream-sediment pebble coatings for simultaneous multi-element analysis in geochemical exploration, Journal of Geochemical Exploration, 21, 361-371.

Johnson, S.F., Sauter, P.C.C., Hyland, S.J. and Bradley, T. 1990. In: Geology of the Mineral Deposits of Australia and Papua New Guinea, F.E.Hughes (ed.), 433-437.

Le Gleuher, M. 2003. Trace elements-mineral associations in the regolith, Scuddles massive Cu-Zn sulphide deposit, Western Australia, CRC LEME Restricted Report 195R, 73p.

Longerich, H.P., Jackson, S.E., and Günter, D. 1996. Laser ablation inductively coupled plasma spectrometric transient signal data acquisition and analyte concentration calculation. Journal of Analytical Atomic Spectrometry, 11, 899-904.

Moore, D.M., and Reynolds, R.C.Jr. 1997. X-ray diffraction and the identification and analysis of clay minerals.Oxford: Oxford University Press., second edition, 378p.

Motelica-Heino, M., Le Coustemer, P., Thomassin, J.H., Gauthier, A., Donard, O.F.X. 1998. Macro and microchemistry of trace metals in vitrified domestic wastes by laser ablation ICP-MS and scanning electron microprobe X-ray energy dispersive spectroscopy. Talanta, 407-422.

Nahon, D.B. 1991. Introduction to the petrology of soils and chemical weathering. John Wiley & Sons, Inc., New York, 313 p.

Proust, D., Eymery, J-P, Beaufort, D. 1986. Supergene vermiculisation of a magnesian chlorite: iron and magnesium removal processes. Clays and Clay Minerals, 34, 572-580.

Radford, N.W. and Burton, P.E. 1999. The geochemistry of transported overburden: the time factor. An example from the Fender deposit, Big Bell, Western Australia. Journal of Geochemical Exploration, 66, 71-83.

Symons, P.M., Anderson, G., Beard, T.J., Hamilton, L.M., Reynolds, G.D., Robinson, J.M., Staley, R.W.and Thompson, C.M. 1990. Boddington gold deposit. In: Geology of the Mineral Deposits of Australia and Papua New Guinea, F.E.Hughes (ed.), 165-169.

Wilde, S.A. 1976. The Saddleback Group- a newly discovered Archaean greenstone belt in the southwestern Yilgarn Block.West.Aust.Geol.Survey, Ann.Rept, 92-95.

Wilde, S.A., and Low, G.H. 1980. Pinjarra, Western Australia - 1:250,000 geological series, Geol.Surv.West.Aust.Explanatory Notes S1, 50-2.

Wilde, S.A., and Pidgeon, R.T. 1986. Geology and geochronology of the Saddleback Greenstone Belt in the Archean Yilgarn Block, southwestern Australia. Aust. J. Earth Sci., 33, 491-501.

## **8. APPENDICES**

# **APPENDIX 1.**

Trace elements concentrations (ppm), silica and alumina contents (%) for the reference synthetic glasses NIST SRM 610 and NIST SRM 612. (From Pearce *et al*, 1996).

	NIST SRN	610	NIST SRM 612		
Element ppm	Average	std dev	average	std dev	
Mg	465.3	26.6	78.00	34.78	
Р	342.5	53.1	55.16	22.71	
K	463.1	8.1	65.51	1.33	
Sc	439.3	10.9	41.05	4.09	
Ti	432.8	12.1	48.51	2.76	
V	440.2	36.4	38.21	2.64	
Cr	388.0	15.2	42.46	13.95	
Mn	436.4	21.4	38.50	1.06	
Fe	453.1	17.9	55.57	15.78	
Со	400.9	22.6	35.09	2.33	
Ni	439.1	15.8	37.77	4.11	
Cu	432.9	16.9	36.82	2.89	
Zn	429.3	16.4	36.64	2.52	
As	317.6	13.9	37.33	6.56	
Se	112.0	2.8			
Rb	430.2	7.0	31.61	0.56	
Zr	439.9	7.8	35.99	1.25	
Nb	381.8		38.06	0.86	
Мо	396.1	38.9	38.30	1.65	
Ag	240.5	19.7	22.06	3.24	
Cd	260.9	4.5	28.02	0.54	
In	439.8	35.5	42.80	4.98	
Sn	390.0	19.8	37.67	2.04	
Sb	388.3	5.1	38.44	2.26	
Ba	415.9	21.5	38.52	1.9	
La	436.6	39.6	35.49	2.16	
Ce	443.3	15.0	38.24	1.71	
Pr	431.2	33.3	37.06	0.97	
Та	361.0	71.6	39.77	2.15	
W	434.5	23.3	39.55	0.78	
Au	22.9	3.7	5.03	0.05	
Pb	419.1	9.4	38.74	1.67	
Bi	373.8	28.7	29.84	5.98	
Th	463.1	11.9	37.31	0.72	
U	462.9	6.2	36.88	1.13	
SiO <sub>2</sub>	72.0		72.00		
wt.%	120		/2.00		
Al <sub>2</sub> O <sub>3</sub>	1.0		100		
wt.%	1.7		1.90		

