



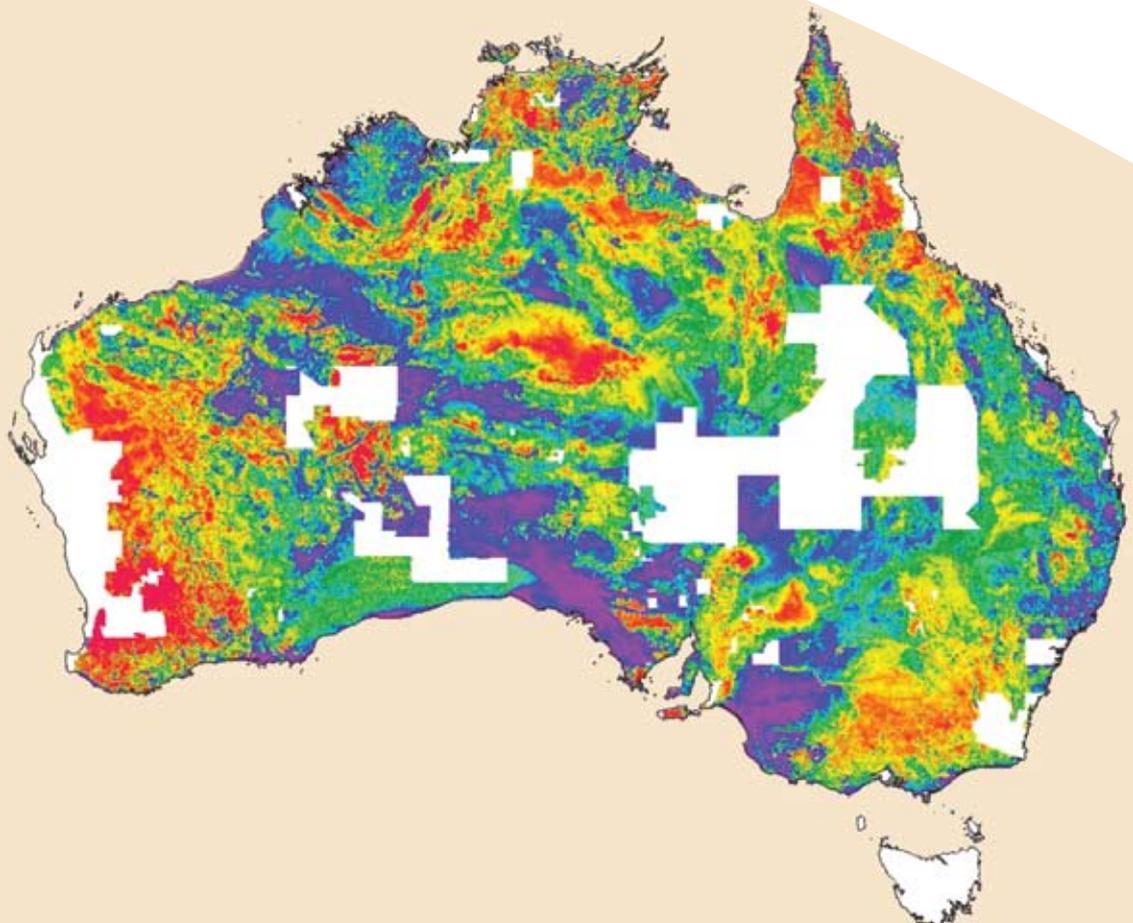
**Australian Government**  
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# A Review of the Geochemical Processes Controlling the Distribution of Thorium in the Earth's Crust and Australia's Thorium Resources

*Terrence P. Mernagh and Yanis Miezitis*

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by

Terrence P. Mernagh<sup>1</sup> and Yanis Miezitis<sup>1</sup>



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**Geoscience Australia**

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Cover Illustration: Image of Geoscience Australia's currently available radiometric data for thorium across the Australian continent with purple/blue regions corresponding to the lowest thorium values and red regions corresponding to the highest thorium values.

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## Executive Summary

Thorium is a naturally occurring radioactive element which is found in the Earth mainly in oxides, silicates, carbonates and phosphates. Thorium exists almost entirely as  $^{232}\text{Th}$  which has a half-life of 14,050 million years. From its natural state,  $^{232}\text{Th}$  decays through a number of stages to eventually form  $^{208}\text{Pb}$ , which is stable.

Thorium occurs in nature either within minerals or as a tetravalent ion. The large, highly charged  $\text{Th}^{4+}$  ion has a marked tendency to form complex ions in solution. The major ones of interest are the complex chloride ions, the complex fluoride ions, the complex nitrate ions, the complex sulphate ions and the complex carbonate ions. In addition there are a number of hydroxide complexes, silicate complexes, phosphate complexes, various citrate, oxalate, tartrate, and acetate complexes and numerous chelate and other organic complexes of thorium, all of which render the element relatively soluble (and mobile) under certain natural conditions.

Thorium and uranium are chemically similar due to the similarities in ionic size and bond character of these elements. This explains why they tend to occur together in igneous rocks and hydrothermal ore deposits that form at high temperature. However, in the surficial environment, uranium is chemically more mobile. This is due to the limited stability of  $\text{Th}^{4+}$  complexes, especially those with carbonate, and the marked insolubility of  $\text{Th}^{4+}$  salts, compared with those of  $\text{U}^{4+}$  and  $\text{U}^{6+}$  at low temperatures.

