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QUARTZ AND THE ACID INSOLUBLE RESIDUE OF ROCKS AND REGOLITH AS A SAMPLE MEDIUM IN MINERAL EXPLORATION

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INTRODUCTION

The characterisation of quartz using a combination of trace element geochemistry and physical methods is a powerful technique for identifying quartz from veins and rocks belonging to mineralisation styles ranging from hydrothermal to pneumatolic (Scherbakova et al. 1971, van Moort and Hotchkis, 1993). The approach relies on the assumption that quartz deposited by mineralising fluids will preserve a distinct trace element composition and physical properties related to specific defects in the mineral lattice or specific solid and fluid inclusions.

Early work by Bambauer (1961) and Poty (1969) concentrated on quartz crystals in fractures and veins, while later work tends to concentrate on the microcrystalline quartz of ore bearing veins (Novgorodova et al., 1984; van Moort and Brathwaite 1988). The issue is complex as veins usually come in stages of varying mineralogy. Considerable simplification occurs if quartz concentrates are obtained from crushed rocks. Studies of variation of quartz concentrates were conducted on silicification associated with the Carlin-type Au deposits (van Moort et al. 1995) and on foot and hanging wall alteration zones associated with volcanic hosted massive sulphide deposits (Aung Pwa et al., 1992; Aung Pwa 1995; Aung Pwa and van Moort 1999a and b.)

The use of the acid insoluble residue has also been tested on a number of regolith case studies over deeply weathered mineral deposits (Stott et al. 1997; Xu and van Moort 1997; van Moort et al. 1999; Aung Pwa et al. 1999). The following discussion is based on some two thousand samples.

SAMPLE PREPARATION

In the case of vein quartz, the material must be hand picked and free of impurities (i.e. carbonates, sulphides, rock fragments, coatings). All samples are finely ground by milling, leached overnight in hot fuming nitric acid, rinsed three times with distilled water and dried at 90° C. This process removes all carbonate, iron and manganese oxides, and sulphide impurities, as well as possible milling contaminants. A similar treatment with hot nitric acid is sufficient for most rock pulps.

Because it is so important to obtain as pure quartz concentrates as possible, preparation of the acid insoluble residue of the regolith samples needs special care. The conventional methods removing carbonates and Fe and Mn oxides from soils and sediments with hydrochloric acid (Milner, 1962; Russell and van Moort, 1987), treatment with nitric acid (van Moort et al., 1995) or even sequential treatment with hot hydrochloric and nitric acid are inadequate for lateritic material. In order to remove the Fe and Mn oxide grains, coatings and cement, hot aqua regia

(Stott et al., 1997) or sequential treatment with hot hydrochloric and hot nitric acid is required. Such treatment also removes Al oxides and hydroxides, phosphates, residual sulphides and most sulphates. The removal of clays is very important as clays influence the chemical and physical analysis of the quartz concentrate. The remaining clays and some other minerals such as alunite can be removed by hot sulphuric acid digestion and subsequent thorough rinsing. Remaining magnetic minerals may be extracted by use of a hand held magnet. Constant vigilance during treatment is required as, for example, talc is acid insoluble, whereas gibbsite, boehmite and resistate spinel and garnet minerals are acid soluble. Important references of the response of individual mineral species to acid treatment are found in Dana and Ford (1966) and Duda and Rejl (1990). A discussion of the poor efficiency of extraction techniques to determine so called "total compositions" of regolith materials is also given by Gedeon et al. (1977).

Aqua regia or hydrochloric acid treatment of lead rich samples will result in the precipitation of amorphous lead and silver chlorides. Further treatment with ammonium acetate may be required to remove these precipitates (Svehla, 1982; Nand and van Moort, 1995). Alternatively a nitric acid treatment may precede an aqua regia treatment.

PURITY OF THE CONCENTRATES

With careful selection, fine grinding and appropriate acid treatment, it is possible to obtain very pure quartz from vein material. The acid insoluble residue of the rock and regolith pulps consists essentially of silicates, especially quartz, minor sericite, traces of alkali feldspar and resistate minerals such as zircon and titania polymorphs. It is rare to encounter more than traces of other silicate minerals as they have either been destroyed by weathering (Loughnan, 1968) or degraded and removed by the acid treatment (Nand and van Moort, 1995).

XRD analysis of the acid insoluble residue from regolith material typically indicates quartz, minor sericite and traces of kaolinite and rutile. Microscopic inspection of residues, however, indicates there is a substantial amount of microcrystalline chalcedony, and more rarely opal, which is the result of hydrolysis during weathering of the silicates. ESEM analysis reveals that the "quartz" in the near surface regolith samples consists in many cases of aggregates of primary quartz embedded in secondary chalcedony, sometimes having trapped clay, sericite and other mineral particles like iron oxides, or just fine grained chalcedony aggregates. Inclusions of rutile are uncommon.

CHEMICAL ANALYSIS

In our work bulk chemical analysis of quartz and quartz concentrates are mostly carried out by simultaneous PIXE/PIGME at the 3 MV van de Graaff accelerator at ANSTO, Lucas Heights (Bird and Williams, 1989). The method uses a defocused proton beam hitting a 3 mm diameter target of finely crushed material that has been homogenised and pelletised with spectrographic graphite. The instrumental conditions of analyses are reported by van Moort et al. (1995), and their precision and accuracy by Russell et al. (1996). The minimum detection limits for the material studied are comparable to, or better than, XRF techniques (Stott et al., 1997). The data

may be complemented by some ICP-MS analyses. The elements consistently present in concentrations above the detection limit are listed in Table 1. Note that the detection limit of Au by PIXE is rather high (5 ppm). The presence of even small amounts of other minerals, such as sericite and feldspar greatly affects the chemical composition of the acid insoluble residues.

There is, however, no particular necessity to perform the analyses by PIXE/PIGME, as comparable results are obtained by other methods. See Table 1.

EPR

Many physical methods are used to characterise quartz in veins and rocks, e.g. morphology as observed by the polarising microscope (Adams, 1920; White, 1943), study of fluid inclusions (Roedder, 1984a) and decrepitation (Roedder, 1984b; Burlinson, 1991), thermal release gas evolution mass spectrometry (Barker and Robinson, 1984), oxygen isotopes (Rye and Rye, 1974); Matsuhisa et al., 1985), trace element studies (Novgorodova et al., 1984), thermoluminescence (Sankaran et al., 1983; Hochman et al., 1984; Charlet and Quinif, 1985) and cathodoluminescence (Nickel, 1978).

Van Moort (1986) and van Moort and Russell (1987) reported the use of electron paramagnetic resonance as a means to characterise quartz as a guide to gold mineralisation. In general it appears that quartz from veins associated with mineralisation is more paramagnetic than quartz from younger rocks. The method requires only a simple EPR spectrometer, present in the chemistry or physics department of most research centres.

Electron paramagnetic resonance (EPR) spectroscopy is defined as the form of spectroscopy concerned with microwave-induced transitions between magnetic energy levels of electrons having a net spin orbital momentum (IUPAC, 1989). The techniques of EPR and nuclear magnetic resonance (NMR) are thus basically the same: the alignments of magnetic moments by externally applied magnetic fields and their reorientation by the absorption of incoming electromagnetic radiation. The essential difference between the two techniques is that, in EPR it is the electronic magnetic moments that are being reorientated, whereas in NMR it is the nuclear magnetic moments.

There are many practical applications of EPR in the fields of biology, life and medical sciences, chemistry, earth and environmental sciences, physics and material science (Rudowicz, 1998). Instrumentation consists of a resonance cavity with a standing microwave of constant frequency between two strong electromagnets. If the magnetic field is swept, the microwave energy is absorbed at specific magnetic flux densities because of resonance of unpaired electrons between the parallel and antiparallel state. The EPR spectra in this study have been recorded as analogue X-band (9.15 GHz) powder spectra. The intensities have been measured as peak heights (in cm) on first derivative absorption spectra obtained under standard instrument conditions, as reported by van Moort and Russell (1987) as shown later in Fig 8. These intensities are relative values only. They are, however, entirely reproducible and have been found to be constant over fifteen years on the JEOL FEX3X ESR spectrometer of the Central Science Laboratory of the University of Tasmania.

The large V shaped EPR signal with a width of about 2 mT and an effective spectroscopic splitting factor of $g \approx 2$ is typically associated with gold mineralisation (Russell and van Moort 1997). The centre shows details reminiscent of the $[\text{AlO}_4]^\circ$ centre in quartz identified by Petrov et al. (1990) and what Scherbakova et al. (1976) and Matyash et al. (1982) called the "Al-O" centre. Other centres are not of practical value (van Moort and Barth, 1992). Fig 8 presented later shows a typical EPR signal in auriferous quartz. All spectra observed in this study are comparable, but for their intensities.

Since EPR requires the presence of unpaired electrons in the sample being studied, its range of applications is restricted to paramagnetic substances. Near ore-bodies, quartz and other minerals contain numerous out-of-place atoms and various substitutional and interstitial impurities (including ore constituents). These cause a considerable amount of lattice defects that result in paramagnetism. It is necessary to use the acid insoluble residue for EPR studies, rather than untreated rocks pulps, because the spectra of untreated material contain strong and unidentifiable interfering signals derived from other minerals. However, as the EPR of quartz is very specific, minor contamination by feldspar, sericite and other minerals in the acid insoluble residue has no significant effect (Nand and van Moort, 1995).

The relationship between EPR signals and gold mineralisation in quartz and rocks has been investigated by various authors (Scherbakova et al. 1976; Matyash et al. 1982; van Moort and Russell; 1987, van Moort and Brathwaite; 1988, Nand 1989; Russell and van Moort 1997). Recently, it was found that auriferous jasperoids from Carlin, Nevada, USA, are more paramagnetic than barren ones (van Moort et al., 1995). Subsequently, a comprehensive study of the EPR spectra of wall rock alteration products of acid and intermediate volcanoclastic rocks in the Mt. Read volcanics of western Tasmania has enabled the distinction between wall rock alteration in general and wall rock alteration associated with VHMS deposits (Aung Pwa, 1995; Aung Pwa and van Moort, 1999c). During the last few years, the use of the acid insoluble residue of rock pulps has been extended to characterise highly weathered regolith (Xu Li, 1999; van Moort et al., 1999)

CASE STUDIES

The use of quartz as a sample medium is given in the following case studies: firstly two auriferous reef systems, secondly the acid insoluble residue of rock pulps from wall rock around a VHMS deposit and thirdly insoluble residue of rock pulps after sequential acid treatment of wall rock alteration products of four deeply weathered regolith occurrences overlying gold deposit.

Case Study 1:

EPR characterisation of quartz vein phases from the Martha Hill gold deposit, Waihi, New Zealand (after van Moort and Brathwaite, 1988)

The quartz vein system at Waihi is a major epithermal gold-silver deposit, with a past production (1883-1952) from underground workings of 11,048,000 kg of Au-Ag bullion (estimated 204,000 kg Au and 9,006,000 kg Ag) and a continuing (1988-1998) production from the Martha Hill open pit of 25,400 kg Au and 141,000 kg Ag. Several stages of vein fill have been recognised,

although a detailed paragenesis is not understood. The succession consists of early bulk vein fill by milky quartz and calcite in the intermediate and deep levels of the old mine, rhythmically banded chalcedonic quartz with fine-grained pyrite, being the dominant vein filling in the upper 120m of the Martha lode and the main ore stage which consists of crustiform banded gold-silver base metal sulphide quartz veins, generally located along the footwall side of the major lodes (Brathwaite and Blattner, 1995).

All material was studied at room temperature as finely ground powders at 9.155 GHz, 10mW microwave power and with magnetic flux density sweeps over ± 250 , ± 100 and ± 2.5 mT (millitesla) respectively. The material collected from musea, the Martha open pit and drill core from the Waihi Gold Company could be classified on the basis of the EPR spectra into seven basic types, as listed in Table 2. The intensity of the paramagnetism in each type of quartz is related to the degree of mineralisation and as such can be used as an exploration tool (e.g. Fig. 3).

The milky barren quartz of the first stage of vein fill is characterised in the ± 250 mT sweep by a steep drop in the first derivative EPR signal as the magnetic field increases, followed by some small peaks in the central region and then a gentle rise. Details of the peaks in the central region, as observed in the ± 100 mT sweep, are first derivative crossovers at spectroscopic splitting factors g 2.14, 2.08, 2.04, 2.00, 1.98, 1.93 and 1.86. The ± 2.5 mT sweep is characteristically very flat. These features are shown in Fig. 1.

The spectra of the quartz replacing calcite in some of first stage veins is similar to the milky-quartz spectra, but show an additional pronounced signal at g 2.26. Again the ± 2.5 mT is flat, with a weakly developed E' centre at g 2.001 (see Fig. 2).

Table 2: Vein Systems Waihi

Milky barren quartz of the first stage veins:			
VM 790-851-933-935-946			Fig.1
Replacement of calcite by quartz, first stage veins:			
VM 791-792-852			Fig. 2
Rhythmically banded chalcedonic quartz of the second stage veins:			Fig. 3
Sequence VM 274-277			
Sequence VM 831-833			
Sequence VM 819			
Sequence VM 820			
Sequence VM 940			
Sequence VM 1312 A to T			
Vug+base VM 798-799			
Small veins in Martha Open Pit:			Fig. 4
VM 793 to 797			
Complex vein VM 931-933			
Rhythmically banded quartz at depth from deep mine workings:			Fig. 5
Core WHD21	204-207m	VM 819-820	
Core WHD15	270 m	VM 821-825	
Chips WHD14	255-258 m	VM 826-830	

Core WHD60	236.47m	VM 837-839
Rhythmically banded quartz at depth, with sulphide bands:		
Core WHD44	244.5m	VM 845-848
Quartz from massive crustiform sulphide ore of third stage veins:		
VM 812-815-816-817-818-942-943-2046-1046a-1047		Fig. 6

The rhythmically banded chalcedonic mineralised quartz in the second stage of vein fill from the Martha Open Pit and drill holes occurs to depth of 120m. This type of quartz has EPR spectra that are different from barren milky quartz. The spectrum of the ± 250 mT sweep does not have such a pronounced drop with increasing magnetic field, with a small signal at g 3.8 and a well developed central signal. The ± 100 mT sweep has peaks in the central region of which the most pronounced peak has a minimum of g 2.0025-2.030, 2.005 and 1.9966 (see Fig. 3). The bands come in sequences, often starting with brecciation of the bottom, followed by massive white chalcedony, sulphide rich chalcedony, grey chalcedony, amethystine quartz and finally clear quartz. The paramagnetism of the material always decreases in this order, as illustrated for the sequence VM274-277 of the inset in Fig. 3.

In some cases the banded veins contain vugs with clear quartz. The bases of the vugs have characteristically flat spectra in the ± 250 mT sweep with a pronounced central signal at g 2.005-2.003. The clear material is like the quartz replacing calcite, with a strong signal at g 2.6, no signal at g 2.0025-2.003 and with a more distinctive centre at g 2.001.

