ALLIGATOR RIVERS ANALOGUE PROJECT

ANNUAL REPORT

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## CONTENTS

1 PREFACE

2 INTRODUCTION

3 OUTLINE OF TECHNICAL PROGRAM

4 SUMMARY OF PROGRESS IN TECHNICAL SUB-PROJECTS

I Modelling of Radionuclide Migration 5
II Hydrogeology of the Koongarra Deposit 7
III Uranium/Thorium Disequilibria 8
IV Groundwater and Colloid Studies 9
V Fission Product and Transuranium Nuclide Studies 10

5 DETAILED REPORTS

5.1 Koongarra Uranium Deposit 11
   - A A Snelling

5.2 Geological History of the South Alligator Region - Retreat of the Escarpment 19
   - Geoff Prowse

5.3 Geochemical Modeling of the Koongarra Uranium Deposit 29
   - Dimitri A Sverjensky

5.4 Modelling of Uranium Sorption to Substrates from the Weathered Zone in the Vicinity of the Koongarra Ore Body 39
   - T E Payne, J A Davis and T D Waite

5.5 Transport Modelling 47
   - C Golian, M Ivanovich, D A Lever and G Longworth

5.6 Comments on the Methods Used to Interpret the Radionuclide Mobility in the Koongarra Uranium Ore Deposit 57
   - Cezary Golian

5.7 Preliminary Hydraulic Characterization of the Koongarra Uranium Deposit 65
   - J R Norris and P Duerden

5.8 The Distribution of Uranium and Thorium between Phases in Weathered Core from Koongarra 79
   - Robert Edghill

5.9 Uranium Distribution in Mineral Phases of Rock by a Five Phase Sequential Extraction Procedure 93
   - N Yanase

5.10 Migration Behaviour of Uranium Series Nuclides in Altered Quartz-Chlorite Schist 103
   - K Sekine, T Ohnuki, T Murakami and H Isobe
5.11 Alteration of Chlorite and its Relevance to Uranium Migration
- Takashi Murakami and Hiroshi Isobe

5.12 Groundwater Sampling and Analysis
- T Payne

5.13 Colloid and Groundwater Studies
- T Seo, Y Ochiai and S Takeda

5.14 Geochemistry of $^{239}$Pu, $^{99}$Tc and $^{129}$I
- JFebryka-Martin and D Curtis

6 VALIDATION ASPECTS

7 COLLABORATING LABORATORIES AND PRINCIPAL INVESTIGATORS
The Koongarra uranium ore deposit in the Northern Territory of Australia is being studied to evaluate the processes and mechanisms involved in the hydrological/geochemical alteration of the primary uranium deposit and model the formation of the secondary uranium dispersion fan. A broad range of research is being undertaken to understand the radionuclide mobilization including hydrogeological studies of the groundwater flow, alteration of the host rock, geochemistry of the rock-water interactions and formation of secondary minerals, colloid transport, adsorption/desorption, and the relative distribution of the uranium/thorium radionuclides in the multiphase system. It is also possible to study the in-situ production and mobility of long-lived fission products such as $^{99}\text{Tc}$ and $^{129}\text{I}$ and transuranic nuclides such as $^{239}\text{Pu}$. A number of models have been developed to describe the radionuclide transport and decay, and satisfy measured uranium/thorium distributions at Koongarra. The eventual aim of the project will be to couple hydrogeological and equilibrium geochemical models, developed on the basis of the field and laboratory studies, to the transport models.

The work is being undertaken by the International Alligator Rivers Analogue Project, which was set up in 1987 following earlier studies in the region, which were funded by the US Nuclear Regulatory Commission (USNRC) and in part by the UK Department of Environment (UKDoE). The Agreement for the new project, which is sponsored by the OECD Nuclear Energy Agency (NEA), was signed by the following organisations: The Australian Nuclear Science and Technology Organisation (ANSTO); the Japan Atomic Energy Research Institute (JAERI); the Power Reactor and Nuclear Fuel Development Corporation of Japan (PNC); the Swedish Nuclear Fuel Inspectorate (SKI); the UKDoE and the USNRC. The project is planned to run for 3 years and ANSTO is the managing participant.
SECTION 2

INTRODUCTION

The nuclear industries in many countries are planning to dispose of high level and long-lived radioactive waste by burial underground using a multiple barrier concept. The spent fuel or high level waste form will be contained in a canister, surrounded by a buffer material, and placed in a stable part of the geosphere at a considerable depth below the biosphere. The objectives of a repository will be to isolate the radioactive waste from the biosphere for a long period of time and to ensure that any migration of radionuclides to the biosphere does not produce an unacceptable level of risk to public health and safety.

The assessment of the optimum design and overall long term safety of a repository will depend heavily on likely disruptive scenarios, processes for migration of radionuclides, and mathematical models. A large data base incorporating data from laboratory and field experiments will also be required and there are limitations on the time period over which these data can be obtained compared with the time period for isolation of the waste.

Natural analogues are an important source of long term data to give assurance that the most important processes, phenomena and scenarios have been included in the models and that these behave as predicted. Evidence on the migration or retardation of radionuclides in natural geological systems can be obtained over distances of metres to hundreds of metres and time periods of thousands to millions of years.

ANSTO has extensively evaluated uranium ore bodies in the Alligator Rivers Uranium Province in Australia as analogues of radioactive waste repositories. The migration of a series of radionuclides through the geosphere was studied in detail supported by contracts from the US Nuclear Regulatory Commission from 1981 to 1987 and from the UK Department of the Environment in 1986 to 1987.

The work was extended for a three-year program (commencing on 1 September 1987) as an international project based on the Koongarra uranium deposit and sponsored by the OECD Nuclear Energy Agency. The Agreement was signed by the following organisations: The Australian Nuclear Science and Technology Organisation (ANSTO); the Japan Atomic Energy Research Institute (JAERI); the Power Reactor and Nuclear Fuel Development Corporation of Japan (PNC); the Swedish Nuclear Fuel Inspectorate (SKI); the UK Department of Environment (UKDOE) and the US Nuclear Regulatory Commission (USNRC). ANSTO is the managing participant and the budget agreed initially for the three-year project was A$2.6 million (US $2 million) in 1987 dollars.
The individual tasks of the project are designed to understand the processes which have contributed significantly to the formation of the present day uranium ore deposit (particularly the secondary uranium mineralization in the dispersion fan). Consequently, the experimental and modelling tasks consider the original weathering of the Koongarra region, the alteration of the host rock and primary uranium, groundwater flow and migration pathways, rock/groundwater interactions, radionuclide transport and the formation and continued development of the secondary mineralization.

The overall objectives of the project are to:

(i) Contribute to the production of reliable and realistic models for radionuclide migration within geological environments relevant to the assessment of the safety of radioactive waste repositories.

(ii) Develop methods of validation of models using a combination of laboratory and field data associated with the Koongarra uranium deposit.

(iii) Encourage maximum interaction between modellers and experimentalists in achieving these objectives.

A Joint Technical Committee of representatives of the participants meets regularly to approve an annual technical program and budget. The technical program comprises six major sub-projects involving modelling and experimental work:

I Modelling of radionuclide migration.
II Hydrogeology of the Koongarra uranium deposit.
III Uranium/thorium series disequilibria studies.
IV Groundwater and colloid studies.
V Fission product studies.
VI Transuranic nuclide studies.

An outline of the technical programs and a summary of progress in the technical sub-projects is given below, and this is followed by a series of technical reports which briefly describe current research tasks.
SECTION 3
OUTLINE OF TECHNICAL PROGRAM

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The Alligator Rivers Uranium Province in the Northern Territory of Australia is located about 200 km east of Darwin. The Koongarra uranium deposit of Denison Australia Ltd which was chosen for the international ARAP study lies about 25 km south of the small town of Jabiru. The area has a monsoonal climate with almost the entire rainfall occurring in the wet season between November and March.

Uranium mineralisation occurs at Koongarra in two distinct but related orebodies separated by about 100 m of barren schists (see Chapter 2). Both orebodies strike and dip broadly parallel to the Koongarra Reverse Fault, which is the footwall to the ore zone. Primary mineralisation is largely confined to quartz-chlorite schists immediately above the fault zone. Secondary uranium mineralisation is present from the surface down to the base of weathering at about 25 m depth and forms a tongue-like body of ore dispersing downslope for about 80 m.

The method of operation is to undertake visits to the Koongarra site to obtain samples of uranium ore, rocks and water from drillholes. The samples are then analysed by a variety of chemical and physical methods in laboratories of the participants or of contractors with special expertise and equipment. At the start of the project samples of cores from 71 drillholes through the orebody were available and samples of water had been obtained from several of the 40 larger diameter drillholes. All of these drillholes were established during the early exploration phase by NORANDA Australia Ltd. In late 1988, 22 additional holes were constructed in and around the No. 1 orebody for the hydrogeological and groundwater geochemistry studies and to provide samples for laboratory studies.

An extensive study of the distribution of uranium, thorium and radium isotopes in and around the No. 1 orebody has identified well-defined areas of leaching and accumulation within the weathered zone. A substantial geochemical data base has been prepared from samples of groundwater collected from more than 80 boreholes in the vicinity of Koongarra, which represent all the distinctive geologic units. Hydrological data have also been obtained in selected parts of the area; both field and laboratory measurement programs are undertaken. The data accumulated so far have been used as input to models established to calculate the extent and timescale of migration of uranium through the secondary dispersion zone. Preliminary analyses of selected long-lived fission products and plutonium have also been obtained with a view to modelling their migration behaviour in the orebody).
Modelling/technical workshops are held at regular intervals to enable maximum interaction to take place between modellers and experimentalists and to guide the direction of the experimental program. Workshops were held in Sydney (February 1988), Tucson (November 1988) and Sydney (July, 1989).

The organisations now taking part as contractors in the project in addition to the six primary participants are: University of Arizona; Johns Hopkins University; University of Sydney; Los Alamos National Laboratory; UKAEA Harwell Laboratory; and the Department of Mines and Energy, and the Power and Water Authority, NT, Australia.
SECTION 4

SUMMARY OF PROGRESS IN TECHNICAL SUB-PROJECTS

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I MODELLING OF RADIONUCLIDE MIGRATION

There is general agreement that the primary uraninite (UO₂) ore at Koongarra was converted into secondary uranium minerals and dispersed over a long period of time through a secondary zone located between the primary zone and the surface. Priority has therefore been given to modelling the processes and timescales involved in the development of the secondary weathered zone. Considerable progress has been made in the following five tasks:

(a) Determination of the sequence and timing of the history of weathering at Koongarra.

(b) Migration of radionuclides in the weathered zone and from the original primary zone.

(c) Open system modelling using radiochemical data for saleeite (magnesium uranyl phosphate) crystals found within the secondary zone to evaluate the timescale of development of this zone.

(d) Geochemical modelling to identify the controlling reactions for formation of the uranium phosphate zone and the uranium silicate zone from the initial pitchblende ore.

(e) Hydrogeological modelling in association with sub-project II.

The data from ARAP are also being modelled as test case 8 in the International Model Validation Study (INTRAVAL) initiated by SKI in October 1987.

a) GEOLOGICAL HISTORY

An initial concept of the Kombolgie sandstone being eroded by scarp retreat during the later Tertiary period to expose the underlying mineralised Cahill formation to sub-aerial and oxidising conditions, appears not to be compatible with features and processes of the Koongarra valley area. A different set of processes appear to have been involved, and these allow for a reasonable time correlation with previous radionuclide transport modelling, which conclude that the uranium mobilisation occurred within the last few million years.
This scenario assumes that prior to and during the Mesozoic the Kombolgie sandstone has been removed from above the orebody, the result of uplifting by faulting along the Koongarra fault and subsequent erosion. The underlying Cahill rocks were planated during the Cretaceous marine transgression and laterised (formation of ferricrete) during the Tertiary, under the tropical conditions which prevailed. In response to significant climatic changes in the later Tertiary and Pleistocene, the laterised schists were eroded by thin scarp retreats of the ferricreted surficial veneer; thus the water table was lowered to the top of the primary orebody and the uranium was mobilised.

b) HYDRODYNAMIC TRANSPORT

A multiphase transport model has been developed, which considers an amorphous iron oxyhydroxide phase coming rapidly into equilibrium with the fluid phase and a crystalline iron oxyhydroxide phase which comes into equilibrium more slowly. Samples from a single representative cross-section through the ore deposit have provided data for the initial modelling but further data are needed for a complete two-dimensional assessment of the uranium dispersion in the near surface, intermediate depth and deep (unweathered) zones. Data are also being provided for a second section, which is parallel to the assumed groundwater flow direction; sequential extraction techniques are used to measure the fractionation of uranium and thorium series nuclides in iron/clay/quartz phases etc. Further modifications of the model have been made to include longitudinal dispersion and develop a quasi two dimensional model, which has been used to describe the mobility of the bulk uranium in the dispersion fan.

c) OPEN SYSTEM MODEL - SALEEITE CRYSTALS

Data for saleeite crystals have been used to gain information on local formation times and hence on the uranium mobility in the weathered zone. The work is based upon a model which considers crystallization being completed in a relatively short time with no significant deposition or leaching during the "younger" stage of the crystal's existence. Loss of $^{227}$Ac through a recoil-related process is however permitted, as is uranium leaching from a radiation-damaged structure in "older" crystals. Although one relatively comprehensive set of results was available for a location within the dispersion fan, the significant age differences for some closely located crystals have suggested that the crystal formation must be spread in time as a result of unknown, possibly geochemical fluctuations.

d) GEOCHEMICAL MODELLING

This task is aimed at understanding the origin of the different U-zones and identify the controlling reactions for formation of uranium phosphates and uranium silicates. Aqueous speciation and saturation state calculations have been carried out using the computer code EQ3NR (Wolery, 1983) and a thermodynamic database generated at the Johns Hopkins University.
The investigation of the chemistry of phosphorus and the states of saturation of the Koongarra waters with respect to the phosphate mineral apatite, based upon the analyses for acid hydrolysable phosphate and anions, suggest that the waters are undersaturated or near saturation with respect to hydroxyapatite, and phosphate is one of the most important ligands for the transport of uranium in the Koongarra groundwaters. The mass transfer calculations now only use the present-day analyses of the Koongarra groundwaters as a guide to the possible initial composition of the fluid before it encounters the orebody. Until now, only thermodynamic equilibrium constants near 25°C that have been derived from experimental measurements have been considered and this has precluded the inclusion of a number of species that may be of importance in the Koongarra waters, such as uranium bicarbonate complexes. These species are now being incorporated in the model.

II HYDROGEOLOGY OF THE KOONGARRA DEPOSIT

A detailed understanding of the hydrogeology of the Koongarra deposit is essential to the successful modelling of radionuclide migration through the deposit. The initial groundwater hydrology data were obtained during the exploratory phase of the deposit by consultants to NORANDA Australia Ltd; a limited amount of work was carried out in 1985 and 1987 in the USNRC funded program. Since then both field and laboratory studies have been restarted to support the development of models describing steady and transient groundwater flow in the Koongarra region.

Two series of field tests were carried out by the University of Arizona in May-June 1988 and June-July 1989 for the ARAP study. The majority of the work comprised constant rate pumping tests, which are the primary means by which quantitative estimates of aquifer coefficients are made. The results of these tests are normally presented as contour maps of final measured drawdown and logarithmic and semilogarithmic plots of drawdown versus time. In 1988, eight tests were conducted in the Cahill Formation aquifer; in 1989 additional tests of drillholes PH73, PH49, C8 and PH58 provided elliptical drawdown patterns which closely matched the results of the 1988 tests.

A series of slug tests was also carried out in 1989, in which a known volume of water was added to either open holes, or packed zones of the holes and the drop in water level to the initial value was monitored. Only a limited series of tests were possible but they suggest that the majority of groundwater flow occurs within the upper 40 m of the system. The monthly measurement of standing water levels (SWL) in all the open wells was restarted in February 1989.

An additional 22 drillholes to monitor aquifer tests, provide an improved network for water analyses and supply drillcore samples in the weathered zone, were completed during October-December 1988. Several of these holes were fitted with special water sampling ports at selected depths.
A series of drillcore physical property measurements is in progress at the University of Sydney on rocks from the weathered, altered and unweathered zones of the orebody, to determine textural characteristics, such as dry bulk density, porosity and permeability.

The preliminary results of the tests indicated a high degree of conductivity. Fracture flow dominated some of the tests, but the overall aquifer response appeared to be that of an equivalent porous medium. Anisotropy is well-developed with north to north-east oriented principal transmissivities. North-east directions represent the large-scale drawdown patterns and are sub-parallel to the bedrock structure and the Koongarra fault. The northerly directions were localised and may reflect a less extensive fracture fabric or a flexure in the bedrock foliation. Basic issues still to be understood are, the interchange of water between different units (sand, clay, weathered, unweathered rock, etc), whether the fault is a semi-barrier or whether it includes conducting zones, and how much water flows in fractures.

III URANIUM/THORIUM DISEQUILIBRIA

A substantial uranium/thorium disequilibria data base for bulk rock and water samples had been collected prior to the commencement of the extended ARAP. A number of new studies on core samples from initial and new drillholes are now underway to assist in the modelling of migration. Radiochemistry/α-particle spectrometry techniques are being used to extend the database for both weathered and unweathered material within the Koongarra uranium ore deposit and extending downstream into the sub-economic zone. Samples from a single representative cross-section through the ore deposit have provided data for the initial modelling studies.

Sequential extraction techniques are used to measure the fractionation of uranium and thorium series nuclides in iron/clay/quartz phases etc. as part of the database preparation and understand how the two (or more) separated "phases" are related to the ore minerals and their accessibility to groundwater. Samples are also being characterised for elemental associations, mineralogical distributions, and attention is being given to those elements which have particular significance for the geochemical modelling including species such as phosphate.

A large proportion of the uranium and thorium is associated with the amorphous phase, which may include associations with ferrihydrite and adsorption onto iron oxides and clay minerals. The areas showing greatest leaching are near the top of drillhole DDH 52, whereas the most rapid accumulation seems to have occurred near the centre of the dispersion fan and near the base of weathering to the edge of the fan. There is possibly preferential movement and accumulation of uranium just above the base of weathering.
Thin section and radiography techniques are being used to investigate the characterisation of uranium in the dispersion fan, its association with the iron oxides and clays, and/or presence in a crypto-crystalline/nodule form. Image analysis is also being used to study variations in the pore structure of drillcore samples for depth profiles through the ore deposit so that the derived porosity and shape factors can be compared with the core permeability measurements obtained by the petrofabric analysis.

The alteration of the Koongarra host quartz chlorite schist is being studied to provide information on the accessibility of the radionuclides to groundwater and how the uranium has been retarded by the transformation from chlorite to vermiculite, then to kaolinite and iron hydroxides. It has been observed that the uranium migration is closely related to the chlorite alteration; uranium has not redeposited in the area where the chlorite is not yet altered but redeposition has started in the area of the vermiculite; high concentrations of uranium are associated with kaolinite and iron hydroxides.

IV. GROUNDWATER AND COLLOID STUDIES

A major aim of the groundwater sampling program is to investigate the chemical composition of groundwater collected in representative zones from the vicinity of the Koongarra ore deposit and prepare a database for the geochemical modelling. A limited set of data is now available from packed off depths in drillholes at Koongarra collected at the end of the wet season (May) and the end of the dry season (November). Seasonal variations are also being studied by monthly sampling of the two point wells to see if there are significant changes in the water chemistry as a result of the variation in standing water levels.

Samples have been collected from depths of about 25 m and 42 m for cations, anions, tritium, stable isotopes, Ra and U analysis. Precipitates from >25 L groundwater volumes were also obtained for $^{230}$Th and $^{38}$Cl analyses. Samples for $^{129}$I determination and for $^{14}$C analysis have also been collected for age measurements to support the hydrogeological modelling. Chemical and physical parameters, such as Eh, pH, conductivity, dissolved oxygen and total alkalinity were measured in the field. Analysis of stable isotopes in samples collected monthly at 13 and 23 m may provide information on the mixing of the near surface groundwaters.

Uranium-238 and $^{234}$U/$^{238}$U activity ratios have been measured for groundwater samples collected at both the end of the wet and dry seasons. Measurable concentrations of $^{230}$Th were generally found, although in most cases they were within an order of magnitude of the detection limit. A uranium and activity ratios database for all representative zones of the ore deposit has still to be completed.
The results of measurements of the colloid content of groundwater at Koongarra show that colloidal transport has been occurring in Koongarra groundwater, and clay particles, and particles containing uranium, lead, titanium and magnesium silicate have been identified. Most of the samples have been obtained from water from the weathered zone, however, it appears that a greater colloid load is carried by deeper water. Some work is in progress to concentrate colloids present in groundwater sampled at three depths in a well and prepare grids for electron-microscopy analysis by centrifugation under controlled atmosphere conditions.

The interactions between sorbed species and those in solution are being studied for core samples from the weathered zone in the leached, uranium ore and downflow regions of the orebody where water sampling points have been installed. The drillholes are almost in line in the direction of the presumed groundwater flow. Batch studies of the sorption of uranium onto the substrates are being analysed with surface complexation modelling techniques so that sorption processes can be incorporated into a general transport code appropriate to the Koongarra weathered zone. Samples from four cores obtained in the November 1988 cable-tool drilling program will be used. They are from the 13-14 m depth where the water sampling intervals are located, so that water from the surrounding zone can be directly analysed and simulated in the laboratory. The preliminary sample characterisation includes sequential extraction to determine the distribution of uranium and thorium, elemental analysis, identification of minerals present, surface area analysis, etc.

The results of early MINTEQA2 speciation modelling for analytical data of Koongarra PH49 groundwater show that equilibration with hematite would result in a concentration of dissolved iron very much lower than the observed value whereas equilibration with ferrihydrite gives total dissolved iron concentrations of a similar magnitude to the observed value. The influence of organic matter and of carbonate and phosphate on uranium solution speciation have also been modelled.

V and VI: FISSION PRODUCT AND TRANSURANIUM NUCLIDE STUDIES

The occurrence of selected long-lived fission products (\(^{99}\)Tc and \(^{129}\)I) and \(^{239}\)Pu is being studied in solid and water samples. Methods of extraction of these isotopes from large volumes of groundwater have been developed, as well as methods for their measurement at the very low natural levels. Only a limited number of ore samples have been analysed to date, however, the results so far suggest that \(^{129}\)I is being leached from the Koongarra primary ore to a greater extent than is uranium or \(^{239}\)Pu.

In water from within and down-gradient of the deposit, \(^{129}\)I/I ratios are higher by one to three orders of magnitude over background levels in the vicinity of the deposit. The down-gradient decrease is not systematic with distance from the orebody and probably reflects differing extents of dilution rather than sorptive losses.
SECTION 5.1
KOONGARRA URANIUM DEPOSIT
A A Snelling

The uranium mineralisation at Koongarra occurs in a layered sequence of schists, rocks that were once shales and siltstones but which have been metamorphosed or changed by heat and pressure. Underneath the schists, and close to the uranium, are layers of dolomite, or metamorphosed limestone. These schist and dolomite layers (called the Cahill Formation) flank, and appear to have been deposited on the sides of, a dome of crystalline granitic rocks (called the Nanambu Complex), that are thus obviously the oldest rocks in the area (see Figure 1). After the limestone, shales and siltstones were deposited on the flanks and on top of the granite, and subsequent to the heat, pressure, folding and fracturing of metamorphism that changed the sediments into dolomite and schists, uplift, weathering and erosion produced a new landsurface on which thick layers of sandstone (the Kombolgie Formation) were then deposited, such that the tilted schist and dolomite layers are now at an angle to the overlying flat lying layers of sandstone.