The average abundance of thorium in the Earth's crust is about 5.6 ppm, but thorium is highly enriched in the upper crust with an average concentration of 10.5 ppm, while the middle crust has an average of 6.5 ppm, and the lower crust an average of 1.2 ppm. The most important thorium minerals are monazite, thorianite, thorite, and thoregummite. Other minerals that contain lesser amounts of thorium are allanite, bastnäsite, pyrochlore, xenotime, fluorapatite and zircon. Many of the thorium-bearing minerals are remarkably resistant to oxidation and tend to become enriched in the oxidised zones of mineral deposits.

Thorium occurs in a large variety of rock and deposit types as follows:

- Placer deposits of which heavy mineral sands are the most important Australian source of thorium.
- Carbonatites (e.g. Mount Weld, Cummins Range and Mud Tank).
- Alkaline and peralkaline igneous complexes (e.g. the Brockman deposit, Yangibana ironstones, Toongi, and the Narraburra Complex).
- Granites (e.g. Yilgarn craton, Arunta region, and Crockers Well).
- Pegmatites (e.g. Greenbushes, the Entia pegmatite field, and Wodgina).
- Iron oxide copper-gold-(uranium) deposits (e.g. Olympic Dam, Ernest Henry, Mt Painter)
- Thorium-bearing veins and lodes (e.g. Nolans Bore, the Peaked Hill Shear Zone, Pine Hill, and the West Bore Shear Zone near Alice Springs).
- Pitchblende (uraninite) veins, lodes, and disseminated bodies in or near major faults, shear zones, or unconformities (e.g. Rum Jungle, the Alligator Rivers, and South Alligator Rivers uranium fields).
- Pyritic quartz-pebble conglomerates (e.g. Witwatersrand and the Blind River-Elliot Lake deposits).
- Skarns and hornfels deposits (e.g. the Mary Kathleen deposit).
- Phosphates (e.g. the Georgina Basin, northern Australia).
- Coal, peat, and carbonaceous material.

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Most of the known thorium resources in Australia are held in the monazite component of heavy mineral sand deposits, which are mined for their ilmenite, rutile, leucoxene and zircon content. Australia's monazite resources are estimated to be of the order of 5.2 million tonnes. Therefore, assuming an average thorium content in monazite of about 7%, Australia's thorium resources in heavy mineral sand deposits could amount to about 364,000 tonnes. Other significant sources of thorium include the Nolans Bore rare earth phosphate uranium deposit, which is in fluorapatite veins and dykes (with about 53,300 tonnes of thorium) and the Toongi zirconia project (with about 35,000 tonnes of thorium).

## Introduction

Consumption of thorium in non-energy applications occurs mainly in chemical catalysts, lighting, and welding electrodes. Worldwide thorium consumption is very small and is estimated at a few hundred tonnes annually (OECD/NEA & IAEA, 2006a). The production of thorium from rare earth bearing minerals continues to create an oversupply of thorium. Because of the cost of disposal of thorium bearing products, non-radioactive substitutes are being developed for the limited thorium applications resulting in depressed demand for thorium (Hedrick, 2007).

The main factors generating current interest in thorium resources are

- its possible use as fuel in nuclear reactors in place of a perceived shortage of cheap uranium, and
- the thorium fuel cycle produces much less plutonium and other transuranic elements, compared with uranium fuel cycles and is considered by some to present less problems in waste disposal and to be more proliferation resistant than uranium fuelled reactors.

Thorium can be used as a nuclear fuel, through breeding to  $^{233}\text{U}$ . Several reactor concepts based on thorium fuel cycles are under consideration, but much development work is still required before the thorium fuel cycles can be commercialised. India is currently testing components for a 300 MWe (Megawatt electric) technology demonstrator thorium-fuelled reactor and may commence construction some time during the period 2007 to 2012.

A collaborative research program involving Moscow's Kurchatov Institute and the US company Thorium Power (with some additional funding from the US government) is aimed at developing thorium-uranium fuel for the existing Russian Vodo-Vodyanoi Energetichesky (VVER)-1000 reactors. At one stage the program was planned for the disposal of weapons grade plutonium by using it as Th-plutonium fuel. Whereas normal fuel uses enriched uranium oxide, the new design has a demountable centre portion and blanket arrangement, with plutonium fuel in the centre and the Th (with uranium) around it. The  $^{232}\text{Th}$  becomes  $^{233}\text{U}$ , which is fissile - as is the core  $^{239}\text{Pu}$ . The blanket material remains in the reactor for 9 years but the centre portion is burned for only three years (as in a normal VVER) (World Nuclear Association Information Paper – Thorium, May 2007 <http://www.world-nuclear.org/info/info.html> ).

Thorium Power (of the US) and Red Star (a nuclear design agency owned by the Russian government) have signed an agreement for Thorium Power's 'seed and blanket' fuel designs to undergo irradiation testing with the goal of moving towards use in commercial reactors (World Nuclear News, 20 April 2007). Thorium Power recently announced the successful completion of three years of testing of experimental thorium fuel rods. Thorium Power is planning further testing to qualify the fuel for widespread use – first in VVERs, then in other current light water reactors. The research program is on track for deployment of lead test assemblies within 3 years.

According to Thorium Power, the fuel could stay in a reactor longer (parts of fuel assemblies could remain in a reactor for three or even nine years) and therefore more of the highly-radioactive actinides produced by fission are 'burnt'. Because of this, there is a 50% reduction in waste volume and 90% reduction in waste toxicity with waste storage time reduced to between 100 and 800 years (personal communication Dr A. Mushakov, Thorium Power Limited, October 2007).