In addition to the rhythmically banded chalcedonic quartz from the upper levels of the lode, isolated thin and slightly pyritiferous quartz veins can be observed in the Martha Open Pit. Their ± 250 mT spectra are much more like the spectra of the first stage milky quartz veins, including the sharp drop in signal with increasing magnetic flux density, the pronounced signal at g 2.26, and the weak signals in the range g 2.13 to 1.86. The spectra of these thinner quartz veins, however, differ in two respects to those of the barren material: they have a weak g 3.8 signal and, most significantly, pronounced signal at g 2.0025 to 2.003. The more pyrite is present the larger the signal (also after destruction of the pyrite). See Fig. 4.

In the Martha Hill complex vein sets it is possible to use EPR spectra to distinguish between the barren early vein phases and later auriferous phases.

Material below the 200m level obtained from drill holes, was used to study milky quartz through the footwall sequences of the Martha lode. These sequences consist of a bottom of white quartz, pyritiferous quartz of these sequences has the same EPR characteristics as the small quartz vein in the Martha Open Pit described above. The main characteristics of the quartz are the cross over at g 2.6 and the minimum at g 2.005-2.003. The intensity of the latter signal decreases gradually, moving upwards through each sequence. See Fig. 5.

The massive crustiform sulphide ore containing pyrite, sphalerite, galena and electrum, is only available from historic collections. The quartz from this material has entirely different paramagnetic characteristics. The ± 250 mT sweep gives a simple spectrum, first sharply decreasing, then with a very strong signal and a crossover at g~2.025, with a distance of about 50

mT between the first derivative maximum and minimum. This same signal does not show any further details in the ± 100 mT and ± 2.5 mT sweeps. See Fig. 6.

The sequence of VM845-848 WHD44 244.5 has an EPR quartz spectrum which is transitional between the simple spectrum of quartz from massive ore and quartz from the sequences of the footwall of the Martha lode described above. The spectra show both the signal at g 2.26 typical of the former as the signal at g 2.025, typical of both. In addition a small signal at g 3.8 is observed.

The above classification enables a better grouping of the veins than was previously possible. The spectra can only be explained in part. The cross over at g 3.8 is caused by Fe^{3+} in the quartz lattice, the six small peaks at between g 2.14 and 1.98 may be attributed to Mn^{2+} , and the peak at g 2.001 represents the oxygen vacancy E' . The nature of the other peaks, including the often pronounced minimum at g 2.0025-2.003, is not well understood; lattice impurities are presumed to be the cause.

Case Study No. 2:

The distribution between auriferous and barren quartz, Beaconsfield Gold Mine, Tasmania (after Russell, 1995)

The 10 km long Beaconsfield/Salisbury goldfield is situated in Ordovician sediments west of the Tamar Fracture System in central northern Tasmania. The main production came from the Tasmania Reef, a Devonian fissure reef with quartz emplaced on a pre-existing fault zone. The reef is 395 m long and varies from 20 mm to 8 m, averaging 3.1 m wide. There are many smaller vein systems in the area, both auriferous and mined or barren and explored only. The veins consist of microcrystalline quartz, sometimes with a core of ankerite. The drill holes from which material was used for the present study intersect the reef below the deepest level of the old mine workings. Gold values in the Tasmania Reef vary with depth. Over the first 120 m an average grade of 38 g/t was maintained, dropping gradually to 4 g/t at 415m. However at 450 m the average Au grades were up to 20 g/t. The geology and mineralogy of the goldfield was discussed in detail by Russell and van Moort (1992) and Russell (1995). Recent development to 925m indicates a total indicated and inferred resource of 1 Mt @18g/t Au.

Early work by van Moort and Russell (1987), based on 112 samples, indicated that by and large quartz from the Beaconsfield reef intersections had higher EPR intensity than quartz from veins outside the reef system. See Fig. 7. Subsequently a total of 307 quartz spot samples from core (with known gold content as determined by assay from 1 m long core splits) were analysed by EPR as a further pilot project. The first stage in determining the relationship between quartz and gold mineralisation was to separate the samples in two subsets. All mineralised samples with a $\text{Au}_{(\text{fire})}$ content >0.02 ppm (the cut-off used at Beaconsfield by the mining company) were extracted from the initial data pool. The result of this subdivision is illustrated in Table 3, where the EPR peak height represents the amplitude of the first derivative signal as indicated in Fig. 8. Both the total data pool and the non-mineralised samples displayed a very strong Spearman rank correlation between the lack of gold and peak height ($R_s=0.469$ and $R_s=0.500$ for 307 and 204 samples respectively, at a 99.999% confidence level, $p=0.001$).

Table 3: Au_(fire) vs EPR Peak Height (cm), with the subdivision of the initial population into mineralised (n=103) and non-mineralised samples (N=204).

Population	Number	Gold Mean (ppm)	Peak Height Mean (cm)	Sp. Rand	@p=0.001
All samples	307	14.5	7.4	0.469	0.190
Au<0.02ppm	204	0	5.7	0.500	0.19
Au>0.02ppm	103	43.1	10.9	-0.084	0.200

The data grouping broadly indicates that the mean peak height of the EPR signal can be used to identify whether a sample is potentially auriferous or not. Both the mean peak height of the non-mineralised group (5.7 cm) and the total data pool (7.4 cm), suggest that a value between 5 cm and 7 cm could be used as a peak height cut-off point for the presence or absence of mineralisation (i.e. for standard instrument settings). To test this hypothesis, the samples were split into two groups of respectively a peak height of less than 5 cm and more than or equal to 5 cm. This process demonstrated that there is a strong relationship between peak heights less than 5 cm and the absence of gold. The group with the higher peak height, however, contained too many samples without gold to give a significant correlation. Consequently the EPR method, provided a cheap and efficient technique to indicate where there is no gold.

From the sample population of 307 samples, 120 samples were re-analysed by EPR at microwave power 0.5 and 100 mW. When the population (N=120) was subdivided into reef samples and barren samples, there were several correlations between the gold fire assay values and the EPR results. In the auriferous subset, the normalised peak height (100 mW), integral (100 mW) and integral (0.05 mW) demonstrated significant correlations of $R_s=0.200$ (N=63), $R_s=0.400$ (N=47) and $R_s=0.300$ (N=51) respectively with Au_(fire) values.

After the removal of surface samples, tiny veins with inadequate information on gold content and duplicate samples, 70 auriferous and barren samples remained in the final pool. Statistical analysis of this group found significant correlations between Au_(fire) and the normalised peak height (100 mW) and standardised integral (100 mW). These correlations were $R_s=0.410$ (N=70, $r=0.380$ at $p=0.001$) and $R_s=0.38$ (N=57, $r=0.33$ at $p=0.01$) respectively with Au_(fire) values. This indicated that the EPR signals at this higher microwave setting could be used as an indicator of gold mineralisation. Frequency histograms were plotted for the reef and barren populations, to determine the most suitable range of EPR values for the prediction of mineralisation. These plots indicated a "cut-off point" of 25 units. Hence, the use of this "cut-off point" (25 units), will select 33 (80%) of the auriferous samples and at the same time will discard 18 (62%) of the barren samples. See Figs 9 and 10. Further statistics highlighting the use of EPR a discriminator for gold mineralisation are listed below in Table 4.

Table 4. Demonstration of the use of the discriminatory Peak Height value of 25 units. N_R = number of reef samples, N_B =number of barren samples.

Population	N_t	Gold Mean (ppm)	N_R	N_B	$N_R:N_B$
Total	70	31.6	41	29	1.41
X>25 units	44	49.3	33	11	3.00
X<25	26	1.5	8	18	0.44

This table demonstrates the concentration of gold samples above the cut-off (mean 53.8 ppm) vs below the cut-off (mean 3.6 ppm). The ratio of reef samples vs barren samples (i.e. $N_R:N_B$) further demonstrates the screening power of this cut-off value (4.36 above the cut-off value vs 0.40 below this value.)

There is a considerable compositional difference between samples from the barren and reef quartz, as shown in the Table below:

Table 5. Chemical composition of samples sorted by gold fire assay (all concentrations in ppm)

Barren Quartz	Au (fire)	Au (pixe)	Ge	As	Cl	K	Mn	Fe	Na	Li	Al
Mean	0	0	0.8	1.6	489	629	6	172	230	3	101
Std. D.	0	0.2	2	9	339	680	15	300	568	6	131
Std. E.	0	0	0.1	0.6	22	44	1	20	37	0.4	86
Min.	0	0	0	0	0	0	0	0	14	0	0
Max.	0	3	16	95	194	5556	128	3554	4343	40	9038
Count	236	236	236	236	236	236	236	236	236	236	236

Reef Quartz	Au (fire)	Au (pixe)	Ge	As	Cl	K	Mn	Fe	Na	Li	Al
Mean	52	28	3	21	410	589	13	231	190	14	1382
Std. D.	78	142	3	67	314	626	34	421	225	11	1284
Std. E.	8	15	0.3	7	33	65	4	44	24	1	135
Min.	0.02	0	0	0	0	0	0	0	41	0	315
Max.	354	993	11	415	1510	3835	264	3018	1322	83	8393
Count	91	91	91	91	91	91	91	91	91	91	91

Case Study No. 3.

The surface expression of VHMS deposits by geochemical and paramagnetic methods: the Rosebery example (after Aung Pwa, 1995).

The Cambrian Rosebery deposit is located within the Mount Read Volcanic belt of western Tasmania, Australia, which hosts more than forty mineral occurrences including major volcanic-hosted massive sulphide (VHMS) deposits at Mount Lyell, Hercules, Rosebery, Que River and Hellyer. The Rosebery deposit is a major Zn-Pb-Cu-Ag-Au mine in Australia, and originally contained 20 Mt ore at 5.0% Pb, 16.2% Zn, 0.7% Cu, 155g/t Ag, and 2.9 g/t Au (Aung Pwa et al., 1992).

One of the most important exploration problems in the search for VHMS deposits is the identification of wallrock alteration related to VHMS mineralisation. During the Devonian Tabberabberan orogeny, shallow level granitic intrusions were emplaced in western Tasmania, including the Rosebery mine area, and the Mount Read volcanics were deformed and metamorphosed to greenschist facies. These overprinting events make it difficult to distinguish between the alteration related to VHMS mineralisation and the alteration related to later metamorphism.

An exploration geochemical study using hot HNO₃ insoluble residues of rock pulps has been conducted in the Rosebery mine area to determine the distribution of elements in surface rocks

(Aung Pwa et al., 1992), to identify the wall-rock alteration related to VHMS mineralisation and to distinguish it from the alteration unrelated to mineralisation (Aung Pwa, 1995; Aung Pwa and van Moort, 1999b).

An independent comprehensive EPR survey has also been conducted to test EPR as an exploration tool (Aung Pwa and van Moort 1999a). The residues after the acid treatment consist mainly of quartz, sericite and feldspar (plagioclase and K-feldspar) with traces of chlorite and kaolinite in some samples.

Quartz, sericite, chlorite, carbonate, etc. are the principal alteration products, however their occurrence relates to both VHMS mineralisation and to metamorphism and deformation in the region. In summary, there are no definitive mineralogical differences between the VHMS related alteration and alteration related to later metamorphism and tectonism.

Two types of geochemical halos exist in the Rosebery area. The type 1 halo trends NW-SW, is related to wall rock alteration, and is defined by enrichment in Cl, and possibly K and Rb, and depletion in Al, Ca, Na, Ti and Sr. It passes discordantly across the White Spur Formation, the altered footwall, the host rock of the Rosebery deposit, the hanging wall and Mount Black Volcanics. The type 2 halo, trending N-S (largely stratabound), is related to massive sulphide mineralisation and is characterised by enrichment in Fe, Mn, Ba, Zn, Pb and possibly K, Rb and F. The type 2 halo outlines the mineralised host rock and footwall alteration zone, and also extends toward the south into the unaltered footwall and hanging wall rocks. Both halos intersect at Rosebery in the zone of mineralisation and associated footwall alteration. The recognition of these geochemical halos has led to the formulation of geochemical indices for identification of alteration related to VHMS mineralisation.

Binary relations between $Mn \times Ba \times F$ and $(Ca \times Na \times Sr)$, and $(Mn \times Ba)$ and $(Na \times Sr)$, and their ratios $(Mn \times Ba \times F)/(Ca \times Na \times Sr)$ and $(Mn \times Ba)/(Na \times Sr)$ identify the alteration related to massive sulphide mineralisation and distinguish it from alteration unrelated to the mineralisation in the Rosebery area. These geochemical indices may also be used for the other VHMS deposits of the Mt Read Volcanic Belt, which all display similar geochemical alteration signatures. The alteration related to VHMS mineralisation can be distinguished from alteration unrelated to mineralisation by higher values of the geochemical indices of $(K \times Mn \times Ba \times Rb)$, $(Mn \times Ba \times F)$ and $(Mn \times Ba)$.

The Ca depletion of the acid insoluble residue in the NE-SW corridor and along the Mt Black fault is related to feldspar destruction. Similar patterns may be observed for Na and Sr. (Fig 11)

High Mn and Ba values of the acid insoluble are recorded in footwall and hanging wall of the Rosebery deposit. (Fig 12)

The ratio of $(Mn \times Ba)/(Na \times Sr)$ in the acid insoluble residue of the surface rocks around the Rosebery deposit broadly outlines the deposit and altered footwall. The strip along the Mount Black fault is due to remobilisation. (Fig 13)

The EPR ± 5 mT and EPR ± 100 mT sweep intensities show a NE-SW lineament and NS lineament respectively. (Fig 14/15)

The EPR index of the product of the 326.5 ± 5 mT and 326.5 ± 100 mT sweep intensities delineate the Rosebery deposit (Fig 16)

Case Study No. 4:

The use of electron paramagnetic resonance spectra and geochemical analysis of acid insoluble residue for recognising primary alteration haloes of gold mineralisation in the regolith (after Xu Li, 1999; van Moort et al., 1999)

A series of studies was conducted to test the hypothesis of a primary signature of mineralisation in intensively weathered rocks of the regolith.

The study sites were the Jim's Find South gold deposit in the Tanami-Granites area in the Northern Territory (Stott, 1994), the Rand Pit, Reedy Mine near Meekatharra, WA (Robertson et al. 1990), the Mystery Zone at Mt Percy, Kalgoorlie WA (Butt, 1991; 1993) and the McKinnons gold deposit near Cobar NSW (Bywater et al. 1996; Rugless and Elliott, 1995; Aung Pwa and van Moort 1999a; Aung Pwa et al., 1999c).

Each site is characterised by a regolith 70-90 m deep overlying primary gold mineralisation in different host rocks and of different genesis. Each site has supergene enrichment of Au and, excepting Reedy Mine, has a sub-surface zone of Au depletion.

