11. MISCELLANEOUS METHODS

11.1   Delayed Neutron Counting

Delayed Neutron Counting is based on the emission of neutrons from a few fission products after the irradiation of ^{235}U with neutrons in a reactor. Approximately 0,03 g of sample was accurately weighed into polythene capsules and sealed. The samples were irradiated in the pneumatic facility for 40 seconds. After a decay of 20 seconds the samples were counted for one minute.

The counting system used was designed and built by the National Institute for Metallurgy. It consists of a ring of eight boron triflouride tubes mounted in a tank of water. Pulses from the tubes pass through an amplifier and a discriminator, and are finally counted.

The standards consisted of standard uranium ores supplied by the Australian Atomic Energy Commission and The International Atomic Energy Agency. A standard calibration graph was drawn and the counts versus $U_3 O_8$ concentration plotted.

11.2   X-Ray Diffraction Analysis

X-ray diffraction was used for qualitative mineralogi= cal identification. All samples were ground down to pass -325 mesh. Clay mineral identification was done on approxima= tely the 2 micron size fraction. A very dilute HCl solution was added to a slurry of this fraction in order to remove any calcite present.

PART III: GEOCHEMISTRY

12. THE GEOCHEMISTRY OF THE BASEMENT ROCKS

The basement rocks constituted the source of all the epigenetic uranium mineralization in the duricrusts from the Gawib River to the Tumas River and also the accumulations in the diatomaceous muds off the coast in the Atlantic Ocean. This, therefore, was the starting point of the geochemical cycle of uranium for the region in this study. A geochemical analysis of certain aspects of some of the basement rocks was very pertinent to this investigation, especially from the point of view of their paragenesis. The rare-earth abundances and trends were found to be useful as indicators of the geochemical and evolutionary sequences.

12.1   Analytical Results

Partial chemical analyses and trace element concen= trations in the Bloedkoppie and Gawib Granites are given in Table 13. Analyses of other basement rock types form part of a geochemical investigation (DAMJU Project) concerning the uranium mineralization of the Damara Orogen, the report of which is still in preparation. A list of the samples used here is given in Table 14.

12.2   Geochemistry of Uranium in Granitic Rocks

The mean uranium concentrations in the Bloedkoppie and Gawib Granite are 18 ppm and 9 ppm respectively. The Gawib Granite has a Th/U ratio of 3,5 which is very close

TABLE 13: PARTIAL CHEMICAL ANALYSIS AND TRACE ELEMENT CONCENTRATIONS IN THE
BLOEDKOPPIE AND GAWIB GRANITES

	BLOEDKOPPIE GRANITE												GAWIB GRANITE		
%	LH 4	LH 5	LH 6	LH 8	LH 10	LH 16	LH 43	HJ2-20	HJ2-26	HJ2-30	HJ2-36	HJ2-39	LH 29	LH 30	LH 45
SiO_2	74,9	74,1	72,0	74,1	74,5	73,4	73,3	69,5	70,3	70,1	70,5	69,7	60,5	59,7	58,4
TiO_2	0,123	0,232	0,219	0,177	0,064	0,051	0,117	0,107	0,091	0,225	0,229	0,229	0,14	0,59	0,59
Al_2O_3	13,17	13,13	13,70	13,14	13,54	13,58	13,04	14,21	13,80	13,16	13,88	13,52	15,53	15,45	16,30
Fe_2O_3	1,38	2,16	2,13	1,79	1,23	1,10	1,48	1,27	1,13	2,06	1,96	1,89	5,70	5,69	6,26
MnO	0,03	0,06	0,063	0,038	0,056	0,06	0,057	0,024	0,036	0,068	0,048	0,056	0,12	0,10	0,12
MgO	0,14	0,28	0,29	0,21	0,12	0,05	0,16	0,36	0,18	0,34	0,35	0,35	1,96	2,01	2,05
CaO	0,87	1,25	1,37	0,86	0,68	0,79	1,19	1,69	1,43	1,55	1,49	1,36	5,79	5,17	4,94
Na_2O	2,78	3,05	3,53	3,04	4,02	4,11	3,54	3,36	3,99	3,42	3,19	3,16	3,35	3,28	2,75
K_2O	5,34	4,91	4,30	5,21	4,30	4,01	4,89	4,42	4,26	4,74	4,48	4,65	3,05	2,83	2,91
P_2O_5	0,05	0,08	0,08	0,113	0,04	0,03	0,04	0,17	0,18	0,12	0,13	0,09	0,27	0,25	0,24
ppm															
Ba	499				184	212	240				658	587	887	1 063	1 003
Ce	112				45	30	95				102	80	137	120	122
Co	2,1				2,9	1,6	2,2				3,1	3,3	13	13	13
Cs	7,4				11,3	24,5	8,1				10,8	13,1	3,2	1,8	2,0
Eu	1,3				0,5	0,3	1				1	1	2,4	2,2	2,3
Hf	3,7				5,3	1,8	4,1				4,5	4,7	5,9	5,8	5,7
La	37				12	7	32				40	32	62	55	58
Li	37	63	97	36	60	113	56	38	40	55	78	79	108	21	29
Lu	0,3				1,0	0,5	0,9				0,8	0,6	0,5	0,5	0,6
Rb	309				375	521	360				317	329	144	130	139.
Sc	3,3				4,1	5,3	3,8				5,5	5,6	12	12	16
Sm	6				6	3	13				9	6	11	10	10
Ta	1,1				5,9	6,5	2,9				4,1	5,1	1,5	1,6	1,1
Tb	0,7				2,0	0,7	2,4				1,4	1,3	1,1	1,3	1,4
Th	27,2				35,8	18,0	52,0				23,0	18,9	20,1	19,2	16,4
U	24	12	14	20	14	21	21	18	15	14	20	10	5	15	6
Th/U	1,1				2,6	0,9	2,5				1,2	1,9	4	4	2,7