In the latest developments, Thorium Power Ltd are shifting their emphasis towards adoption of their thorium fuel designs in commercial reactors in the US. They are developing two primary fuel designs for commercial applications that have similar thorium-uranium blanket but different seed: (1) U-Zr seed, and (2) Reactor-grade Pu-Zr seed. The third design with weapons-grade Pu-Zr seed is intended for US-Russia government programs relating to excess WG Pu disposition. Thorium Power are currently focusing on the first two designs for commercial applications. Of those two designs, the U-Zr seed design is intended for countries that already have operating light water

reactors as well as currently non-nuclear countries that would like to pursue peaceful nuclear power and could benefit from enhanced proliferation resistance, reduced volume and long-term radio-toxicity of spent fuel, and improved fuel cycle economics. The RG Pu-Zr seed design is intended only for those countries that already have stockpiles of separated RG Pu or have adopted a policy of reprocessing spent fuel that generates additional stockpiles of RG Pu (i.e., primarily EU countries and Japan) (personal communication Dr A. Mushakov, Thorium Power Limited, December 2007).

### **AUSTRALIA'S THORIUM RESOURCES IN WORLD CONTEXT**

The Organisation for Economic Co-operation and Development (OECD), which includes the Nuclear Energy Agency (NEA) and the International Atomic Energy Agency (IAEA) have reported estimates of thorium resources on a country-by-country basis (OECD/NEA & IAEA, 2006a). The report notes that the estimates are subjective due to variability in the quality of the data, a lot of which is old and incomplete. Table 1 has been derived by Geoscience Australia from information presented in the OECD/NEA & IAEA analysis; the total identified resources refer to Reasonably Assured Resources plus Inferred Resources recoverable at less than US\$80/kg Th. Table 1 also shows quantitative estimates that have been made of undiscovered thorium resources for some countries. Australia currently accounts for about 18% of the world's thorium resources followed by United States (16%), Turkey (13.8%) and India with (12.8%).

**Table 1.** Estimated thorium resources by country

Country	Total Identified Thorium Resources ( <sup>'000 t Th</sup> ) <USD 80/kg Th		Undiscovered Resources ( <sup>'000 t Th</sup> )
		%	
Australia	452	18.1	Not available
United States	400	16.0	274
Turkey	344	13.8	400 - 500
India	319	12.8	Not available
Venezuela	300	12.0	Not available
Brazil	221	8.9	329 - 700
Norway	132	5.3	132
Egypt	100	4.0	280
Russian Federation	75	3.0	Not available
Greenland	54	2.2	32
Canada	44	1.8	128
South Africa	18	0.7	130
Others	33	1.3	81
<b>TOTAL</b>	<b>2492</b>	<b>99.9</b>	<b>1786 - 2257</b>

*Sources: Data for Australia compiled by Geoscience Australia; estimates for all other countries are from OECD/NEA & IAEA, 2006b.*

### **WORLDWIDE DISTRIBUTION OF RESOURCES BY DEPOSIT TYPE**

OECD/NEA & IAEA (2006a) have grouped thorium resources according to four main types of deposits as shown in Table 2. Thorium resources worldwide appear to be moderately concentrated in the carbonatite type deposits accounting for about 30% of the world total. The remaining thorium resources are more evenly spread across the other three deposit types in decreasing order of abundance in the placers, vein type deposits, and alkaline rocks.

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**Table 2** World and Australia's thorium resources according to deposit type (modified after OECD/NEA & IAEA 2006a)

World Deposits			Australian Deposits	
Major Deposit Type	Resources (1000 t Th)	Percentage of World Resources	Resources (1000 t Th)	Percentage of Australian Resources
Carbonatite	1,900	31.3	No data	-
Placer deposits	1,524	24.6	364	80.5
Vein-type deposits	1,353	21.4	53	11.7
Alkaline rocks	1,155	18.4	35	7.7
Other	258	4.2	No data	-
<b>Total</b>	<b>6,190</b>	<b>100.1</b>	<b>452</b>	<b>99.9</b>

In Australia, a larger proportion of the known thorium resources are located in placers where the heavy mineral sand deposits account for about 80% of the known thorium resources. The reason for more thorium resources being reported in the placers in Australia is probably due to the greater amount of data being generated by the active heavy mineral sand mining industry in Australia compared to the lack of analyses for thorium of the other types of deposits. Even for deposits where thorium resources have been assessed, the results have not been well publicised since thorium is not considered to have economic significance.

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# Part 1 – Geochemical Processes Controlling the Distribution of Thorium in the Earth's Crust

## GENERAL CHEMISTRY

Thorium (Th), with atomic number 90, is the second element in the actinide series. Thorium has six natural isotopes of which the most abundant and longest lived is  $^{232}\text{Th}$ . This isotope, the first member of the natural radioactive series  $4n$  decays in a series of steps to ultimately yield  $^{208}\text{Pb}$  (Table 3). Only two long-lived isotopes occur in nature. The major one is  $^{232}\text{Th}$  with an abundance of more than 99.99% and a half-life of  $1.405 \times 10^{10}$  years. The isotope  $^{232}\text{Th}$  is of particular interest as it can absorb slow neutrons and is converted to  $^{233}\text{U}$ , which in turn is fissionable by slow neutrons and is thus utilisable as a nuclear fuel in breeder reactors. The other important natural isotope of thorium  $^{230}\text{Th}$  is generally present in minerals that contain uranium and has a half life of 80,000 years. Thorium isotopes 227, 228, 230, 231, and 234 are short lived nuclides which are members of the  $^{235}\text{U}$ ,  $^{238}\text{U}$ , and  $^{232}\text{Th}$  decay series (Wedepohl, 1978).