The primary style of mineralisation in the four occurrences varies considerably. At Jim's Find, Au is associated with quartz carbonate veining and has an envelope of sericite-pyrite alteration, hosted by interbedded graywackes, phyllites and basalts. At Reedy, mineralisation is hosted by quartz veins and shears within altered mafic/ultramafic rocks that are intruded by porphyries. At Mt. Percy, mineralisation is associated with finely disseminated pyrite and quartz veining in quartz albite porphyries and fuchsite-carbonate alteration zones in talc-chlorite ultramafic rocks. In the McKinnons deposit, primary epithermal Au-Ag mineralisation is associated with pyrite-illite wall rock alteration and extensive silicification. All areas have been affected by deep chemical weathering under humid climatic conditions, probably during the late Cretaceous to early Tertiary. Subsequently, the regolith profiles have been modified (and partly eroded) under arid conditions that persist to the present day.

THE DISTRIBUTION OF AU AND EPR SIGNALS

The Au values in all cases were determined by INAA on the bulk samples prior to their acid treatment and are given in the references cited for the individual deposits. The EPR intensities have been determined on the acid insoluble residue of the same samples used for Au determinations.

JIM'S FIND SOUTH, TANAMI, NT

In order to compare the trends of the distributions of the EPR intensity and the Au mineralisation, 144 samples from the surface down to depths of 90 m were selected from three regolith sections (Stott, 1994). Where the complete regolith profile is preserved, Au determined by INAA is present as laterally extensive sub-horizontal zones of secondary Au enrichment (0.01-3 g/t) in lateritic gravels and within the saprolite above the primary ore zone; there is also a zone of subsurface Au depletion (Fig 17).

The acid insoluble residue from the primary mineralisation shows two separate EPR haloes over and above the Au anomalies (Fig 18). The intensities are approximately three times stronger than those from near the surface and the barren zone. There is no EPR expression of the near surface secondary gold enrichment and the EPR anomaly does not reach the surface (Xu Li and van Moort, 1997).

RAND PIT, REEDY MINE, NEAR MEEKATHARRA, WA

Gold is present in and around two sub-economic ore shoots on the south face of the Rand Pit, broadly conformable approximately to two mica schist zones within mafic schists (Figure 19). The profile is truncated and saprolite occurs close to the surface. Accordingly, there is no surface Au enrichment and a lateral dispersion halo is weak (<50 ppb), extending for less than 20 m.

One hundred and ten samples were selected for the EPR study. The EPR values of the acid insoluble residue change in proportion to the log Au content of the bulk rock (Figure 19). There are high EPR values near the surface, especially above the mica schist, and close to the mica schists at depth (Figure 20). The barren ultramafic rocks have low EPR values.

MYSTERY ZONE, MT. PERCY, NEAR KALGOORLIE, WA

One hundred and eighty seven regolith samples from section 15850N were selected. The geology, regolith subdivisions and Au concentrations, determined by INAA on bulk samples prior to acid treatment, are shown on Figure 21. An additional 197 samples were analysed from a background area, about 1 km north of the Mystery Zone (Aung Pwa and van Moort, 1998b).

Primary Au mineralisation is associated with the porphyries and adjacent fuchsite-carbonate-altered ultramafic rocks. In the regolith, there is a widespread zone of high Au concentrations (>100 ppb) in calcareous soils, lateritic residuum and mottled clays in the upper 3-5 m. Below this there is a 5-10 m zone of Au depletion (from the upward projection of primary mineralization) corresponding approximately to the upper clay-rich horizons, overlying a zone of supergene enrichment. The gold mineralisation at depth occurs in alteration zones.

Unfortunately, surface samples were not available for EPR measurements. However, lateritic gravels just below the surface have high values, whereas Au is depleted. This indicates that the EPR of the acid insoluble residue is not affected by weathering. At depth, the high EPR values are found in the mineralised porphyries and fuchsite-carbonate rocks (Fig 22). The background area has a flat EPR spectra (Aung Pwa and van Moort, 1998b).

MCKINNONS, NEAR COBAR, NSW

This study involves 101 drill core regolith samples from the 15150N mine section through the open pit and 39 surface soil samples from a line 400 m to the north. The McKinnons open pit averaged 1.9 g/t Au; the outline of the supergene enrichment zone (Au>0.3 g/t) is shown in Fig 23.

The distribution map of EPR intensities in the drill core samples of the mine section reveals a significant EPR halo outlining the Au mineralisation. The halo is open to the west, which is an area of weak mineralisation, and at depth (Fig 24). The EPR response of the surface line 400 m north of the McKinnons open pit is very weak (Aung Pwa and van Moort, 1998b; McQueen et al., 1999).

GEOCHEMICAL SIGNATURES RELATED TO GOLD MINERALISATION

The multi-element data permit a more structured discussion of the relationship with mineralisation than the EPR data alone. Space allows only a summary of the results here.

The Au concentrations discussed below are those determined on the whole samples, not the acid insoluble residues. The Au concentrations in the residues never show zones of supergene enrichment, as secondary Au is dissolved by the acid digestion. Primary dispersion patterns in the untreated and acid treated material are comparable.

JIM'S FIND SOUTH, TANAMI, NT

There is a spatial relationship between the occurrence of Au and acid insoluble F, Al, K, V, Mn, Fe, Ga, Rb and W that is essentially related to sericitic wall rock alteration. The distribution of K expresses the relationship between sericite and the primary occurrence of Au (Fig 25). The data presented by Stott et al., (1997) with respect to the concentration of Al are superseded, as the analysed material still contained residual kaolinite. Sodium, Ca and Sr depletion at depth is related to wall rock alteration and, near the surface, to weathering.

A high Rb/K ratio and of elevated As, Cu, Ni, Pb and Zn contents yield a good surface expression of the mineralisation. An association between As and primary mineralisation is preserved throughout the regolith.

RAND PIT, REEDY MINE, MEEKATHARRA, WA

Potassium, Rb, V and, in particular, Ga and W have a spatial relation with the occurrence of Au that appears to relate to sericitic alteration. The K distribution is shown in Fig 26. Copper and Pb show surface enrichment over the mineralisation, best expressed as (Cu×Pb). Sodium, Ca and Sr are not systematically depleted in the ore zones.

MYSTERY ZONE, MT. PERCY, KALGOORLIE, WA

Primary mineralisation at Mt. Percy is associated with felsic porphyries and the fuchsite-carbonate alteration of the ultramafic rocks they intrude. The alteration zone is typically pyritic and, in addition to Au, is characterised by high abundances of K, Rb, W and Ga in the acid insoluble residue. There is also a good correlation between Ge and Au.

The mineralisation is characterised by high Rb/K and Rb/Al ratios at the surface. This is consistent with the presence of sericitic (fuchsite) alteration. The K distribution is shown in Fig

Figure 7. Relative EPR 326.5 ± 5 mT signal distribution in the Mystery Zone, Kalgoorlie. The EPR halo is undiminished in the subsurface Zone

Tungsten is consistently enriched throughout the primary mineralisation with concentrations of 10-40 ppm over the porphyries and between 5-27 ppm in the fuchsite bearing ultramafic rocks compared to < 2 ppm in the barren talc chlorite rocks. Tungsten is the best indicator element for Au in the Mystery zone.

MCKINNONS, NEAR COBAR, NSW

The geochemical halo associated with the McKinnons gold mineralisation is characterised by enrichment in Cu, Zn, Pb, Ag, As, Sb, Ba and Bi and depletion of K, Al, Fe, Mg, Ca, Na, Ti, Cl, F, Ga, Rb, Zr, Y, V, and Tl. Most of these depleted elements, except possibly Ti and V, are considered indicators of wall rock alteration involving sericite *destruction* during the emplacement of Au mineralisation along zones of intense fracture. Some of these elements exhibit geochemical zonality in the regolith. The zonality is characterised by enrichment in Cu, Pb, Ag, As, Sb, Ba, Bi, Mo and W, and depletion in Zn and Ni in the upper level of the deposit and at the surface. These geochemical features are considered to be primary geochemical signatures associated with Au and base metal mineralisation.

Copper, Zn, Pb, Ag, As, Sb, Ba, Bi and Mo have potential as surface indicators of concealed mineralisation.

EPR of quartz is unaffected by the degree of weathering of the material in which the quartz is present (Hamdorf 1987; Nand, 1989). The present study indicates that EPR can detect surface indications of concealed Au deposits in highly weathered terrain and that it can be used to differentiate between barren and mineralised regolith at the surface, e.g., at Reedy, Mt Percy and McKinnons. The failure of this study to detect an EPR surface expression of underlying Au mineralisation at Jim's Find (Figure 3) may be attributed to admixtures of microcrystalline secondary chalcedony resulting from the hydrolysis of silicates during weathering. Such material does not show a strong EPR signal. Some of the surficial material may also have a transported component. It should be noted that the EPR signal is not necessarily related to the presence of sericite, as the McKinnons deposit is characterised by sericite destruction yet exhibits a very strong EPR signal.

The chemical composition of the acid insoluble residue reflects the type of wall rock alteration in all four areas associated with feldspar destruction and sericitisation, but sericite destruction in the McKinnons case. There is further evidence that the wall rock alteration is associated with the formation of a Rb- and V-rich sericite. Of further importance is the reliability of Rb/K ratios and Cu, Pb, Zn and As abundances in acid insoluble residues as indicators of mineralisation throughout the regolith to and including the surface soil. The haloes of these elements are larger than the associated Au mineralisation. In the case of the McKinnons deposit, Pb, Ag and Sb occur at the upper level of the mineralisation and Ni and Zn are enriched at the lower level. Similar distributions and relationships are also generally shown by total element analyses of rock pulps.

CONCLUSION

Powder EPR and chemical composition of quartz veins enables distinction of vein phases. Powder EPR spectra of the acid insoluble residue (quartz concentrate) of veins, rocks or regolith inclusive of soil form a reliable indicator of wall rock alteration and are unaffected by the degree of weathering, unless dilution occurs. The EPR spectra are the result of substitutional and interstitial impurities in quartz and are associated with a wide variety of mineralisation.

The chemical expression in the acid insoluble residue of sericitic wall rock is K and Rb enrichment, increased Rb/K and Rb/Al ratios, except where wall rock alteration is characterised by sericite destruction. Sodium, Ca and Sr depletion invariably occurs as a result of plagioclase destruction. Where appropriate Mn and Ba enrichment of the acid soluble residue can be used as indicator of mineralisation. Not all mineral deposits have an associated suite of pathfinder elements, whereas research to date suggest that there is always an EPR signal.

EPR and composition of quartz veins and quartz concentrates obtained from acid treatment of rock, regolith and soil facilitates distinction between mineralisation and barren systems.

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Table 1. Typical detection limits for INAA, PIXE/PIGME and XRF for geological materials

Element	INAA ^a	PIXE/PIGME ^b	XRF ^c
Ag	5	80	2
Au	5ppb	7	3
Al	--	400	0.01%
As	1	3	2
Ba	100	50	30
Ca	1%	45	0.01%
Cl	--	75	20
Co	1	3	20
Cr	5	13	10
Cu	--	2	4
Fe	200	5	1%
Ga	--	2	5
Ge	--	2	3
K	2000	35	0.01%
La	1	600	10
Mg	--	1500	0.01%
Mn	--	8	0.01%
Na	100	40	250
Nb	--	5	4
Ni	50	4	5
P	--	40	0.005%
Pb	--	4	5
Rb	30	3	5
S	--	140	0.005%
Sc	0.1	40	2
Si	--	1100	1%
Sn	0.01%	100	5
Sr	0.05%	3	10
Th	0.5	10	10
Ti	--	17	0.01%
V	2	13	5
Y	1	4	10
Zn	50	2	5
Zr	500	5	10

a: Bequerel Laboratories, Lucas Heights, NSW, Australia

b: This study conducted at Physics Division, Ansto, Lucas Heights, NSW, Australia

c: CSIRO, Wembly, W.A., Australia

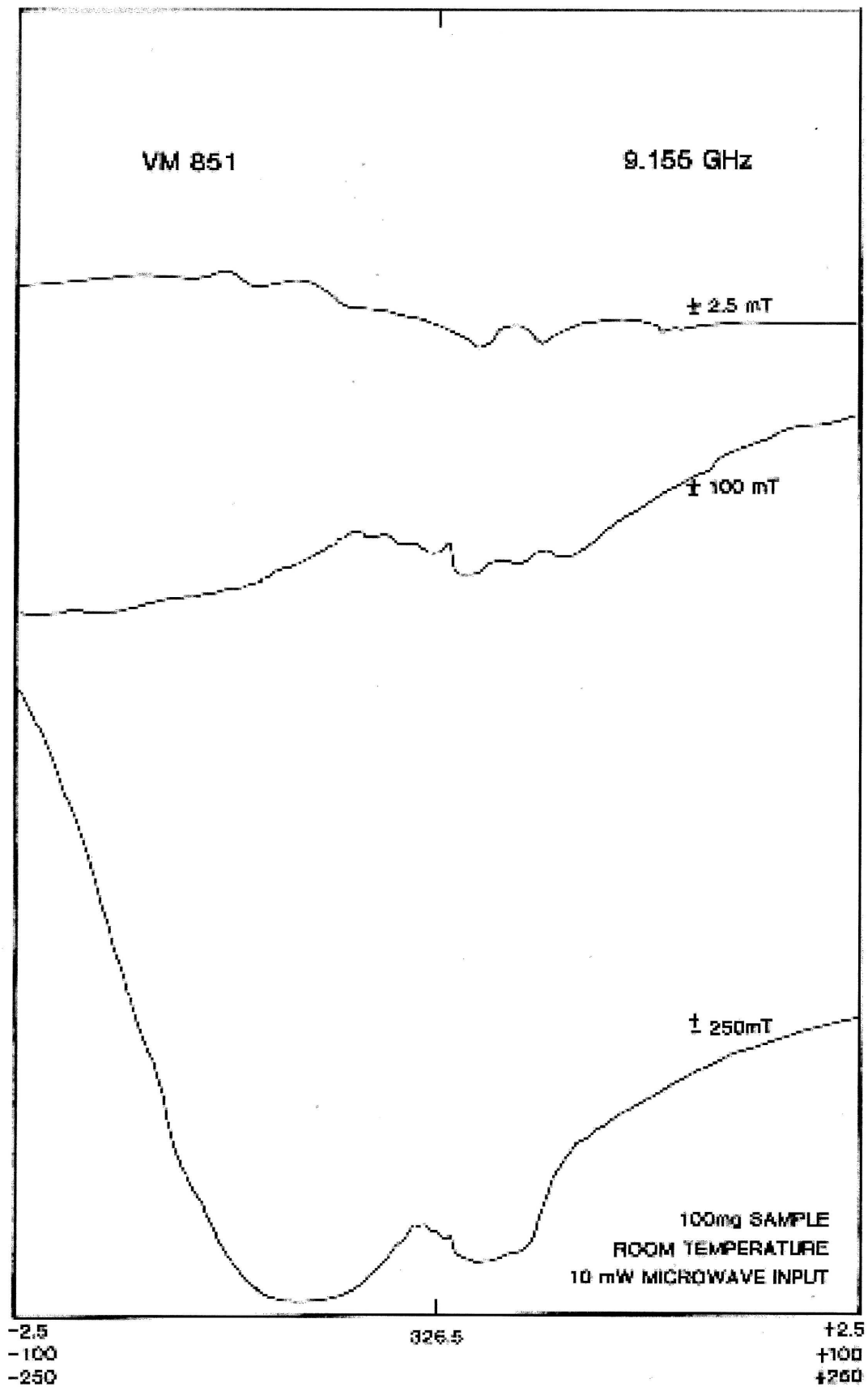


Fig. 1 Martha Hill deposit. Milky barren quartz of 1st stage veins EPR spectra at magnetic sweeps over ± 2.5 , ± 100 and ± 250 mT at 9.155GHz of barren first stage quartz. The ± 2.5 mT sweep is characteristically flat