Within the schist layers, probably within 100 metres above the dolomite, the uranium ore occurs in two distinct but clearly related bodies, separated by about 100 metres of barren schists (see Figure 2). Both orebodies are elongated and dip at 55° broadly parallel to a prominent fault (the Koongarra Reverse Fault), the movement along which has reversed the normal sequence of strata by bringing the overlying younger sandstone down underneath the older tilted schist layers (see Figure 3). This fault zone forms the lower boundary (or footwall) to the uranium ore zone. The primary mineralisation is largely confined to a schist layer consisting of grains and flakes of the minerals quartz and chlorite respectively (quartz-chlorite schist), immediately above the fault zone, and a thin layer of similar schist that also contains large amounts of graphite forms a distinctive upper boundary or hanging wall unit (see Figure 3). At the northern end of the No. 1 orebody, and in the No. 2 orebody, mineralisation persists into the overlying schists that contain graphite, garnet and mica, as well as quartz and chlorite.
The more south-westerly of the two orebodies, the No. 1 orebody (Figure 2), is elongated over a distance of 450 metres and persists to a depth of about 100 metres. Secondary uranium mineralisation, derived from decomposition and leaching of the primary mineralised zone, is present from the surface down to the base of weathering over some 25 metres, and forms a tongue like body of ore grade material dispersed down slope for about 80 metres to the south-east (Figure 3). There is also some dispersion of secondary uranium mineralisation within the main fault zone. In cross-section the primary ore zone consists of a series of partially coalescing lenses, that have the appearance of being stratabound, that is, confined within and parallel to the host schist layer (see Figure 3). The width of the primary ore zone averages 30 metres at the top of the unweathered schist, tapering out at the extremities of the elongation, and down dip to about 100 metres below surface. The strongest mineralisation with most assay values in excess of 1% uranium, is over a thickness of several metres just below the graphite bearing hanging wall schist layer. This high grade ore is persistent both along the elongation and down dip. Mineralisation of varying grades, however, occurs down through the host schist layer and along minor fractures. Closer to the footwall fault breccia (crushed rock) zone the ore is of lower grade, is more sporadic, and tends to fade more rapidly with depth.

In the No. 2 orebody, the mineralisation is elongated over a distance of about 100 metres and persists down dip at 55° to at least 250 metres. Because the top of the primary mineralisation is at 50 metres depth, there is no secondary uranium mineralisation in the weathered schists. In cross-section the ore zone tends to be oval in shape, and is made up of a series of partially coalescing lenses. Ore grades are generally lower than in the No. 1 orebody, but the mineralisation is present over greater widths.

The primary ore consists of pitchblende (or uraninite - uranium oxide) veins and veinlets which either follow or cross cut the layering in the schist. Associated with the high grade ore, just below graphite bearing hanging wall schist layer particularly, are minor amounts of scattered sulphide minerals, primarily galena (PbS), chalcopyrite (CuFeS₂) and pyrite (FeS₂), but also some rare native gold. In and around the ore is a geochemical halo, representing the elements with which the ore is enriched, of copper, lead, sulphur, arsenic, nickel, cobalt, vanadium and magnesium, the latter reflecting the chlorite in the host schist.
One of the most important features of the uranium mineralisation at Koongarra is the occurrence of abundant secondary uranium minerals, principally within the dispersion fan above the No. 1 orebody, but also to a lesser extent within the top of the primary ore zones just below the weathered zone and at the bottom of the primary zones along and just above the fault. These secondary uranium minerals are noted for their variety of brilliant colours, so their presence is easily recognised both in subsurface samples and in drill core.

Much of the secondary mineralisation is derived from in situ oxidation and alteration of grains and veins of the primary uranium mineral, pitchblende, and by the dissolving and retransporting of the uranium. These processes therefore represent the latest stage in the genesis of the deposit as we know it today, processes which may still be in operation. Uranyl phosphate minerals are found in the tail of the secondary dispersion fan in and down slope from what was the upwards extension of the primary ore zone, while uranyl silicates are either in the primary ore zone below or at the interface between the two (see Figure 3). In the No. 2 orebody, which has no secondary dispersion fan, only uranyl silicates have been found.

The differences in distribution and style between the uranyl silicates and phosphates strongly suggests a two stage process for their development under different physico-chemical conditions. The first stage was the in situ alteration of pitchblende to form uranyl silicates associated with chlorite veining at depth within the primary ore zones of both the No. 1 and No. 2 orebodies. Subsequent intersection of the zone of surface weathering with the top of the primary ore zone of the No. 1 orebody only, has resulted in the leaching and decomposition of both pitchblende and uranyl silicates to form the uranyl phosphates within the secondary dispersion fan.

In the primary ore zones at Koongarra, where the mineral apatite (the source of phosphorus) is stable, the soluble uranyl silicates precipitated under slightly reducing and weakly acidic conditions with negligible to zero concentration of phosphate and vanadate in the ground waters. In the weathered zone, however, the precipitation of relatively insoluble uranyl phosphates has been favoured by oxidising conditions and much higher phosphate concentrations (due to weathering of apatite) in the ground
waters. It is also possible to conclude that vanadium concentrations in the circulating fluids at Koongarra were very low compared to phosphorus because carnotite is sparse in its occurrence in the weathered zone.

Groundwater movements at Koongarra have been investigated and are shown schematically in Figure 3. The depicted groundwater paths indicate the source and direction of the ground waters responsible for the oxidation, hydration and silicification of the pitchblends and contemporaneous chlorite production in the primary ore zone above the fault, and of the ground waters responsible for the weathering and dispersion of the primary ore in the weathered zone. The distribution of secondary uranium minerals thus produced is also shown schematically in Figure 3.

Recharge of ground waters to the weathered schists appears to occur via downflow parallel to, and in close proximity to, the reverse fault in both the underlying sandstone and the schists. Although the fault zone was found to be practically impermeable, some water still appears to flow from the sandstone into the schists via cross fractures which offset the fault, producing hematite alteration in the fault zone and in the schists above. Once in the schists ground water flow is towards the south-east, away from the sandstone cliffs behind the deposit. The weathered zone essentially acts like a capping that appears to prevent downwards circulation of surficial waters. Nevertheless there is a separate flow of surficial waters within the weathered zone, again flowing down slope towards the south-east away from the sandstone cliffs. Below the weathered zone water flow rates appear to be very low.

The weathered zone ground waters are by nature oxidising, being essentially surficial, and this is supported by the oxidation mineralogy in the weathered zone, including the rare occurrence or carnotite, and the non-occurrence of pitchblende. Below the base of weathering, conditions are slightly reducing, particularly in the presence of graphite where pitchblende and sulphide minerals are stable. Consequently, any dissolved uranium still present in the ground waters may well have been reprecipitated as supergene pitchblende, thus further upgrading the high grade ore zones.

These groundwater movements are believed to have been active for at least the last 350,000 years, as this is the estimated age of the leading edge of the secondary dispersion fan. However, removal of the sandstone originally
covering the deposit is estimated to have taken place in excess of one million years ago. The reverse fault and its offsetting fractures must have developed even earlier still, as they have facilitated erosion of the sandstone cover and later provided access for the penetrating ground waters responsible for alteration of the pitchblende ore. These timescales are more than adequate for the observed alteration to be produced at depth. The present state of the No. 2 orebody provides a clear picture of what No. 1 orebody was probably like prior to surficial weathering and attendant destruction of primary ore. Once surficial weathering processes commenced to destroy pitchblendes and uranyl silicates producing uranyl phosphates in their place, lateral groundwater flow dissolved and dispersed the uranium down slope in the direction away from the sandstone cliffs (Figure 3) to form the prominent dispersion fan above the No. 1 orebody.

The following references give more details -


Figure 1. Regional geology map showing the location of the Koongarra uranium deposit.
Figure 2. Local geology map showing the location of the Koongarra No. 1 and No. 2 orebodies. Because of surficial cover the geological units and outline of the mineralisation are projected to the surface from the base of weathering.
URANIUM MINERALOGY
- Uraninite with Pb-U oxides
- Uranyl silicates
- Uranyl phosphates
- Dispersed uranium, adsorbed on clays and iron oxides
- Groundwater flow

ALTERATION
- Primary
  - Outer halo
  - Chlorite-alter-biotite (in schists)
- Silification (in sandstone)
- Inner halo
  - Pervasive chloritisation and quartz removed (in schists)
- Secondary
  - Limits (approx.) of hematite alteration

GEOLOGY
- WZ Weathered zone
- Base of weathering
- MIDDLE PROTEROZOIC
  - Kombolgie Formation (sandstone)
- LOWER PROTEROZOIC
  - Mica-quartz-feldspar schist
  - Amphibolite
  - Garnet-mica-quartz schist
  - Graphite-mica-quartz schist
  - Graphite-quartz-chlorite schist
  - Quartz-chlorite schist
- Reverse fault breccia

Figure 3. Simplified cross-section through the Koongarra No. 1 orebody showing geology, distribution of uranium minerals, distribution of alteration, and present groundwater flow.
INTRODUCTION

In an attempt to solve the problem of the exact time interval during which the Koongarra orebody was exposed to oxidising conditions and the resulting dispersion fan developed, a brief study was applied to existing data. Information has been gathered to present the history of the South Alligator Region from a perspective of the geomorphological evolution. This included an evaluation from the maps Cahill 1:100 000 scale both - geological (1982) and topographical, Landsat imagery 1974 and 1983, aerial photographs and publications as listed below. A summary of the geological history of the region is given in Table 1, which is reprinted from the commentary for the Cahill 1:100 000 map.

Geological cross sections from the Northern Australian Research Unit, Kapalga, Cahill and East Alligator present evidence of Tertiary and Quarternary aged sections, derived from erosion of the South Alligator Rivers and the Magela Creek catchments. They are downstream of the drainage of the Mt Brockman Massif and the Koongarra Valley system. For convenience in this discussion the valley system between the Mt Brockman Massif and the Arnhem Land Escarpment 10 km to the South East is referred to as the Koongarra Valley. Koongarra Creek drains the South Western margin of the Massif and Namarrgon Creek drains the major part of the valley and Sawcut Gorge headwaters.

In general over the northern half of the Northern Territory geomorphological processes are of great antiquity. The tectonic stability of the North Australian Craton since the mid Proterozoic has resulted in widespread peneplanation, and the development of extensive duricrusts. However, as an introduction to this discussion it was generally thought that the Arnhem Land Plateau and the Mt Brockman Massif form the Wave Hill Surface, while the northern plains including the immediate Koongarra area can be identified as the Koolpinyah Surface which is thought to have been developed in Pleistocene times (1.8 My). The literature also mentions older surface systems eg Tennant Creek, Ashburton and Bradshaw Surfaces. Further work is required to assign the probable surface system at Koongarra, as some conflict is believed to exist with the period of development of this system.
It is essential to understand that the present day dry monsoonal climate is not assumed to have occurred during the period of development of the oxidised ore at Koongarra. Clearly the parameters of climate have altered significantly since the Mesozoic. The multicyclic episodes of laterisation are much in evidence.

GEOLOGICAL HISTORY OVERVIEW

This is summarised in Reference 1 pp 26-30. Selected extracts follow:

Most deposition and virtually all of the tectonism, metamorphism and igneous intrusion took place in the Early Proterozoic. The Kakadu Group were laid down on Archean granite basement and were overlain by the Cahill Formation, predominantly sandstone and siltstone. Black shale and limestone at the base of the Cahill Formation probably were deposited in shallow-marine to supratidal conditions.

The braided alluvial-fan sandstone of the Kombolgie Formation was deposited from a northerly provenance in mid Carpentarian time. The interbedded volcanic and sandstone units may have once extended across Cahill but, if so, have since been removed by erosion. The main faulting of the formation possibly preceded retrogressive metamorphism and metasomatism of the uranium orebodies and surrounding rocks at 1610 My as indicated by chloritised down-faulted blocks of Kombolgie Formation sandstone.

A very long stable-to-erosional period followed for about 1400 My Minor phonolite and dolerite were emplaced about 1370, 1320 and 1200 My ago. Carpentarian rocks were peneplanated and Mesozoic aged seas eroded much of these to expose Early Proterozoic rocks, exhume the pre Kombolgie land surface and form sea cliffs in Kombolgie Formation sandstone. The only remaining evidence of Mesozoic deposition is scattered mesas of epicontinental sediments in the northwest. None of the generally unconsolidated Cainozoic sediments are recognisably marine, but the dominance of marine faunas in floodplain archaeological sites to the north indicated Pleistocene to mid-Holocene high-stands. Sea level has been constant for the last 7000 years. The dominant forces which have moulded today's landscape were chemical weathering to produce laterites, sheet washing of sands derived from the Kombolgie Formation and "cut and fill" modification of the land surface by repeated erosional and aggradational cycles.

GEOLOGICAL PROCESSES AND DEPOSITION DURING MESOZOIC, TERTIARY AND QUATERNARY

Mesozoic

Laterised Cretaceous sediments cover a large part of the Darwin - Alligator Rivers Area. The escarpment cliffs have largely been formed as shoreline erosion during the Cretaceous marine transgression.
No Cretaceous rocks outcrop across the Koongarra Valley nor further west across the area which is close to the postulated Cretaceous sea cliffs. It could be assumed that an extensive series of coalescing wave cut platforms were developed thus stripping the lower areas to a plain. The Mt Brockman Massif would have formed an island or narrow necked peninsular feature, at least towards the end of the period. Cretaceous aged sediments were deposited in deeper off shore areas (eg the location of present outcrop which occurs 35 km north west) with more extensive occurrences further north again extending under the northern Magela swamps (Ref.4 Fig.26).

Tertiary

During the Tertiary modification of the Mesozoic sea cliffs by sub-aerial erosion produced the Arnhem Land Escarpment.

Tertiary deposits also do not outcrop in the study area. However, sections of Tertiary rocks from elsewhere could possibly be correlated to the time of erosion of the surface of the catchment area of the South Alligator River. For example coarse gravelly bedded rocks can be observed on the road cutting of the Arnhem Highway where a section up to 81 metres deep has been drilled (see Figure 2). This figure illustrates the significant trizonal laterite profile developed on these rocks and the subsequent erosion and backfill with Quaternary Sediments, which are not laterised. The text accompanying this data states -"The gravels form a poorly consolidated band up to 40 m thick at or near the unconformity with the Early Proterozoic rocks. The relief of the unconformity appears to be largely controlled by faulting rather than resistance of bedrock to weathering."

Further relevant information on the Tertiary history is quoted below from Stuart-Smith.

"These Tertiary deposits formed as extensive colluvial mantles on the Early Proterozoic erosional surface during the Middle to Late Tertiary. Gravels were deposited on valley floors, on lower wash slopes, and locally adjacent to active fault scarps.

Monsoonal climatic conditions throughout the Cainozoic resulted in the development of a lateritic or weathering profile during a sedimentary hiatus in the late Tertiary. (The Koolpinyah Surface). The presence of ferricrete pebbles in gravels and a ferruginised zone in some of the Early Proterozoic rocks beneath the unconformity indicates that laterite also developed before Tertiary sedimentation."

Quaternary

Quaternary sediments have backfilled Namarrgon Creek and a significant degree of maturity is in evidence for this drainage system. Koongarra Creek exhibits a more youthful stage of development. Extensive Quaternary
sediments have aggregated along the Norlangie Creek system, which probably reflects the shallowness to bedrock\(^{11}\). The shallowness of bedrock has maintained and controlled the base level of erosion for the upstream modifications.

It is probable that the metre or so cover of sand over the ore body at Koongarra is a result of sandstone erosion of the dissected wedge of Mt Brockman Massif immediately to the north of the orebody. Archeological evidence existing in the region indicates that up to a few metres of sand overlie Aboriginal middens approximately 30,000 years old along the base of the escarpment (J Mulvany ANU public Seminar Darwin 1978). Additional information on Holocene and Pre-Holocene sediments are presented in Reference 3. This reference provides both information on sea level changes in this region and relevant climatic data. Note that the Holocene seas did not transgress into the study area, and that the climate in the last 10,000 years has been variable with plus or minus 50% rainfall conditions.

**GEOMORPHOLOGY OF KOONGARRA VALLEY**

Kombolgie Sandstone Erosion From Valley

The removal by erosion of the formerly continuous cover sheet or tabular body of Kombolgie Sandstone Formation across the Koongarra Valley has occurred prior to the planation and laterisation of the valley floor. An evaluation of the geological and topographical map data points to this interpretation. It is suggested that the mechanism of removal would have commenced by upward tilting, maximised along the Koongarra reverse fault, and with the corresponding hinge zone close to and subparallel to the Arnhem Land Escarpment along the south west margin of the valley. The amount of vertical throw is speculative. However, estimates have ranged from 600 metres\(^{7}\) to probably less than 100 metres and possibly only 50 m\(^{8}\).

Following uplift the unconformity of the Kombolgie/Cahill contact would have been elevated thus exposing the relatively softer Cahill schists to erosion. Consequently at the scarp, erosion by undercutting then gravity block felling of the resistant Kombolgie Sandstone and followed by removal by mechanical processes, would have occurred probably by marine activity. The time interval for this removal is probably no later than Mesozoic (Cretaceous) when marine transgression shaped the main outline of the Arnhem Land Escarpment. However, removal during the long period of erosion since faulting and mineralisation is not discounted. (Reference 1 pp 26-30).

Kombolgie scarps with talus deposits are common but their absence along the southern margin of the Mt Brockman Massif is notable. The coincidence of the location of the Koongarra reverse fault dipping 60 degrees south along the length of this southern margin does provide evidence of the processes involved here. It suggests the faulting has bevelled and stabilised this scarp in antiquity with little resultant erosion in geomorphic recent
times. It is suggested that this stable relief has existed for the majority of the Tertiary and Quaternary. For this reason an alternative model of overburden removal is required for the initiation of the oxidised ore development at Koongarra.

Valley Planation

The Mesozoic seas formed sea cliffs on the Kombolgie scarp with partial or near complete erosion of the up faulted horst block of Kombolgie/Cahill in the Koongarra Valley. It is apparent that the Mesozoic marine transgression was the dominant factor via wave cutting mechanical processes in this peneplanation resulting in the levelling of a variety of lithologies (eg Namambu Complex to Cahill) over a wide area. Modification of any pre-existing landscape to planated areas resulted once the resistant Kombolgie was removed.

The planated nature of the valley with occasional remnants of insitu and reworked remnants of the standard laterite profile (commonly above the topographical 40 m AHD contour) permits a reconstruction of the valley grade prior to an event of later erosion as evidenced by stream channel incision below the 20 m AHD contour.

Stream Morphology

Within the valley a study was conducted of stream morphology, ie drainage patterns, channel sediments and topographical contour map intervals. As previously mentioned Namarrgon Creek has the features of a more matured stage of development than Koongarra Creek. A steeper stream bed gradient exists for Koongarra Creek than exists for Namarrgon Creek. Stream capture of tributaries flowing off the Mt Brockman margin has probably occurred. This would result in the ground surface of Koongarra being lowered from approximately 40 m AHD to the present 20 + m AHD. The only mapped Kombolgie talus along the southern margin (GR63 766 Cahill 1:100 000) occurs midway along the length of Koongarra Creek coincident with a valley scarp edge supporting the proposition that an active erosional event has recently been in progress. The dominant directional pattern of the smaller tributaries in the Koongarra Valley have the same orientation with the structural lineaments exposed on the Kombolgie sandstone and Cahill rocks. But Koongarra Creek differs. Thus it can be suggested that the direction of stream drainage has been altered from a flow to the south east with connection to Namarrgon Creek, to a westerly flowing direction via the present Koongarra Creek.

It is proposed that prior to stream capture Namarrgon Creek was the dominant stream subsequent from Sawcut Fault, with tributaries draining the whole southern margin of the Mt Brockman Massif. This model could explain the observed direction of the oxidised ore zone at Koongarra as shallow groundwater flow directions are dictated by the direction of the surface drainage. This situation would have predated the progressive channel
erosion to form Koongarra Creek, as evidenced by the stream pattern and elevation changes. Rejuvenation by base level changes would precipitate headward erosion and eventual stream capture of those that drain the southern Brockman Massif.

**SUMMARY**

The common concept for the Koongarra site is that the Kombolgie Sandstone Formation has been eroded by scarp retreat during the later Tertiary period exposing the underlying mineralised Cahill Formation to sub-aerial and oxidising conditions.

However this is not compatible with the geomorphological features and processes of the valley area nor with the geological history of the evolution of the Arnhem Land Escarpment. The literature notes that Mesozoic aged sea cliffs essentially shaped the Escarpment and that only minor modification has occurred since the marine sea regression approximately 65 My ago.

In consequence it has been concluded from this assessment study that a different set of processes have been involved. These are:

1. Prior to and during the Mesozoic the Kombolgie Sandstone had been removed from above the orebody, the result of uplifting by faulting along the Koongarra Fault and erosion.

2. The underlying Cahill rocks were planated during the Cretaceous marine transgression and laterised during the Tertiary, under the tropical conditions which prevailed.

3. In response to significant climatic changes in the later Tertiary and Pleistocene, the laterised schists were eroded by thin scarp retreats of the ferricreted surficial veneer. Thus the water table was lowered down to the top of the primary ore body and the uranium was mobilised.

The concepts as proposed allow for a reasonable time correlation with radionuclide studies, which conclude that the ore mobilisation occurred within the last few million years.

Further investigation is required to refine the time period during which the Koongarra Creek evolved as the groundwater flow direction today varies from the orientation of the oxidised ore.

**ACKNOWLEDGEMENTS**

I wish to acknowledge the many useful discussions with, and editorial assistance given by Peter Jolly, Groundwater Evaluation Section, Hydrology Branch, NT Power & Water Authority.
REFERENCES


2 Cahill NT 1:100 000, National Topographic Map Series, Division of National Mapping, Canberra, Australia.


## TABLE 1

**SUMMARY OF GEOLOGICAL HISTORY 1982**

<table>
<thead>
<tr>
<th>Age</th>
<th>Deposition</th>
<th>Intrusion events</th>
<th>Metamorphism</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RECENT</strong></td>
<td>Aggradation of valleys and valleys</td>
<td></td>
<td>Coastal emergence ~ 7 m;</td>
<td>Dissolution of Koolpinyah Surface</td>
</tr>
<tr>
<td><strong>PLEISTOCENE</strong></td>
<td>Aggradation of major valleys, formation of sand plains, minor deep weathering</td>
<td></td>
<td>Dissolution of Koolpinyah Surface</td>
<td>Oesulation of shallow uranium ore zones probably triggered by flushing water table</td>
</tr>
<tr>
<td><strong>MIocene-</strong></td>
<td>Deep weathering and inter-weathering, followed by deposition of</td>
<td></td>
<td></td>
<td>Modelling of Mesozoic sea cliffs by subaerial erosion to produce</td>
</tr>
<tr>
<td><strong>Pliocene</strong></td>
<td>unconsolidated sand in coalescing fans and further deep weathering</td>
<td></td>
<td></td>
<td>Anhem Land escarpment</td>
</tr>
<tr>
<td></td>
<td>and inter-weathering to form Koolpinyah Surface</td>
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<td></td>
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<td></td>
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<tr>
<td><strong>CRETACEOUS</strong></td>
<td>Deposition of sandstone and siltstone in northwest</td>
<td></td>
<td></td>
<td>Paralic-epicontinental to continental sedimentation</td>
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<td></td>
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<tr>
<td><strong>ADELAIDIAN</strong></td>
<td>Interal of phaneritic dikes at 1320 m.y. and dolerite at 1370 m.y.</td>
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<tr>
<td><strong>CARPENTARIAN</strong></td>
<td>Interal of differentiated phaneritic dikes of Oenpelli Dolerite in south</td>
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<td></td>
<td>and east.</td>
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<tr>
<td><strong>EARLY PROTEROZOIC</strong></td>
<td>Interal of quartzites and minor sandstone at Mundorie</td>
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<tr>
<td><strong>PROTEROZOIC</strong></td>
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<tr>
<td><strong>EARLY PROTEROZOIC</strong></td>
<td>Interal of quartzites and minor siltstone at Zama Dolerite</td>
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<td><strong>EARLY PROTEROZOIC</strong></td>
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<tr>
<td><strong>ARCHAEOIAN</strong></td>
<td>Interal of quartzites and minor siltstone at Mundorie</td>
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<tr>
<td><strong>EARLY PROTEROZOIC</strong></td>
<td>Interal of quartzites and minor siltstone at Mundorie</td>
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</tr>
</tbody>
</table>

### Notes
- **UNCONFORMITY**: Extrapolated from known unconformable relationships to southwest.
- **POSSIBLE DISCONFORMITY**: Probable syngenetic concentration of uranium in black shales in intertidal to supralal environment east of Nanambu high.
- **POSSIBLE LOCAL UNCONFORMITY**: Inferred by converging photo-trends east of Koongarra.
- **UNCONFORMITY**: Probable correlatives of Wildman Sillstone west of region; may contain some metamorphosed Koolpinyah Formation and Fisher Creek Sillstone.
- **UNCONFORMITY**: Probable period of non-deposition.
- **UNCONFORMITY**: Probable mild faulting at close of deposition.
- **UNCONFORMITY**: Probable period of non-deposition.
Figure 2 Diagrammatic cross-section of Cainozoic deposits, along drill traverse, Kapalga 1:100 000 Sheet area
Figure 1 The Koongarra Valley.
SECTION 5.3
GEOCHEMICAL MODELLING OF THE KOONGARRA URANIUM DEPOSIT

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INTRODUCTION

The main purpose of this report is to summarize geochemical modelling studies of the Koongarra deposit carried out to August 31, 1989. Consistent with the goals of the research as originally defined, two major themes have been pursued.