## APPENDIX 2: In situ Laser Ablation Inductively Coupled Plasma Mass Spectrometry analyses: Boddington gold deposit

#### Data acquisition and reduction

The ablation pits were systematically observed with the SEM to check their morphology, and to confirm the expected mineralogy of the site.

#### Saprolite

Two batches of LA-ICP-MS analyses are presented:

1) In the first batch, 20 sites were ablated with a 29 μm probe. Isotopes <sup>26</sup>Mg and <sup>29</sup>Si were analysed to facilitate the mineralogical identification of the ablated material, as well as 17 minor and trace elements: <sup>49</sup>Ti, <sup>51</sup>V, <sup>52</sup>Cr, <sup>55</sup>Mn, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>75</sup>As, <sup>90</sup>Zr, <sup>95</sup>Mo, <sup>121</sup>Sb, <sup>138</sup>Ba, <sup>140</sup>Ce, <sup>184</sup>W, <sup>208</sup>Pb, <sup>209</sup>Bi, <sup>232</sup>Th, <sup>238</sup>U.

2) From the first batch results ten areas were selected for the measurement of gold and silver in particular. In order to maximise the detection of gold and silver in the clays and iron oxides, a large probe (50  $\mu$ m) has been used. In addition to <sup>197</sup>Au, the following isotopes were measured: <sup>27</sup>Al, <sup>29</sup>Si, <sup>49</sup>Ti, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>95</sup>Mo, <sup>98</sup>Mo, <sup>107</sup>Ag, <sup>109</sup>Ag, <sup>115</sup>In, <sup>184</sup>W, and <sup>209</sup>Bi. Isotopes <sup>91</sup>Zr, <sup>93</sup>Nb, <sup>181</sup>Ta were also analysed to check on potential oxide interferences with silver and gold: <sup>91</sup>Zr <sup>16</sup>O = <sup>107</sup>Ag, <sup>93</sup>Nb <sup>16</sup>O = <sup>109</sup>Ag; <sup>81</sup>Ta <sup>16</sup>O = <sup>197</sup>Au. In some cases (Ag and Mo) two isotopes were measured.

The calibration of the analytical results was carried out using the NIST SRM 612 glass reference standard (Appendix 1). The NIST SRM 616 (0.18% Au) was also randomly used to check the gold concentration of the NIST 612. The calculations of the isotopic concentrations were performed using silica (batch 1) and alumina (batch 2) as internal standards. Silica and alumina concentrations are microprobe data or stoichiometric values normalised to 100% wt. Where the signal had to be decomposed into slices representing "purer" phases, the most suitable internal standard was chosen for each slice.

## Clay zone

A 29 μm probe was used to ablate the samples (depth profiling). The following isotopes were analysed: <sup>26</sup>Mg and <sup>29</sup>Si for "navigation", and <sup>49</sup>Ti, <sup>51</sup>V, <sup>52</sup>Cr, <sup>55</sup>Mn, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>75</sup>As, <sup>90</sup>Zr, <sup>95</sup>Mo, <sup>121</sup>Sb, <sup>138</sup>Ba, <sup>140</sup>Ce, <sup>184</sup>W, <sup>208</sup>Pb, <sup>209</sup>Bi, <sup>232</sup>Th, <sup>238</sup>U.

The NIST SRM 612 reference glass was used as external standard to calculate the isotopic concentrations of two samples. The silica contents used as internal standard are microprobe  $SiO_2$  wt. % values normalised to 100.