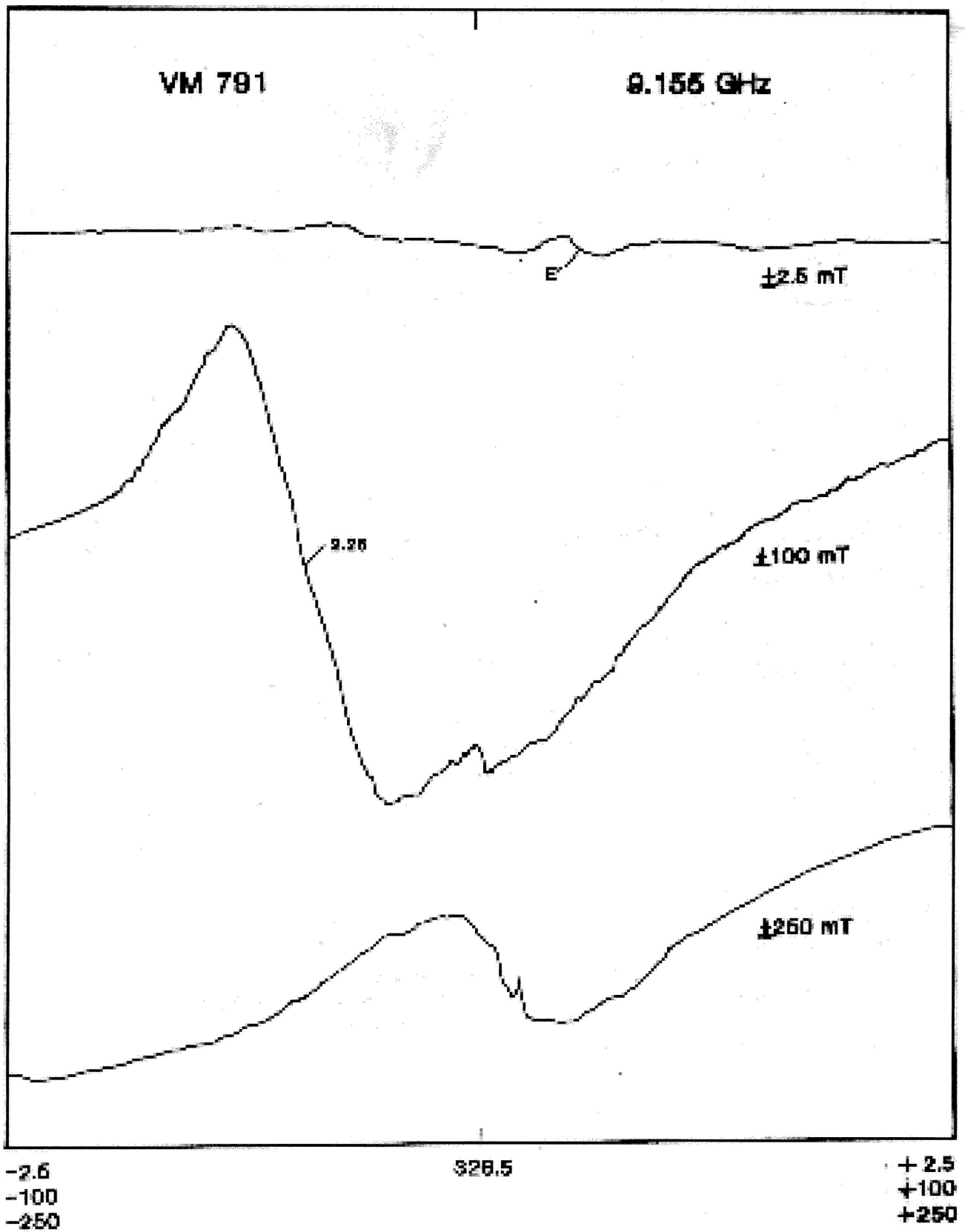


Fig. 2 Replacement of calcite by quartz in first stage vein Martha Hill deposit, N.Z. The ± 2.5 mT sweep is characteristically flat. Note differences in the sweeps over sweeps over ± 100 and ± 250 mT compared with Fig.1

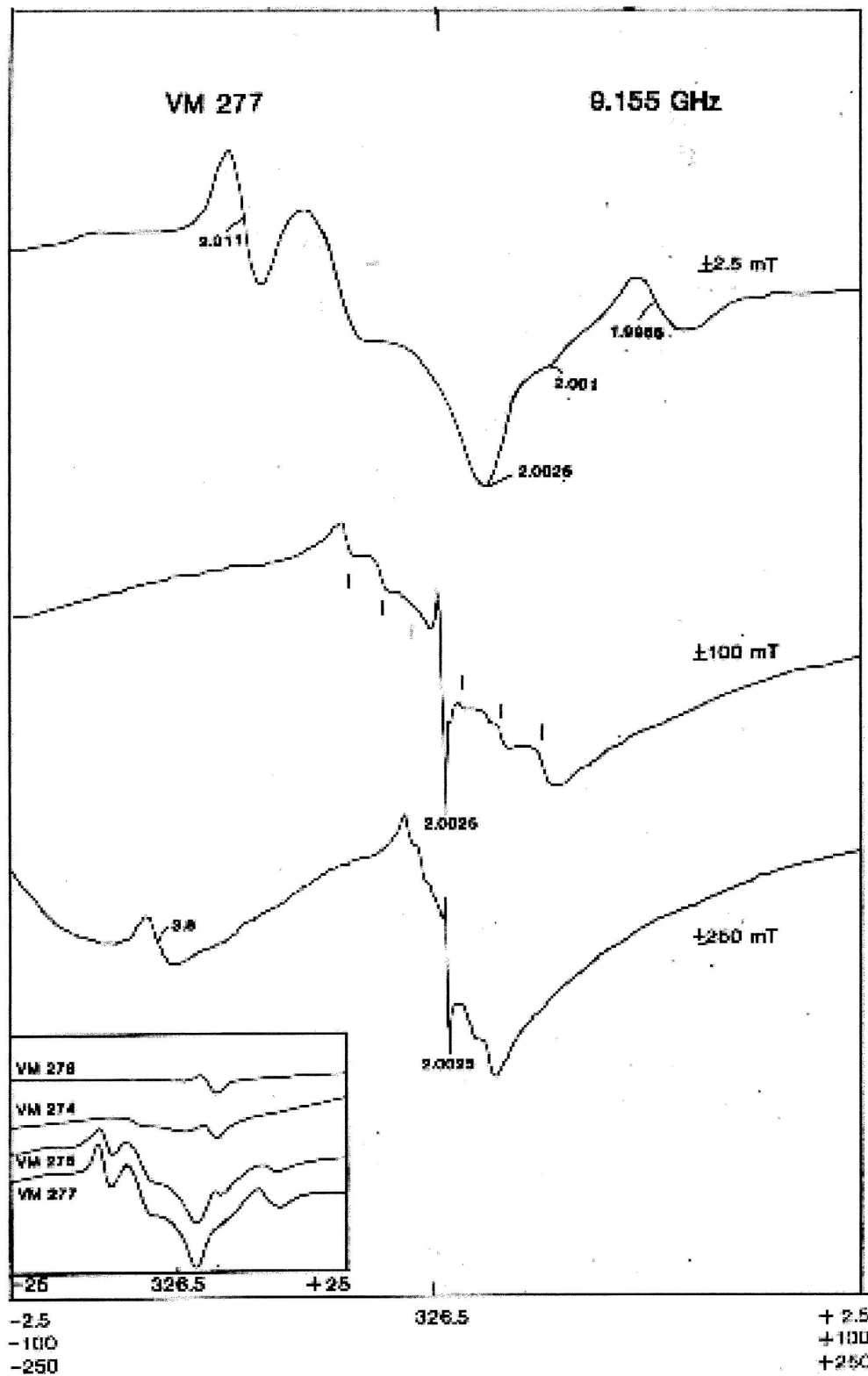


Fig. 3 EPR spectra of rhythmically banded ore from second stage veins from the Martha Hill deposit. Note the highly characteristic spectra of the ± 2.5 mT sweep. Paramagnetism decreases from the bottom upwards in each sequence, as shown in the inset

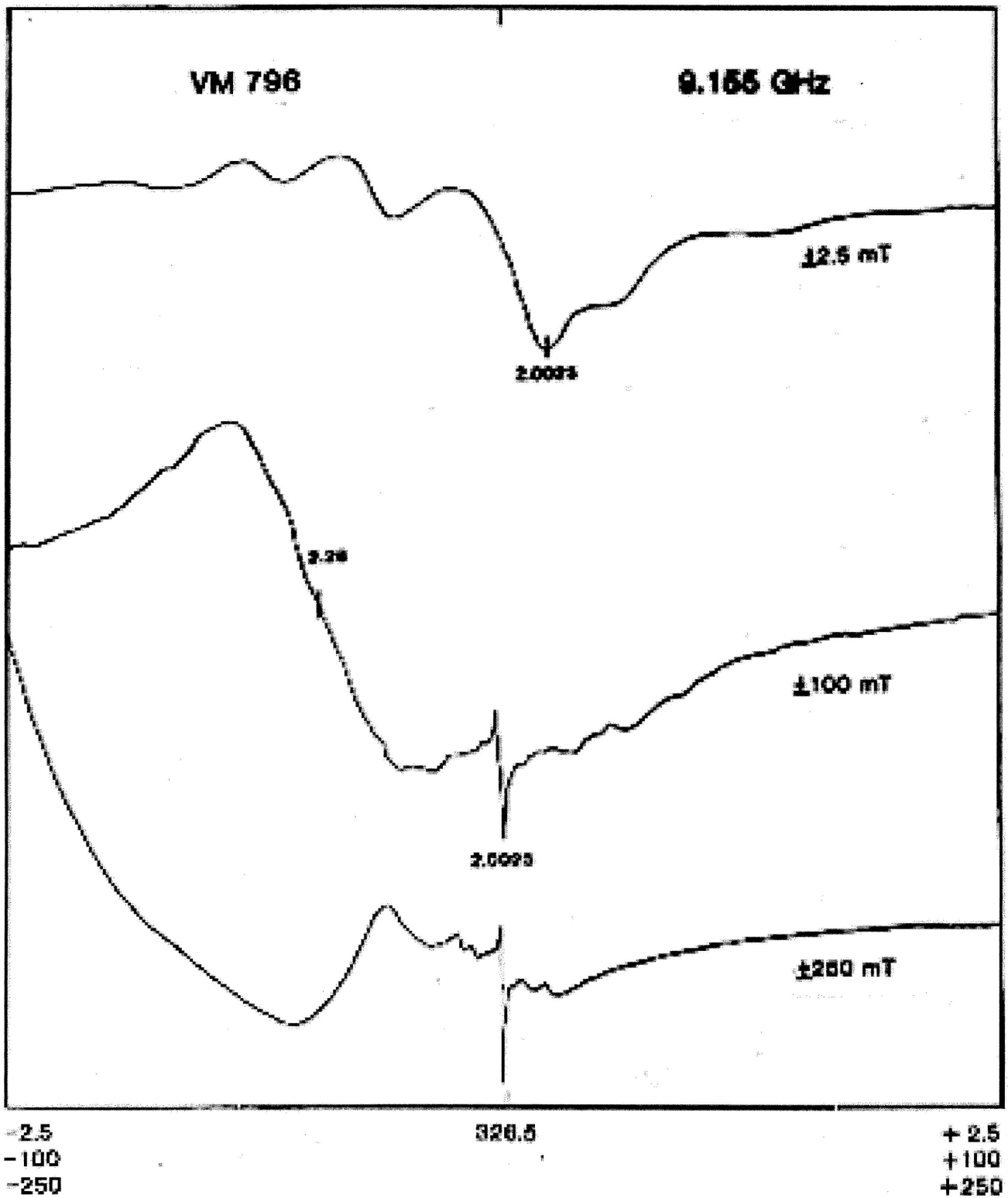


Fig. 4 EPR spectra of thin vertical veins in the Martha Open Pit. The ± 2.5 mT sweep signal is similar to the rhythmically banded quartz of Fig. 3. Note however, the differences between the ± 100 mT and ± 250 mT sweeps

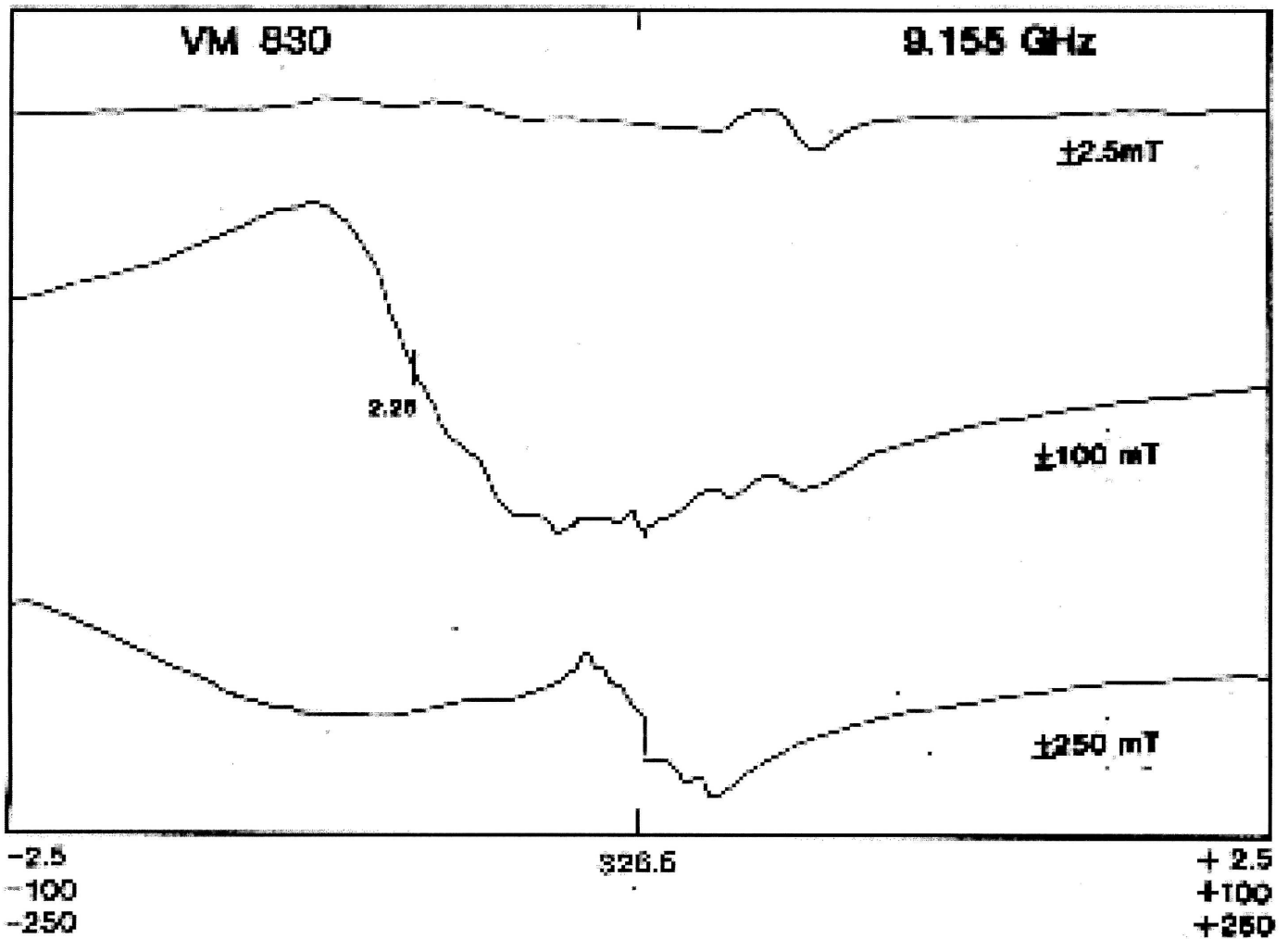


Fig. 5 EPR spectra of a non mineralised sample high up a sequence in the banded material of deeper mine levels, Martha Hill. This material is rather similar to the material in Fig. 4