The first has utilized previous and current studies of the mineralogy and petrology of the Koongarra deposit, together with available chemical analyses of present-day groundwaters from the deposit, in order to make a quantitative assessment of the speciation and state of saturation of the present-day groundwaters. The complex geologic history of the Koongarra deposit (Snelling, 1980, 1989; Foy and Pederson, 1975) makes it imperative to establish what role the present-day groundwaters play in the alteration and dispersion of the deposit. It is currently assumed that the chemistry of these groundwaters reflects interaction with the different zones of the ore deposit from which they are sampled and that the formation of the uranium phosphate zone and its associated dispersion fan are a consequence of present-day groundwater movement (e.g. Giblin and Snelling, 1983). These assumptions have not previously been tested by quantitative speciation, saturation state and chemical mass transfer calculations.

The second line of research has used theoretical mass transfer calculations (e.g. Helgeson, 1970) to investigate the kinds of waters that could produce the uranium phosphate zones at Koongarra. These calculations aim to use the geological and mineralogical data for the Koongarra weathered zone to constrain the initial compositions and reactions undergone by groundwater during the formation of the uranium phosphate zone. In contrast to the line of research described above, the mass transfer calculations only use the present-day analyses of Koongarra waters as a guide to the possible initial composition of the fluid associated with the formation of the phosphate zone. However, it is anticipated that this line of research will yield results for comparison with the interpretation and evaluation of the present-day groundwaters from the Koongarra deposit.

In the research summarized below, aqueous speciation, saturation state and chemical mass transfer calculations were carried out using the computer programs EQ3NR and EQ6 (Wolery, 1983; Wolery et al., 1984) and a thermodynamic database generated at The Johns Hopkins University.
AQUEOUS SPECIATION CALCULATIONS AND STATES OF SATURATION OF THE PRESENT-DAY GROUNDWATERS AT KOONGARRA

Samples were selected to represent as wide a range of groundwater compositions as possible over a line of section within the weathered zone parallel to the dispersion fan of the ore deposit. It is important to note that all groundwater analyses considered to date were of samples taken through the May, 1988 and November, 1988 field trips. More recent samples of waters from the new wells drilled late in 1988 (see Snelling, ARAP Report, November, 1988) will be interpreted and modeled using similar techniques when the analytical results become available. Samples from these new wells may yield different results to those obtained to date.

Input parameters for the aqueous speciation calculations include: measured total dissolved concentrations of cations and anions, temperature and pressure, oxidation state of the fluid, and measured pH values. The actual input data used and the detailed results are documented in the quarterly reports for 1988 and 1989.

All the present-day groundwaters sampled from Koongarra were found to be near saturation with respect to chalcedony and approaching saturation with respect to dolomite in the orezone. They are strongly undersaturated with respect to chlorite and illite, two abundant minerals in the flow path. However, there is a trend towards saturation along the line of section from KD1 to PH94. This suggests that the analyzed water compositions are reflecting modification by water-rock interactions along the inferred flow path.

In contrast, all the groundwaters are strongly undersaturated with respect to uranium-bearing minerals. Despite uncertainties in the thermodynamic data supporting calculations involving uranium-bearing species, the degree of undersaturation appears significant. In part this may be attributable to loss or dilution of uranium during sampling (e.g. due to adsorption or mixing with fresh surficial waters). However, even samples with high uranium contents (e.g. from hole PH49, which contains about 560 micrograms per litre uranium) are undersaturated with respect to the uranium phosphates saleeite and torbernite. If the waters sampled are representative of the actual groundwaters in the uranyl phosphate zone at Koongarra, such groundwaters should be actively dissolving the uranium phosphate zone.

Consequently, based on the calculations summarized above, it appears that the analysed groundwaters may not be responsible for the formation of the uranium phosphate zone, but rather with its alteration and removal into the dispersion fan. The form of the uranium in the dispersion fan is not well established and is currently being further investigated by Koppi and co-workers at the University of Sydney.
CHEMICAL MASS TRANSFER CALCULATIONS MODELLING THE FORMATION OF THE URANIUM PHOSPHATE ZONE AT KOONGARRA

In order to carry out a series of mass transfer calculations to constrain the geochemical processes operating during the formation of the uranium phosphate zone at Koongarra it is necessary to assume both an initial water composition and an initial rock mineralogy with which the water will react to produce the phosphate zone assemblages. Uncertainties in the latter are minimized by taking into account the known geologic history of the deposit as described in previous ARAP reports and Snelling (1980). The mass transfer calculations then serve to refine the initial fluid composition or range of compositions that could have reacted to produce the mineral assemblages of interest. These assumptions are detailed below.

The waters associated with the formation of the uranyl phosphate zone may be quite different from those found in the present-day wells at Koongarra. Consequently, in the present study, I have used the known mineralogy, mineral chemistry and textural observations to attempt to constrain both the kind of water that might have been involved in the formation of the uranyl phosphate zone and the nature of the geochemical processes operating during the formation of this zone at Koongarra. This is an iterative process. To start, it is first necessary to assume an initial water composition and an initial rock composition with which the water will be permitted to react.

Assumptions for the initial water composition

The following initial assumptions have been made for the series of calculations carried out to August, 1989:

(1) The analytical values of waters from the well KD1 were used as a guide for construction of a hypothetical water composition that may have existed at Koongarra at some time in the past. KD1 samples were selected for this purpose because they may represent the best sample available of the current groundwater before it encounters the orebodies at Koongarra (Duerden, 1988).

(2) The initial water is saturated with respect to hematite, kaolinite, and quartz.

(3) A simplified water chemistry is being considered initially. No Cu, Mn, or Pb are included. In the future, inclusion of Cu will permit consideration of torbernite precipitation in addition to saleeite.

(4) The temperature of the water-rock system is taken to be 31.0°C consistent with temperatures recorded for the May, 1988 and November, 1988 analyses.
(5) A range of initial pH values have been adopted based on the May 1988 measurements.

(6) The oxidation state of the initial water has been assumed to be uniformly consistent with dissolved oxygen in equilibrium with the atmosphere (log fugacity of -0.70).

These assumptions permitted definition of an initial fluid composition. It is important to stress that this is a trial fluid composition only. Most of the above assumptions can be relaxed or changed during the course of the series of mass transfer calculations.

**Assumptions for the initial rock mineralogy**

(1) The non-uranium bearing minerals in the initial rock were chlorite (Mg-clinochlore), quartz, muscovite, biotite (phlogopite), hematite, and accessory apatite (hydroxyapatite). These minerals were selected based on the information presented in Snelling (1980), and the availability of thermodynamic data. The assumed initial rock type should correspond to the Cahill Formation prior to exposure to weathering above the water table, but after formation of the uranium oxide/silicate zones. No pyrite or graphite have yet been included in the calculations, but they will be included as soon as the pyrite and graphite-free system is well understood.

(2) The uranium-bearing minerals considered for the initial rock mineralogy included uraninite, $\text{UO}_3^{3\frac{1}{8}}$, and uranophane. Of these, $\text{UO}_3^{3\frac{1}{8}}$ and uranophane were used in order to approximate partially oxidized uraninite and the uranium silicate alteration, respectively. This assumes that the formation of the uranyl phosphate zone proceeded primarily by weathering of uranyl and uranium silicate and oxide assemblages (Snelling, 1980, 1989). The latter are found in both the No. 1 and No. 2 orebodies at Koongarra.

(3) The relative reaction rates of apatite, uranophane and $\text{UO}_3^{3\frac{1}{8}}$ were set at 10.0 times the overall reaction progress variable $z_i$. The relative reaction rates of the other reactant minerals were set at 1.0 times $z_i$. No attempt has been made in these preliminary runs to include actual reaction kinetics for the reactant minerals. The relative rates described in the calculations reported here were chosen in order to maximize the amount of saleeite precipitated.

(4) The amounts of initial reactant minerals for the calculations reported below were 1.0 moles of quartz, muscovite, chlorite and hematite, $2.5 \times 10^{-4}$ moles of $\text{UO}_3^{3\frac{1}{8}}$ and of uranophane, and $6.0 \times 10^{-5}$ moles of apatite.
Results of mass transfer calculations

An example of the overall course of reaction progress can be seen in Figures 1 and 2. The upper part of Figure 1 depicts the number of moles of reactant minerals destroyed in the initial rock as a function of the reaction progress \( z_i \). The lower part of Figure 1 depicts the number of moles of minerals precipitated as a function of \( z_i \). The latter is repeated in a clearer fashion in Figure 2 by separating out the numerous product minerals from the lower part of Figure 1.

It can be seen that the amount of saleelite precipitated in Figures 1 and 2 maximizes between values of \( \log(z_i) \) from about \(-5.0\) to about \(-0.5\) and then is replaced by apatite at the end of the reaction path. The maximum amount of saleelite precipitated is about \( 10^{-4} \) moles/kg \( H_2O \) during the reaction path. As described above in the assumptions section, numerous input parameters to the calculations were chosen in order to maximize the amount of saleelite precipitated. For example, the small amounts and relatively fast reaction rates of the uranium-bearing and apatite reactant minerals appear to be required to put enough uranium and phosphorous into the reacting fluid so that saturation with respect to saleelite is reached before the fluid becomes saturated with respect to the initial uranium-bearing phases or apatite. The fluid saturated with respect to saleelite has a very high uranium content (255 mg/l). Such concentrations are difficult to achieve if the fluid becomes saturated with respect to uraninite, \( UO_2 \), or uranophane before reaching saturation with respect to saleelite. Similarly, if the pH of the fluid increases too rapidly because of reaction with the chlorite then apatite saturation is reached before saleelite can precipitate.

The appearance of saleelite as a product mineral during the course of the reaction progress is also strongly influenced by the chemistry of the initial water. As might be expected, the higher the initial concentrations of Mg, U, and P, the sooner saleelite will precipitate during the reaction path calculation. The initial U value (0.88 mg/l) is high compared to the water sample from KD1, but is small compared to the value at which saleelite becomes saturated (255 mg/l). The bulk of the dissolved U is added to the fluid during reaction progress by destruction of the initial uranium-bearing phases. In contrast, the Mg content of the fluid decreases throughout the reaction path overall, associated with the conversion of chlorite to montmorillonite and saleelite. Higher initial Mg values (e.g. 50 mg/l) result in saleelite precipitation all the way thorough to the end of the reaction path (work in progress). Consequently, the initial Mg content of the fluid in the calculations reported in Figures 1 and 2 (10.0 mg/l) may represent a minimum value for the formation of saleelite (with the given initial pH).
PRELIMINARY CONCLUSIONS

(1) Quantitative aqueous speciation calculations for the Koongarra groundwaters suggest that the uranium in the aqueous phase is predominantly complexed by phosphate or carbonate depending on the relative abundances of these ligands, which vary systematically with sample location (laterally) in the weathered zone at Koongarra.

(2) Waters considered to date from Koongarra are undersaturated with respect to chlorite, illite, carbonate minerals, and the uranium minerals uraninite, uranophane, saleeite, torbernite, and carnotite. If these analyses are truly representative of the pore fluids in the uranyl phosphate orezone then the present-day groundwaters may be actively dissolving and altering the uranyl phosphate zone and dispersing uranium and other elements of interest along the present flow paths. Interpretation of analyses from the new wells drilled in late 1988 should help to resolve this issue.

(3) Chemical mass transfer calculations suggest that the waters associated with the formation of the uranyl phosphate zone at Koongarra were probably quite different to those sampled to date at the present day. However, a considerable number of simulations need to be carried out in order to more closely constrain the conditions under which the phosphate zone formed. This work is currently in progress and the results will be reported in subsequent reports.

REFERENCES


LOG (MOLES OF MINERALS)

LOG (MOLES MINERALS DESTROYED)
MODELLING OF URANIUM SORPTION TO SUBSTRATES FROM THE WEATHERED ZONE IN THE VICINITY OF THE KOONGARRA ORE BODY

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INTRODUCTION

The goal of this sub-project is the modelling of the sorption of uranium to substrates from the weathered zone in the vicinity of the Koongarra ore body under conditions typical of this region. This goal is being achieved through application of the "surface-complexation" modelling approach to laboratory-derived sorption data. Investigations of uranium sorption to natural substrates under both batch and column arrangements are either underway or are planned.

A major difficulty in application of the surface complexation modelling approach to interpretation of the partitioning of uranium between solid and solution phases is the identification of major sorbing phases and their characterisation in terms of required model parameters (surface site density, acid-base and complexation characteristics). This will be achieved here through a variety of approaches:

i) assumption that amorphous iron oxides are the major sorbing phase and comparison of the results of modelling under this assumption with laboratory derived sorption results;

ii) comparison of uranium sorption characteristics to complex (natural) substrates before and after removal of Tamm's acid oxalate extractable materials (particularly amorphous iron oxides);

iii) comparison of the uranium sorption characteristics to selected (well characterised) weathered zone substrates with sorption characteristics to single substrates (particularly ferrihydrite).

Studies have commenced with a thorough analysis of the chemistry of groundwaters from the weathered zone down-field of the Koongarra ore body. Of particular interest is the possible impact of groundwater composition (such as the presence of carbonate, phosphate or silica) on uranium speciation and thus adsorbability to the solid matrix. We have followed this with surface complexation modelling of previously obtained data on the pH dependency of uranium (VI) sorption to both Ranger and Koongarra solids.
In addition, fresh core material from the Koongarra weathered zone has been selected for further investigation and physico-chemical characterisation has commenced. These aspects are described in more detail below.

**SOLUTION PHASE SPECIATION AND IMPLICATIONS TO SORPTION**

In general, the results of MINTEQA2 (Version 2.01; an updated version of MINTEQA1, Brown and Allison, 1987) solution phase modelling of analytical data for Koongarra waters are in agreement with those obtained by Sverjensky (Duerden, 1988) using the code EQ3/6. An assumption of no precipitation of any mineral species results in predicted oversaturation of many crystalline species though the solution phase is close to equilibrium with respect to the amorphous oxides ferrihydrite, SiO$_2$(am) and Al(OH)$_3$(am). Under these conditions, essentially all the iron in the system is present as Fe$^{2+}$(aq). It is also noteworthy that the CO$_2$ partial pressure is significantly above atmospheric ($10^{-3.5}$ atm). Again, as reported by Sverjensky (Duerden, 1988), all uranium minerals considered in these computations, including the secondary minerals saleeite, autunite, torbernite and bassetite, are significantly undersaturated.

In the absence of significant concentrations of phosphate, the solution chemistry of U(VI) is controlled by carbonate complexation. For a solution in equilibrium with the atmosphere (P$_{CO_2} = 10^{-3.5}$ atm) and a total uranium concentration of $10^{-6}$M (approx. 250ppb), the carbonate containing species $UO_2CO_3^-$, $(UO_2)^{2-}(OH)^-$, $UO_2(CO_3)^{2-}$ and $UO_2(CO_3)^{4-}$ are of varying significance for pH values greater than 5.5 (Figure 1a). Tripathi (1983) found that the pH and concentration dependency characteristics of uranium adsorption to goethite at $P_{CO_2} = 10^{-3.5}$ atm could be accounted for satisfactorily by assuming that the hydroxy carbonate species adsorbed while the others did not. At higher carbonate concentrations, where the hydroxy carbonate species is no longer important (Figure 1b), it appears necessary to consider binding of other uranyl carbonate species in order to properly account for uranium partitioning between solid and solution phases (Hsi and Langmuir, 1985).

Phosphate is a strong complexing agent for uranyl ion and, if present in sufficient quantity, would appear to outcompete carbonate for U(VI). Indeed, the results of MINTEQ calculations for waters from a number of bores are shown in Table 1 and indicate that the proportion of uranyl ion complexed by phosphate increases from less than 5% at KD1 (upgradient of the ore body) to 98.9% at PH55 which is in the dispersion fan immediately down gradient of the primary ore zone. It should be noted however that considerable confusion still surrounds the role of phosphate in controlling solution speciation and influencing sorption behaviour. Literature values for the formation of the $UO_2(HPO_4)^{2-}$ species have been used in these calculations however the results of Tripathi (1983) and Markovic and Pavkovic (1983) cast doubt on the existence of this species. Interestingly, Tripathi (1983) has shown that there is very little difference between the extent of uranium adsorption in ligand-free systems and phosphate-bearing systems, and that almost complete removal of uranium is possible by
"adsorption" when $\text{UO}_2(\text{HPO}_4)_{2-}^2$ is calculated to be the dominant uranyl species in solution. This issue is of considerable relevance to the Koongarra system and will be pursued further in laboratory investigations and field measurements.

SURFACE COMPLEXATION MODELLING

While the interaction of uranyl species with a variety of solid substrates has been frequently studied, only a few authors have attempted to present a coherent mathematical description of sorption results obtained over a range of solution conditions. The most commonly used method for describing the interaction of solution phase species with solid substrates is the "surface complexation" approach and has been used by both Tripathi (1983) and Hsi and Langmuir (1985) in modelling the adsorption of uranyl species to iron oxides. In the surface complexation approach, surface charge is considered to develop on oxides via chemical reactions at specific surface sites. Adsorption of ions on oxide surfaces is viewed as analogous to the formation of soluble complexes; i.e. ions (including $\text{H}^+$ and $\text{OH}^-$) bind to functional (reactive) groups at the surface, and these reactions can be described by mass law equations. With knowledge of the number of functional groups and ion-binding constants, surface charge and ion adsorption can be computed for different conditions in solution.

As indicated earlier, Hsi and Langmuir (1985) found that the presence of carbonate resulted in significantly more uranium adsorption to iron oxides than could be accounted for by formation of uranyl hydroxy surface complexes alone and successfully modelled the experimental results by assuming the formation of uranyl di- and tricarbonate surface complexes; i.e.

$$\text{FeOH} + \text{UO}_2^{2+} + 2\text{CO}_3^{2-} + \text{H}^+ \rightarrow [\text{FeOH}^+\text{UO}_2(\text{CO}_3)_2^{2-}] \quad (1)$$

$$\text{FeOH} + \text{UO}_2^{2+} + 3\text{CO}_3^{2-} + \text{H}^+ \rightarrow [\text{FeOH}^+\text{UO}_2(\text{CO}_3)_3^{4-}] \quad (2).$$

Under the conditions used by Hsi and Langmuir (1985), $(\text{UO}_2)_{2-}^2\text{CO}_3(\text{OH})_3$ was not a significant species.

Preliminary results of studies of the adsorption of uranium (VI) to was selected solid substrates from the Alligator Rivers Region have been modelled using a surface complexation model with triple layer description of the electrical double layer (Payne and Waite, 1989). The major purpose of this modelling exercise was to ascertain our ability to model the sorption of uranium (VI) to a complex substrate for which one phase (the amorphous ferric oxyhydroxide component) has been proposed to dominate the interaction with groundwater solutes (Lowson et al., 1986).

Particular attention in this preliminary modelling exercise has been given to the experimental results for uranium adsorption to the Ranger S1/146 sample. This sample contains 1.92 mg/g of Tamm's acid oxalate extractable iron. While this reagent will attack a variety of crystalline minerals
including iron-rich chlorite and biotite, magnetite, maghemite and some secondary manganese minerals, the proportion of these in sample S1/146 is low and the bulk of the iron extracted can be considered to be amorphous. This corresponds to a surface site concentration of $8.82 \times 10^{-5}$ M for suspensions used in these studies assuming a surface site density of 20 sites/nm$^2$ and a surface area of 700 m$^2$/g. Approximately 24% of the total uranium content of the sample is associated with the Tamm's acid oxalate fraction and it is this component that has been assumed to be in dynamic equilibrium with the solution phase (Payne and Waite, 1989). For the purpose of modelling the sorption results, this corresponds to $1.68 \times 10^{-7}$ U(VI) or 0.045 mg UO$_2$/L.

Application of a similar approach in modelling uranium adsorption to the amorphous iron oxide component of our samples to that used by Hsi and Langmuir (1985) in which only uranyl di-and tri-carbanato species were considered to interact significantly with the iron oxide surface resulted in large deviations between computational and experimental results. Inspection of the solution phase uranyl speciation diagram in Figure 1b indicates that major problems in modelling using only reactions (1) and (2) arises because of the dominance of the UO$\text{CO}_3^-$ species in the pH 4.8-6.4 region and the assumed lack of interaction of this species with the surface. As indicated in Figure 2a, inclusion of a uranyl monocarbonate complex in the suite of possible surface species provides a very reasonable fit to the adsorption data for the Ranger S1/146 sample.

While preliminary adsorption data for a Koongarra sample (sample DDH 52) is somewhat scattered, use of identical constants to those found to fit the Ranger data provides a reasonable description of this data also (see Figure 2b). Such a fit is satisfying given that the Koongarra sample contains significantly more Tamm's acid oxalate extractable $^{238}$U (215 ppb) than the Ranger sample and contains a smaller proportion of amorphous iron oxide (1mg Fe$_2$O$_3$·H$_2$O per gram of solid). Interestingly, consistent deviation between the model results and experimental data is still observed in both the Ranger and Koongarra studies in the region of predominance of UO$\text{CO}_3^-$ indicating that our description of the interaction of uranium (VI) with the solid substrate in this pH region requires further attention. More comprehensive studies of U(VI) adsorption to both simple and complex substrates are underway in an attempt to further clarify the role of carbonate in uranium sorption processes.

**SELECTION OF SUBSTRATES FOR FURTHER INVESTIGATION**

Three W-series cores and one M-series core have been selected for more detailed and rigorous sorption experimentation. Core from the recently drilled W-series has been taken from a depth of 13-14 m as this lies within the weathered zone but is below the water table and the sandy surface layers. In addition, in the W-series boreholes, a water sampling interval has been installed over the depth 13-15 m. This enables water from the contacting aquifer to be analyzed and more closely simulated in laboratory
experiments. Comparison of solid and aqueous phase radionuclide concentrations will provide information on the in-situ distribution of radionuclides between solid and aqueous phases. The three W-series boreholes selected, W1, W2 and W7, provides a set of samples lying approximately linearly in the proposed direction of groundwater flow. The M2 (13 m) sample is from the high grade area of the secondary dispersion fan, immediately down-gradient of the primary ore zone. It has been included to ensure adequate coverage of the dispersion fan (in terms of soil type and intrinsic uranium content) but it is not co-linear with the three W-series cores selected and water sampling from the 13 m depth is not possible. The order of increasing distance from the fault is W1, M2, W2 and W7.

REFERENCES


Table 1. Uranium (VI) speciation computed using MINTEQA2 for groundwater samples from selected bores in the Koongarra region with and without the uranyl phosphate species UO₂(HPO₄)₂²⁻ excluded from consideration. Thermodynamic data for uranium species from Tripathi (1983).