TABLE 14: SAMPLES USED IN THE GEOCHEMICAL INTERPRETATION
OF THE RARE-EARTH ELEMENT DISTRIBUTIONS

Rock Type	DJP Sample No.
Salem Granite	44, 49, 50, 114
Tinkas Formation	98, 100
Banded gneiss	22, 24, 29, 80
Etusis Formation	25, 26, 29, 31, 33, 34, 43

Analyst, Dr R.J.N. Brits - Chemistry Division, Atomic Energy
Board.

to the world average of 3,0. In the Bloedkoppie Granite,
on the other hand, the Th/U ratio varies between 0,9 and 2,6,
indicating an over-abundance of uranium. This is responsible
for the weak aeroradiometric anomaly associated with the
Bloedkoppie Granite. Uranium does not correlate with any other
element in Table 13. This is not entirely surprising when one
considers the high degree of weathering of the Bloedkoppie
Granite.

The common rock-forming minerals do not easily
accommodate uranium for it cannot substitute for any element
of its own size, e.g. calcium and sodium, as the balancing
of excess electrical charges is virtually insurmountable, and
more so if uranium occurs in the form of the uranyl cation,
UO_2^{2+}. Consequently it is either concentrated in late magmatic
fluids or expelled from the magma chamber (Armstrong, 1974,
p. 628). In the first instance the tendency will be to form
its own minerals such as uraninite, or to substitute in the
crystal lattices of accessory minerals. In granite rocks which

contain <u>low</u> concentrations of uranium, e.g. the Bloedkoppie *high!*

Granite, the uranium is dispersed as ionic or molecular

disseminations. These molecules are usually found in

crystal structures, adsorbed on crystal surfaces, in lattice

defects or in fluid inclusions. The tendency will therefore

be for uranium to be progressively concentrated within a

differentiated suite of igneous rocks.

The mode of transportation of uranium in a magma has

been the subject of several investigations. Poty <u>et al</u>

(1974, p. 569) studied fluid inclusions in granites and

demonstrated a correlation between the uranium and carbon

dioxide contents of the fluid. This suggested to them that

the uranium was transported as a uranyl carbonate complex.

Bhose <u>et al</u> (1974, p. 50) drew attention to the affinity of

uranium for the halogens and the subsequent removal of

volatile uranium hexafluoride in the escaping gases.

Furthermore the role of the uranium-halogen complex formation,

rather than increasing oxygen fugacity, prevents the precipi=

tation of uranium. Thermodynamically Kaspar and Hejl (1970,

p. 301) calculated that uraninite crystallizes at low oxygen

fugacities, that is, a reducing atmosphere favours its

precipitation whereas an oxidizing atmosphere suppresses it.

Precipitation of uranium from a magma is nevertheless

still a partly unsolved problem. Poty <u>et al</u> (1974, p. 569)

suggest that precipitation is promoted by unmixing of the

uranyl carbonate complex from the solution. They further

state that the reduction of uranium by the oxidation of iron

(II) to iron (III) is largely an inadequate mechanism to

precipitate uranium as the occurrence of hematite is not always

associated with uranium mineralization. In the Damara

orogen the correlation between the aeroradiometrics and air-

borne magnetics suggests an association of uranium with iron.