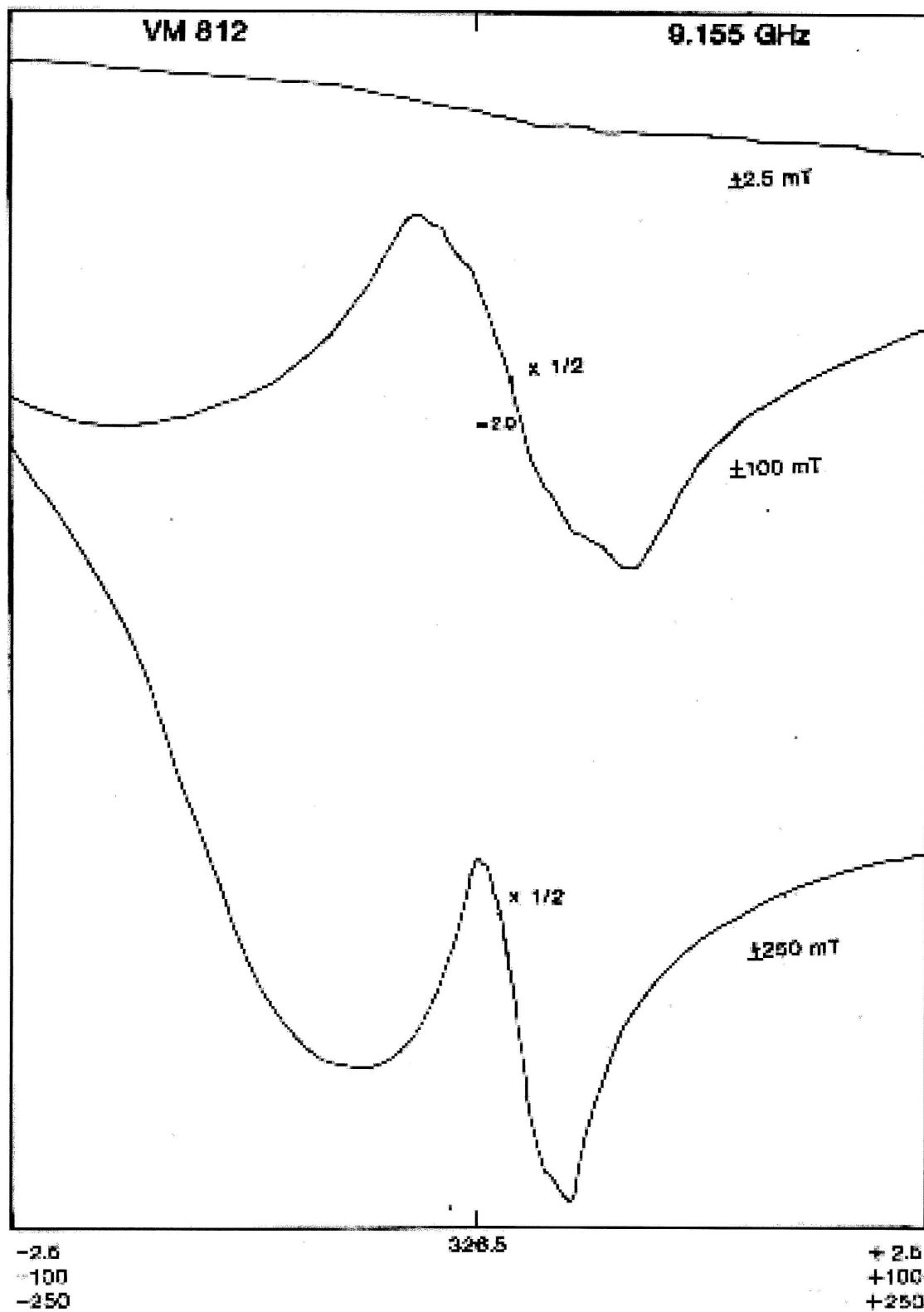


Fig. 6 EPR spectra of quartz from the massive crustiform gold-silver-sulphide ore, Martha Hill. Very strong and simple spectra in the ± 100 and ± 250 mT sweeps.

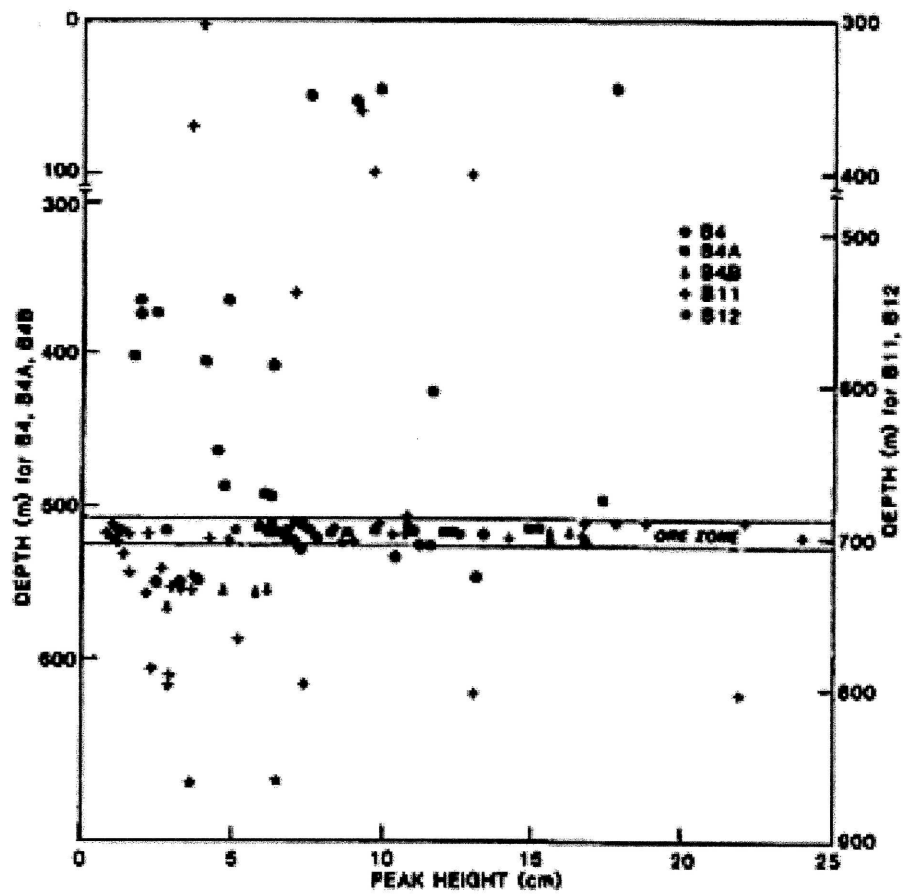


Fig. 7 A plot of EPR peak heights as a function of depth for quartz powders from diamond drill holes intersecting mineralisation at Beaconsfield. The position of the reef intersection of DDH B₁₂ has been adjusted to coincide with that of DDH B₁₁ (after van Moort and Russell, 1987).

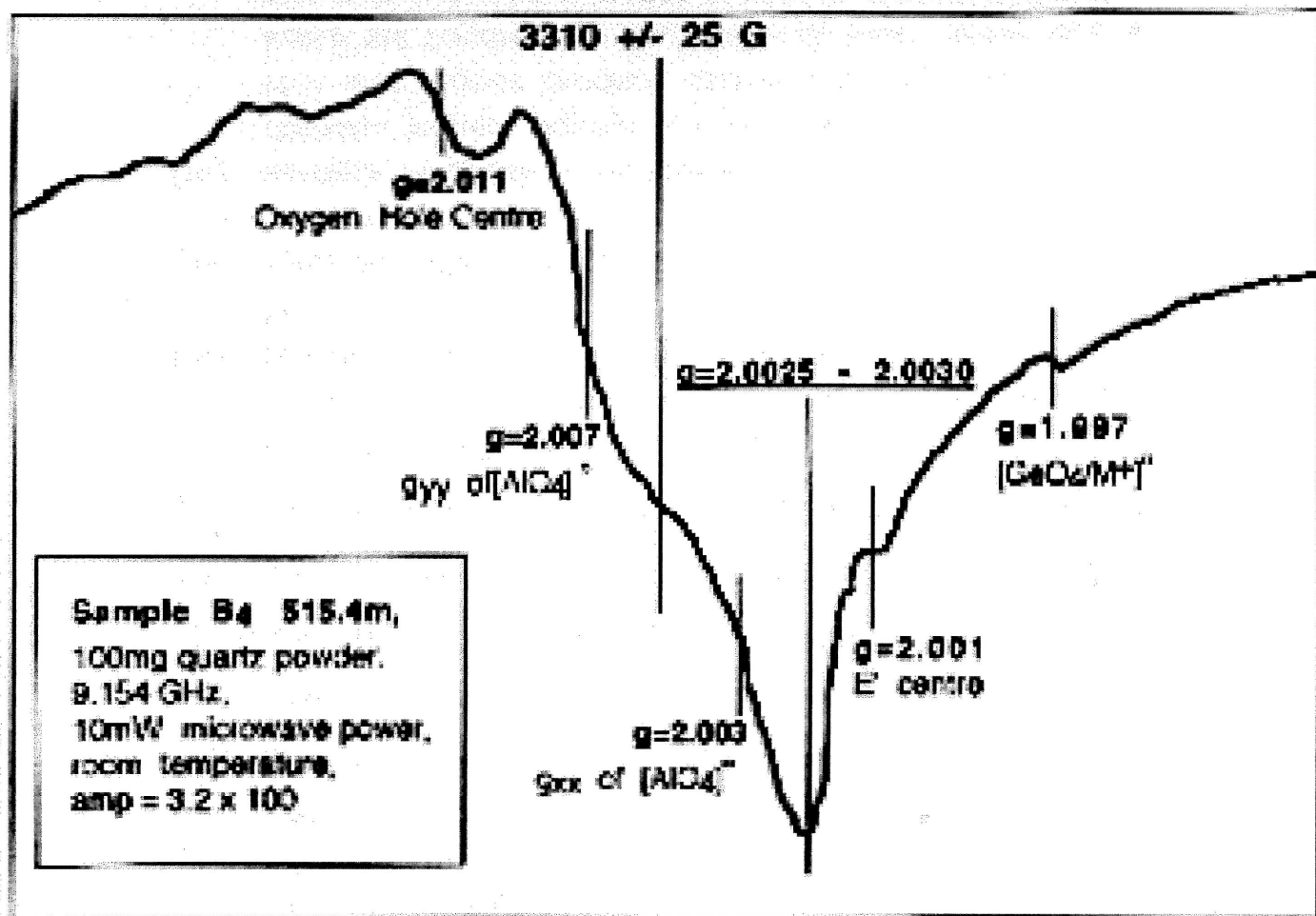
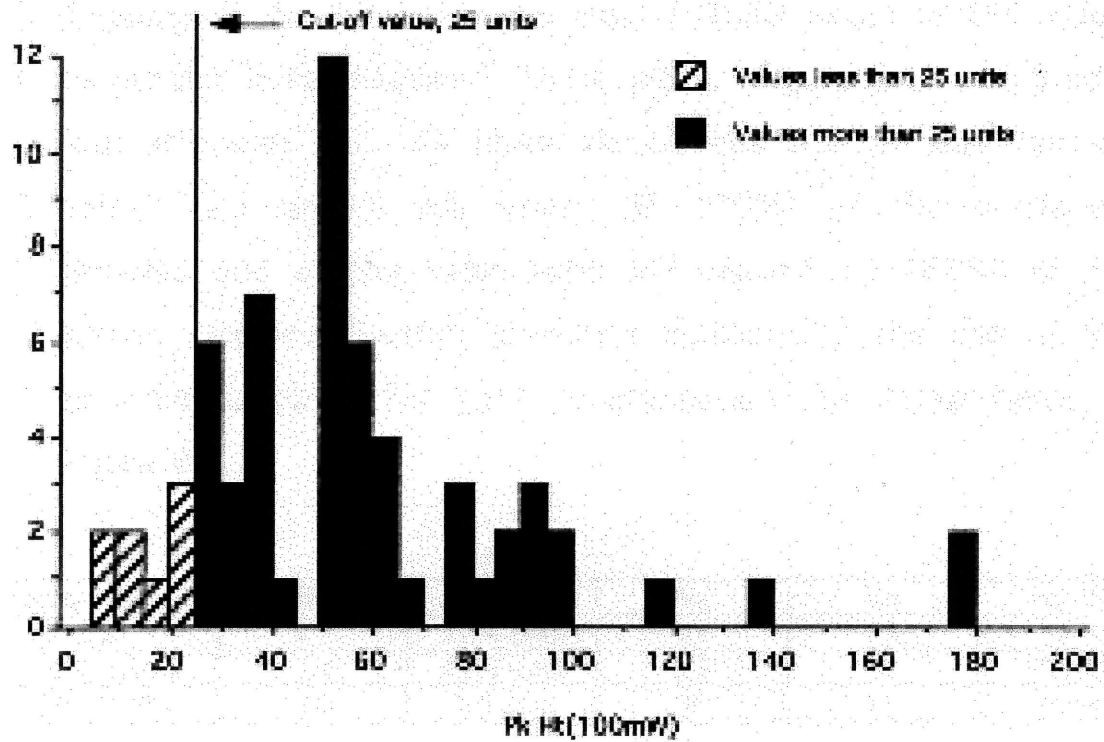


Fig. 8 First derivative EPR X-band spectrum at room temperature of powdered quartz with identified g values. Sample B4 (515.4 m) with crossovers at $g=2.011$ (oxygen hole centre), $g=2.007$ (g_{yy} of $[AlO_4]^-$), $g=2.003$ (g_{zz} of $[AlO_4]^-$), $g=2.001$ (E') and $g=1.997$ $[GeO_4/M+]^+$ as per Petrov et al., 1990.