<table>
<thead>
<tr>
<th>Bore No.</th>
<th>Depth (metres)</th>
<th>Total Mg (mg/L)</th>
<th>Total U (µg/L UO₂)</th>
<th>Total P (µg/L PO₄)</th>
<th>Alkalinity (mg/L CO₃²⁻)</th>
<th>pH</th>
<th>% U(VI) Species (&gt;1%)</th>
<th>% U(VI) Species (&gt;1%) (UO₂(HPO₄)₂²⁻ excluded)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH49</td>
<td>28-30</td>
<td>26.4</td>
<td>240</td>
<td>310</td>
<td>46.8</td>
<td>6.80</td>
<td>86.8</td>
<td>2.0</td>
</tr>
<tr>
<td>PH55</td>
<td>26-28</td>
<td>17.9</td>
<td>0.47</td>
<td>650</td>
<td>62.2</td>
<td>6.57</td>
<td>98.9</td>
<td>2.7</td>
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<tr>
<td>PH61</td>
<td>43.3-43.5</td>
<td>18.0</td>
<td>4.6</td>
<td>130</td>
<td>74.0</td>
<td>7.03</td>
<td>54.0</td>
<td></td>
</tr>
<tr>
<td>PH94</td>
<td>26-28</td>
<td>5.7</td>
<td>0.20</td>
<td>290</td>
<td>18.6</td>
<td>7.17</td>
<td>98.8</td>
<td>2.7</td>
</tr>
<tr>
<td>PH14</td>
<td>70.3-72.5</td>
<td>8.9</td>
<td>0.55</td>
<td>160</td>
<td>62.7</td>
<td>6.42</td>
<td>78.6</td>
<td>5.2</td>
</tr>
<tr>
<td>PH88</td>
<td>28-30</td>
<td>14.1</td>
<td>2.5</td>
<td>110</td>
<td>43.1</td>
<td>6.54</td>
<td>83.7</td>
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<tr>
<td>K11†</td>
<td>70.3-72.5</td>
<td>8.9</td>
<td>0.55</td>
<td>10</td>
<td>32.8</td>
<td>6.18</td>
<td>6.3</td>
<td>49.1</td>
</tr>
</tbody>
</table>

* Phosphate at detection limit (10 µg/L PO₄)
† Phosphate at half detection limit
Figure 1. Mole percent distribution of major (>1%) uranyl species as a function of pH for a total uranyl concentration of $10^{-6}$M (approx. 250 ppb) and (a) at equilibrium with the atmosphere (i.e. partial pressure of $P_{CO_2} = 10^{-3.5}$ atm, and (b) at fixed total carbonate content of $2 \times 10^{-3}$ M.
Figure 2. Preliminary data for adsorption of uranium to (a) Ranger sample S1/146 and (b) Koongarra sample DDH 52 as a function of pH. The best fit results of surface complexation modelling assuming formation of surface complexes $\text{FeO}^{-}\text{UO}^{2+}$, $\text{FeOH}^{-}\text{UO} \cdot \text{CO}^{2-}$, $\text{FeOH}^{-}\text{UO} \cdot (\text{CO})_{2}^{2-}$, and $\text{FeOH}^{-}\text{UO} \cdot (\text{CO})_{4}^{4-}$ with intrinsic formation constants $\log^{2}K$ of 8.2, 23.3, 31.2, and 34.7 respectively are also shown.
BACKGROUND

It is important to build confidence in the models used in support of the long-term safety assessments of geological repositories for radioactive waste by validating them. There are three complementary types of investigation that can be used: laboratory experiments, field experiments and natural analogues.

In laboratory experiments, the initial and boundary conditions and the geometry are probably well defined. In addition they can be designed so that a small number of processes are involved. However, there are severe restrictions on the size of experiments ($\leq 1$ m) and their duration ($\leq 1$ yr).

With field experiments, substantially longer transport distances can be examined (up to 100 m), but again there are similar time constraints to those in laboratory experiments. Boundary conditions may not be as well defined as with laboratory experiments, and there may be uncertainty with the geometry.

The great advantage of natural geochemical systems over the other validation tools is that they give access to the long timescales required for repository safety assessments. There are a number of counterbalancing disadvantages in that the initial and boundary conditions are often poorly characterised and there may be a number of changes in conditions in the intervening time that are also difficult to characterise. In addition, a number of processes may be coupled together, making the analysis more complicated.

So all three types of study have advantages and disadvantages, and none is the perfect validation tool. However, if they are used together, they can build confidence in the models being used.

The main features that set Koongarra apart are that transport of radionuclides has been taking place in the weathered zone. The purpose of the studies in this sub-project is to build confidence in the type of model used in safety assessments to describe radionuclide transport through the
geosphere. This is being achieved by using the same type of model to analyse the data from Koongarra. The aim is to build a consistent picture of the transport that has been taking place. It is perhaps worth noting that not only are the same type of models being used, but that the experimental techniques being used to collect data are similar as well.

The following data are available from the Koongarra study. First there are many estimates of the activity of uranium and significant daughters on rock samples throughout the ore body. The application of different extraction techniques has yielded estimates of the same quantities for the different phases of the rock, such as the amorphous iron hydroxides and crystalline phases. There are also estimates of the activities of uranium and daughters in the rock porewater. To date these have been comparatively crude as the porewater samples have not been packered. Laboratory experiments have been carried out to get estimates of the distribution coefficients of the different elements of interest, to give insight into the interaction of radionuclides on the rock and in the porewater. Finally there are laboratory and field measurements of hydrogeological parameters used in groundwater flow models. These can be used in the models to give insight into the way groundwater is and has been moving at the site.

The aim of this report is first to review the early work on transport modelling that was undertaken before the current international project was started. Then the work that was carried out during the first part of the international project is summarised.

THE ORIGINAL TRANSPORT MODEL

The first model that combined the effects of transport by flow and radionuclide interaction between the solid and liquid phases was developed by Lever. This was a very simple one-phase model, which assumed a one-dimensional groundwater flow with constant velocity and linear equilibrium sorption. Other processes, such as the kinetics of leaching and deposition, non-linear sorption, hydrodynamic dispersion and variation of properties along the path were not included. The effects of α-recoil were modelled approximately by allowing different members of the same chain to have different retardation factors, even for different isotopes of the same element ($^{238}\text{U}$ and $^{234}\text{U}$). This can be thought of as accounting for the greater availability of some radionuclides as the decay products recoil into different phases of the rock. Thus the concentration $c_i$ in the groundwater of the $i$th member of the chain satisfies the equation

$$\frac{R_i}{\lambda_i} \frac{\partial c_i}{\partial t} + u \frac{\partial c_i}{\partial x} + R_i \lambda_i c_i = R_{i-1} \lambda_{i-1} c_{i-1}$$

where $\lambda_i$ and $R_i$ are the decay constant and retardation factor for the $i$th member of the chain, and the subscript $i-1$ refers to the parent of the $i$th member.
When certain assumptions are made, this model allows simple analytical solutions. These assumptions are:

(i) the different members of the $^{238}\text{U}$ chain are locally in what would be termed secular equilibrium if flow were absent,

(ii) the concentration of U in the porewater only varies slowly with distance.

In the original analysis, these solutions were used to interpret the available data to give two estimates of the time that transport of uranium had been taking place in the weathered zone:

(i) based on the migration distance, an estimate of the groundwater velocity (from preliminary groundwater flow simulations) and the elemental distribution coefficient (from laboratory sorption experiments and from crude field estimates),

(ii) based on the disequilibria between $^{238}\text{U}$, $^{234}\text{U}$ and $^{230}\text{Th}$ on whole rock samples. This estimate of the migration time is given by

$$ t = \frac{R_i/R_{i-1} - 1}{l-a_i/a_{i-1}} \frac{L}{\int_a^1 \frac{da}{a}} \frac{dx}{dx} $$

where $L$ is the migration distance and $a_i$ is the activity on the whole rock sample of the $i$th member. This is given by $a_i = \phi R_i \lambda c_i$, where $\phi$ is the rock porosity.

The original analysis suggested that a consistent picture was being developed if the uranium had been migrating for around $10^8 - 3 \times 10^6$ years. At the time it was recognised that these estimates were very preliminary, nevertheless they pointed to this approach being valuable for the understanding of transport in the weathered zone.

The data used in this analysis are shown in Figure 1, where the activity ratios between $^{238}\text{U}$ to $^{234}\text{U}$ and $^{230}\text{Th}$ to $^{238}\text{U}$ on whole rock samples are shown. A systematic trend is seen and the fit to the model is encouraging.

One of the obvious shortcomings of the above analysis is that the rock was treated as a single phase. The experimental evidence clearly shows that the activity ratios are different for different phases of the rock, suggesting that they do not immediately come into equilibrium. The consequences of these differences were examined by using the data for the amorphous iron phase in the model (the other phases being treated as a quasi-closed system). A procedure was developed to correct the results for the transport from the amorphous iron phase to the crystalline phase, and using this a timescale of around $1 \times 10^6$ years was obtained.
The differences between the various estimates of the timescale was interpreted as arising from the shortcomings of the one-phase model. In the earlier applications the inaccessible uranium was disregarded and in the last application its presence was only treated approximately.

**DEVELOPMENTS IN THE TRANSPORT MODEL**

So the next development in the model\(^3\) took the differences between the phases into account explicitly by having two solid phases: one in equilibrium with the porewater and the other only coming into equilibrium after some time. This model has two extra parameters: the sorption capacity of the second phase \(K'\) and the relaxation time \(\xi_1\). Thus equation (1) is replaced by two equations

\[
\begin{align*}
R \frac{\partial c_i}{\partial t} + u \frac{\partial c_i}{\partial x} + R \lambda_i c_i &= -\xi_1 \phi^{-1}(K'c_i - s_i) + R \lambda_{i-1} c_{i-1}, \\
\frac{\partial s_i}{\partial t} + \lambda_i s_i &= \xi_1(K'c_i - s_i) + \lambda_{i-1} s_{i-1},
\end{align*}
\]

where \(s_i\) is the quantity sorbed per unit volume on the second phase of the rock.

These equations no longer allow the simple solutions that could be obtained from (1), and so a different solution technique has to be used. A partly analytical and partly numerical technique has been adopted that has been successful elsewhere\(^4\). In this the Laplace transform of the equations is taken to give ordinary differential equations that can be solved analytically. Then the transform of the solution is inverted numerically using an algorithm due to Talbot\(^5\).

Hydrodynamic dispersion is not included in the present analysis, but it can be incorporated in a straightforward manner using the same solution technique. However, non-linear sorption cannot be included within this framework, as it is limited to linear systems.

The initial testing of this second model was done on the same region of the weathered part of the ore body as was used with the first model above. The results of the application of this model are shown in Figure 2, where there is a similar type of plot of activity ratios to that in Figure 1. The two rock phases considered are the amorphous iron hydroxide phase, which is believed to be in equilibrium with the rock porewater, and the remaining crystalline phase. The data come from the depositional region of the ore body.
The Figure shows that the data for the amorphous samples follow a systematic trend in the bottom half quadrant reserved for samples with ratios less than unity, and the crystalline samples follow a trend in the upper half quadrant, reserved for samples with ratios greater than unity. The lines represent the model calculation. These are capable of fitting the amorphous phase data trends quite well. No equivalent fit could be found for the crystalline phase data since the two calculated curves tend to be in the same region on the plot. Thus the results suggest that this model is not adequate to fit the trends seen in the experimental data.

In an attempt to remove this discrepancy, the model has been extended to include the effects of recoil rearrangements of the daughter radionuclides between the amorphous and crystalline phases. This is achieved by adding extra flux terms between the two equations above\(^1\). So they become

\[
\begin{align*}
R \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} + R \lambda c_i &= \xi_1 \phi^{-1} (K_i c_i - s_i) + (1 - B_1) \lambda c_i - 1, \\
&+ \phi^{-1} B_i \lambda s_i - 1, \\
\frac{\partial s_i}{\partial t} + \lambda s_i &= \xi_2 (K_i c_i - s_i) + (1 - B_2) \lambda s_i - 2 \\
&+ \phi B_i \lambda c_i - 1, \\
\end{align*}
\]

where \(B_1\) and \(B_2\) are the recoil factors between amorphous and crystalline phases and vice versa. As the equations are very similar, the same solution technique to that described above can be used to solve them.

Example results are shown in Figure 3. The same input parameters are used with the exception of recoil factors of 0.2. The curves now represent a considerably better fit to the data points. The direction of flow of the streamline is thought to be 2c, 3d, 4c to 58. Thus the direction BE agrees reasonably with the relative positions of the data points for the amorphous phases are tightly bunched but again position 58 seems to be anomalous.

Some of the most recent data are shown in Figure 4. An examination of the order in which the samples are believed to lie suggests that if the data have a structure, it is complicated. So no direct comparison with the model has been attempted.

In summary, the modified model gives a better fit to the data than the earlier ones. Further evaluation is, however, required to examine it more thoroughly and to see where systematic trends in the data occur. In this examination, developments in hydrogeological modelling and more precise sampling of porewater play key roles.
REFERENCES


Figure 1  Plot of activity ratios on whole rock samples, and fit to the original model [1].
Figure 2  Plot of activity ratios for amorphous (+) and crystalline oxide (*) phases. The curves represent model calculations for the amorphous (——) and crystalline oxide (— — —) phases with no recoil between the phases. B and E denote the beginning and end of the leaching/deposition process.
Figure 3  Plot of activity ratios for amorphous (+) and crystalline oxide (*) phases. The curves represent model calculations for the amorphous (—) and crystalline oxide (— — —) phases with recoil terms $B_1 = B_2 = 0.2$. B and E denote the beginning and end of the leaching/deposition process.
Figure 4  New data for the amorphous (+) and crystalline oxide (Δ) phases from depths between 11 and 20 m. The order of the boreholes is 2, 3, 4, 55, 58, 60, 89.
COMMENTS ON THE METHODS USED TO INTERPRET THE RADIONUCLIDE MOBILITY IN THE KOONGARRA URANIUM ORE DEPOSIT

Cezary Golian

The geology of an analogue system, such as the Koongarra uranium deposit, poses many challenges owing to its complex geochemistry and hydrology and their evolution in time. The migration modelling studies have therefore to be supported by a comprehensive range of hydrology, geochemistry, geomorphology, experimental and interpretative tasks.

Several different approaches have been developed for migration modelling. So-called "open system" methods are characterised by the simplicity of their assumptions and experimental data base requirements, but usually produce a qualitative or semi-quantitative result. The hydrodynamic transport modelling techniques are more data base and computer demanding, and require a more formal description of the rock-water interaction processes.

The general aim of the different methods is to achieve a non-contradictory understanding of the system complexity.

OPEN SYSTEM METHODS

Open system methods are based on the concept that the final composition of the mobile components and their radiogenic products in the rock sample, is the result of continuous processes of leaching and/or deposition and radioactive decay.

In the basic model developed at Lucas Heights\(^{[1]}\) it was assumed that leaching and deposition were first order processes proportional to the concentration of accessible uranium in investigated strata. Although this was satisfactory for the leaching process, it restricted the physical interpretation of deposition processes. For specific applications, the general model required suitable extensions and modifications. In particular an adaptation of its applicability to a complete system, rather than as is typical for open system models, to individual samples. Later a more realistic representation of the leaching/deposition processes was introduced, so that the leaching/deposition rate was related to the actual uranium concentration in the rock and in the water, and the respective adsorption coefficient \((K_d)\).

Examples of the applications of the model are: methods for dating of saleeite crystals, and a combined open system/transport model to describe the development of uranium series activity ratios (ARs) in the dispersion zone.
Dating Secondary Uranium Minerals

Saleeite occurs extensively throughout the 30 m deep weathered zone of the deposit and originates both from in situ alteration of the primary pitchblende and from deposition of mobilised uranium. The $^{234}$U/$^{238}$U, $^{230}$Th/$^{238}$U and $^{227}$Ac/$^{235}$U ARs were measured in crystals from several locations, with the ARs showing large deviations from secular equilibrium.

Various possible sequences of the crystal growth were considered, but the concept that a crystal is formed in a short single event, then behaves as a system closed to groundwater activity, was examined in detail.

It was found that the experimental data sets for samples from some particular locations, such as DDH64 samples (Figure 1), can show a distinctive trend which may be extrapolated in the direction of a secular equilibrium point. A modified version of the Lucas Heights open system model was adopted to test this observation. The fit to the data seen in figure 1 was obtained for the initial activity ratio $^{234}$U/$^{238}$U(0) = 0.76, and indicates a common origin for the crystal forming solute.

The subsequent calculation of the crystal ages showed however significant inconsistencies when compared with $^{231}$Pa/$^{235}$U data (Figure 2). It was however noted that these ARs were obtained via a measurement of $^{227}$Th, and not through a direct determination of the $^{231}$Pa. Closer examination of the differences in the pathways of these two uranium series radionuclides leads to the conclusion that $^{227}$Th, the immediate parent of $^{227}$Ac ($T_1 = 22$ y) can be ejected from the crystal and hence may not be as readily readsoerd as thoria, or remain for a considerable time in a relatively unstable, prone to leaching, environment created by the recoil process. In such a case, the $^{227}$Ac/$^{235}$U activity ratios will be reduced.

The model was modified to include the assumption that $^{227}$Ac can escape from the crystal, and the effect of nucleus recoil and the substantial actinium chemical activity was estimated. A further modification to take account of radiation damage effects in aged crystal samples was also considered.

The saleeite mineral contains an impressive concentration of uranium (~50%) and the very high radiation density may, with time, produce substantial changes in the crystal structure. The initial leach rate of uranium from a radiation damaged crystal will most probably increase very slowly in time until major cracks and surface deterioration develop. The subsequent, sharp increase in the rate, levels off by a self-repair mechanism, and is a function of the surface to volume ratio. The total initial loss is probably negligible in comparison to the uranium loss in the latter stage. In this modification, the leach rate is described by a step function, where before time $t_{c/o}$ the system was totally closed to uranium mobility.

The "escape" corrected quasi-closed system modelling approach results in the determination of general ranges of crystal ages in various locations along the second dispersion deposit. The spatial relationship between those
regions can be used to calculate the rate of uranium mobility, if it is assumed that the arrival of uranium coincides with the onset of saleeite mineralization.

Using this simplistic approach, a total timescale for the formation of the dispersion zone was determined to be of the order of $1.2 \times 10^6$ years.

One-Dimensional Open System/Transport Model

In this model, open system ideas were combined with assumptions typically found in hydrodynamic transport modelling. Radionuclide movement in porous rock was modelled as a groundwater induced transport along a quasi 1D pipe consisting of a series of 1D elementary rock volumes (Figure 3).

It is assumed that, during a time period $\Delta t$, an elementary volume $V_i$ is filled in a negligibly short time with water which originated from volume $V_{i-1}$. The amount of radionuclide brought in, is instantaneously deposited into the rock and then the radionuclide is released back to water (by leaching) until a new sorption equilibrium is established. Equilibrium is determined by the local $K_d$ factor. Thus, the rock/groundwater interactions are encompassed by two general processes - leaching and deposition. However, the precise nature of these processes was not considered.

The concentration ($C$) of the $k$th-member of the uranium decay series in an elementary rock volume $(j)$ was then described by

$$\frac{dC_k}{dt} = \lambda_k C_k - \lambda_{k-1} C_{k-1} + \frac{\phi}{K_d} r_k g_L C_k - r_k g_d C_w$$

and in the corresponding groundwater by

$$C_k^w(j,t) = C_k^w(j,t_0) \exp(-\lambda_k t),$$

$$C_k^w(j,t) = \frac{\phi}{K_d} C_k(j-1,t),$$

where $r_k = \lambda_k C_k / \lambda C_1$, in the leachate/groundwater, $w$ denotes groundwater and $g_L, g_d$ - leaching and deposition rates.

The equations are obviously valid in a general time-space scale. But in the model, an attempt is made to combine elements of the open system approach and hydrodynamic transport formalism. As a result, the open system like equations are applied in a discreet way for each $\Delta t$ period and computational techniques allow the transfer of the locally calculated values to the next point on the time and distance scales. In practice, the hydrodynamic transport elements of advection and longitudinal dispersion are included only during the computation stages, and are not present in the mathematical formalism.
In an advection only mode (Figure 4a), the radionuclide transfer can occur only in the direction of water flow. However, in an advection and dispersion mode (Figure 4b) radionuclide mobility in the direction of any concentration gradient is also permitted. The initial results of this model seemed to indicate the usefulness of this uncomplicated conceptual and mathematical approach. In particular, the distribution curves obtained when dispersion was included did not exhibit the "travelling" concentration pulse, and more realistically modelled the Koongarra uranium dispersion fan. In the next stage of developing this model, inclusion of the multiphase concepts is planned.

CONCLUSIONS

Open system methods, together with transport modelling, when applied to the secondary uranium mineralisation in the weathered zone at the Koongarra ore deposit have yielded a range of values for the timescale of the formation of the dispersion fan (0.7-3.0 x 10^5 y). Subsequent continuation of these investigations have to concentrate on a more precise definition of the already identified interaction processes and a systematic evaluation of their effect on the formation of the dispersion fan.

REFERENCES


FIGURE 1  DDH 64 samples. Development of activity ratios (ARs). Fitting curve ($^{234}\text{U}/^{238}\text{U}(0) = 0.76$ - closed system).

FIGURE 2  Development of $^{230}\text{Th}/^{227}\text{Th}$ activity ratios (ARs) with time for different initial urania ratios ($^{234}\text{U}/^{238}\text{U}(0) = 0.75, 1.00, 1.25$).

Insert $^{234}\text{U}/^{238}\text{U}(0) = 0.76$ - positions of sample DDH 64a, b.
ID ELEMENTARY VOLUMES $v_i$

<table>
<thead>
<tr>
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<th>$v_{i-1}$</th>
<th>$v_i$</th>
<th>$v_{i+1}$</th>
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</table>

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I. TRANSPORT PROCESSES

1. Advection

$$a_i \rightarrow \quad u$$

2. Advection (a) and longitudinal dispersion (d)

$$a_i \rightarrow \quad u$$

$$du_i > 0 \quad \text{for} \quad C_i > C_{i-1} \quad \text{and} \quad du_i = 0 \quad \text{for} \quad C_i \leq C_{i-1}$$

$$dd_i > 0 \quad \text{for} \quad C_i > C_{i+1} \quad \text{and} \quad dd_i = 0 \quad \text{for} \quad C_i \leq C_{i+1}$$

where $C_i$ - radionuclide concentration in $v_i$

II. OPEN SYSTEM PROCESSES

Removal (leaching), deposition (adsorption)

![Conceptual schemes of the transport and open system processes.](image)

FIGURE 3 Conceptual schemes of the transport and open system processes.
FIGURE 4 Radionuclide distribution along 1D groundwater flow direction. Typical result for a) advection only model, and b) advection and dispersion model.
PHYSIOGRAPHY AND RAINFALL

Koongarra is located along the southeastern edge of the Mount Brockman massif, an outlier of the Arnhem Land plateau. The southeast margin of the massif is defined by an escarpment rising above gently sloping woodlands containing the deposit. The orebody lies within the catchment of the westerly draining Koongarra Creek. Several ephemeral streams issue from small catchments in the rocky escarpment northwest of the deposit. These streams are steep (53-212 m/km) until emerging from the escarpment where topographic gradients decrease to as little as 0.003.

Rainfall in the Alligator Rivers region occurs during a humid monsoonal wet season from November to March or April. Relatively dry conditions exist for the remainder of the year. Rainfall intensity is variable during the wet season while June, July, and August usually lack rain. Rainfall records have been kept at a number of sites at Koongarra since 1971. A six year record (ending with the 1976/77 water year) has an annual mean of 1798 mm with 95% of the rain falling between November and April (Noranda Australia Ltd., 1978). The mean annual pan evaporation rate was 2580 mm.

HYDROGEOLOGY

All the geologic units ranging from bedrock to unconsolidated sands are capable of transmitting water. However, several materials appear to have sufficient relative permeability contrasts that they can be considered distinct hydrogeologic units.

Surficial Deposits

Unconsolidated sands and gravel, lateritic zones cemented with iron oxide, and residual soils form the uppermost hydrologic unit. These are up to 9 m thick and cover most of the site with the exception of a small area of subcropping schist above Orebody No. 1. The sands have a high infiltration capacity and are likely highly transmissive when saturated during the wet season. Earlier geotechnical studies characterized the surficial deposits with over 200 backhoe pits and 44 shallow drill holes both north and south of Koongarra Creek (AGC, 1980a and 1980b).

Weathered Cahill Formation

Underlying the surficial deposits is a zone of weathered Cahill Formation, which can be transitional into overlying residual soil and underlying unweathered schist. Though variably foliated and fractured, in its most
developed state weathered zone material consists of a bleached white, structureless deposit of disaggregate quartz and muscovite grains in a clay matrix. This material is plastic when wet and shows little of the fabric of the original schist. The permeability of the weathered zone is considered to be low due to its high clay content and relative lack of fractures. The transition from weathered to unweathered rock occurs over several meters. Transition zone rock is iron stained and clay altered but clearly exhibits fractures and the foliation of the unweathered schists.

Variable rate injection tests were conducted in weathered schists and amphibolite at six sites north of Koongarra Creek and 26 sites south of it (AGC, 1980a; McMahon, Burgess and Yeates, 1981). A (geometric) mean hydraulic conductivity of $5.2 \times 10^{-4}$ m/d was determined; an order of magnitude variation in conductivity between adjacent test intervals is commonly observed.

### Unweathered Cahill Formation

The unweathered schists and amphibolite are competent, well foliated rocks. Drill core shows the schist to be fractured; some fractures show oxidation. Mean apparent transmissivities calculated from aquifer tests completed during the 1988 field program (see below), average about 60 m$^2$/d, suggesting a substantial degree of secondary permeability. The effective saturated thickness of the unweathered Cahill Formation is not known, though drill logs indicate water inflows occur to depths of at least 125 m.