Thorium belongs to the series of actinide elements, which are characterised by an incomplete  $5f$  shell. It is markedly oxyphile in nature, occurring mainly as oxides, silicates, and phosphates. It also has a biophile tendency and is found in various organisms, and under certain conditions, can be concentrated in organic compounds such as humus, coal, petroleum, bitumen, and pyrobitumen. Three positive oxidation states are possible for thorium, 2, 3, and 4, but the tetravalent state is of principal importance in geochemistry (Boyle, 1982).

**Table 3:** The thorium ( $4n$ ) decay series (modified from Boyle, 1982).

RADIOELEMENT	NUCLIDE	ATOMIC NUMBER	TYPE OF DECAY (RADIATION)	HALF-LIFE
Thorium	$^{232}\text{Th}$	90	$\alpha$	$1.405 \times 10^{10}$ years
↓				
Mesothorium 1	$^{228}\text{Ra}$	88	$\beta^-$	6.7 years
↓				
Mesothorium 2	$^{228}\text{Ac}$	89	$\beta^-, \gamma$	6.13 hours
↓				
Radiothorium	$^{228}\text{Th}$	90	$\alpha$	1.91 years
↓				
Thorium X	$^{224}\text{Ra}$	88	$\alpha$	3.64 days
↓				
Thoron	$^{220}\text{Rn}$	86	$\alpha$	55.3 seconds
↓				
Thorium A	$^{216}\text{Po}$	84	$\alpha, \beta^-$	0.158 seconds
↓				
Thorium B	$^{212}\text{Pb}$	82	$\beta^-, \gamma$	10.64 hours
↓				
Thorium C	$^{212}\text{Bi}$	83	$\beta^-, \alpha, \gamma$	60.5 minutes
↓				
<div style="display: flex; justify-content: space-around;"> <span><math>\beta^-</math> 64%</span> <span><math>\alpha</math> 36%</span> </div>				
Thorium C'	$^{212}\text{Po}$	84	$\alpha$	$3.04 \times 10^{-7}$ sec
↓				
Thorium C''	$^{208}\text{Tl}$	81	$\beta^-, \gamma$	3.1 minutes
↓				
Thorium D	$^{208}\text{Pb}$	82	stable	

## **THORIUM ABUNDANCE ON EARTH**

The true average abundance of thorium in the Earth may never be precisely known but its abundance has been measured extensively at the Earth's surface and interpreted for the Earth's interior from indirect evidence. The three main sources of data are:

1. Chemical and radiometric analysis of meteorites interpreted to be representative of different Earth layers,
2. Chemical and radiometric analysis of surficial rocks, and
3. Estimation of values for the Earth's interior from heat-flow and rock-conductivity data.

The principal division of the Earth into core, mantle, and crust is the result of two fundamental processes:

- (i) The formation of a metal core very early in the history of the Earth. Core formation was complete at ~30 million years after the beginning of the solar system (Kleine et al., 2002).
- (ii) The formation of the continental crust by partial melting of the silicate mantle. This process has continued with variable intensity throughout the history of the Earth.

### **The Mantle**

The composition of the primitive mantle has been estimated from chondritic meteorites (i.e. meteorites with chemical compositions essentially equivalent to the average solar system composition). Alternatively, the mantle composition has been reconstructed by mixing appropriate fractions of basalts (i.e. partial melts from the mantle) and peridotites (the presumed residues from the partial melts) or it has been calculated from trends in the chemistry of depleted mantle rocks. The concentration of thorium in the primitive mantle has been estimated to be 29.8 ppb (as derived from chondritic meteorites) or 83.4 ppb (as derived by Palme and O'Neill, 2004).

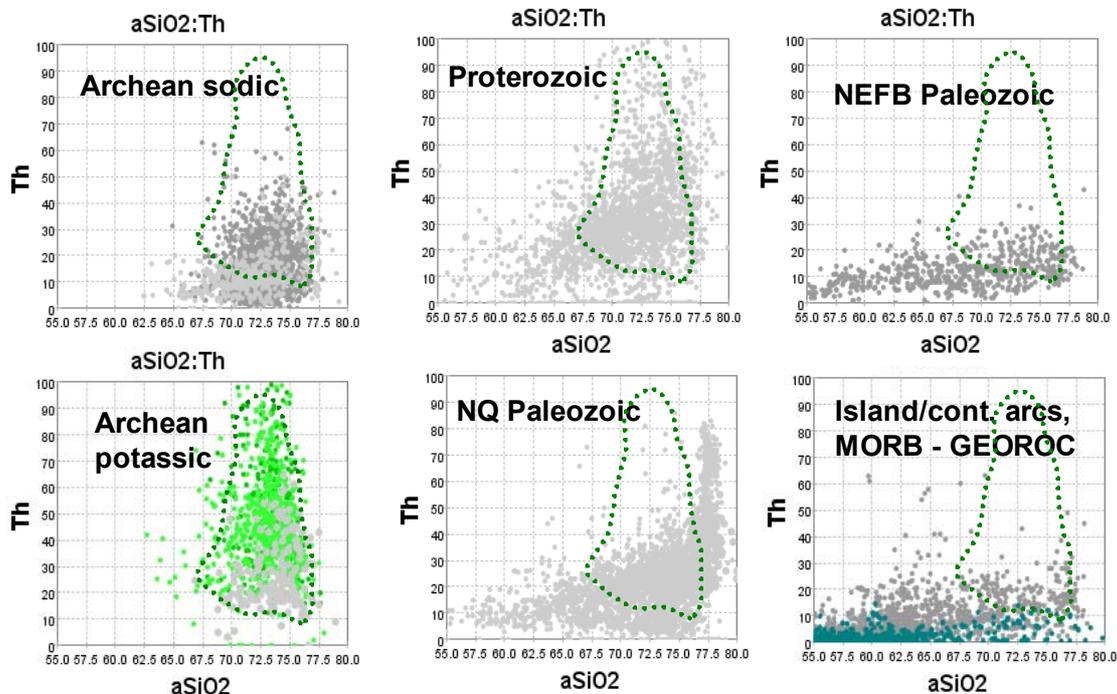
A large majority of the mantle (~70%) is made of magnesium perovskite, which has great potential for fractionating elements. It is interesting to note that calcium perovskite [ $\text{CaSiO}_3$ ], which is also expected to exist in the mantle, has enormous storage potential for lithophile elements. Its ability to host thorium and uranium make it an especially important phase to understand with respect to long-term storage of these elements in the deep Earth (Righter, 2004).