## Pisolitic Duricrust

Two lots of LA-ICP-MS analyses were carried out:

1) In the first lot, 21 sites were ablated with a 29 μm probe. The mineralogical study has shown that nodule and matrix roughly consist of microcrystalline plasmas with various Al/Fe ratios. In order to identify the type of plasma, and enable the calculation of a value for the internal standard, the isotopes of three major elements <sup>27</sup>Al, <sup>29</sup>Si and <sup>57</sup>Fe were analysed. The following isotopes were also measured: <sup>24</sup>Mg, <sup>31</sup>P, <sup>47</sup>Ti, <sup>51</sup>V, <sup>53</sup>Cr, <sup>55</sup>Mn, <sup>59</sup>Co, <sup>60</sup>Ni, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>75</sup>As, <sup>95</sup>Mo, <sup>121</sup>Sb, <sup>138</sup>Ba, <sup>140</sup>Ce, <sup>181</sup>Ta, <sup>184</sup>W, <sup>208</sup>Pb, <sup>209</sup>Bi.

Two modes of ablation were used: depth profiles in relatively homogeneous phases (11 analyses), and scans across nodules and between nodules (10 analyses) to visualise the spatial

distribution of the trace elements. The isotopes concentrations have only been calculated for the depth profiling analyses.

2) Gold, <sup>107</sup>Ag and <sup>109</sup> Ag, as well as <sup>91</sup>Zr, <sup>93</sup>Nb, <sup>95</sup>Mo, <sup>98</sup>Mo, <sup>107</sup>Ag, <sup>109</sup>Ag, <sup>181</sup>Ta, <sup>184</sup>W, and <sup>209</sup>Bi were measured in selected phases, using a 50 µm laser probe. Isotopes <sup>27</sup>Al, <sup>29</sup>Si, <sup>49</sup>Ti, <sup>55</sup>Mn and <sup>57</sup>Fe were also analysed.

The calibration of the data was performed with the NIST SRM 612 glass reference standard (Appendix 1), and the NIST SRM 616 (0.18% Au) when analysing for gold. Aluminium stoichiometric values normalised to 100% wt oxides were used for the internal standard concentrations.

## Loose Pisoliths and Nodules

Routine LA-ICP-MS analyses were first conducted measuring 24 isotopes. A few sites were selected thereafter for analyses of gold and 15 others isotopes.

The following elements were measured. using a 29 µm probe: <sup>24</sup>Mg, <sup>27</sup>Al, <sup>29</sup>Si, <sup>31</sup>P, <sup>47</sup>Ti, <sup>51</sup>V, <sup>53</sup>Cr, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>59</sup>Co, <sup>60</sup>Ni, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>75</sup>As, <sup>95</sup>Mo, <sup>121</sup>Sb, <sup>138</sup>Ba, <sup>140</sup>Ce, <sup>181</sup>Ta, <sup>184</sup>W, <sup>208</sup>Pb, <sup>209</sup>Bi. The samples were ablated along transects (8 scans) and depth profile (10). The isotope concentrations have been calculated using the data from depth profiles and scans which are spatially restricted to the core or the cortex.

Gold, <sup>107</sup>Ag and <sup>109</sup>Ag, as well as <sup>27</sup>Al, <sup>29</sup>Si, <sup>49</sup>Ti, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>91</sup>Zr, <sup>93</sup>Nb, <sup>95</sup>Mo, <sup>98</sup>Mo, <sup>107</sup>Ag, <sup>109</sup>Ag, <sup>118</sup>Sn, <sup>181</sup>Ta, <sup>184</sup>W, and <sup>209</sup>Bi were analysed using a 50 µm laser probe.

The calibration of the data was performed with the NIST SRM 610 and 612 glass reference standards (Appendix 1), and the NIST SRM 616 (0.18% Au) when analysing for gold. Aluminium stoichiometric values normalised to 100% wt oxides were used for the internal standard concentrations.

## APPENDIX 3: In situ Laser Ablation Inductively Coupled Plasma Mass Spectrometry analyses: Mt Percy gold deposit

#### Data acquisition and reduction

#### Saprolite

Thirty two LA-ICP-MS analyses were performed on the saprolite minerals of the saprolite (Sample MW1711).