### Kombolgie Formation

The Kombolgie Formation is silica cemented and contains little primary permeability. Secondary permeability occurs dominantly from well developed vertical fractures. Subsidiary sources of permeability are flat lying fractures developed by weathering along bedding planes. The predominance of northwest to west-northwest vertical fractures suggests that permeability may be enhanced in these directions. Because it is not mineralized, this rock has not been extensively studied.

### Koongarra Fault Zone

The Koongarra fault is a complex zone of disruption and sympathetic faults. No direct measurements of its hydraulic conductivity have been made. Weathering extends to a depth of 50 m along portions of the fault (Pederson, 1978) indicating a deeper circulation of oxidizing waters along the fault than in the schists. While this suggests permeability along the fault, no evidence exists for permeability across it. In core samples, the fault zone is brecciated and fractured with quartz and chlorite alteration minerals filling void spaces and fractures. The cores show little apparent permeability. The fault is a boundary between hydrologic systems of contrasting character. The portion of the aquifer composed of the Cahill Formation and surficial sands is multilayered and has a northeasterly bedrock structural fabric, whereas water in the Kombolgie Formation
consists dominantly of water stored in northwesterly fractures. The function of the Koongarra fault in groundwater flow between the escarpment rocks and the schist is unclear. However, unless transected by cross fractures, the fault probably acts as a barrier of low permeability.

**Joints and Fractures**

Well developed vertical joints are evident in the Kombolgie Formation along the escarpment. Aerial photographs show that these joints form a penetrative northwest to west-northwest fracture fabric with strike lengths up to several kilometers. In the study area, obvious offsets of the Koongarra fault by the northwest fractures are not evident.

**LABORATORY AND FIELD EXPERIMENTAL PROGRAM**

Despite numerous studies at Koongarra, little reliable information existed on the hydraulic properties of the various geologic units at the start of the present project. Since then both field and laboratory studies have been restarted to support the development of models describing steady and transient groundwater flow in the Koongarra region.

**Physical Property Measurements**

A series of samples were selected in May 1989 for petrophysical measurements from both the general zone of the orebody and from the sandstone. The first phase of the work, at the Department of Geology, Sydney University, for bulk and grain densities, porosity, permeability and susceptibility, are on diamond drill hole (DDH) samples from the core shed at Koongarra. The samples are from the weathered, alteration and unaltered zones. The second stage of the work, will study the permeabilities of the clayey samples obtained during the November 1988 cable tool drilling program (see below), whilst phase three will investigate the electrical and acoustic properties of the lithologies.

**Water Levels**

The exploration percussion drilling at Koongarra, left an array of drill holes suitable for a water level monitoring network, and water levels in 61 wells have been monitored since 1971 for various periods up to 7 years in duration. The bores are usually cased but not cemented through the surficial deposits and weathered zone and are open in the unweathered schist. Water levels probably represent the hydraulic head for the unweathered Cahill Formation and the base of the weathered zone. However, because the majority of casings are not cemented, the possibility that water levels represent a composite potentiometric head for entire bore cannot be discarded. Only a few bores are in the Kombolgie Formation.

In late 1988 the NT Power and Water Authority drilled an additional 22 holes in and around the No. 1 orebody. These holes were positioned to maximise each hole's usefulness to the hydrogeological and groundwater
geochemistry studies and similarly the drilling method for each hole was chosen so that the best possible samples could be obtained for laboratory studies and best suit the various modelling studies. Seven wells were drilled to 25 m and back filled to encase slotted PVC tubes as water sampling ports at 13-15 m and 23-25 m. Fifteen monitoring wells were also drilled; thirteen of these were to 40 m and the other two to 50 m.

The NT Mines and Energy Dept has recently recommenced the monthly measurement of standing water levels (SWL) in all the presently open wells at Koongarra. This study started in February 1989 but as a result of very heavy rains it was not possible to gain access to the site in March 1989.

Water levels across the property exhibit seasonal variations reflecting groundwater recharge during the wet season and discharge for the remainder of the year. During the wet season, fluctuations of up to 15 m occur in some bores. Static water levels throughout the year define southerly hydraulic gradients. At the northeast end of the project area, the gradient is east to southeast oriented due to the presence of a perennial recharge area in the Cahill Formation. The areal extent of the water mound is dependent on seasonal rainfall. Recharge appears to spread out laterally along the Koongarra fault in a zone with anomalously deep weathering (Figure 1), which suggests either preferential permeability along the fault or anisotropic conditions in the Cahill Formation. Over the rest of the area, water levels rise during the wet season, but no large water mounds develop, suggesting that recharge across the fault is either minor or uniformly distributed. Springs and seeps in the vicinity of the Koongarra fault and steep water level gradients across it suggest that the Koongarra fault acts as barrier to flow. During the wet season, the surficial deposits become fully saturated and form an unconfined aquifer discharging into Koongarra Creek or its channel deposits. As a result of discharge from springs or leakage from the schists, the surficial deposits may contain a limited amount of flow throughout the year resulting in a two layer aquifer system.

The overall continuity of water levels suggests good hydraulic communication in the aquifer at the scale of the property. Water level anomalies between bore holes indicate macroscopic heterogeneities in the aquifer and suggest local scale (10-100 m) permeability contrasts. The annual recurrence of artesian pressures in the same bores suggests confined aquifer conditions rather than temporary confinement due to air entrapped by surface infiltration. Given the lack of streamflow during the latter part of the dry season, the daily water level declines must indicate aquifer discharge by underflow from the basin or evapotranspirative loss. These observations were interpreted to indicate that the Cahill aquifer is partially confined and locally heterogeneous.

Several springs and seeps occur within the Kombolgie Formation along the escarpment. The elevation of the springs indicates that water levels in the escarpment are several meters higher than in the eroded Kombolgie Formation at the base of the escarpment and the adjacent Cahill Formation.
Aquifer Tests

Constant rate pumping tests are the primary means by which quantitative estimates of aquifer coefficients have been made. The results of the tests are normally presented as contour maps of final measured drawdown and logarithmic and semilogarithmic plots of drawdown versus time. During the preparation of the Koongarra Environmental Impact Statement, 24 drawdown and recovery tests and 50 water pressure tests were carried out (AGC 1979). Two further drawdown tests, of KD1 (Salama 1985) and PH85 (Davis 1988), were carried out in 1985 and 1986 respectively in the USNRC funded program. In 1988, as part of the ARAP project, eight tests were conducted in the Cahill Formation aquifer (Norris 1989). Three of the tests had pumping periods longer than 2,000 minutes and produced significant drawdown in observation wells. Water level recoveries were monitored for a time equal to the duration of pumping or until daily declines resumed; elongate, north to northeast trending, asymmetric patterns were seen in the contour maps of the drawdown. A further series of tests was undertaken in 1989 by Bob Marley, University of Arizona, when aquifer tests of PH73, PH49, C8 and PH58 provided elliptical drawdown patterns which closely match the results of the 1988 tests. The W series of bores, which are completed in the weathered zone, reacted to the pumping suggesting that there is hydraulic connection between the weathered and partially weathered zones. Figure 2 shows the drawdown patterns for three of the tests from the 1979 (KD2), 1988 (PH56) and 1989 (PH58) measurements.

Cascading water was observed in a few of both the 1988 and 1989 tests, when discharge exceeded inflow to the bore. This indicates that the weathered zone does restrict vertical flow at least in response to a short term stress and that hydraulic communication between the unweathered zone and overlying units can occur along the casing. Borehole PH81, which is terminated in the weathered zone and is not hydraulically connected to the unweathered schist as are surrounding bores, showed anomalously low drawdown compared to surrounding bores and substantiates the interpretation of a lower hydraulic conductivity for the weathered zone.

A series of slug tests was also carried out during the 1989 field program, in which a known volume of water was added to either open holes, or packed zones of the holes, then monitored the drop in water level to the initial value. Although only a limited number of tests were possible on that occasion, they suggest that the majority of groundwater flow occurs within the upper 40 m of the system. Further measurements, with a modified packer system will be carried out in October 1989.

Analysis

Estimates of transmissivity and storativity for the 1988 tests and the 1979 test at KD2 have recently been calculated by Norris (1989) from the aquifer response data, using a number of homogenous isotropic, homogenous anisotropic and fracture controlled models. However, only the results for the homogenous anisotropic analysis for PH56 and KD2 and an interpretation
of the fracture modelling of the PH88 test is included here. Though the models applied to fractured media require more data for numerical estimates, they were able to provide some qualitative information.

The data were analyzed as a homogenous, anisotropic medium in three ways. First, all three well combinations in a test were evaluated using the approach of Papadopolous (1965) for drawdown around a well discharging at a constant rate from an infinite anisotropic aquifer. With these data, the magnitude and orientation of the major and minor principal transmissivity axes can be determined. Secondly, each test was analyzed for a least squares approximation, (Neuman et al. 1984), using all observation bores and then a least squares solution was sought using combinations of tests in an attempt to define large scale aquifer properties.

Test PH56b

The principal transmissivities for 42 three well combinations show two main orientations (Figure 3a): a dominant northeast to east-northeast direction and a subordinate northerly direction. Northeasterly directions were obtained primarily from combinations of bores PH14, PH55, PH58, PH80, PH83, and PH84, while combinations of PH73, PH74, PH80, PH83, and PH84 were north directed. Transmissivity ellipses for the two groups show good agreement with directional transmissivity for the bores on which the approximation was calculated (Figure 3b) but not for bores outside the group. These data suggest that two components compose the total system response to pumping. One is represented by a northerly principal transmissivity and appears to be influential at a scale of about 100 m around the pumped well. The other component has a northeasterly principal transmissivity effective at a scale of hundreds of meters.

Test KD2

Data for test KD2 gave principal transmissivities for 43 three well combinations but no least squares solution. A rose diagram of the results shows a single northerly maximum. A minor northeasterly peak accounts for less than 10% of the calculations. Drawdowns show north-south trends near KD2 and northeast orientations for the large scale patterns. As in test PH56b, these data suggest that two components make up the total system response. A north oriented transmissivity fabric is defined by observation wells closest to the pumped bore and a northeast principal transmissivity represents more distal bores.

Analysis of Fracture Flow - Test PH88

The 1988 aquifer test data showed similarities to fracture flow type curves. Though the ambiguity of type curve fitting and the lack of supporting data prevent unique solutions, some qualitative interpretations were possible. The PH88 test produced relatively little drawdown in the pumped bore while equivalent drawdowns occurred rapidly in adjacent bores as well as one 100 m away. This was interpreted as representing a well
intersecting a high angle fracture system of finite conductivity. Drawdowns at PH88, KD2, PH87, PH85, PH92, and PH93 were identical, indicating a good hydraulic connection to a fracture system with a strike length of at least 100 m in a northerly direction.

Summary of Aquifer Test Results

Table 1 summarizes the best estimates of aquifer parameters using an anisotropic model. The principal transmissivities are north to east-northeast oriented with anisotropy ratios ranging from 4 to 17. The northeasterly direction is representative of large scale drawdown patterns and is subparallel to the Koongarra fault and features such as foliation, fold axes, and lithologic layering in the bedrock schists. The north direction is important at smaller scales (<150 m) and may reflect a less extensive fracture fabric in the unweathered schist or lower weathered zone. An alternative interpretation is that the transition from north to northeast directions may be continuous and represent flexure or open fold in the schistosity or relict bedding of the bedrock. These results show that the magnitude and orientation of the principal transmissivity varies with spatial position and the scale of the test and suggest that a representative elementary volume cannot be determined for the entire aquifer but only subregions of it.

CONCLUSIONS

Five hydrologic units compose the Koongarra site. These are: the Kombolgie Formation, unweathered Cahill Formation, weathered Cahill Formation, surficial sands and the Koongarra fault. Water level and aquifer test data support the concept of a "hangingwall" aquifer consisting of: (1) unweathered Cahill Formation forming a partially confined fractured rock aquifer, (2) weathered Cahill Formation acting as a laterally variable aquitard, and (2) the surficial sands which likely form an unconfined aquifer during the wet season. The vertical hydraulic conductivity of the weathered zone and the amount of leakage possible through it are not known. The Kombolgie Formation composes a "footwall" aquifer containing water in well developed fracture sets. The Koongarra fault forms the hydraulic boundary between the two aquifers. The hydraulic characters of the Kombolgie Formation and Koongarra fault are poorly understood. Localized permeability across the fault is indicated by a recharge zone at the northeast end of the site. Elsewhere recharge is diffuse suggesting permeability across the fault is either evenly distributed or the fault is relatively impermeable and recharge occurs by infiltration through hangingwall rocks.

Water levels at Koongarra are dynamic showing yearly, daily and semidiurnal cyclic fluctuations. Semidiurnal cycles are correlated with earth tides. The hydraulic gradient dips primarily to the south and varies slightly in magnitude with the season. Property wide water level trends and results of
aquifer tests indicate good hydraulic connectivity in the unweathered Cahill Formation aquifer. No impermeable boundaries have been detected although data does indicate heterogeneity at small scales (10-100m).

Drawdown patterns during aquifer tests indicate a heterogeneous aquifer with pronounced north to east-northeast anisotropy, and logarithmic drawdown curves for early time data are frequently linear suggesting fracture controlled flow. Intermediate and late time data indicate pseudo radial flow conditions modified by leakage or fracture storage. Analysis of drawdown data using a homogeneous, anisotropic model has provided consistent results though interpretations must be constrained by drawdown patterns. Principal transmissivities are north to northeast oriented with anisotropy ratios from 4 to 17. Northeast anisotropy represents large scale drawdown patterns and is controlled by bedrock geologic fabrics and the Koongarra fault. North anisotropy is areally restricted and may be controlled by localized fracture fabrics. A representative elementary volume cannot be defined for the entire area but only subregions of it. The combination of southerly hydraulic gradients and north-south to east-northeast to west-southwest oriented major transmissivity axes will result in southerly to southwesterly groundwater flux vectors. Groundwater velocities will be fastest when the gradient and major transmissivity are co-linear.

Further measurements with a modified packer system are planned to be carried out during October 1989 to improve our knowledge of the vertical distribution of hydraulic conductivity. Differences between wet season and dry season hydraulics, the lateral continuity of hydrostratigraphic units and the hydraulic connection between units still need to be addressed. All hydrogeologic data is presently being assessed by the CSIRO Dept. of Groundwater and the Dept. of Hydrology at the University of Arizona; further site testing will be carried out based upon these recommendations.

REFERENCES

Australian Groundwater Consultants, 1979, Report on investigation of groundwater and the design of the water management and tailings retention system for the Koongarra project, V.1 Groundwater Studies, January 1979, unpublished consultants report.


Pederson, C.P., 1978, The geology of the Koongarra uranium deposits including investigations of contained elements, In: Koongarra project draft environmental impact statement, Noranda Australia Limited, Melbourne, Appendix V.

Table 1  Summary of aquifer parameters obtained from anisotropy analysis

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<th>Test</th>
<th>$T_{xx}$ ($m^2/d$)</th>
<th>$T_{yy}$ ($m^2/d$)</th>
<th>$T_{xy}$ ($m^2/d$)</th>
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Symbols:

- $T_{xx}$, $T_{xy}$, $T_{yy}$: Components of the transmissivity tensor in arbitrary coordinate system
- $S$: Storage coefficient
- $T_a$, $T_b$: Major and minor principal transmissivities
- THETA: The angle between the major principal transmissivity and the arbitrary coordinate system
- $T_a/T_b$: The anisotropy ratio of major to minor principal transmissivities
Figure 1a Contour map of water-level elevations during the dry season (data for 21/11/79 from AGC, 1980c).

Figure 1b Contour map of water-level elevations during the wet season (date for 27/2/80 from AGC, 1980c).
Figure 2. Contour map of final measured drawdowns in aquifer tests KD2 (1979), PH56b (1988) and PH58 (1989).
Figure 3a  Rose diagram of principal transmissivities for three well combinations in aquifer test PH56b. The least squares solution for all wells is denoted as LSS.

\[ T_a = 324.63 \text{ m}^2/\text{d} \]
\[ T_b = 38.28 \text{ m}^2/\text{d} \]
\[ T_a/T_b = 8.5 \]
\[ S = 7.7 \times 10^{-4} \]
\[ \Theta = 9.5^\circ \]

Figure 3b  Polar plot of the least squares transmissivity ellipse obtained with data for PH14, PH55, PH80, PH88 and PH84. The directional transmissivities shown are for all observation bores.
SECTION 5.8
THE DISTRIBUTION OF URANIUM AND THORIUM BETWEEN PHASES IN WEATHERED CORE FROM KOONGARRA

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INTRODUCTION

This report presents data for uranium and thorium concentrations, and \(^{234}\text{U}/^{238}\text{U}\) and \(^{230}\text{Th}/^{234}\text{U}\) activity ratios in "amorphous" and "crystalline" phases of drillcore samples from the vicinity of the Koongarra uranium ore deposit. The amorphous material was defined as poorly ordered material accessible to, and therefore in approximate equilibrium with, the groundwater. Crystalline phases were defined as highly ordered materials with contained species inaccessible to the groundwater. Here amorphous material includes species adsorbed onto the surface of crystalline phases. How the disequilibria and concentrations differ between the phases with the position of the sample, was also considered.

For Koongarra, the two phase extraction work has mainly concentrated on a single transect of the ore body running from DDH52 to PH89, perpendicular to the major fault and along the dispersion fan for about 400 m. This information is helpful in elucidating the zones of leaching and deposition of the uranium series nuclides in the ore deposit.

TAMMS ACID OXALATE EXTRACTIONS

The amounts of elements associated with amorphous phases can be estimated by performing a Tamms acid oxalate (TAO) extraction and analysing the extract. The use of oxalate extractions to remove amorphous inorganic "gel-complexes", was first proposed by Tamm in 1922\(^{11}\), and has been extensively used and modified by soil scientists\(^{2,3}\). It has mostly been used to extract amorphous iron oxides such as ferrihydrite and amorphous aluminium complexes\(^{14}\). The procedure involves shaking the soil sample with 40 mL/g sample of 0.2 M ammonium oxalate, buffered to pH 3.0 with oxalic acid. The slurry is shaken for 4 hours. Shaking is done in the dark since dissolution of crystalline iron oxides/oxyhydroxides by oxalate occurs in the presence of light\(^{15}\). The removal of species and dissolution of amorphous materials, especially ferrihydrite, is by complexation with oxalate. Most metal-oxalate complexes are strong at pH 3.

Saleeite \((\text{Mg[UO}_2\text{]}_2[\text{PO}_4]_2\cdot8\text{H}_2\text{O})\) was found to be quite soluble by Nightingale\(^{6}\), and this may explain the high uranium concentrations, and near unity \(^{234}\text{U}/^{238}\text{U}\) activity ratios in some extracts of Koongarra core, e.g. DDH27 - 29 m (Table 1). However, uranium in saleeite crystals should not be considered to be accessible to groundwater, and therefore does not fit our definition of amorphous material. The samples analysed by TAO extraction should therefore contain no uranium minerals.
The TAO extraction does not give a distinct cut-off between the amorphous and crystalline phases. Rather it gives only an estimate of the amount of the accessible material. After about 4 hours most of the amorphous iron, probably as ferrihydrite, is usually removed\(^7\). Slow dissolution of crystalline iron oxide phases such as goethite, then continues until all the iron oxides are removed, which may take several weeks. The distinction between the amorphous and crystalline phases also varies between soils. The effect of extraction on unweathered rocks is unclear, and the results are generally too ambiguous to be useful.

**MATERIALS AND METHODS**

**Extraction**

Crushed air dry samples, 0.5-2 g, were shaken with Tamms acid oxalate reagent (10.9 g/L oxalic acid, 16.1 g/L ammonium oxalate, pH3) for 4 hours in darkness. After shaking, the slurry was filtered through a 0.45 μm filter. The filtrate containing the dissolved amorphous material and associated elements was analysed for uranium and thorium by α-spectrometry.

**Residual Digestion**

The material retained by the 0.45 μm filter, i.e. crystalline phases, was dried at 65°C and weighed. It was then dissolved by an HF/HClO\(_4\) digestion, followed by alkaline fusion, and analysed for uranium and thorium by α-spectrometry.

The mass of material extracted by TAO reagent was estimated by difference. The amount of water removed at 65°C was estimated and included in calculations.

**Characterisation**

A range of techniques were used to characterise the samples. These have included Si and Al solid state Nuclear Magnetic Resonance, random powder X-ray diffraction using Co Kα radiation (patterns were collected between 10 and 70° 2θ) and Transmission Electron Microscopy; samples were analysed both before and after extraction. Three samples were also studied by Mössbauer Spectroscopy at room temperature.

**RESULTS AND DISCUSSION**

Data for 46 core samples from the DDH52-PH89 transect have been reported by Nightingale\(^8,9\), Yanase\(^9,10,11\) and Edghill\(^12\) and are listed in Table 1. A surface plan of boreholes is given in Figure 1. Holes from which samples have been, or will be, analysed are also shown. The majority of the samples were weathered, with an occasional unweathered sample also being studied.
The variables considered in this work were -

- the concentration of $^{238}$U and $^{232}$Th,
- the activity ratios of $^{234}$U, $^{238}$U and $^{230}$Th,
- accessible or inaccessible phases, and
- position in the transect.

Table 1 gives the values for uranium concentration, $^{234}$U/$^{238}$U and $^{230}$Th/$^{234}$U activity ratios in the TAO extractable phases, TAO residual phases and bulk samples. In some cases "extractable" is a combination of Morgan's and TAO extractions, and residual is a combination of citrate dithionite bicarbonate and HCl extractions and residual digestion.

### Uranium Concentrations

9-98Z of the uranium in the samples was extractable by TAO, with an average of 45.4Z. The mass of material extracted by TAO was 1.5-12Z of the total sample, with an average of 5.1Z. There was no obvious pattern of percent uranium or percent mass extracted with position.

Figures 2a and 2b show the distribution of uranium concentration in the transect in the TAO extractable and TAO residual phases. The uranium concentrations in both phases follow similar patterns, resembling that of the bulk uranium concentration. Near the end of the dispersion fan the drop in uranium concentration appears to be more abrupt in the residual phases than in the extractable phases. Down-gradient of the dispersion fan, the uranium appears to be increased in the top 5 to 10 m in both the extractable and residual phases. The distribution of total uranium concentration of the top 15 m, also shows a higher concentration of uranium in the top approximately five metres, down-gradient of the ore zone, especially in the vicinity of the base of surficial sands. This suggests possible rapid transportation of uranium moving with groundwater in the surficial sands, especially during the wet season.

It has been postulated that extractable uranium is associated with ferrihydrite, although no clear evidence exists. Elemental analyses of some TAO extracts by Nightingale$^{[6]}$ gave levels of TAO extractable iron of 0.35 to 10.9 mg/g sample. Assuming that all this iron comes from ferrihydrite, which has an approximate composition of $5 \text{Fe}_2 \text{O}_3 \cdot 0.9 \text{H}_2 \text{O}$, then the amount of ferrihydrite in the samples would be $0.6-19 \text{mg/g}$. The largest amounts were in the top 5 m, 2.6-19 mg/g. Below 5 m, the amounts were 0.6-6.3 mg ferrihydrite/g sample. Citrate dithionite bicarbonate (CDB) extractions (for dissolution of crystalline iron oxides) removed over ten times as much iron as TAO$^{[6]}$. It is possible that TAO extractable uranium is mostly strongly sorbed onto crystalline phases.
The $^{234}\text{U}/^{238}\text{U}$ activity ratios for the TAO extract and residual phases are shown in Figures 3a and 3b. In the extract, $^{234}\text{U}/^{238}\text{U}$ was usually less than unity; in the residual it was greater than unity. The $^{234}\text{U}/^{238}\text{U}$ ratios in the extracts suggest a preferential mobility of $^{238}\text{U}$ over $^{234}\text{U}$. The most popular explanation proposed for this phenomenon is $\alpha$-recoil of the daughter $^{234}\text{Th}$ nucleus into inaccessible phases, while atoms recoiled into the groundwater are rapidly reequilibrated with the solid phase. Other possible explanations consider the behaviour of $^{234}\text{Th}$, finding sites inaccessible to uranium by a process of specific adsorption; and the effect of transformations of iron oxides, with the possibility of Th being preferentially entrapped in newly formed crystals of iron oxides.