### **The Crust**

Two distinct types of crust are present on the Earth. The low-lying oceanic crust is thin (~7 km on average). It is composed of relatively dense rock types such as basalt and is young ( $\leq 200$  Ma). In contrast, the high-standing continental crust is thick (~40 km on average). It is composed of highly diverse lithologies (virtually every rock type known on Earth) and contains the oldest rocks and minerals observed on Earth (currently the 4.0 Ga Acasta gneisses (Bowring and Williams, 1999) and 4.4 Ga detrital zircons from the Yilgarn Block, Western Australia (Wilde et al., 2001)), respectively. The abundances of thorium, uranium and potassium for some terrestrial rocks are given in [Table 4](#).

Based on seismic investigations the crust can be divided into three regions: upper, middle and lower continental crust. The current consensus is that the modern Earth's continental crust has a bulk andesitic composition (~61 %  $\text{SiO}_2$ ) but is lithologically and chemically stratified, such that a mafic lower crust depleted in granitic components underlies and evolved middle and upper crust (Kemp and Hawkesworth, 2004).

Continental rocks are highly differentiated, and so the crust is enriched in incompatible components compared to the mantle. The average abundance of thorium in the Earth's crust is about 5.6 ppm, but thorium is highly enriched in the upper crust with an average concentration of 10.5 ppm, while the middle crust has an average of 6.5 ppm, and the lower crust an average of 1.2 ppm (Rudnick and Gao, 2004). Lambert and Heier (1967) obtained an average thorium concentration of 2 ppm from pyroxene granulite subfacies rocks from the Australian shield and this correlates well with the more recent estimation for the lower crust by Rudnick and Gao (2004). More recently, Champion and Smithies (2007) have compared the Th concentrations in granites from different Australian provinces and world-wide island and continental arcs. They noted particularly high concentrations of Th in mid-late Archaean, Proterozoic and most Palaeozoic granites of Australia (Figure 1). All these elevated Th concentrations represent the results of crustal recycling coupled with fractionation and illustrate the importance role of pre-existing continental crust in producing elevated Th concentrations in granitic rocks.



**Figure 1:** The evolution of Th through time as indicated by  $aSiO_2:Th$  plots for various Australian granites and world-wide island and continental arc rocks (the latter are from the GEOROC database <http://georoc.mpch-mainz.gwdg.de/georoc/>). NEFB = New England Fold Belt, NQ = North Queensland, MORB = Mid-Ocean Ridge Basalt. The green dotted polygon compares the results for Archaean potassic granites with the other analyses.  $aSiO_2$  refers to anhydrous  $SiO_2$ , i.e. the percentage of  $SiO_2$  neglects any water in the samples as this would be very minor anyway (Figure taken from Champion and Smithies, 2007).

The above data indicate a strong fractionation of thorium into the more siliceous material, which equates with the Earth's middle and upper crust. Thorium is enriched in the lower crust by 15 – 40 times compared to primitive mantle Th concentrations and is further enriched by up to 350 times in the upper crust. It is unusual that a heavy element such as Th should fractionate with the light silicates in the crust rather than with other heavy metals in the core. However, one possible cause may be its large ionic size.

**Table 4:** Radioelement abundances in terrestrial rocks. (Modified from Boyle, 1982 and Gabelman, 1977)

CHEMICAL ANALYSES				INTERPRETATION		
Average Rock	Average Abundance			Earth Layer		
	Th ppm	U ppm	K %			
Arenites	5	1.5	1.8	Sedimentary Cover	Upper Crust	Crust
Lutites (shales)	12	4.2	2.5			
Carbonaceous shales	11.5	53				
Limestone	1.2	1.9	0.63			
Evaporites	0.2	0.1				
Tuffs	6	3				
Granite - Rhyolite	15	4.5	2.75	Continental Basement	Upper Crust	Crust
Phonolite, nepheline syenite	17.1	6.5	5.78			
Latite, rhyodacite, granodiorite	11.0		2.53			
Metamorphic basement	10.9	3.5	2.66			
Alkali basalt	4.6	0.99	0.61			
Plateau basalt	1.96	0.53	0.61	Lower Crust	Upper Crust	Crust
Gabbro	3.84	0.84	0.58			
Basement amphibolite	5.0	2.3	0.91			
Basement granulite	21.0	0.5		Continental Margin	Upper Crust	Crust
Andesite	1.90	0.79	1.7			
Alkali olivine basalt	3.90	0.53	0.57	Oceanic Crust	Upper Crust	Crust
Tholeiitic basalt	0.50	0.14	0.65			
Spilite	0.26	0.22				
Dunite			716 ppm	Upper Mantle	Upper Crust	Crust
Peridotite	0.05	0.01	225 ppm			

#### **MECHANISMS OF THORIUM TRANSFER TO THE CRUST**

In simplified terms, the continental crust has grown magmatically, directly from the underlying mantle, and by the tectonic accretion of thicker portions of oceanic crust, such as island arcs or ocean plateaus. However, these materials are predominantly basaltic, whereas the continental crust is andesitic, and neither most andesites, nor the large complement of silicic igneous rocks of the Earth's crust, can be extracted directly from a peridotitic source. Therefore, crust formation must occur in at least two stages. The first stage involves melting of the mantle to produce basaltic magma, and the second stage involves either fractional crystallisation or remelting of the basalt to ultimately produce the more evolved rocks of which the continental crust is dominantly composed. The products of the second stage may subsequently undergo further differentiation by one or more cycles of remelting (termed anatexis or "intracrustal melting"), which is integral to stabilisation of new continental crust, or by weathering and erosion at the Earth's surface (Rudnick, 1995).