Many alaskites have a red hematitic halo which indicates a

relationship between uranium and iron. The following

reaction might have been responsible for the precipitation

of uranium in this instance:

$$4Fe_3O_4 + UO_2(CO_3)_2 \cdot 2H_2O^{2-} \rightleftarrows 6Fe_2O_3 + UO_2 + 2CO_2 + 2H_2O$$

magnetite   uranyl dicarbonate   hematite   uraninite
             complex

        Dissociation of magnetite and oxidation of the iron

(II) component took place within the framework of the redox

reaction. Complete dissociation of the uranyl dicarbonate

complex took place by the acceptance of four electrons from

the decomposing magnetite.

        Preliminary results of the DAMJU project indicate

that uranium was precipitated when the magmatic fluids were

very alkaline and in particular at the stage when potash

feldspar predominated over the sodium-rich feldspars at low

oxygen fugacity.

12.3   Geochemistry of the Rare-Earth Elements and Their
        Bearing on the Origin of the Granitic Rocks

        Before discussing the rare-earth element distributions

in the basement rocks, it is pertinent to briefly review the

geochemistry of the rare earths in granitic rocks (Taylor,

1965, p. 160; Haskin et al, 1966, p. 231; Philpotts and

Schnetzler, 1968; Koljonen and Rosenberg, 1974).

In general, through the whole sequence of magmatic differentiation, the rare earths concentrate in the more acid phases and the lighter elements tend to become enriched relative to the heavier ones. This is due to the lanthanide contraction according to which the ionic radius decreases with increasing atomic number and results in preferential depletion of the smaller elements (gadolinium to lutetium) in the residual melt.

Normally the rare earths are trivalent, but depending on the environmental conditions, Eu^{2+} and Ce^{4+} may exist. The well-known europium anomaly is due to the preferential inclusion of Eu^{2+} in the Ca^{2+} sites of plagioclase feldspars. It was found that during differentiation processes the crystal-lization of approximately 15 per cent plagioclase feldspar results in a 5 per cent depletion of europium in the remaining melt. Continuing crystallization of plagioclase will bring about larger europium anomalies in the residue.

Relationships between the rock types of the Damara orogen were established by Jacob (1974) through field and petrological evidence. An attempt was made here to see whether the geochemical relationships of the rare earths in the respective rock types fitted his postulates concerning the origin of the Banded Gneiss, Salem, Gawib and Bloedkoppie Granites. The problems to consider are, firstly, the relationships between the sedimentary rocks and their ultrametamorphic equivalents, and secondly, the relationships between the granites. The procedure adopted was to normalize the rare-earth concentrations in the rocks with the correspon=

ding concentrations of the rare-earth elements in chondritic
meteorites. This eliminated the odd-even effect as shown
in Figs. 38, 39 and 40.

        Jacob (1974, p. 86) considered that the banded gneisses
were derived from sediments characterizing the Khan and
Etusis Formations. The rare-earth trends in the Etusis
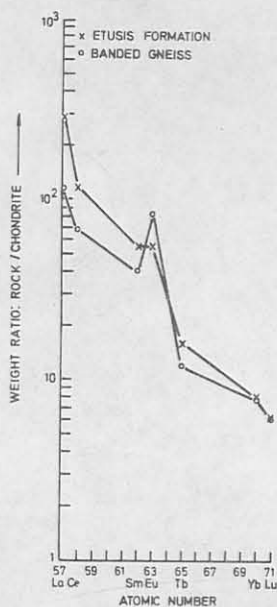Formation and the banded gneiss are similar (Fig. 38).

Fig. 38:   Rare-earth abundances in the Etusis
           Formation and banded gneiss divided
           by the rare-earth abundances in chondrites,
           plotted against atomic number.

Both rock types have positive europium anomalies, but the
banded gneiss has the greater relative europium enrichment
of the two suites. The trends agree with the postulate,
suggested by Jacob, that the origin of the banded gneiss was
due to metamorphic differentiation. The large positive euro=
pium anomaly of the banded gneiss resulted from a depletion
of the more volatile constituents of the Etusis Formation,
leaving a more basic residue rich in plagioclase. Depletion

of the lighter rare earths in this basic residue is typical
of a partial fractional melting process.