In weathered samples, the TAO extract gave the highest $^{234}\text{U}/^{238}\text{U}$ ratios near the top of DDH52, and in barren zones down-gradient of the dispersion fan. Unweathered samples also gave high ratios. Lowest ratios in the extract occur near the edge of the dispersion fan. Uranium-234/uranium-238 ratios in residuals followed a similar pattern, with the lowest values around DDH3 to DDH4 and DDH55, and in some areas beyond the dispersion fan. The ratios were most different between the extractable and residual around DDH4, PH55 and the bottom of DDH3. They were nearest in holes down-gradient of the dispersion fan. This suggests that the zones at the tip of the dispersion fan, and at the base of weathering, are the sites where recent deposition of $^{238}\text{U}$ has occurred, and/or where the groundwater is most $^{234}\text{U}$ depleted.

$^{230}\text{Th}/^{234}\text{U}$ Activity Ratios

The ratio in the extract is generally lower than unity and lower than the ratio in the residual phases. The ratio is highest in the extracts from near to the top of DDH52, and deeper than about 5 m at PH60 and PH89. Particularly low values, about 0.4 or less, occur near the surface at DDH1, DDH2, PH58 and PH60. Low values also occur near the base of weathering along the dispersion fan. The residual $^{230}\text{Th}/^{234}\text{U}$ ratios appeared to follow similar trends, but so far there are much fewer data points. The very low $^{230}\text{Th}/^{234}\text{U}$ ratios near the surface, and near the base of weathering, suggest that these are the sites of most recent deposition.

The activity ratio data can be plotted on a graph of $^{234}\text{U}/^{238}\text{U}$ versus $^{230}\text{Th}/^{238}\text{U}$ in the style of Osmond et al.\textsuperscript{15}, to recognise samples where deposition and leaching may have occurred. This is done for the TAO extract data in Figure 4a. The data points appeared to group together in clusters which were then numbered. The origin of the samples from each cluster can be seen in Figure 4b.
Zone 1 in Figure 4b appears to represent an area of rapid accumulation of uranium, with $^{238}\text{U}$ accumulating preferentially to $^{234}\text{U}$. Zone 2 may be similar to zone 1, but is not as intensely accumulating. Zone 3 may be an area of intense accumulation, but does not accumulate $^{238}\text{U}$ preferentially to $^{234}\text{U}$ as much as zones 1 and 2. This may be because of the different nature of the solid material; surficial sand versus weathered schist, or the type of water flow; rapid and seasonal versus slow and continuous. Zone 4 is possibly a zone where slight leaching has occurred, and zone 5 may be where strong leaching has occurred. Nightingale suggested that an upward extension of the ore body in the vicinity of DDH52-DDH1 had been eroded and leached away, leading to very high $^{230}\text{Th}/^{234}\text{U}$ ratios in this area.

$^{232}\text{Th}$

Thorium-232 was mostly present in residual phases, but a small significant proportion was in the TAO fraction. The distribution of $^{232}\text{Th}$ was not related to that of uranium. The concentrations of $^{232}\text{Th}$ in the TAO extracts was 0.54-2.23 µg/g and in the residuals 2.95-17.26 µg/g.

Phase Characterisation and Extraction Validation

Some attempts to characterise the extracted material have been made. When using transmission electron microscopy, no differences were observed for the sample before and after extraction. Many grains of iron oxide were present in both subsets, suggestive of little if any dissolution of iron oxides in the samples by TAO. Some likely sources of $^{232}\text{Th}$ were identified as monazite (Ce, La, Nd, Th) PO$_4$ and zircon (ZrSiO$_4$), and thorium peaks were observed for some monazite grains.

Three samples, chosen to represent different depths and mineralogies, were analysed before and after extraction, by XRD. For all three samples a peak present of $d = .286$ nm was completely removed after treatment with TAO. The identity of the phase removed has not yet been fully uncovered, but may be a carbonate. (If a mineral is removed, it does not necessarily mean that uranium, etc also extracted, was associated with that mineral.)

CONTINUING AND FURTHER WORK

Many of the samples from the DDH4-PH89 section are being extracted and prepared for analysis for $^{226}\text{Ra}$ activity and total elemental analysis by ICP-MS.

Since the samples appear heterogeneous, the question of near field heterogeneity needs to be addressed and this may involve extraction of samples near one another but with apparent differences in mineralogy. The concentration of uranium is probably the most sensitive variable to near field heterogeneity. Iron oxides, which are probably the major sorbers of uranium, constitute only a minor part of the sample mass and are often distributed very unevenly through the samples, sometimes forming
concentrations and nodules. However, the uranium activity ratios may be more robust to the heterogeneity of the sample, since even in areas of lower iron oxide concentration, the bulk of the uranium is still likely to be associated with iron oxides. The nodules of iron oxides may present a different case however, if they are effectively closed systems compared to iron oxides dispersed over clay particles. Activity ratios on TAO extracts should be similar in the near field, since the phases are accessible to the groundwater and in near equilibrium with it. Concentrations are likely to be more variable than activity ratios.

CONCLUSIONS

A large proportion of the uranium and thorium is associated with amorphous phases. This may include associations with ferrihydrite and adsorption onto iron oxides and clay minerals. This uranium is possibly accessible to, and at near equilibrium with, the groundwater. There is an apparent preferential mobility of $^{238}\text{U}$ to $^{234}\text{U}$ in the groundwater, reflected by low $^{234}\text{U}/^{238}\text{U}$ activity ratios in extractable phases. This may occur due to an $\alpha$-recoil effect, emplacing $^{234}\text{Th}$ and $^{234}\text{U}$ nuclei into crystalline phases, from surface and amorphous sites. Other processes may, however, be important.

Areas showing greatest leaching are near the top of DDH52. Most rapid accumulation seems to have occurred near the centre of the dispersion fan and near the base of weathering to the edge of the fan. There is possibly preferential movement and accumulation of uranium just above the base of weathering. Possible rapid movement of uranium containing waters through the surficial sands may occur seasonally.

More work is required on near field heterogeneity, alternative transects and directions, extractant validation, phase characterisation and the nature of associations of uranium with phases, the causes of disequilibria, and the stability of uranium containing phases and the effect of transformations on associations and disequilibria.

REFERENCES


13 Noranda/Denison Drilling Core Logs.


17 N Yanase et al. Migration Behaviour of Uranium Series Nuclides: Relevant to Alteration (3). Section 9, this volume.
### TABLE 1

**URANIUM SERIES IN TOTAL SAMPLES AND TAO EXTRACTABLE AND RESIDUAL PHASES**

<table>
<thead>
<tr>
<th>Hole</th>
<th>Length (m)</th>
<th>Actual Depth (m)</th>
<th>( ^{238}U/\text{Th} ) Extractable (( \mu g/g ))</th>
<th>( ^{234}U/\text{Th} ) Residual (( \mu g/g ))</th>
<th>Bulk ( ^{234}U/\text{Th} ) (( \mu g/g ))</th>
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<td>98 0.910 1.87 526 1.42 1.45</td>
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<td>1.5-3</td>
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| DDH1 3.0 | 2.2 | 641 1.120 1.17 | 8 |
|          | 6.7 | 835 1.18 1.09 | 11 |
|          | 1028 0.597 0.287 1277 1.336 1.150 | 2305 1.007 0.918 | 10 |
|          | 1044 0.609 0.293 1175 1.320 1.236 | 2271 1.004 1.01 | 10 |
|          | 13.1 | 9.3 | 2353 0.953 0.87 | 8 |
|          | 20.4-21.3 | 14.4-15.1 | 813 1.034 1.02 | 9 |
|          | 27.4-29.0 | 19.4-20.5 | 70170 0.972 0.866 | 5691 1.070 1.700 | 82300 0.985 1.04 | 8,10 |
|          | 41.5 | 29.3 | 8.5 0.888 0.40 | 21 1.07 | 30 1.015 0.94 | 8,6 |
|          | 48.8-50.3 | 34.5-35.6 | 103 1.042 0.90 | 112 0.96 | 214 1.001 1.04 | 8,6 |

<p>| DDH2 | 3.3.7 | 2.6-3.2 | 183 0.848 0.40 340 1.10 | 555 1.017 0.87 | 8,6,15 |
|       | 13.7-15 | 11.9-13.2 | 336 0.669 0.32 597 1.17 | 935 0.991 0.97 | 8,10 |
|       | 15-16.8 | 13.2-14.5 | 464 0.703 0.42 668 1.21 | 1120 1.000 1.00 | 8,6 |
|       | 18.3-18.4 | 15.9-16.0 | 1070 0.890 0.90 | 16 |
|       | 20-21.3 | 17.2-18.5 | 310 0.750 0.47 485 1.16 1.14 | 864 0.996 1.04 | 8,6 |
|       | 38.1-39.6 | 33.0-34.3 | 21700 1.108 0.874 79770 0.963 | 0.966 82500 0.999 0.99 | 8,9 |
|       | 73-74.7 | 63.4-64.7 | 35700 0.990 1.00 | 8 |</p>
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<td>Residual ( ^{234}\text{U} / ^{238}\text{U} ) U (µg/g)</td>
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KOONGARRA AREA N.T.

Alligator Rivers Analogue Project

DRILL HOLE PLAN

- Diamond Drill Holes (Inclined)
- @ Rotary (or cable tool) Vertical Open Holes
- ◦ Rotary Vertical Closed Holes
FIGURE 2a  TAO extractable uranium (µg/g).

FIGURE 2b  TAO residual uranium (µg/g).
FIGURE 3a Uranium-234/uranium-238 activity ratios in TAO extract.

FIGURE 3b Uranium-234/uranium-238 activity ratios in TAO residual.
FIGURE 4a  Uranium-234/uranium-238 versus thorium-230/uranium-238 in TAO extracts, with numbered clusters.

FIGURE 4b  Uranium-234/uranium-238, thorium-230/uranium-238 cluster zones from Figure 4a, along DDH52-PH89 transect.
INTRODUCTION

Selective extraction procedures which had been adopted first to extract traces of metals in specific phases of soil or sediment\cite{1,2,3}, were applied to the disequilibrium study of uranium series radionuclides in the rock. The geology, geochemistry and mineralogy of the Koongarra uranium deposit have been investigated and reviewed in a recent report\cite{4}. The ore body consists of a primary ore body and a secondary ore body formed by the leaching of uranium from the primary ore body and its subsequent deposition; the host rock is quartz chlorite schist (Figure 1). The migration of radionuclides through the Koongarra ore body has been studied as an analogue of radioactive waste repositories. In order to clarify migration mechanisms, it is valuable to identify the significant mineral phase in which isotope disequilibrium has occurred. Nightingale earlier investigated the disequilibrium of $^{238}$U, $^{234}$U and $^{230}$Th in drillcore samples\cite{5}. In this study the sequential extraction procedure used by Nightingale was slightly modified and applied to the rock samples to obtain information on the distribution of uranium in the rock at Koongarra. On the basis of the distribution of uranium, the significant mineral phase of the rock was determined.

EXPERIMENTAL

The analysis of nine rock samples, collected mainly from diamond drill holes in the Koongarra 6109 mN cross section (Figure 1) is reported here. One gram of crushed material was sequentially treated by the following extraction solutions and the residual mineral and liquid phases were separated by centrifugation and filtration using a 0.45 µm Millipore filter.

The probable minerals dissolved and the extraction reagents used in this study are as follows.
1) Adsorbed trace materials and carbonate minerals by Morgan's solution\(^{2,5}\).

2) Ferrihydrate, amorphous minerals of Fe, Al and Si, and secondary U minerals by Tamm's solution\(^{1,5}\).

3) Crystalline iron minerals by CDB solution\(^{3,5}\).

4) Clay and some refractory minerals by 6 M HCl\(^{5}\).

5) All remaining resistant minerals by fusion\(^{5}\).

The uranium and thorium extracted from each mineral phase, was separated by an anion exchange resin (AGX 1x8, 100-200 mesh) after adding the \(^{232}\)U tracer. For the uranium fraction, iron was removed by a di-isopropylether extraction. The uranium was electroplated and measured by alpha spectrometry using a silicon surface barrier detector.

RESULTS AND DISCUSSION

1 Extraction Procedure

The uranium concentrations and the major minerals found in the rock samples are listed in Table 1. It can be seen that quartz, mica, clay minerals such as kaolinite, iron minerals (pyrite, hematite, limonite and chalcopyrite) and uranium minerals (pitchblende, autunite and torbernite) are the major minerals in the rock samples. Consequently Nightingale\(^{5}\) used a sequential extraction procedure for amorphous iron, crystalline iron, residual crystalline, clay and the remaining resistant mineral phases. However, in this study the extraction of uranium by Morgan's solution was added so that we could determine the uranium fraction in the adsorbed or associated carbonate mineral phases, which are more accessible to the groundwater than the amorphous iron mineral phase. On the other hand, the extraction of uranium in the residual crystalline mineral phase was omitted because the amount of uranium in the residual crystalline mineral phase was very small and the \(^{234}\)U/\(^{238}\)U activity ratio was always similar to that of the crystalline iron mineral phase.
Duplicate analyses were carried out to check the reproducibility of the sequential extraction procedure using the sample DDH1, 4.7 m. The results showed fairly good reproducibility.

2 Uranium Distribution

Figure 2 shows the distribution of uranium in the mineral phases of the rock samples. In the secondary ore body, most of the uranium was contained in the CDB fraction (42-60%) of all the rock samples, because the iron minerals such as limonite and pyrite are contained in these rock samples and an iron mineral usually incorporate with the uranium in the secondary ore body.

On the other hand, in the primary ore body, 72% of the total uranium was incorporated with the Tamm's solution extractable minerals in the 19.4-20.5 m region of the drill hole DDH1. This rock sample contains the hematitic mica schist and the uranyl phosphate such as autunite and torbernite. The large amount of uranium in the Tamm's fraction seems to result from the dissolution of uranyl phosphate such as autunite and torbernite.

In the deeper, 33.0-34.3 m, region of the drill hole DDH2, 70% of the total uranium was extractable with 6 M HCl which mainly dissolves the uranium in the clay mineral phase. However, at the present time we have no evidence for clay mineral existences in this region. As this rock sample contains pitchblende, its insolubility in CDB solution and solubility in 6 M HCl needs to be investigated.

3 234U/238U Activity Ratio

The 234U/238U activity ratios of mineral phases of rock samples are shown in Figure 3. In the secondary ore body, the 234U/238U activity ratios of the fusion fraction are greater than unity (2.8-6.3). The mechanism proposed to explain these results suggested that the high enrichment of 234U relative to 238U occurs when 234U recoils into the uranium-poor phase from the adjacent uranium-rich phase and the former phase is isolated from the leaching solution (e.g. groundwater) which causes a preferential leaching of 234U. Therefore the quartz mineral phase in the rock at Koongarra seems to be surrounded by the uranium-rich mineral phase and isolated from the groundwater.
It can be seen from the data that the $^{234}\text{U}/^{238}\text{U}$ activity ratios for the Morgan's and Tamm's extractions are similar and significantly below unity for all the samples (0.59-0.79 and 0.61-0.78 respectively) in the secondary ore body, and these values are consistent with $^{234}\text{U}/^{238}\text{U}$ activity ratios for groundwater in this zone. The results support Nightingale's interpretation, that is, leaching of uranium and preferential leaching of $^{238}\text{U}$ relative to the $^{234}\text{U}$ in the rock up-gradient, and deposition of uranium in the rock down-gradient are occurring.

In the primary ore body, the $^{234}\text{U}/^{238}\text{U}$ activity ratio of the fusion fraction was higher than unity in the 19.4-20.5 m region of the drill hole DDH1, a similar result to that obtained in the secondary ore body. However, recoil enrichment of $^{234}\text{U}$ in the fusion fraction appears not to have occurred in the 33.0-34.3 m region of the drill hole DDH2, where the $^{234}\text{U}/^{238}\text{U}$ activity ratio in the fusion fraction was unity. There is a possibility that the quartz mineral phase in the deeper region is not surrounded by the uranium-rich mineral phase.

CONCLUSION

The distribution of uranium, as determined by sequential extraction, can be explained on the basis of the mineral composition of the rock.

In the secondary ore body, the CDB extractable minerals (crystalline iron minerals such as limonite and pyrite) are the significant mineral phase associated with uranium accumulation. The Morgan's and Tamm's solution extractable minerals (adsorbed and carbonate, and amorphous iron minerals respectively) are accessible to groundwater and so their $^{234}\text{U}/^{238}\text{U}$ activity ratios, less than unity, are equal to that of the groundwater. The remaining resistant minerals (mainly quartz) are the significant mineral phase found to be enriched with $^{234}\text{U}$ by the alpha recoil effect.

However, in the shallow region of the primary ore body, the Tamm's solution extractable minerals (secondary uranium minerals such as autunite and torbernite - uranyl phosphates) are the significant mineral phase associated with the uranium accumulation. In the deeper region of the primary ore body, the 6 M HCl extractable minerals are significant. The relationship between the extraction solutions and the mineral phases has
not yet been precisely identified; the mineral phases dissolved by the sequential extraction procedure should be examined by the X-ray diffraction analysis using rock samples from Koongarra.

REFERENCES


Table 1  Uranium concentrations and the major minerals in the rock samples analyzed by the sequential extraction procedure.

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<th>Depth (m)</th>
<th>Concentration of U (ppm)</th>
<th>Major minerals contained*</th>
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<td>Quartz and limonite stained kaolinitic mica schist.</td>
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<td>19.4-20.5</td>
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<td>323 (2.5)</td>
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</table>

The figures in parenthesis denote counting error (%).

*: The data on the major minerals contained in the samples is from the Koongarra geological log of Denison Australia Pty Ltd.
Figure 1 6109N geological section through the Koongarra uranium ore body and the location of the drillholes.
Figure 2 Distributions of uranium in mineral phases of rock by the five-stage sequential extraction procedure.
Figure 3 Variations of $^{234}\text{U}/^{238}\text{U}$ activity ratios in mineral phases of rock by the five-stage sequential extraction procedure.
INTRODUCTION

Part of the primary uranium ore deposit, at Koongarra, has been weathered to form a secondary ore deposit. The secondary ore deposit is located in the "weathered zone", which is present below the surface for a depth of about 20 m (Fig. 1a). With increase in weathering, uraninite, the primary form of the uranium mineral at Koongarra, is changed to uranyl silicates, and then to uranyl phosphates. Uranium is finally associated with clay minerals and iron minerals in the downstream of the secondary ore deposit. The clay minerals and the iron minerals are altered products of chlorite, which is a major rock-forming mineral of the quartz-chlorite schist, the host rock of the ore deposit. Murakami and Isobe have noted the significance of the degree of alteration to the uranium distribution, and examined the relationship between U concentrations and chlorite and its altered products, vermiculite and kaolinite, in and near the transition zone just below the weathered zone.

The disequilibria of the uranium series nuclides have been discussed previously with migration velocities in the order of $^{238}\text{U} > ^{234}\text{U} > ^{230}\text{Th}$ in the weathered zone being reported. In the present paper, we will examine the relationship between alteration and the uranium disequilibria.

EXPERIMENTAL TECHNIQUE

Twelve rock samples from a section through the ore zone (Fig. 1) were collected, and their uranium series nuclides concentrations were measured by alpha-ray spectrometry. An outline of procedure is as follows.

1. 0.5 g of each sample powder was decomposed by pyrosulfate fusion.

2. The pyrosulfate cake was dissolved in hydrochloric acid, and thorium was separated by co-precipitation with barium sulfate.

3. Uranium and thorium were extracted into amine (Aliquat-336) and back-extracted.

4. The purified uranium and thorium were electro-deposited onto a stainless steel disk from ammonium sulfate solution, and then quantitatively measured by alpha-ray spectrometry.
The coexistent minerals of three of the rock samples, PH58-8, DDH3-47, and DDH4-101, were examined by the X-ray diffraction method so that the relationship between the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ Activity Ratios (ARs), and the mineral species could be studied. The locations of the three samples correspond to the surface, intermediate, and deep layers mentioned below.

RESULTS AND DISCUSSION

The activity ratios of $^{238}\text{U}$, $^{234}\text{U}$ and $^{230}\text{Th}$ are good indicators for the different migration behavior of the three nuclides$^{[2]}$. In order to visualize the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ ARs in the section shown in Fig. 1a, contour maps are given in Figs 1b and 1c, respectively, of the activity ratios obtained here, and for samples previously reported by Nightingale$^{[6]}$. Because groundwater has flowed from left to right in the weathered zone shown in the figure$^{[1]}$, Fig. 1b suggests that $^{238}\text{U}$ has moved faster than $^{234}\text{U}$. Uranium-234 is though a more mobile nuclide than $^{230}\text{Th}$ as is suggested in Fig. 1c. Interestingly, the $^{230}\text{Th}/^{234}\text{U}$ ARs in the secondary ore deposit are about 1 like those of $^{234}\text{U}/^{238}\text{U}$.

The variations of the $^{230}\text{Th}/^{234}\text{U}$ ARs (Fig. 1c) as a function of horizontal distance were then drawn for the surface (about 2 m depth), intermediate (16 m), and deep (31 m) layers (Fig. 2) so that the differences in the migration behavior of the uranium series nuclides at different depths could be examined. The DDH52 drillhole is taken to be the zero distance position. Figure 2 clearly shows that the migration trends of the two nuclides are different between depths.

In the surface layer, the leaching zone (denoted as I) may correspond to the remnant of the primary ore deposit, which has released nuclides to the secondary ore deposit (the zone denoted as II is part of the ore deposit), and further downstream. In the intermediate layer, the leaching zone (denoted as I) and the deposition zones (denoted as II and IV) are similar in location to their counterparts in the surface layer, with more moderate leaching and deposition, respectively. However, there is another leaching zone (denoted as III) in the intermediate layer, which corresponds approximately to the center of the secondary ore deposit. In the deep layer, the $^{230}\text{Th}/^{234}\text{U}$ ratio is almost 1 at any position, meaning that either migration or nuclides fractionation has hardly occurred.

The ratios of $^{234}\text{U}/^{238}\text{U}$ to $^{230}\text{Th}/^{238}\text{U}$ were calculated from the data obtained here and by Nightingale$^{[6]}$, to examine the relative mobility between $^{234}\text{U}$, $^{234}\text{U}$ and $^{230}\text{Th}$. Data from positions between 0 and 10 m deep, 10 and 20 m deep, and greater than 20 m depths, are regarded as being in the surface, intermediate and deep layers, respectively. The ratios of $^{234}\text{U}/^{238}\text{U}$ to $^{230}\text{Th}/^{238}\text{U}$ along the surface and intermediate layers are plotted in Figs. 3a and 3b, respectively. Figures 3a and 3b indicate that the ARs of $^{234}\text{U}/^{238}\text{U}$ are linearly proportional to those of $^{230}\text{Th}/^{238}\text{U}$ along the surface and intermediate layers, respectively. If we assume that $^{230}\text{Th}$
is immobile, then the gradient of $^{234}\text{U}/^{238}\text{U}$ against $^{230}\text{Th}/^{238}\text{U}$ gives a relative retardation factor of $^{238}\text{U}$ to $^{234}\text{U}$ by the following equation\(^{5,7}\):

$$\frac{R_{\text{238}}}{R_{\text{234}}} = 1 + \left\{ \frac{G}{(1-G)(\lambda_{\text{234}}/\lambda_{\text{230}})} \right\}$$

where $R_{\text{238}}$ and $R_{\text{234}}$ are the retardation factors of $^{238}\text{U}$ and $^{234}\text{U}$, respectively, $G$ is the gradient, and $\lambda_{\text{234}}$ and $\lambda_{\text{230}}$ are the decay constants of $^{234}\text{U}$ and $^{230}\text{Th}$, respectively. The gradients of the figures 3a and 3b give a retardation factor for $^{234}\text{U}$ greater than that of $^{238}\text{U}$ by a factor of 1.1 and 1.9 in the surface and intermediate layers, respectively. The retardation factor of $^{234}\text{U}$ is the same as that of $^{238}\text{U}$ in the deep layer.

The results reveal that the migration of the uranium series nuclides differs between depths although the mobility of the uranium series nuclides in the weathered zone is in the order of $^{238}\text{U}$, $^{234}\text{U}$ and $^{230}\text{Th}$, which agrees well with Lever's results\(^{5}\).

The X-ray diffraction patterns of the three rock samples from the different layers (Fig. 4) show that quartz is found in all layers, and that chlorite in the deep layer has been altered to become kaolinite-smectite and goethite in the intermediate layer, and kaolinite-smectite, goethite and hematite in the surface layer. The co-existent mineral species and their relative abundances are different between depths as also pointed out by Murakami and Isobe\(^{4}\). The differences in the pattern of migration between depths may be related to the different mineral assemblages and abundances between depths as the U concentrations are directly related to them\(^{4}\).