PEAK HEIGHTS FOR ALFIFEROUS SAMPLES



PEAK HEIGHTS FOR BARREN SAMPLES

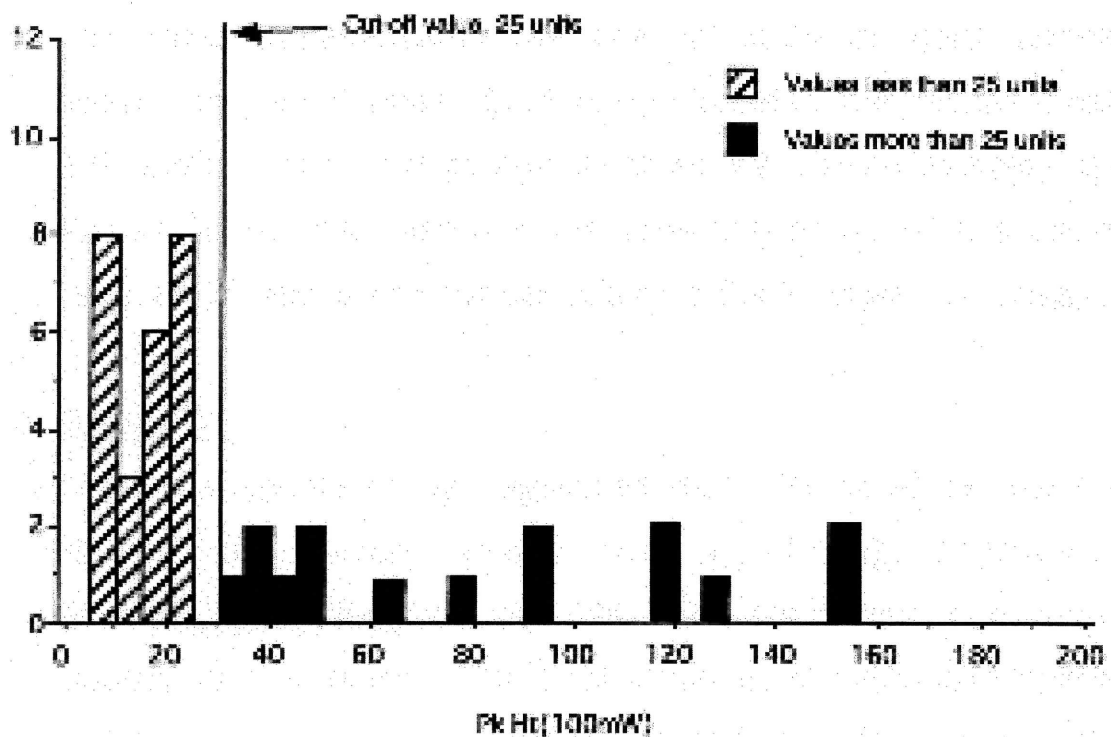


Fig. 9 and Fig. 10 Frequency histograms plotted for mineralized samples, N=44 (top) and barren samples, N=26 (bottom). These FPR values are relative Peak Height units measured at a power of 100 mW. These plots demonstrate the "cut-off" at 25 units.

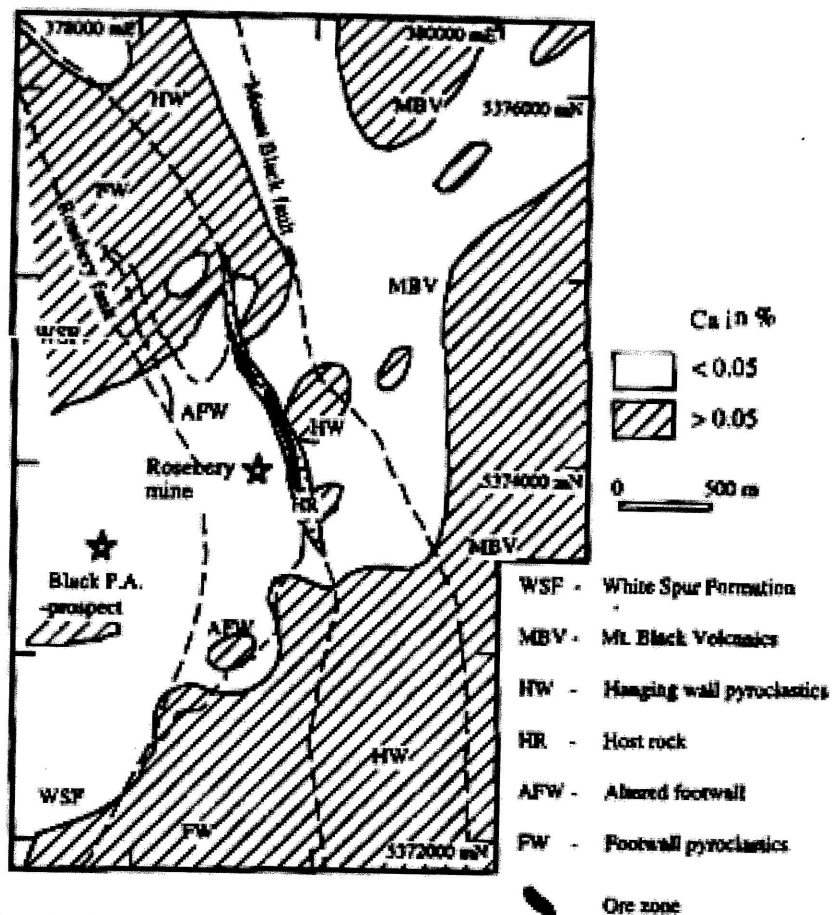


Fig. 11 The Ca depletion in the acid insoluble residue in the NE-SW corridor and along the Mt Black fault is related to feldspar destruction. Similar patterns may be observed for Na and Sr

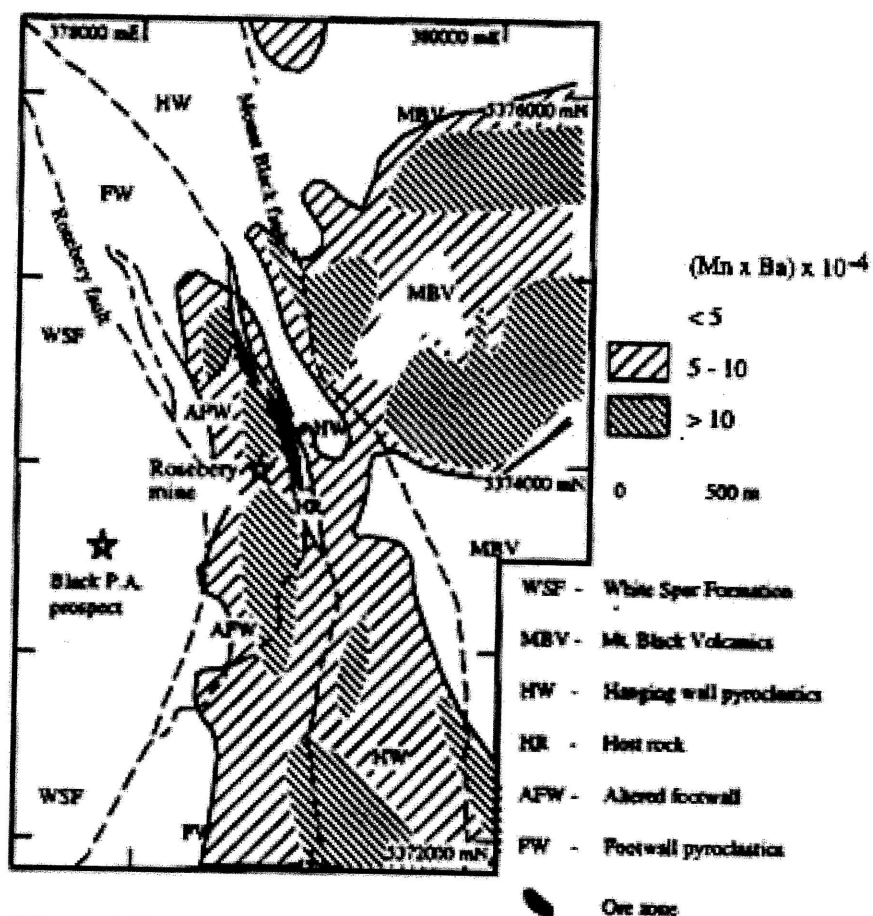


Fig. 12 High Mn and Ba values are recorded in footwall and hanging wall of the Rosebery deposit

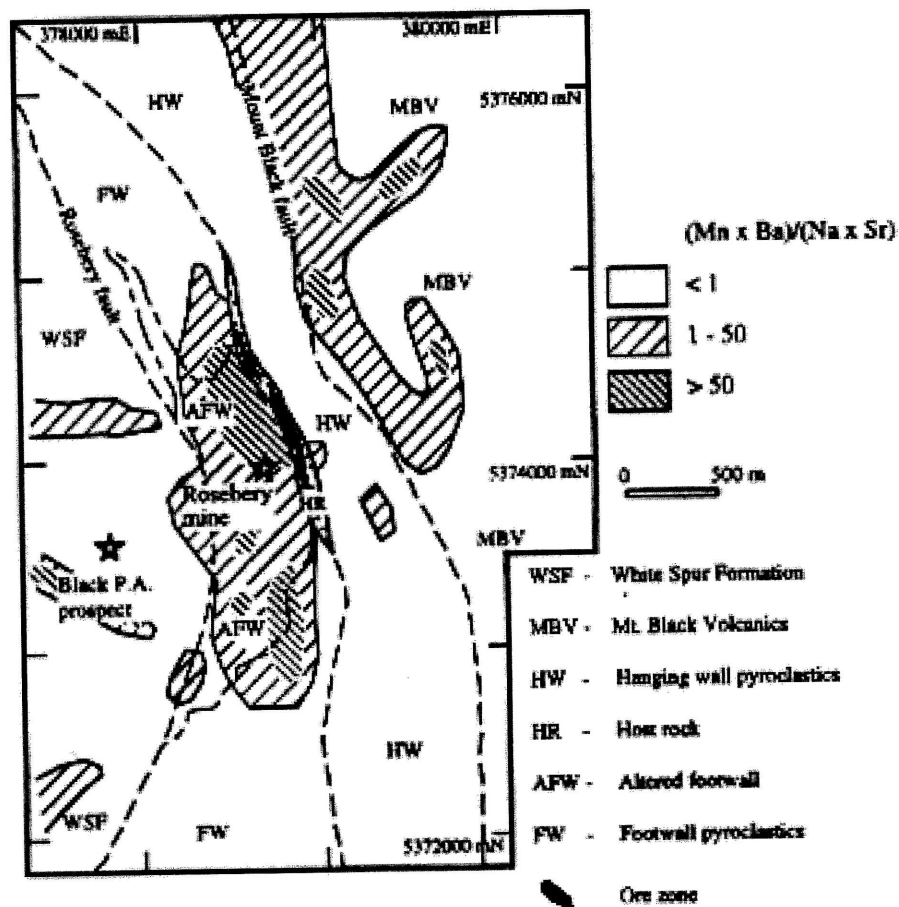
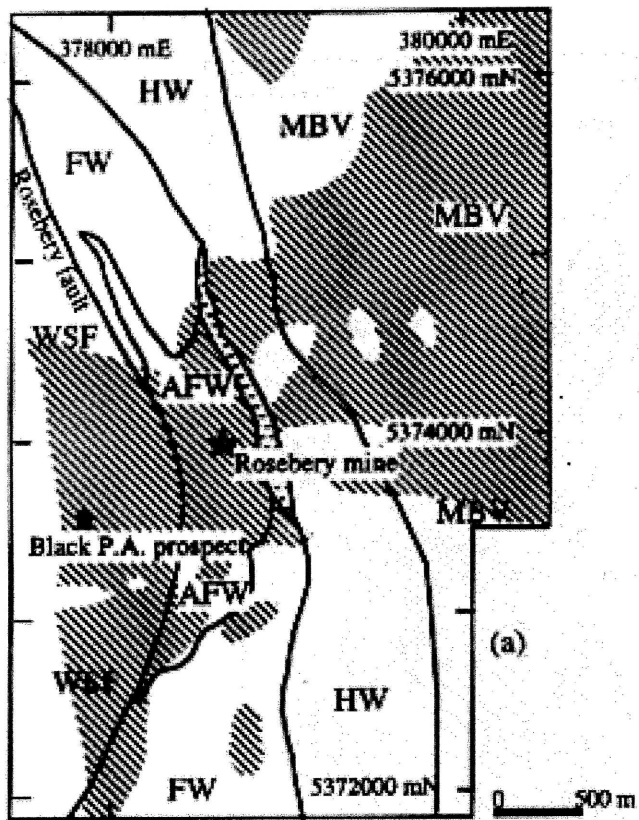
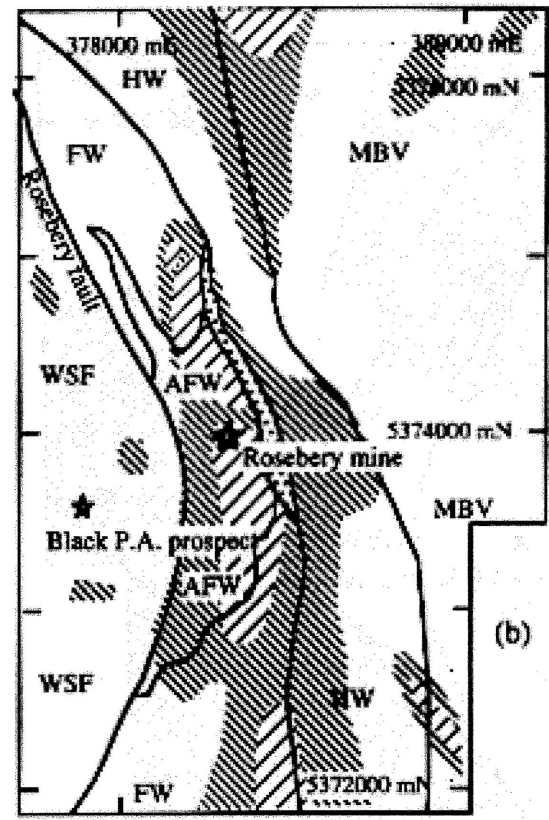


Fig. 13. The ratio of $(Mn \times Ba)/(Na \times Sr)$ in the acid insoluble residue of the surface rocks around the Rosebery deposit broadly outlines the deposit and altered footwall. The strip along the Mount Black fault is due to remobilisation.