The sites were ablated with a 29 µm laser probe. The following isotopes were analysed: <sup>26</sup>Mg, <sup>27</sup>Al, <sup>29</sup>Si and <sup>57</sup>Fe for mineralogical identification, and <sup>31</sup>P, <sup>45</sup>Sc, <sup>49</sup>Ti, <sup>51</sup>V, <sup>53</sup>Cr, <sup>55</sup>Mn, <sup>59</sup>Co, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>75</sup>As, <sup>85</sup>Rb, <sup>95</sup>Mo, <sup>121</sup>Sb, <sup>137</sup>Ba, <sup>140</sup>Ce, <sup>184</sup>W, <sup>208</sup>Pb, <sup>209</sup>Bi. Unfortunately, Sn not being analysed, In data had to be disregarded as pollution could not be ascertained. However In concentrations and distribution were considered to interpret Sb anomalies.

The calibration of the analytical results was carried out using the NIST SRM 610 glass standard reference (Table 1). Alumina was chosen as internal standard to calculate the isotopic concentrations. Alumina concentrations are microprobe data and stoichiometric values normalised to 100 % oxides.

#### Clay saprolite

Forty six LA-ICP-MS analyses were performed on the clay saprolite (Sample MW1140).

The routine analyses involved the measurement of isotopes of 23 isotopes, of 4 major elements and 19 minor and trace elements: <sup>26</sup>Mg, <sup>27</sup>Al, <sup>29</sup>Si and <sup>57</sup>Fe, and <sup>31</sup>P, <sup>45</sup>Sc, <sup>49</sup>Ti, <sup>51</sup>V, <sup>53</sup>Cr, <sup>55</sup>Mn, <sup>59</sup>Co, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>75</sup>As, <sup>85</sup>Rb, <sup>95</sup>Mo, <sup>115</sup>In, <sup>121</sup>Sb, <sup>137</sup>Ba, <sup>140</sup>Ce, <sup>184</sup>W, <sup>208</sup>Pb, <sup>209</sup>Bi. The material was ablated with a 29 µm without pre-ablation.

A further batch of analyses was conducted using a 50 µm probe to measure gold and silver <sup>107</sup>Ag and <sup>109</sup> Ag, as well as <sup>91</sup>Zr, <sup>93</sup>Nb, <sup>95</sup>Mo, <sup>98</sup>Mo, <sup>181</sup>Ta, <sup>184</sup>W, and <sup>209</sup>Bi using a 50 µm laser probe. Isotopes <sup>27</sup>Al, <sup>29</sup>Si, <sup>49</sup>Ti, <sup>55</sup>Mn and <sup>57</sup>Fe were also analysed.

Considerations about the oxide interferences and pollution have been commented in Section 2.

The calibration of the analytical results was carried out using the NIST SRM 610 glass standard reference (Appendix 1). Alumina was chosen as internal standard for the two sets of analyses.

## Mottled and plasmic clay

Thirty-nine sites, including cutans and ferruginised material, were analysed by LA-ICP-MS. Twenty-nine depth profiles were conducted using a 29 µm laser probe. The following isotopes were measured: <sup>27</sup>Al, <sup>29</sup>Si, <sup>57</sup>Fe, <sup>24</sup>Mg, <sup>31</sup>P, <sup>47</sup>Ti, <sup>51</sup>V, <sup>53</sup>Cr, <sup>55</sup>Mn, <sup>59</sup>Co, <sup>60</sup>Ni, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>75</sup>As, <sup>95</sup>Mo, <sup>121</sup>Sb, <sup>138</sup>Ba, <sup>140</sup>Ce, <sup>181</sup>Ta, <sup>184</sup>W, <sup>197</sup>Au, <sup>208</sup>Pb, <sup>209</sup>Bi. Using a larger probe (50 µm), analyses of Gold, <sup>107</sup>Ag and <sup>109</sup> Ag, <sup>91</sup>Zr, <sup>93</sup>Nb, <sup>95</sup>Mo, <sup>98</sup>Mo, <sup>107</sup>Ag, <sup>109</sup>Ag, <sup>181</sup>Ta, <sup>184</sup>W, <sup>209</sup>Bi, as well as a few majors <sup>27</sup>Al, <sup>29</sup>Si, <sup>49</sup>Ti, <sup>55</sup>Mn and <sup>57</sup>Fe.

The calibration of the data was performed with the NIST SRM 612 glass reference standard (Appendix 1), and the NIST SRM 616 (0.18% Au) when analysing for gold. Aluminium stoichiometric values normalised to 100% wt oxides were used for the internal standard concentrations.