The finding of mobility in the order of $^{238}\text{U}$, $^{234}\text{U}$ and $^{230}\text{Th}$ is however inconsistent with that by other workers\(^{6,9,10,11}\) who have reported mobility in the order of $^{234}\text{U}$ and $^{238}\text{U}$ resulting from the alpha-recoil effects and preferential leaching. Shirvington has inferred the important role of $^{234}\text{Th}$ in $^{234}\text{U}/^{238}\text{U}$ fractionation\(^{12}\). Thorium-234 is a daughter nuclide of $^{238}\text{U}$ and Th is much more strongly adsorbed to materials such as clay minerals than U. If water containing $^{238}\text{U}$ flows into a rock, almost all the $^{234}\text{Th}$ decayed from the $^{238}\text{U}$, is adsorbed onto clay minerals and iron minerals while some of the $^{238}\text{U}$ continues to be transported by groundwater. The $^{234}\text{Th}$ then decays to $^{234}\text{U}$. Some of the $^{234}\text{U}$ may remain adsorbed onto the clay minerals and iron minerals, and some of the $^{234}\text{U}$ may be incorporated into the crystallographic sites of the clay minerals. Thus, the greater mobility of $^{238}\text{U}$, which accounts for the distributions of the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ ARs shown in Fig. 1, may be explained. Further work to investigate the relationships between the migration behavior of the uranium series nuclides and the minerals is under way.
CONCLUSIONS

The present study of alteration and the migration behavior of uranium series nuclides has led to the following conclusions:

The distributions of the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratios in the surface, intermediate and deep layers, indicate that the migration behavior of the uranium series nuclides differs between depths.

The relationship between the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ activity ratios along the surface, intermediate and deep layers reveals that the mobility of the nuclides is in the order of $^{238}\text{U}$, $^{234}\text{U}$, and $^{230}\text{Th}$, and that the retardation factors of $^{234}\text{U}$ are greater than those of $^{238}\text{U}$ by a factor of 1.1, 1.9, and 1 in the surface, intermediate, and deep layers, respectively.

The difference in the migration behavior of the nuclides between depths may be related to the different mineral assemblages identified by X-ray diffraction analysis.

REFERENCES


Use reference to previous Section in Annual Report by Murakami + Isobe


Fig. 1  (a) Section used for the present study. Shaded area is a high uranium concentration area (approximately corresponding to the ore deposits).

(b) Contour map of $^{234}\text{U}/^{238}\text{U}$ ARs.

(c) Contour map of $^{230}\text{Th}/^{234}\text{U}$.

Fig. 2 Variation of $^{230}\text{Th}/^{234}\text{U}$ ARs against distance along the (a) surface, (b) intermediate, and (c) deep layers. Leaching zones are shown by I and III, and deposition zones, by II and IV.

Fig. 3 Relationships between $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ARs along the (a) surface and (b) intermediate layers.

Fig. 4 X-ray diffraction patterns of the samples from the (a) surface, (b) intermediate, (c) deep layers.
Fig. 1 (a) Section used for the present study. Shaded area is a high uranium concentration area (approximately corresponding to the ore deposits).
(b) Contour map of $^{234}\text{U}/^{238}\text{U}$ ARs.
(c) Contour map of $^{230}\text{Th}/^{232}\text{U}$. 
Fig. 2 Variation of $^{230}$Th/$^{234}$U ARs against distance along the (a) surface, (b) intermediate, and (c) deep layers. Leaching zones are shown by I and III, and deposition zones, by II and IV.

Fig. 3 Relationships between $^{234}$U/$^{238}$U and $^{230}$Th/$^{238}$U ARs along the (a) surface and (b) intermediate layers.
Fig. 4 X-ray diffraction patterns of the samples from the (a) surface, (b) intermediate, (c) deep layers.
IntRODUCTION

Transuranic elements are a major concern for the disposal of high level radioactive waste because of their long-lasting (tens of millions of years) hazard. If we consider radionuclide migration over the above period, the host rocks cannot be static, but are dynamic. The rock-forming minerals will be changed structurally and chemically with time by the water-rock interaction, so-called alteration. The authigenic or secondary minerals formed by the alteration are usually metastable. The attainment of equilibrium may be delayed by as much as $10^7$ years, longer than the time required for the safety assessment of high level waste disposal. The relationships between the alteration and transuranic elements are characterized by reactions, especially, adsorption and desorption of transuranic elements to the then co-existent minerals, which vary with time owing to the alteration mechanism and kinetics. This suggests that the retardation of transuranic elements will also vary with time, that is, with the co-existent minerals. Knowledge of the alteration mechanism and kinetics is, therefore, essential if we are to understand radionuclide migration over a long, geologic time.

Koongarra provides us with a good testing site in terms of the relevance of the radionuclide migration to alteration. Quartz-chlorite schist, the host rock, has been subjected to alteration. Quartz persists even in the surface while chlorite has been altered to clay minerals and iron minerals in the weathered zone, which is present below the surface for a depth of about 20 m. Uranium is found to be associated with the altered products of chlorite in the downstream of the secondary ore deposit which is located in the weathered zone.

This preliminary report on our work to examine the alteration mechanism and cation redistribution during the alteration in Koongarra work focuses on the relationship between the alteration and uranium distribution.

SAMPLES AND EXPERIMENTAL TECHNIQUES

Thirteen samples were used for the present study. Nine of these were chosen from the DDH3 core, so that we could examine the mineral profile with depth in detail. However, all samples from depths between 4.5 and 47 m along the DDH3 core were initially inspected by the naked eye. Samples located at depths greater than 25.2 m are not generally altered but alteration does occur along fractures in samples between 25.2 and 24.8 m deep. The alteration then gradually extends into the schistosity in samples between 24.8 and 24.1 m deep and the samples are completely altered at depths less than 24.1 m.
A part of the samples were powdered and then centrifuged to obtain fine-grained clay fractions less than 2 μm in size for the identification of clay minerals in the samples by X-ray diffraction analysis (XRD). Each sample was treated with ethylene glycol and heated at 450 and 600°C to distinguish one clay mineral species from another. The textures of the samples were examined by optical microscopy (OM) and scanning electron microscopy (SEM), and their compositions, by electron microprobe analysis (EMPA).

RESULTS AND DISCUSSION

A series of XRD patterns of the clay fractions in the DDH 3 samples indicate the possible existence of chlorite, vermiculite, mica, smectite, and kaolinite for all specimens. On the basis of the criteria used to identify the clay minerals\textsuperscript{[1]}, the XRD studies are well summarized; the alteration of chlorite occurs as a function of depth; chlorite is transformed to vermiculite through regularly interstratified chlorite/vermiculite; vermiculite is converted to kaolinite and probably smectite; an iron mineral, possibly ferrihydrite, is formed during the alteration; and goethite and hematite are found in the weathered zone.

The chlorite in the first alteration stage is indicated by its change in color from green to brown, which is due to oxidation of Fe\textsuperscript{2+}. Such grains of altered chlorite, showing a layer texture in SEM images, consist of slabs of chlorite and vermiculite 1 μm thick. Between the slabs an iron phase (possibly ferrihydrite), distinguished by the whitest contrast, occurs as a short slab. The layer texture suggests that the crystallographic orientation of the chlorite structure is retained during the transformation of chlorite to vermiculite. The occurrence of the iron phase reveals that Fe reprecipitation takes place out of the original chlorite during the transformation.

The chlorite compositions are rather consistent; MgO, 9-12; Al\textsubscript{2}O\textsubscript{3}, 15-19; SiO\textsubscript{2}, 24-27; and FeO, 26-34 (in wt%). The chlorite compositions in the present study are lower in Mg and higher in Fe than that given by Gray and Davey\textsuperscript{[2]}. Higher Fe content in chlorite may cause faster vermiculitization because of greater charge imbalance and/or structural distortion owing to the Fe oxidation. This suggestion accounts for the narrow zone (1 m thick) of co-existed chlorite and vermiculite below the weathered zone. The decrease of iron during the transformation from chlorite to vermiculite is remarkable while the decrease of Si, Al, and Mg is much smaller. On the other hand, Ti and K, which are rarely contained in chlorite, are accommodated in vermiculite. If we use average compositions of chlorite and
vermiculite to express the reaction from chlorite to vermiculite, the following reaction equation can be written:

\[
(\text{Chlorite}) \\
(\text{Vermiculite}) \\
(\text{Ferrihydrite?})
\]

During the transformation, excess Fe forms possibly ferrihydrite around vermiculite, which is perfectly consistent with the SEM observation. K and Ti, required to form vermiculite, may be released from mica and anatase of the quartz-chlorite schist, respectively. Excess of Mg, Si, and Al may be consumed in the formation of kaolinite and possibly smectite. Additional Fe, Mg, Si, and Al are released during the decomposition of vermiculite, and these may be used again for the formation of ferrihydrite, kaolinite, and smectite. The layered texture of altered chlorite and the similar crystal structures of chlorite and vermiculite suggest that the formation of vermiculite from chlorite may be explained by cation diffusion. However, we have not found any evidence in the SEM images of textural relationships between kaolinite and chlorite or vermiculite and there is a difference in crystal structure between them. This suggests that the formation of kaolinite may be by dissolution and reprecipitation.

It is possible, on the basis of the XRD intensities to qualitatively estimate the abundances of the minerals as a function of depth. Figure 1 schematically compares the uranium concentrates and mineral abundances in drill hole DDH3. The amount of chlorite, which is not altered even at 111 feet (25.9 m deep from the surface vertically), rapidly decreases between 107 and 103 feet (25 and 24 m deep) and chlorite disappears at 103 feet. Vermiculite appears at 107 feet (25 m deep) and is at a maximum at 103 feet (24 m deep) where kaolinite begins to persist. Vermiculite disappears at 86 feet (20 m deep) where kaolinite is predominant as it is in the shallower zone.

The mineral abundances were then compared to the uranium concentrations in ppm along the DDH3 corehole. The comparison indicates that the mineral abundances of chlorite, vermiculite, and kaolinite (smectite) are closely related to the uranium concentrations. The chlorite predominant zone corresponds to the zone of lower U concentrations, the vermiculite predominant zone, to the zone of intermediate U concentrations, and the kaolinite predominant zone, to the zone of highest U concentrations Figure 1). The crystal chemistry of chlorite and its altered minerals may well account for this close relationship.
In any of the minerals, large cations like U cannot be accommodated in the tetrahedral or octahedral sites. Because the chlorite structure has little capacity for large cations in the interlayers, large cations are not accommodated. However, large cations can easily enter the interlayers of vermiculite, hence after the initiation of chlorite alteration U is accommodated in the interlayers. Because ferrihydrite or iron phases, which occur as interstitial materials between vermiculite and chlorite slabs, are adsorbents, it is also possible for U to be adsorbed onto them during the transformation. The kaolinite structure, like that of chlorite, only allows a very limited number of large cations to enter. Therefore, in the kaolinite zone, U is associated with iron phases, ferrihydrite, goethite, and hematite which are formed with the decomposition of vermiculite and the transformation of chlorite to vermiculite. Smectite has a large space for large cations. However, the amount of smectite is small and its role in the accommodation of U remains unknown.

This is illustrated in Figure 2 where the crystal structures of kaolinite, vermiculite, smectite, and chlorite projected on the (101) plane (modified from Bailey) are compared. In the kaolinite structure, there are no interlayers where larger cations such as potassium, uranium can be accommodated. Although the chlorite structure has interlayers, they are occupied with (Mg, Fe, Al) octahedral layers, which leaves little space for large cations. On the other hand, the interlayers of smectite and vermiculite have much greater flexibility; exchangeable cations such as K, Mg are more loosely bound to water molecules. The interlayers of smectite and vermiculite can therefore be possible crystallographic sites for uranium.

REFERENCES


FIGURE 1 Comparison of U concentrations (µg g⁻¹) and mineral abundances in DDH3. The arrows indicate the sampling locations for the XRD measurements.
FIGURE 2 Comparison of the crystal structures of kaolinite, vermiculite, smectite, and chlorite projected on the (101) plane (modified from Bailey\(^3\)).
FIELD TRIPS TO KOONGARRA

Sampling

Rainfall in the Alligator Rivers region occurs during a humid monsoonal wet season from mid November to March or April, whilst relatively dry conditions exist for the remainder of the year. Rainfall intensity is variable during the wet season while June, July, and August usually lack rain. Field trips for groundwater sampling were held during May and November 1988 as these months coincide with the end of the wet (May) and dry (November) seasons. A selection of boreholes throughout the deposit were sampled at two depths (approximately 28 metres and 42 metres). The deeper depth is well into unweathered rock, whereas the shallower depth is in a transition zone near the weathering front. Boreholes sampled in May were resampled in November to investigate possible seasonal variations.

In November 1988, an extensive drilling program was undertaken, and this greatly improved the coverage of the area for groundwater sampling purposes. A total of 22 boreholes were drilled, including several intersecting the primary and secondary mineralisation. Seven new boreholes have water sampling points in the previously unsampled weathered zone (13-15 m depth) and also between 23-25 m. A monthly sampling program of these boreholes commenced in February 1989. A further field trip was undertaken in May 1989 with the main aims being to sample the new boreholes and to collect large volume samples for $^{14}C$, $^{129}I$, $^{99}Tc$ and $^{239}Pu$ analyses.

Field Work

A double packer/pump system has been constructed for water sampling. A feature of this equipment is inflatable packers above and below the pump which define a sampling interval approximately 1.5 m in length. Until the development of this system the depth from which pumped groundwaters originated was unknown.

Groundwater samples obtained at Koongarra alter upon exposure to air, consequently in-line filtration is normally used to obtain filtered water samples. For samples requiring more complex treatment a portable glovebox was designed, which permits operations to be carried out in a N$_2$/CO$_2$ atmosphere. The glovebox has been used for colloid separations and will be used in sampling for sulfide which is very sensitive to oxidation.
The sampling procedure is as follows:

After setting the pump and packers at the required depth, the interval is pumped whilst the pH and conductivity are monitored until constant values are achieved. At this time pH, conductivity and Eh are recorded, and alkalinity is determined by titration with standardised HCl. A portable spectrophotometer is used to determine Fe(II) and S²⁻ levels in samples which have not been exposed to air.

Samples for chemical analysis are normally filtered through a 0.45 μm filter without air contact. The type of bottle and sample treatment are selected as appropriate for each sample.

Samples are taken for the following analyses: uranium, radium, cations (Mg, Ca, K, Na, Fe etc), anions (Cl⁻, SO₄²⁻, F⁻, I⁻), phosphate, total organic carbon and stable isotopes (³H, ¹⁸O).

A sample for thorium analysis is often taken. Thorium isotopes are precipitated from 20 L volume with iron carrier.

Larger volume samples, which are taken when required and flow rates permit, include ¹⁴C (precipitated from 140 L), ¹²⁹I (collected by passing 500-1000 L of groundwater through resin), and ³⁸Cl (precipitated from 20 L). Samples for ²³⁹Pu and ⁹⁹Tc analysis were obtained on the May 1989 field trip.

The pH, conductivity, Eh and alkalinity are usually measured again at the end of sampling.

REVIEW OF RESULTS

Chemistry of Groundwaters Intersecting the Orebody

As an example of this work, the major ion chemistry for borehole PH49, which intersects the primary orebody, is given in Table 1. This borehole has been sampled on several occasions using packers to restrict the source of water; a previous sampling of the unpacked bore is also included in Table 1. As noted above, the compositions given in Table 1 are from the transition and unweathered zones.

The water chemistry is fairly constant, without major seasonal or depth-related variations, and is representative of groundwaters intersecting the orebody. Relatively high levels of Mg²⁺ are present, which corresponds to the abundance of magnesium in the chloritised mine-series rocks which accompany uranium mineralisation. This enrichment of magnesium is characteristic of the four known uranium deposits in the region¹¹. Significant levels of Ca²⁺ are also present in the PH49 samples, particularly from deeper depths. The main anion is bicarbonate (HCO₃⁻) and these groundwaters tend to outgas CO₂ when brought to the surface. The concentration of phosphate, although much smaller than HCO₃⁻ is significant
because of the potential importance of uranyl phosphate complexes in the groundwater and the presence of phosphate-containing secondary uranium minerals in the weathered zone at Koongarra. Dissolved silica is also present.

Redox and pH measurements indicate that dissolved uranium is present in its oxidised U(VI) state, which is more mobile than U(IV).

Trends in Groundwater Chemistry

At the beginning of the ARAP project, all existing chemical data on Koongarra groundwaters was assembled and tabulated. The data was grouped into several zones, each with a characteristic chemistry (Figure 1).

Direct infiltration and the Kombolgie sandstone formation (Zone I, Figure 1) are the sources of groundwater entering the flow system of the deposits. This flow occurs both at depth across the fault and also close to the surface in the weathered zone. The pH of the Kombolgie groundwater is slightly acidic (approximately 5.5-6.0) and the Eh is relatively oxidising. Kombolgie groundwaters moving across the fault zone below the base of weathering have caused in situ alteration of uraninite veins to secondary minerals.

As discussed previously, the groundwaters intersecting the orebody have a distinctive chemistry. Within the orebody (Zone II), the pH is higher, and the conductivity is over twice that of Kombolgie groundwaters.

The flow paths of groundwater down-gradient of the orebody are not yet fully understood. The uranium dispersion fan in the weathered zone appears generally to be towards the south-east, however the groundwaters sampled from Zone VI have a different character to those taken from the orebody. The chemistry of Zone V groundwaters is very similar to Zone II, and this suggests a more southerly direction of groundwater flow. The possibility of movement from Zone II to Zone V is supported by data from pumping tests, and helium levels, as well as uranium and magnesium concentrations.

Several other groundwater zones are shown on Figure 1. Zones IV E and IV W are along the strike of the orebody (east and west respectively), Zone VII is a zone of dolomite with a characteristic groundwater chemistry, and Zone III may be influenced by the presence of the Koongarra No 2 orebody.

In summary, it appears that the sequence of groundwater chemistry relevant to the deposit initially involves a Kombolgie type groundwater moving into the Cahill formation. This leads to the distinct groundwater type found within the orebody. Groundwater flow away from the deposit appears most likely to occur in a southerly direction where groundwater character closely resembles the groundwater of the mineralised zones. Groundwater sampling in the weathered zone is now underway and this will provide a more detailed understanding of groundwater flow at Koongarra.
Concentrations of Uranium and Thorium

Uranium concentrations in filtered groundwater were determined using α-spectrometry for all samples taken on the field trips in 1988. The sample set from November was also analysed using quantitative ICP-MS, which was found to be in excellent agreement with the α-spectrometry results. The range of uranium concentrations was between 0.2 µg/L (PH94) and 270 µg/L (PH49) for samples taken in May 1988.

Slightly elevated uranium concentrations (2-14 µg/L) were found in the two sampled boreholes from geochemical region V which indicated the movement of uranium bearing groundwater in a southerly direction. These two boreholes had higher uranium concentrations than PH94, PH96, PH55 and PH58 which lie to the south-east of the primary ore (range 0.2-2 µg/L).

Samples taken in November had generally lower uranium levels than in May, and the measurements indicated a possible relationship between dissolved uranium and phosphate levels.

The α-spectrometry measurements showed that the measured $^{234}$U/$^{238}$U isotope ratio differed between samples taken at two depths in the same borehole. These results are shown in Figure 2. Of the seven boreholes sampled at two depths, five (PH49, PH55, PH56, PH58 and PH61) had higher isotope ratios at the deeper depth. These boreholes are all in the geochemical Zone II in the immediate vicinity of the orebody. The two exceptions (PH88 and PH94) are both some distance away from the primary ore, in Zones V and VI respectively. Isotope ratios ($^{234}$U/$^{238}$U) below unity are common in the weathered zone of the Koongarra deposit in both accessible mineral phases (as determined by sequential extractions, see Sections 5.8 and 5.9) and in the groundwater.

Measurements of thorium isotopes ($^{232}$Th, $^{230}$Th, $^{228}$Th) by α-spectrometry in 0.45 µm-filtered samples collected during the November 1988 field trip have been completed. The levels of $^{232}$Th were below 0.002 dpm/L and could not be accurately determined. The concentrations of $^{230}$Th were also extremely low (Table 2), and the $^{230}$Th/$^{234}$U ratio showed that $^{230}$Th is far less mobile than $^{234}$U, as would be expected. Considering the tendency of thorium to be associated with particulate rather than dissolved forms, it is probable that the true dissolved level of $^{230}$Th is even lower than reported in Table 2. It seems reasonable to consider $^{230}$Th to be virtually immobile in this system. The data for $^{228}$Th are difficult to interpret due to ingrowth of $^{226}$Th from $^{228}$Ra in the time between sampling and analysis. The significant levels of $^{228}$Th which were measured probably reflect the mobility of $^{228}$Ra in these groundwaters.
Phosphate Analyses

A program to determine phosphate in Koongarra groundwaters has been undertaken on account of the potential importance of uranyl phosphate complexes in uranyl speciation, and the presence of uranyl phosphate minerals in the tail of the dispersion fan at Koongarra. The results indicated that the concentration of phosphate was sufficient to play a major role in uranyl speciation in Koongarra groundwaters. Uranium speciation calculated using the geochemical code MINTEQA2 showed that for many groundwaters compositions representative of Koongarra groundwaters, the uranyl phosphate complex $\text{UO}_2(\text{HPO}_4)^{2-}$ would be the dominant solution phase complex (Table 3). The potential importance of phosphate in uranium mobilisation has therefore been clearly established.

We have also made measurements for copper and total organic carbon levels, as previously reported. At present this data has not been fully assessed. Measurements of redox couples ($\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{SO}_4^{2-}/\text{S}^{2-}$) are also in progress.

SUMMARY

In the period under review, progress has been made in the following areas:

- Packer/pump design and construction.
- Field glove box design and construction.
- Phosphate measurement.
- Thorium levels.
- Uranium levels and isotope ratios.
- Variations with depth.
- Seasonal variations.
- Spatial zones of groundwater chemistry.
- ICP-MS analysis.
- Analyses for several trace groundwater components.
- Geochemical speciation calculations.

Further work to be completed includes:

- Full sampling of newly drilled boreholes.
- Monthly sampling program.
- Further detailed chemical analyses.
- Further shallow sampling in weathered zone.