EPR intensity measured at magnetic density sweeps 326.5 ± 5 mT

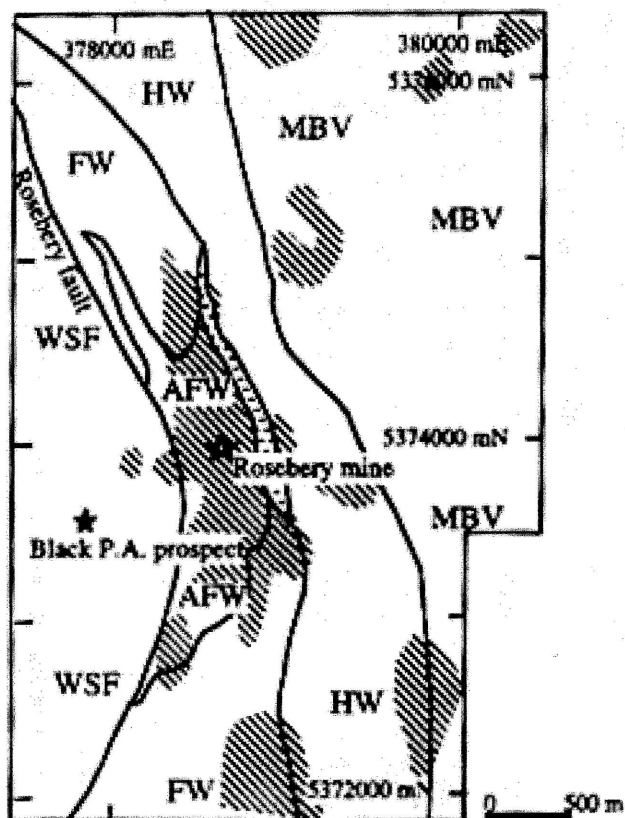
> 10 cm



EPR intensity measured at magnetic density sweeps 326.5 ± 100 mT

< 5 cm 5 - 10 cm > 10 cm

Figure 14 and 15. The EPR ± 5 mT and EPR ± 100 mT show a NE-SW lineament and NS lineament respectively



 EPR index > 60

Fig. 16. The EPR index of the product of the in of the 326.5 ± 5 mT and 326.5 ± 100 mT sweeps delineates the Rosebery deposit

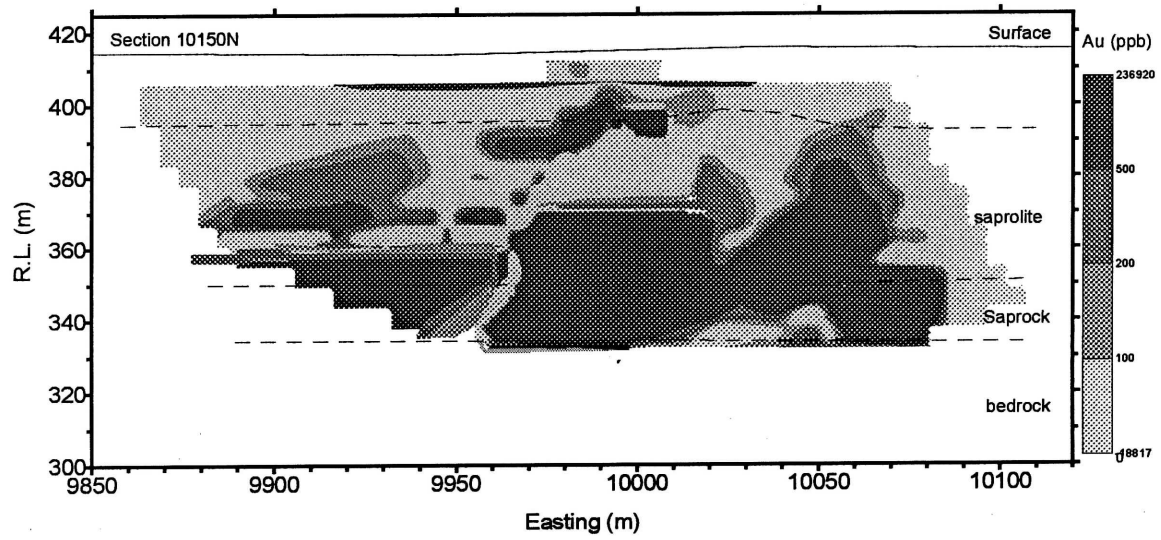


Figure 17. Distribution of Au (determined by INAA) at Jim's Find South, Tanami, N.T.; Section 10150N; Note secondary surface enrichment and subsurface leaching.

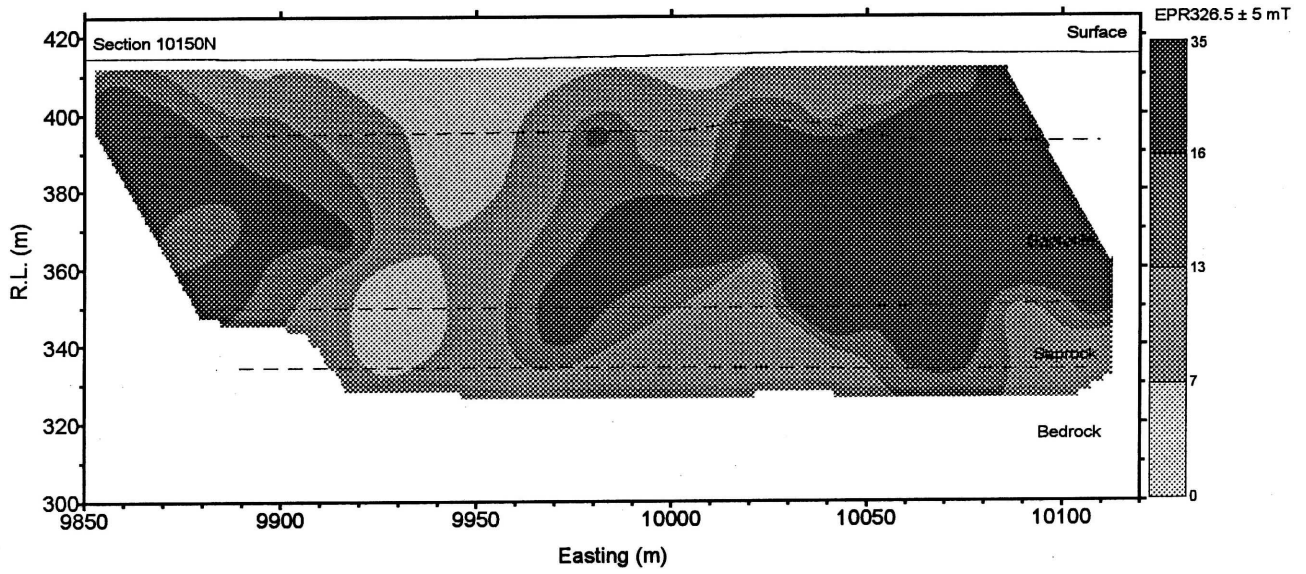


Figure 18. Relative EPR326.5 ± 5 mT signal distribution at Jim's Find South. The paramagnetic halo is larger than the extent of the primary Au mineralisation.

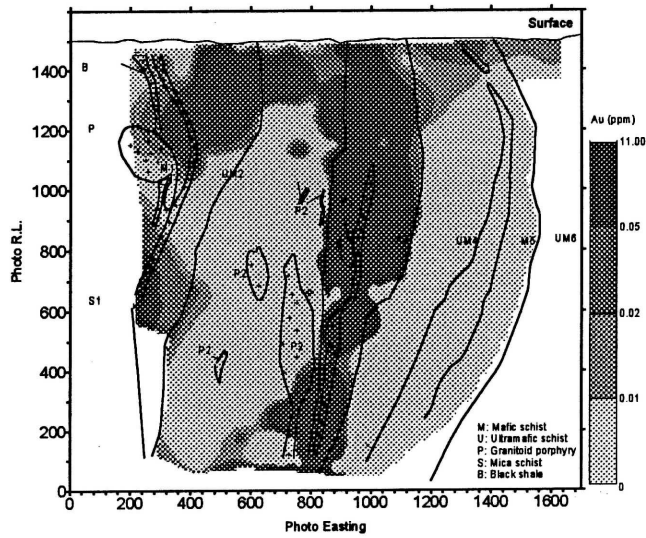


Figure 19. Distribution of Au (determined by INAA) at Rand Pit, Reedy Mine, near Meekatharra, W.A.

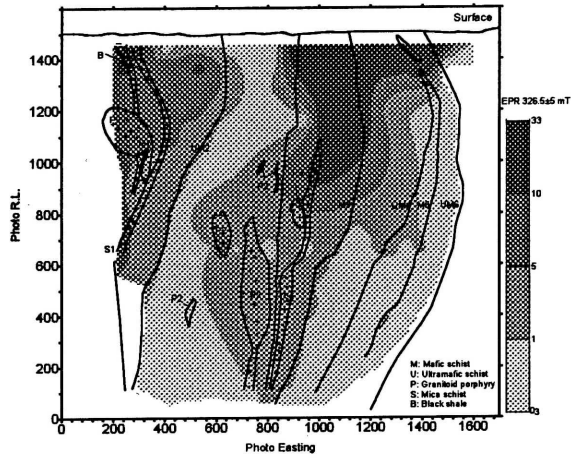


Figure 20. Relative EPR 326.5 ± 5 mT distribution at Rand Pit, Reedy Mine, W.A. The EPR halo is larger than the primary Au occurrence.

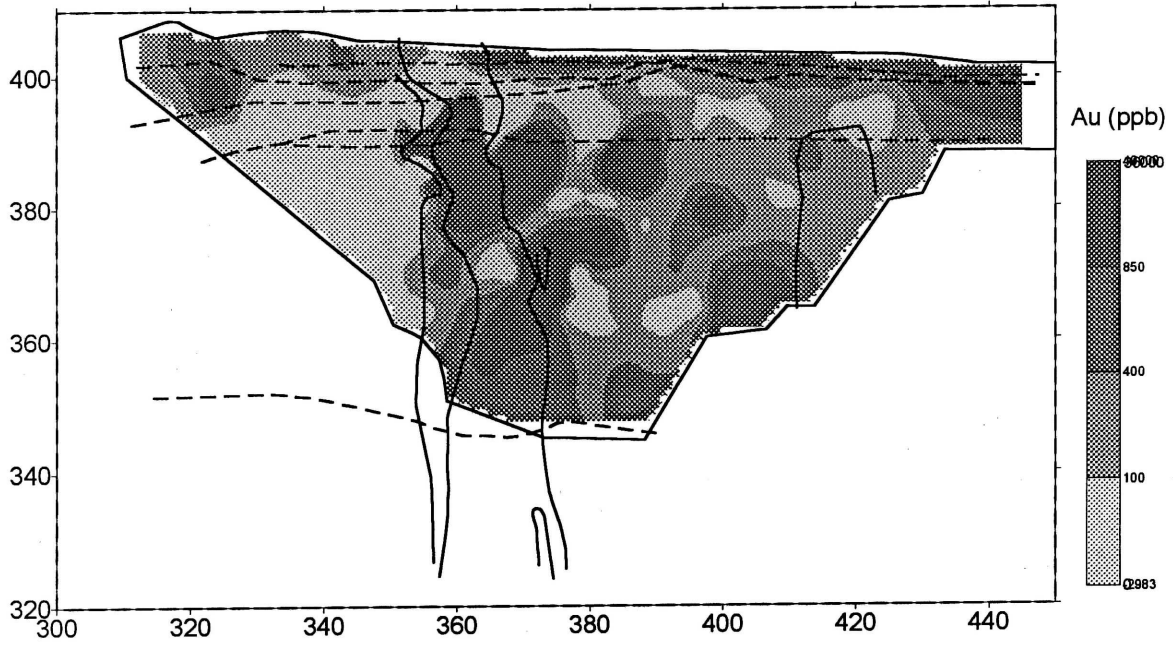


Figure 21. Distribution of Au (determined by INAA) in the Mystery Zone, Mt. Percy, W.A. Note the secondary surface enrichment and subsurface leaching.

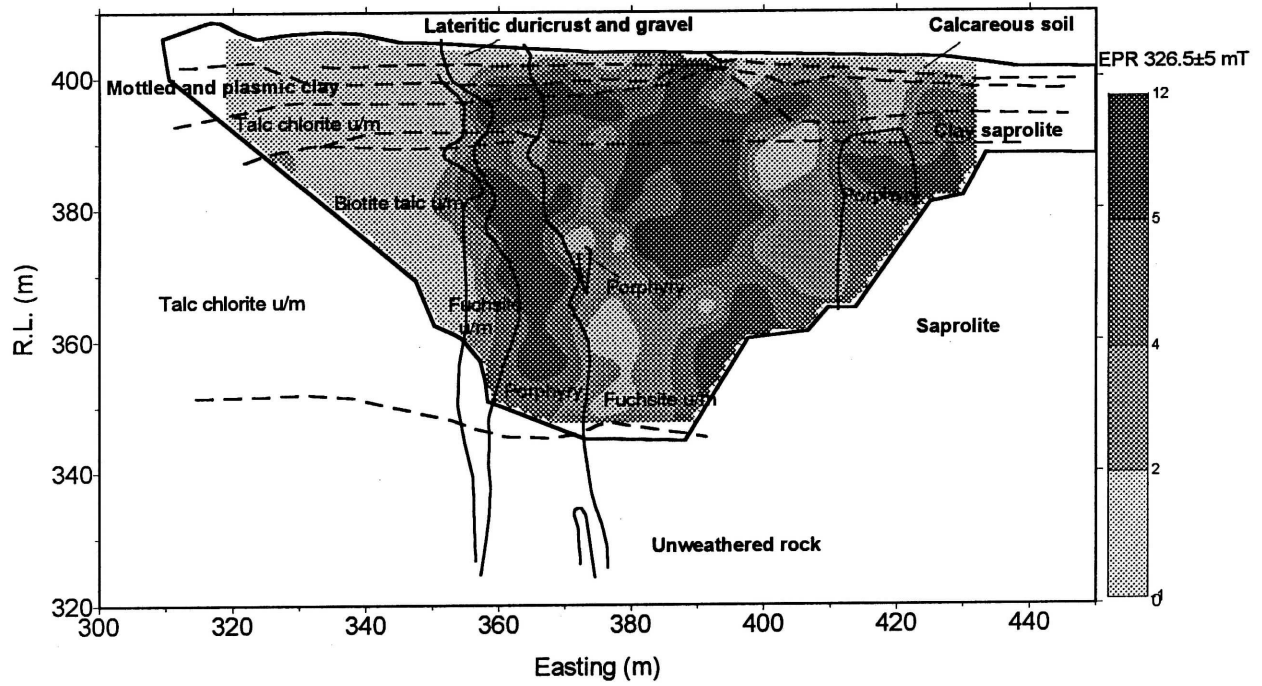


Figure 22. Relative EPR 326.5 ± 5 mT signal distribution in the Mystery Zone, Mt. Percy, W.A. The EPR halo is undiminished in the subsurface Zone.