Isotopic studies have established that the continental crust is old, in that more than half of it was formed by the end of the Archaean (Kemp and Hawkesworth, 2004). The distinctive igneous components of Archaean cratons, coupled with evidence that the crust at this time was overall less

mafic, provide clues that crustal growth mechanisms during this period differed significantly from those operating today. The apparent periodicity in crustal growth, the bimodal nature of Archaean magmatism, and the lack of a consistent subduction signal in certain greenstone belts provide strong evidence for the role of plume-related magmatism (Kemp and Hawkesworth, 2004). However, regardless of the tectonic setting, the thermal conditions necessary for remelting of basaltic rocks in the garnet stability field were rarely attained after the Archaean. From the Late Archaean onwards, the formation of relatively mafic granites ( $\text{SiO}_2 < 70\%$ ) with elemental ratios more like the continental crust required higher temperature melting reactions and direct heat input from mantle-derived magmas. Chemical and isotopic considerations from specific case studies demand that juvenile mantle-derived magmas have also made a material contribution to granites generated from a range of crustal protoliths; i.e., that the Moho has acted as an open interface during post-Archaean granitic generation (Kemp and Hawkesworth, 2004).

The alkaline and kimberlite-related rocks are not as common as other mantle-derived magmas but they are significant because of their generally higher thorium content. (Note however, not all kimberlites contain abundant thorium). The alkaline rocks are believed to have been strongly enriched in volatiles and alkalis while still at great depth in the mantle, and possibly have received significant additions of melted crust as well. These rocks are several orders of magnitude richer in thorium than are any other known mantle-derived products (Table 5). For example, the Gardar Province in Greenland contains carbonatite with 843 ppm Th and aplite dykes with 360 ppm Th (Pearce and Leng, 1996). The thorium is contained in refractory complex silicates and multiple oxides and is associated with rare earths.

**Table 5:** Average thorium and uranium concentrations in alkaline rocks (Bergman, 1987).

<b>ALKALINE ROCKS</b>	<b>THORIUM (ppm)</b>	<b>URANIUM (ppm)</b>
Lamproites	46	4.9
Kimberlites	16	3.1
Alkali basalt	3	0.7
Alkaline/calc-alkaline lamprophyres	24	5.0
Ultramafic lamprophyres	22	8.0

The upper crust has a large negative europium anomaly that is largely complimented by the positive europium anomaly of the lower crust. Similar complimentary anomalies exist for strontium. These features and the greater light rare earth element enrichment of the upper crust relative to the lower crust, suggests that the upper crust is largely the product of intracrustal magmatic differentiation in the presence of plagioclase (see Taylor and McLennan, 1985). That is, the upper crust is dominated by granite that differentiated from the lower crust through partial melting, crystal fractionation and mixing processes. The middle crust has an overall trace-element pattern that is similar to the upper crust, indicating that it too is dominated by products of intracrustal differentiation (Rudnick and Gao, 2004). As previously mentioned, all segments of the crust are characterised by an overall enrichment of the most incompatible elements including thorium.

#### **DISTRIBUTION OF THORIUM IN THE CRUST**

It has long been recognised that the thorium content of igneous rocks tends to increase with increasing silica content and also with increasing differentiation index. Reversals in these trends occur in some cogenetic suites of igneous rocks, especially in S-type granites. In sedimentary rocks there is no well-defined trend except that some shales and other argillaceous rocks with high alumina tend to have elevated amounts of thorium. In sandstones and other psammitic rocks an increase in thorium is associated with an increase in resistate minerals such as biotite, monazite, allanite, and zircon.

Certain suites of cogenetic igneous rocks exhibit increasing amounts of thorium with increases in sodium or potassium contents or with total alkali content. Elements such as Zr, Hf, rare earths, Nb, and Ta, with which Th is often associated, typically follow a similar trend in igneous rocks, although they only have a loose correlation with Th. Thorium has elevated concentrations in kimberlites compared to ultramafic and mafic rocks, and the Th/U ratio is often erratic and anomalous with values as high as 30 or more. Igneous rock series exhibiting an increase in total alkali content and a consequent increase in Th are often marked with increasing amounts of readily extractable Th (in sodium carbonate and mildly acid solutions), especially when such rocks are deuterically or otherwise altered. A number of alkali-rich igneous rocks (e.g. small stocks, sills, or dykes) are greatly enriched in thorium (up to 100 ppm or more), far above the average for most alkali granites and syenites and tend to also have very low calcium contents (Boyle, 1982).

In differentiated series of granitic rocks (with the exception of S-type granites) there is a tendency for thorium to increase with differentiation, with maximum amounts in the more leucocratic, and alkalic varieties. Similar features can be noted in some effusive sequences. Many granite and syenite bodies have internal variations in their thorium concentrations, and there may be marked regional variations among granite, granodiorite, and syenite batholiths, stocks, sills and dykes. The available data on metamorphic rocks indicate that their uranium and thorium concentration decreases with an increase in metamorphic grade from greenschist to granulite facies (Boyle, 1982). A decrease in the Th/U ratio with increasing metamorphism is also apparent, although in some terranes the trend may be erratic. Igneous differentiation in particular appears to mobilise thorium which ultimately concentrates in pegmatites and certain lodes, a feature that is amplified subsequently (See Part 2).