ACKNOWLEDGEMENTS

The assistance of the NT Department of Mines and Energy, particularly Mr Bob Treloar, in supporting the field trips and carrying out the monthly sampling program; and of Mr D Garton (ANSTO) who designed the field packer/pumps systems and provides technical assistance both in the field and at Lucas Heights is gratefully acknowledged.
REFERENCES


## Table 1

### Chemistry of PH49 Groundwater

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<td>---------------</td>
<td>------------------</td>
<td>------------------</td>
<td>-------------------------</td>
<td></td>
</tr>
<tr>
<td>PH94 (40-42 m)</td>
<td>0.0052</td>
<td>0.25</td>
<td>2.1 x 10^{-2}</td>
<td></td>
</tr>
<tr>
<td>PH61 (43.5-45.5)</td>
<td>0.0024</td>
<td>1.63</td>
<td>1.5 x 10^{-3}</td>
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</tr>
<tr>
<td>PH14</td>
<td>0.0014</td>
<td>11.6</td>
<td>1.2 x 10^{-4}</td>
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<tr>
<td>PH15</td>
<td>0.0034</td>
<td>22.5</td>
<td>1.5 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>PH49 (28-30 m)</td>
<td>0.050</td>
<td>76.5</td>
<td>6.5 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>PH49 (44-46 m)</td>
<td>0.036</td>
<td>105</td>
<td>3.4 x 10^{-4}</td>
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</tr>
</tbody>
</table>

Note that this table only includes boreholes for which U and Th data for 0.45 μm filtered samples (November 1988 field trip) are available.
**TABLE 3**

URANIUM (VI) SPECIATION COMPUTED USING MINTEQA2 FOR GROUNDWATER SAMPLES FROM SELECTED BORES IN THE KOONGARRA REGION

<table>
<thead>
<tr>
<th>Bore No</th>
<th>Depth (metres)</th>
<th>Mg (mg/L)</th>
<th>Total U (μg/L)</th>
<th>Total P (μg/L)</th>
<th>Alkalinity (mg/L CO₂)</th>
<th>pH</th>
<th>UO₂⁺</th>
<th>UO₃⁻</th>
<th>UO₂⁻</th>
<th>UO₃⁻</th>
<th>UO₄⁻</th>
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<tr>
<td>PH49</td>
<td>28-30</td>
<td>26.4</td>
<td>240</td>
<td>310</td>
<td>46.8</td>
<td>6.80</td>
<td>86.8</td>
<td>2.0</td>
<td>10.8</td>
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<tr>
<td>PH55</td>
<td>26-28</td>
<td>17.9</td>
<td>0.47</td>
<td>650</td>
<td>62.2</td>
<td>6.57</td>
<td>98.9</td>
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<td>18.0</td>
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<td>130</td>
<td>74.0</td>
<td>7.03</td>
<td>54.0</td>
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<td>7.17</td>
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<td></td>
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<td>61</td>
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<td>6.42</td>
<td>78.6</td>
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<td>15.8</td>
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<tr>
<td>PH88</td>
<td>28-30</td>
<td>14.1</td>
<td>2.5</td>
<td>110</td>
<td>43.1</td>
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<td>83.7</td>
<td>4.3</td>
<td>11.6</td>
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<tr>
<td>KD1⁺</td>
<td>70.5-72.5</td>
<td>8.9</td>
<td>0.55</td>
<td>10</td>
<td>32.8</td>
<td>6.18</td>
<td>6.3</td>
<td>49.1</td>
<td>43.0</td>
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<tr>
<td>KD1⁺</td>
<td>70.5-72.5</td>
<td>8.9</td>
<td>0.55</td>
<td>5</td>
<td>32.8</td>
<td>6.18</td>
<td>1.7</td>
<td>51.6</td>
<td>45.2</td>
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</tr>
</tbody>
</table>

* Phosphate at detection limit (10 μg/L PO₄).  
† Phosphate at half detection limit.
LOCATION OF OPEN WELLS

KOONGARRA CREEK

KOONGARRA
LOCATION OF OPEN WELLS

FIGURE 1
Figure 2

Change in U234/U238 with depth (May 1988)
INTRODUCTION

PNC has been taking part in the technical area of Sub-project IV, "Colloid and groundwater studies", which focuses on the role of colloids on radionuclide migration. Colloids in groundwater are a significant factor in specifying the chemical form in geochemical processes of solubility-adsorption reactions and have a great influence on the retardation effect in radionuclide migration. Thus, an understanding of the geochemical and physical properties of colloids in groundwater is considered to be important in the evaluation of the radionuclide migration. To identify the significance of colloid transport of radionuclides through the geosphere, the following investigations have been carried out at the Koongarra uranium deposit in Australia in the period to 31 August 1989.

a) To investigate the amount of colloids and to identify the colloid species.
b) To investigate the adsorption of trace elements such as uranium, thorium and Rare Earth Elements (REE) on colloids, which seem to be chemical analogues of actinides.
c) To investigate the chemistry of the groundwater.
d) To investigate the concentration of trace elements in the host rock.
e) To investigate the differences in the colloid characteristics between the weathered and unweathered zones.

FIELD TRIP

PNC participated in the field trips of May 1988 and May 1989. In 1988 five colloid concentrate, filtrate and ultrafiltered samples from PH80, together with five rock samples from the immediate region of the sampling, were taken from the weathered zone of the Koongarra No 1 ore body for analysis. Twelve additional colloid concentrate, filtrate and ultrafiltered samples from four drill holes (M1, M2, M3 and PH49), together with rock samples from DDH65, were taken from the unweathered zone in 1989. These groundwater samples were collected from the aquifer along the secondary ore dispersion fan.
ANALYSES AND RESULTS

To determine the concentration of REE, uranium and thorium, all of the rock and groundwatersamples collected in 1988, Instrumental Neutron Activation Analysis (INAA) was used, whilst bulk composition of rock samples was determined by wet analysis and atomic absorption spectroscopy. In addition, the uranium concentrations and the uranium series activity of the rock samples were determined by wet analysis and alpha spectrometry, respectively.

There were no significant differences detected in the concentrations of the REE, uranium and thorium between the colloid concentrate, the filtrate and the ultrafiltered samples. The concentrations of the REE in the groundwater were extremely low in comparison with the uranium concentration, and consequently the measurement of REEs such as La, Ce and Sm there was interference to the energy dispersion peaks from the fission products of $^{235}\text{U}$ which occurred during the sample activation. Therefore, it is necessary to preseparate the uranium prior to the INAA.

The concentrations of major elements in rock samples show that there are compositional variations especially in Al$_2$O$_3$, Fe$_2$O$_3$, FeO and MgO, and the sample taken from the unweathered zone has a slightly higher value of K$_2$O than the other samples from the weathered zone. The wide compositional variation of major elements might be caused by the degree of weathering. The REE chondrite normalised plots of rock samples clearly show similar patterns for all the samples analyses. The enrichment in light REE relative to heavy REE and the depletion in La and Eu can be seen in the REE patterns. A positive correlation between uranium and total REE concentrations is observed. The activity ratios of the uranium series nuclides for the rock samples show that the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ ratios in the weathered samples are slightly higher than unity. This result can be interpreted on the basis that excess deposition of uranium from solution and then some leaching has taken place.

For the colloid concentrated, groundwater and rock samples collected from unweathered zone in 1989, the following analyses are being undergone -

a) Physical and chemical analysis of four colloid concentrate samples by transmission electron microscopy with X-ray dispersive spectrometry.

b) Trace element analysis of eight filtrate and ultrafiltered groundwater samples by ICP mass spectrometry.

c) Major element analysis of eight filtrate ultrafiltrated groundwater samples by ICP, atomic absorption spectroscopy and wet chemical analysis.

d) Trace element analysis of four rock samples by INAA.

e) Major element analysis of four rock samples by wet chemical analysis.
FURTHER WORKS

In order to evaluate the geochemical and physical properties of the colloids relevant to radionuclide migration, the following factors affecting the role of colloids will have to be investigated -

a) The hydrogeological environment along the secondary dispersion fan such as flow direction and velocity of groundwater.

b) The physico-chemical condition of the groundwater and the characteristics of natural colloids present in the groundwater.

c) The groundwater-host rock interaction and their influence on radionuclide transport.

REFERENCE

SECTION 5.14
GEOCHEMISTRY OF $^{239}$Pu, $^{99}$Tc AND $^{129}$I

J. Fabryka-Martin and D. Curtis
Los Alamos National Laboratory (LANL)


RESEARCH OBJECTIVES

The radionuclides $^{99}$Tc, $^{129}$I and $^{239}$Pu are long lived components of nuclear waste and, in theory, can be mobile in aqueous systems. Hence, they are of concern to those responsible for safety assessment of geological repositories for high level nuclear waste. The overall objective of the LANL program is to test assumptions about the mobility of these radionuclides. Specifically, our program is: (a) to measure concentrations of these radionuclides in different geochemical environments; (b) to compare measured concentrations with those predicted for closed or static systems; and (c) to interpret measured concentrations in terms of retention by the ore, migration in ground water, or retardation down gradient of the ore body. Funding for our research has been provided by ARAP, the U.S. Department of Energy Repository Technology Program, and the U.S. Department of Energy Office of Basic Energy Science.

OVERVIEW OF OUR APPROACH

Measurement of these three radionuclides required development of new analytical techniques for extraction and isolation of each nuclide from the ore matrix. Interpretation of measured concentrations requires measurement of many other sample characteristics in order to model nuclide production rates in a closed system, the baseline against which measured concentrations are compared. These ancillary measurements include neutron production rates, bulk density, mineralogy, elemental composition, and U-Th activity ratios for each sample.

We have focussed on samples from unweathered and unaltered zones in primary ore deposits, i.e., samples that we believe closely approximate systems which are closed with respect to retention of nuclear products. A wide range of uranium contents and ore mineralogies were selected in order to identify factors controlling nuclide production rates and degrees of nuclide retention. In addition to being source terms for radionuclide migration in the ground water, these ores can also be considered as natural analogues of spent fuel. During the next year, we will expand the program to include ore samples from dynamic open systems: specifically, altered or weathered zones of two ore deposits, Koongarra and Pocos de Caldas, and ground waters from Koongarra.
PLUTONIUM-239 ANALYSES OF PRIMARY ORES

Plutonium-239 contents have been measured in ten primary ores. Samples are prepared for mass spectrometric analysis using a microwave to dissolve the ore in a concentrated solution of HF-HNO₃ acids. This novel technique gives quicker and cleaner results than alternative methods. The blank associated with microwave dissolution was 8 x 10⁷ atoms, lower than the value of 3 x 10⁸ atoms associated with alkaline fusion.

Pu-239 concentrations in the ores range from 0.3 to 6 x 10⁹ atoms/g; ²³⁹Pu/U ratios from 0.8 to 5 x 10⁻¹² (See Table 1). Neither set of measurements is correlated with U content. Oklo sample Z9-005, 64% U, has the lowest ²³⁹Pu/U ratio, 8 x 10⁻¹³; and Katanga sample NBL-6, 45% U, has the highest ratio, 5 x 10⁻¹². This lack of correlation agrees with predictions of the Monte Carlo neutron transport code (see section 8), which show that the environment which determines the neutron energy spectra and hence the rate of ²³⁹Pu production is considerably larger than that of a hand specimen. Hence, because of the heterogeneity of most ore bodies, the elemental characterization of a hand specimen will not generally be adequate for predicting ²³⁹Pu production.

IODINE-129 ANALYSES OF PRIMARY ORES

Three suites of ore samples have been processed for ¹²⁹I over the past year and analyzed by accelerator mass spectrometry at the University of Rochester. The first two sets were prepared by alkaline fusion, a standard technique for iodine extraction from rocks which has the advantage of complete dissolution of the ore. However, reproducibility of results was poor, and variably high blanks suggested the presence of ¹²⁹I contamination in the reagents. Blanks ranged from <2 x 10⁸ to 1 x 10⁶ atoms; in some cases, the blanks contained more ¹²⁹I than did the uranium ores. Encouraged by the success of the microwave technique for ²³⁹Pu samples, a modified version of the same method was applied to the uranium ores for ¹²⁹I analysis. The blanks in this case were consistently and negligibly low, averaging 1 x 10⁶ atoms.

Preliminary ¹²⁹I concentrations for the ores range from 0.3 to 9 x 10⁹ atoms/g; ¹²⁹I/U atom ratios range from 0.8 to 8 x 10⁻¹². As in the case of ²³⁹Pu, the highest concentration is obtained for Katanga NBL-6. Measured ¹²⁹I/U atom ratios for ore samples prepared by the microwave technique are considerably lower, by factors of 2-5 in some cases, than those obtained by alkaline fusion. The higher values for the fused samples can probably be attributed to contamination, and experiments are planned to test this conclusion. Assuming that the production rate of ¹²⁹I can be scaled to that of ²³⁹Pu as suggested by our modeling results, then the results thus far suggest that ¹²⁹I is being leached from the Koongarra primary ore to a greater extent than is uranium or ²³⁹Pu.
MEASURED $^{129}$I/I RATIOS IN KOONGARRA GROUNDWATERS

Thus far, $^{129}$I/I results are available for groundwater samples collected in 1983, 1985 and 1986. Samples from the 1988 and 1989 field trips will not be processed until reproducibly low reagent blanks can be obtained. The 1983-86 data clearly demonstrate that $^{129}$I is being lost from some part of the ore body to a great extent, probably during weathering of the primary ore. In water from PH49 intersecting the primary ore body, $^{129}$I/I ratios are higher by three orders of magnitude over background levels. Down gradient, $^{129}$I/I ratios in groundwater are lower than that in PH49 by factors of 2 to 7 but are still far above background (See Figure 1). The down gradient decrease is not systematic with distance from the ore body. The decrease probably reflects differing extents of dilution with meteoric waters which have not flowed through the deposit rather than evidence for sorptive losses of this radionuclide.

TECHNETIUM-99 ANALYSES OF PRIMARY ORES AND KOONGARRA GROUNDWATER

Thus far, we have measured $^{99}$Tc in one sample from the unweathered primary ore zone, G2698, and in one Koongarra water sample. The atom ratio $^{99}$Tc/U for the ore, $6 \times 10^{-12}$, suggests that $^{99}$Tc is being retained relative to uranium in this part of the deposit because the ratio predicted for a closed system is $1.6 \times 10^{-12}$. On the other hand, the result for PH49 groundwater, 11 atoms/ml, indicates that $^{99}$Tc is being released to the water from some part of the deposit.

As in the case of $^{129}$I, the analyses thus far have been obtained by alkaline peroxide fusion, which gave variably large blanks. Hence, the results have considerably large uncertainties associated with them and should be considered preliminary. We have now developed a procedure using acid dissolution of the ore in a microwave, for which we expect that the blanks will be at least an order of magnitude lower than those obtained by the previous method.

MEASURED $^{36}$Cl/Cl RATIOS IN KOONGARRA GROUNDWATER

Together with $^3$H, measured $^{36}$Cl/Cl ratios in Koongarra ground waters provide a check for the presence of bomb pulse radionuclides in the waters. The presence of bomb pulse nuclides would complicate, if not negate, the use of $^{14}$C for age dating at this site or the interpretation of $^{129}$I, $^{99}$Tc and $^{239}$Pu concentrations in groundwater in terms of migration. $^{36}$Cl/Cl ratios can also be used to constrain the residence time of ground water in the ore deposit.

Thus far, $^{36}$Cl/Cl results are available for samples collected in 1983-86 and 1988. All analyses were by accelerator mass spectrometry, first at the
University of Rochester until 1987 and then at the Australian National University starting in 1988. The 1989 suite of samples are scheduled to be analyzed at ANU during the next quarter.

The $^{36}\text{Cl}/\text{Cl}$ ratio measured for PH61, $1 \times 10^{-13}$, is close to the value predicted for water recharged prior to nuclear testing. This relatively low result confirms the absence of bomb pulse fallout or radionuclides leached from the ore, and supports the selection of this well for determining background concentrations of $^{129}\text{I}$, $^{99}\text{Tc}$ and $^{239}\text{Pu}$.

In the absence of sources other than natural atmospheric $^{36}\text{Cl}$, the relatively young ages of the waters (< 4000 years) indicated by the $^{14}\text{C}$ measurements suggest that the $^{36}\text{Cl}/\text{Cl}$ ratios should be fairly constant throughout the flow system due to insufficient time for $^{36}\text{Cl}$ decay, and this is more or less what one finds for waters nearest the ore body. Ratios in this region are very slightly elevated above background as represented by PH61, which could result from in-situ production of $^{36}\text{Cl}$, either by leaching of $^{36}\text{Cl}$ from the uranium ore or by production within the water itself due to the high neutron flux in the deposit. In either case, the $^{36}\text{Cl}$ data indicate a maximum residence time of water in the primary ore zone on the order of a few thousand years.

Finally, $^{36}\text{Cl}$ data in bores at the down gradient edge of the sampled flow field clearly show the presence of bomb pulse waters (See Figure 2). $^{36}\text{Cl}/\text{Cl}$ ratios in these waters exceed meteoric background levels by factors of 4 to 10, as well as being greater than any waters from the ore body itself. This interpretation of a bomb pulse contribution is consistent with (and less ambiguous than) $^{14}\text{C}$ and tritium analyses.

**PREDICTION OF RADIONUCLIDE CONCENTRATIONS FOR CLOSED SYSTEMS**

Once the nuclide concentrations have been measured, the next step is to compare them to the concentrations expected if the ores had behaved as closed systems with respect to uranium and its products. All of the primary ores being studied have formation ages on the order of 108 years or more, sufficiently old to have allowed secular equilibrium to have been attained. The assumption of undisturbed uranium has been confirmed for each sample by the lack of secondary mineralization in XRD scans and by activity ratios $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ that are essentially 1.0.

Under conditions of secular equilibrium in closed systems, radionuclide concentrations are solely a function of neutron flux and uranium content. For $^{239}\text{Pu}$, the only production mechanism is neutron capture by $^{238}\text{U}$. Fission products $^{99}\text{Tc}$ and $^{129}\text{I}$ are produced by two mechanisms: spontaneous fission of $^{238}\text{U}$, which is of course independent of neutron flux, and neutron induced fission of $^{235}\text{U}$ and $^{238}\text{U}$.

The prediction of production rates, however, is complicated by the need to estimate the neutron flux as a function of energy. We solve this problem by directly measuring the neutron production rate in each ore sample, then by
using a Monte Carlo Neutron/Photon Transport Code (MCNP) to track the fate of these neutrons. A neutron coincidence counter was used to measure the rate of primary neutron production in each sample. Primary neutrons are produced by spontaneous fission of $^{238}$U and by capture of $\alpha$-particles by light nuclei, resulting in neutron emission. In pure uranium metal, only spontaneous fission contributes neutrons, at a measured rate of 0.88 n/min/g $^{238}$U. The relative importance of $(\alpha,n)$ reactions can be seen by comparing this to the rates measured for the ores, which ranged from 1.25 to 1.88 n/min/g $^{238}$U. When normalized to uranium content, the highest rates are seen for those ores with a high clay content, and the lowest rates for those ores hosted by metal sulfides in the absence of clays. This enhancement probably reflects the influence of $\alpha$-targets with larger cross-sections than 0, particularly Mg, Al and Si in the clays.

By combining MCNP calculations with the measured neutron production rates, we have estimated the maximum possible radionuclide concentrations for our samples. In addition, MCNP modeling allows us to identify the critical elemental parameters controlling radionuclide production rates, and to test for expected correlations among product/target radionuclide pairs. Some important conclusions of the modeling are that: a) contrary to common expectations, no correlation should be expected between concentrations of uranium and $^{239}$Pu or $^{129}$I; b) considerable variability should be expected in $^{239}$Pu/U and $^{129}$I/U ratios within a given deposit, due to the effects of elemental heterogeneities on neutron fluxes; c) spontaneous fission of $^{238}$U should account for more than 80% of the total $^{99}$Tc production rate, such that the $^{99}$Tc/U atom ratio predicted for a closed or static system should be fairly constant throughout the Koongarra deposit; and d) the thermal component of neutron fluxes in uranium deposits is probably quite small, with the vast majority of neutrons being absorbed in higher energy ranges. The latter complexity makes it nearly impossible to estimate $^{239}$Pu and $^{129}$I concentrations and correlations by any simplistic calculations.
TABLE 1

$^{239}$Pu CONCENTRATIONS AND $^{239}$Pu/U ATOM RATIOS IN URANIUM
ORES, CORRECTED FOR BACKGROUND

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Z U ID</th>
<th>Date prepared</th>
<th>Total $^{239}$Pu (x $10^8$)</th>
<th>$^{239}$Pu at/g (x $10^8$)</th>
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<td>Koongarra</td>
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<td>G4674</td>
<td>12.2</td>
<td>870303</td>
<td>16.7 ± 3.1</td>
<td>3.34 ± 0.61</td>
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<td></td>
<td>890630</td>
<td>3.81 ± 0.67</td>
<td>3.39 ± 0.60</td>
<td>1.10 ± 0.20</td>
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<td></td>
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<td>6.25 ± 0.85</td>
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<td>1.99 ± 0.29</td>
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<td></td>
<td>890815</td>
<td>20.6 ± 0.7</td>
<td>4.14 ± 0.14</td>
<td>1.34 ± 0.08</td>
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<td>2.33 ± 0.15</td>
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<td>880321</td>
<td>59.5 ± 3.0</td>
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<td>2.57 ± 0.18</td>
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<td>11.3 ± 0.7</td>
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<td>2.30 ± 0.18</td>
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<td>15.2 ± 0.8</td>
<td>3.15 ± 0.22</td>
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<td>CS235L</td>
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<td>138 ± 3</td>
<td>25.8 ± 0.6</td>
<td>1.83 ± 0.10</td>
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<td>890630</td>
<td>23.9 ± 0.7</td>
<td>24.4 ± 0.7</td>
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<td>W83A</td>
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<td>31.3 ± 1.7</td>
<td>31.1 ± 1.7</td>
<td>3.15 ± 0.24</td>
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<td>W83C</td>
<td>46.8</td>
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<td>32.7 ± 0.7</td>
<td>33.4 ± 0.7</td>
<td>2.82 ± 0.15</td>
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<td>NBL-6</td>
<td>44.9</td>
<td>890630</td>
<td>60.0 ± 1.1</td>
<td>59.0 ± 1.1</td>
<td>5.19 ± 0.11</td>
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<tr>
<td></td>
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<td>890815</td>
<td>32.0 ± 0.7</td>
<td>62.9 ± 1.4</td>
<td>5.54 ± 0.14</td>
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<td>Z9-028</td>
<td>65.8</td>
<td>890916</td>
<td>25.1 ± 0.7</td>
<td>47.8 ± 1.3</td>
<td>2.87 ± 0.16</td>
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Notes:

a) All preparations and analyses done at Los Alamos National Laboratory.

b) Sample results are corrected for background as follows: background for fused samples, $3 \pm 3 \times 10^8$ atoms; background for microwaved samples, $7.5 \pm 6.6 \times 10^8$ atoms.

c) The total uncertainty associated with the ratio $^{239}$Pu/U includes 5% uncertainty for uranium concentration, except for NBL-6 for which the estimated uncertainty is 1%.
$^{129}$I/I RATIO $\times 10^{12}$ IN KOONGARRA GROUND WATERS, 1983, 1985 AND 1986

![Diagram of Koongarra Ground Waters with markers for various points and a legend for primary and secondary ore zones.](image)

- **Primary Ore Zone**: PH139, 68 ± 8
- **Secondary Ore Zone**: PH49, 645 ± 106; PH55, 45 ± 5; PH14, 298 ± 22; PH56, 153 ± 9

FIGURE 1
$^{36}\text{Cl}/\text{Cl}$ RATIOS $\times 10^{13}$ IN KOONGARRA GROUND WATERS, 1983, 1985 AND 1988

KOMBOLGIE SANDSTONE  
CAHILL SCHIST  
PRIMARY ORE ZONE

PH55  
1.5 ± 0.2  
2.0 ± 0.2  
1.8 ± 0.2  
2.4 ± 0.2

PH139  
3.9 ± 0.4

PH58  
4.0 ± 0.3

PH94  
17.2 ± 0.2

SECONDARY ORE ZONE

PH61  
1.0 ± 0.1

PH80  
1.9 ± 0.2  
5.0 ± 0.4

PH88 (2 depths)  
5.6 ± 0.4

FIGURE 2
The principal aims of the Alligator Rivers Analogue Project are -

to contribute to the production of reliable and realistic models for radionuclide migration within geological environments relevant to the assessment of the safety of radioactive waste repositories, and
to develop methods of validation of models using a combination of laboratory and field data associated with the Koongarra uranium deposit.

There are several features of the Koongarra ore deposit which make it particularly suitable for such a validation study, and the extensive experimental program to understand significant processes and evaluate the formation of the uranium dispersion fan has provided substantial databases with which it is possible to test flow, geochemical and transport models used for performance assessment studies. These features include:

The deposit has a fairly straightforward geology, with distinct regions of primary, weathered primary and secondary ore zones, and a well defined fan of dispersed uranium associated with weathered schists.

The site is undisturbed, except for exploration drilling.

Large spatial (~ 100 m) and time (~ 1 My) scales are provided in the formation of the uranium dispersion fan.

An extensive hydrogeological database is available.

The base of weathering intersects the ore zone. This provides a basis for estimating the timescales of radionuclide migration since the time of initial mobilization may be assumed to coincide with the onset of weathering.
The origin of the uranium distributed through the dispersion fan is the former upward extension of the primary orebody. Hence the horizontal distance of migration is relatively well defined. The primary ore below the weathering front provides a good indication of the original nature of the mineralization of the present weathered zone.

There is a substantial body of data on the geochemistry of the deposit (including uranium series radionuclides, fission products and transuranic elements) for both groundwater and drillcore samples.

The following factors are also of significance,

Colloidal transport seems relatively unimportant in the system.

Surficial (stormwater) erosion has not caused major radionuclide dispersion.

The movement of uranium and other radionuclides in the dispersion fan therefore appears to be predominantly the result of precipitation/dissolution and adsorption/desorption processes. In principle it should be possible to test various aspects of geochemical models and databases such as rock/water interactions and radionuclide solubility/speciation calculations using the range of groundwater chemistry regimes present at Koongarra; the formation of the various zones of specific secondary uranium minerals; and surface complexation modelling using the results of sorption of uranium to substrates from the leached and deposition zones in the weathered zone.
<table>
<thead>
<tr>
<th>Institution</th>
<th>Research Areas</th>
<th>Principal Investigators</th>
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</thead>
<tbody>
<tr>
<td>ANSTO</td>
<td>Mineralogy/Colloids/Rock U Series</td>
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<td>A Snelling</td>
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<td>D Emerson</td>
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<td>B Treloar</td>
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$^*$ Retired
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