       According to Jacob (1974, p. 167) the Salem Granite
was derived from the Khomas Subgroup rocks 'on the high
temperature side of the anatexis-in-gneiss boundary'. Crystalli=
zation of the Salem Granite anatectic melt by 'filter-press'
action resulted in the Bloedkoppie Granite forming from the
displaced acid residues. The Gawib Granite was late to
post-tectonic in age (Jacob, 1974, pp. 30 and 167).
Smith (in Jacob, 1974, p. 30) considered the Gawib
Granite to be older than the Salem Granite due to the
intrusive relationships of the latter.

       The rare-earth patterns of both the Tinkas Formation
and the Salem Granite are very similar (Fig. 39) which
suggests that the Salem Granite was derived from the former.
Both rock types are enriched in samarium, and Koljonen and
Rosenberg (1974, p. 254) report a similar anomaly in a granite
derived from a sediment. It appears that the rare earths are
essentially resistant to metamorphic and metasomatic processes
(ibid., p. 249) and consequently their distributions in the
original rock and the derivitives remain very similar. The
close similarities (Fig. 39) indicate that the Salem Granite
was a product of complete melting of the Khomas Subgroup.
These trends confirm the findings of Jacob.

       The rare-earth patterns for both the Bloedkoppie and
Gawib Granites (Fig. 40) show that both granites are depleted
in europium, the degree of depletion in the former being
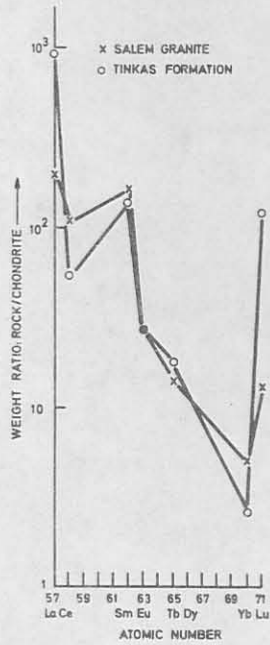the most significant.

Fig. 39: Rare-earth abundances in the Tinkas Formation and Salem Granite divided by the rare-earth abundances in chondrites, plotted against the atomic number.
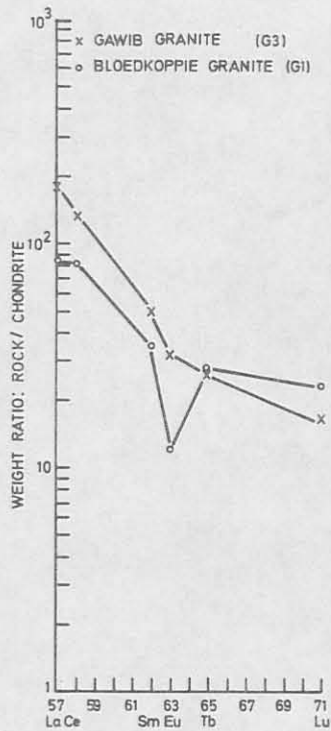

Fig. 40: Rare-earth abundances in the Gawib and Bloed= koppie Granites divided by the rare-earth abundances in chondrites, plotted against the atomic number.

The patterns of the Bloedkoppie and Gawib Granites
are generally similar, implying that both are genetically
related and that the Bloedkoppie Granite is the most frac=
tionated of the two. It is evident that the rare-earth
distributions for these granites are similar to the trends
of the Etusis Formation and the banded gneiss. There is no
resemblance to the distributions in the Salem Granite
(Fig. 39).

It is considered, therefore, that as a result of partial
melting of the Etusis Formation at depth, the resultant melt
fractionated into the acid Bloedkoppie Granite phase and the
more basic Gawib Granite phase. Both granites are more
differentiated than the parent rocks from the evidence of
the negative europium anomaly. This evidence and that of
the north-east orientation of the xenoliths in the Bloedkoppie
Granite tends to fall more in line with Smith's work and that
the Bloedkoppie and Gawib granites might well be of late
syntectonic age. The close proximity of the Etusis Formation
comprising the Langer Heinrich Mountain provided the source
material for these granites.

12.4   Summary

The banded gneiss was derived from the Etusis Forma=
tion by metamorphic differentiation. The Salem Granite was
the product of complete melting of the Tinkas Formation, or
more broadly, the Khomas Subgroup. Finally, a magma derived
from partial melting of the Etusis Formation crystallized
into an acid Bloedkoppie Granite phase and a residual, but

more basic, Gawib Granite phase. Both granites are therefore

late syntectonic in age. Tne significance behind the

paragenesis of the Bloedkoppie Granite is that it was

derived from the Nosib Group rocks. Therefore the Nosib

Group was the initial source of the uranium in this later-

forming granite which ultimately contributed to the supply *formed*

of the epigenetic uranium in the Gawib River Valley.