15150 N

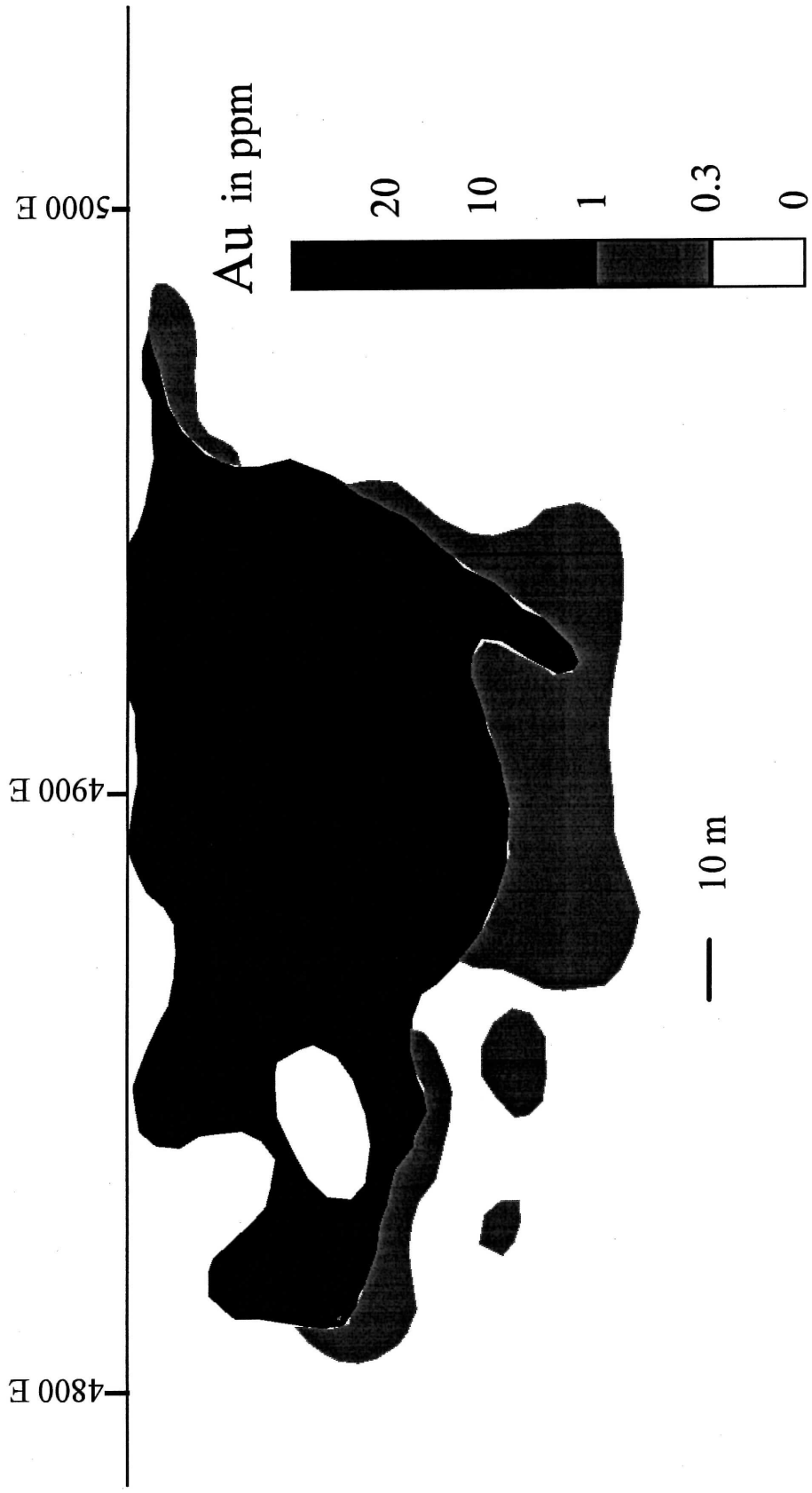


Fig. 23 Distribution of gold in the McKinnons deposit, Cobar (Mashall et al., 1996)

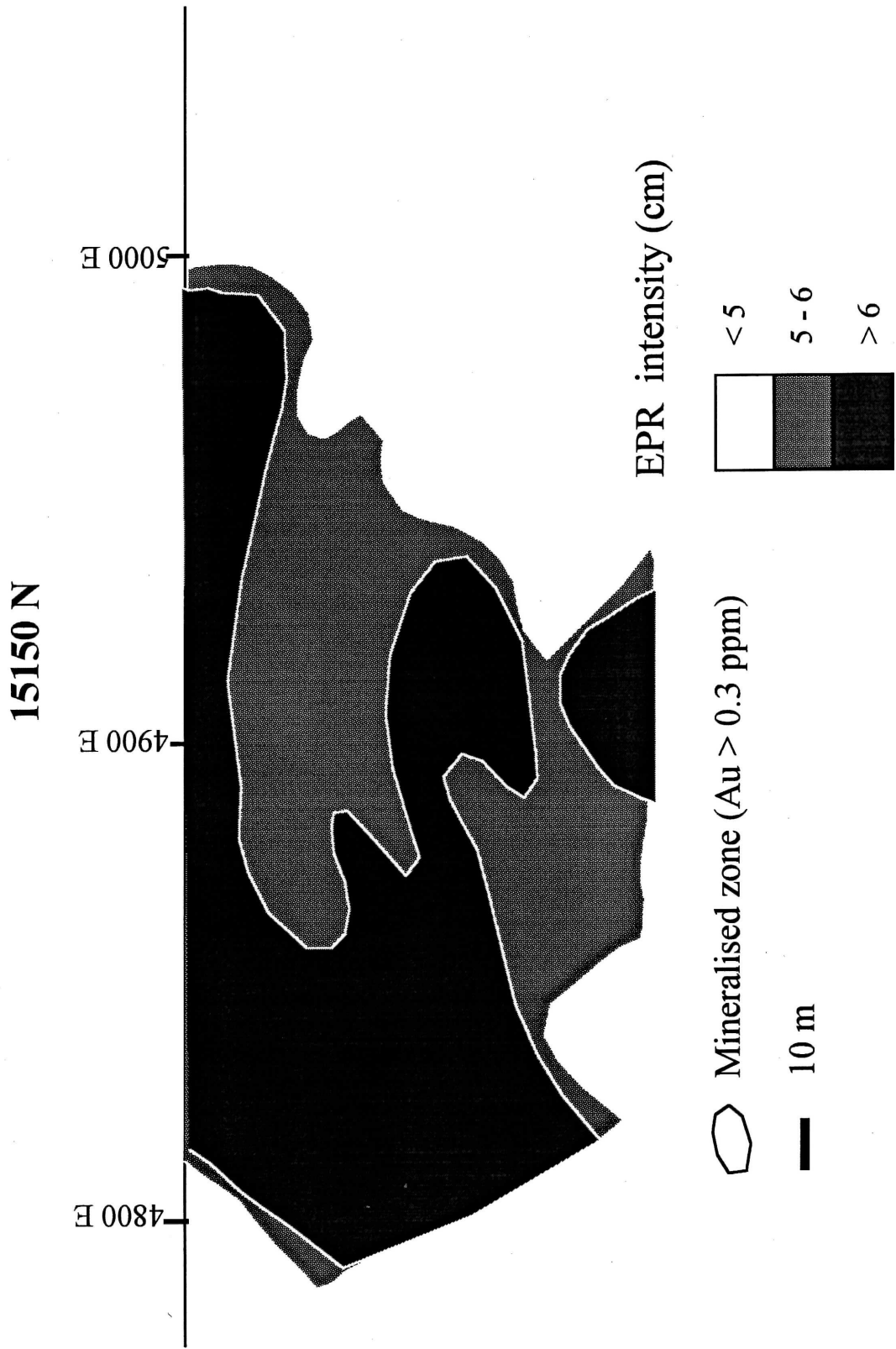


Fig. 24 Distribution of EPR signal intensities measured at magnetic flux density sweeps 326.5 ± 5 mT in acid insoluble residue Of regolith samples from 15150 N section, McKinnons gold deposit

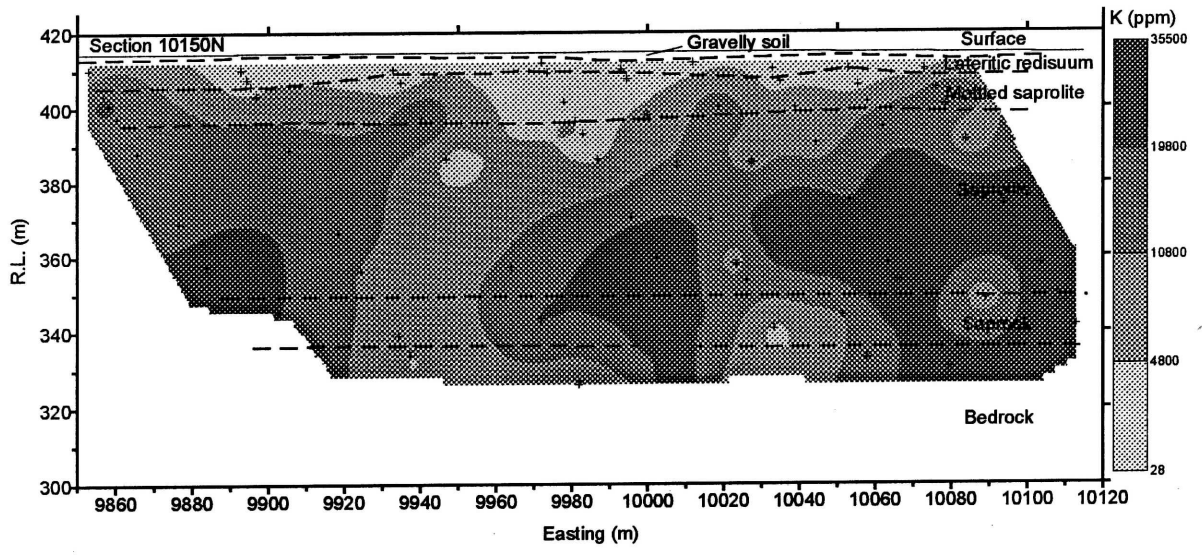


Figure 25. Distribution of K in the acid insoluble residue at Jim's Find South, Tanami, N.T.

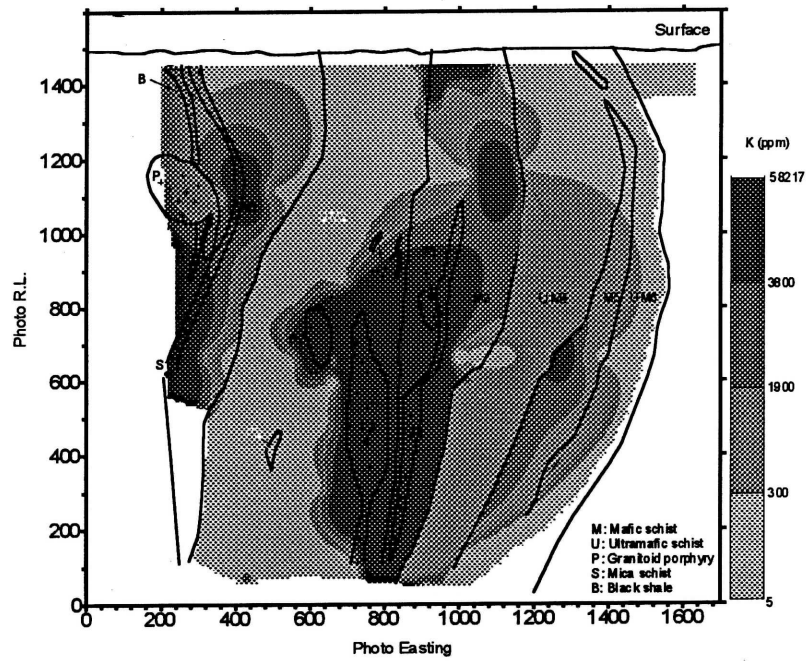


Figure 26. Distribution of K in the acid insoluble residue at Rand Pit, Reedy Mine, W.A. (Xu Li, 1998)

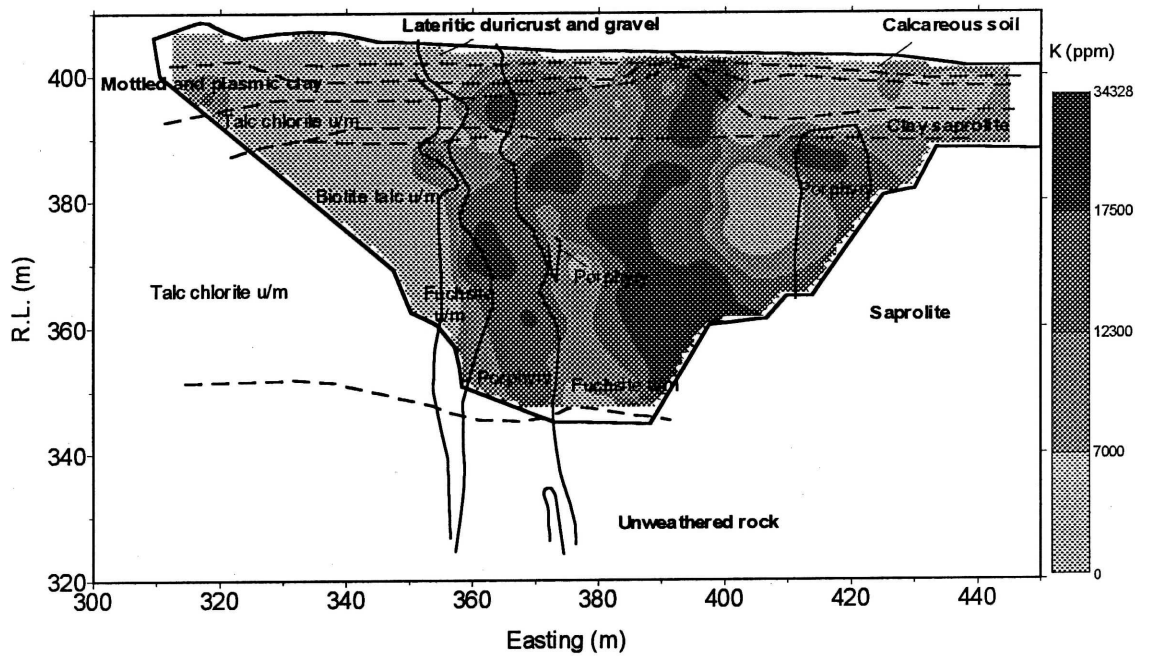


Figure 27. Distribution of K in the acid insoluble residue at Mystery Zone, Mt. Percy, W.A. (Xu Li, 1998)