In typical igneous rocks, thorium is mainly present in the accessory minerals, particularly thorite, monazite, allanite, zircon, titanite, anatase, rutile, and perovskite. Small to trace amounts occur in other minerals such as fluorite, apatite, epidote, hematite, quartz, feldspar, and mica (mainly in inclusions) and the remainder is present as an adsorbed phase or in minute mineral grains such as thorite along grain boundaries, microfractures, and other discontinuities in the rocks. The same is true for sedimentary and metamorphic rocks but in some sedimentary rocks the resistates such as monazite, zircon and titanite may be quite abundant, and there may be considerable thorium bound in the clays and in limonite and other colloidal materials.

The thorium content of soils is highly variable and ranges from 0.1 ppm to 50 ppm with an average of about 1 ppm (Boyle, 1982). The thorium concentration of residual soils depends on the type of parent rock, being the highest in soils developed on granites, alkalic igneous rocks, schists, and gneisses and lowest on basic igneous and carbonate rocks. Exceptionally high thorium concentrations (200 – 1000 ppm or higher) may be present in soils, clays, laterites, and bauxites developed on alkaline rocks, high heat-producing granites, carbonatites, and in the vicinity of thorium-rich pegmatites and veins. Most of the thorium in soils is present in resistates such as zircon, monazite, allanite, titanite, thorianite, and thorite but some is present in secondary minerals such as baddeleyite and thorumite, and the remainder resides mostly in the clay fractions, and in limonite, wad, and bauxitic complexes (Boyle, 1982).

#### **THE TRANSPORT OF THORIUM**

Thorium is the largest of the tetravalent cations with an ionic radius comparable to that of  $U^{4+}$  and  $Ce^{4+}$ . For a comprehensive list of the chemical properties of thorium see <http://environmentalchemistry.com/yogi/periodic/Th.html#Overview>. The similarities in ionic size, outer electron configuration and bond character are the main reasons for the close relationship between the crystal chemistry of thorium, cerium, uranium, and zirconium. There are many examples for isostructural compounds, e.g. ThS, US, CeS, ZrS (NaCl-type);  $ThO_2$ ,  $UO_2$ ,  $CeO_2$ ,  $ZrO_2$

(fluorite-type);  $\text{ThSiO}_4$ ,  $\text{USiO}_4$ ,  $\text{ZrSiO}_4$  (zircon-type);  $\text{ThGeO}_4$ ,  $\text{UGeO}_4$ ,  $\text{CeGeO}_4$ ,  $\text{ZrGeO}_4$  (scheelite-type); and  $\text{BaThO}_3$ ,  $\text{BaUO}_3$ ,  $\text{BaCeO}_3$ ,  $\text{BaZrO}_3$  (perovskite-type). Although there is a definite preference by thorium for 8- and 6-fold coordination in non-metallic compounds, higher coordination numbers such as 9, 10, and 11 are also found. A list of thorium-bearing minerals is given in [Appendix 1](#). Pure thorium minerals, like thorianite ( $\text{ThO}_2$ ) or thorite ( $\text{ThSiO}_4$ ), are rather rare, but this element occurs as a minor constituent of a large number of minerals containing uranium and rare earths such as monazite (Wedepohl, 1978).

Thorium melts at 1842 °C, but halides of chlorine, bromine, and iodine begin to form at 450 °C, and hydrides and nitrides form above 600 °C.  $\text{ThCl}_4$  is reported to sublime at 750 °C (Kirk and Othmer, 1955). Thorium dioxide is much more basic than the dioxides of the preceding elements of Group IV (i.e. Si, Ge, Sn, Pb, Ti, Zr, Hf). Unlike uranium, thorium does not form simple oxyions, a feature that explains the absence of these compounds in nature. The hydroxide  $[\text{Th}(\text{OH})_4]_n$ , dissolves readily in strong acids, and the hydrated normal salts (e.g.  $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) can be precipitated from solution. Addition of alkalis to solutions of the normal salts precipitates basic salts (e.g.  $\text{ThOSO}_4 \cdot \text{H}_2\text{O}$ ), and various double salts are readily formed with the alkali, alkaline earth, and other ions.

Thorium undergoes extensive interaction (hydrolysis) with water at pH values  $>3$ , the products being first monomeric and oligomeric species and later polymeric complexes of colloidal particles. In this respect the chemistry of thorium is similar to that of silicon, titanium, zirconium, and hafnium. Various colloidal forms of thorium compounds are known. Of these the most important are the hydroxide and silicate. The former generally carries a positive charge but may be negative under certain conditions, the latter is essentially a negative colloid (Boyle, 1982). Thorium hydroxide is very insoluble in water and possesses marked colloidal properties. The hydroxide absorbs carbon dioxide strongly forming insoluble  $\text{ThOCO}_3$ . This compound can also be precipitated from carbonate solutions (Boyle, 1982).

The thorium content of most natural terrestrial waters is very low (0.005 – 0.5 ppb, Paunescu, 1986). Ground waters that leach thorium-rich terranes are typically higher by an order of magnitude, especially if they are enriched in sulphates, fluorides, nitrates, phosphates, carbonates, or organic matter. For example, waters with pH  $<3$  may contain up to 100 ppb Th and waters charged with alkaline carbonates at pH 8-10 may contain up to 70 ppb Th or more. Boyle (1982) suggests that thorium in terrestrial waters is probably largely present as the carbonate complex  $[\text{Th}(\text{CO}_3)_5]^{6-}$ , as the soluble sulphate or its complexes; as a complex nitrate, fluoride, or phosphate, as various hydrolytic products (e.g.  $[\text{Th}_6(\text{OH})_{14}]^{10+}$ ); as the positive colloid  $[\text{ThO}_2 \cdot n\text{H}_2\text{O}]$ ; and as soluble or colloidal humates and other organic complexes. Langmuir and Herman (1980) suggest that dissolved thorium is almost invariably complexed in natural waters, and state that the predominant complexes below pH 4.5 are  $[\text{Th}(\text{SO}_4)_2]^0$ ,  $[\text{ThF}_2]^{2+}$ , and  $[\text{Th}(\text{HPO}_4)_2]^0$ ;  $[\text{Th}(\text{HPO}_4)_3]^{2-}$  from pH 4.5 to 7.5; and  $[\text{Th}(\text{OH})_4]^0$  above pH 7.5. None of the soluble thorium species, except perhaps the colloids, are particularly stable at natural pH conditions (5-8), and hence, this severely restricts the mobility of thorium (Boyle, 1982).

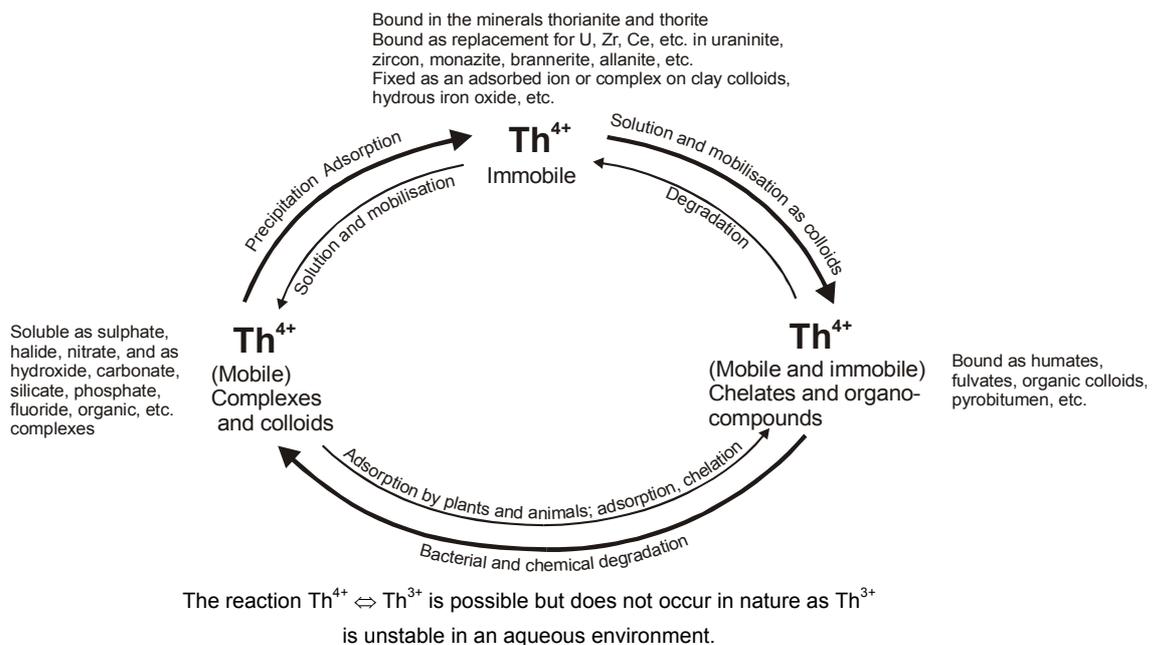
As noted above, the large highly charged  $\text{Th}^{4+}$  ion has a marked tendency to form complex ions with anions which may be present in solution. Among those of interest in the geochemistry of thorium are the various complex chloride ions  $[\text{ThCl}]^{3+}$ ,  $[\text{ThCl}_2]^{2+}$ ,  $[\text{ThCl}_3]^+$ , and  $[\text{ThCl}_4]^0$ ; the complex fluoride ions  $[\text{ThF}]^{3+}$ ,  $[\text{ThF}_2]^{2+}$ ,  $[\text{ThF}_3]^+$ , and  $[\text{ThF}_6]^{2-}$ ; the complex nitrate ions  $[\text{Th}(\text{NO}_3)_2]^{2+}$ ; the complex sulphate ions  $[\text{ThSO}_4]^{2+}$ ,  $[\text{Th}(\text{SO}_4)_2]^0$ ,  $[\text{Th}(\text{HSO}_4 \cdot \text{SO}_4)]^+$ , and  $[\text{ThO}(\text{SO}_4)_2]^{2-}$ ; and the complex carbonate ions  $[\text{Th}(\text{CO}_3)_3]^{2-}$ ,  $[\text{Th}(\text{CO}_3)_5]^{6-}$ , and  $[\text{Th}(\text{CO}_3)_4(\text{OH})_2]^{6-}$ . In addition there are a number of hydroxide complexes e.g.  $[\text{Th}(\text{OH})_4]^0$ ,  $[\text{Th}(\text{OH})]^{3+}$ ,  $[\text{Th}(\text{OH})_2]^{2+}$ , silicate complexes, phosphate complexes, various citrate, oxalate, tartrate, and acetate complexes and numerous chelate and other

organic complexes of thorium, all of which render the element relatively soluble (and mobile) under certain natural conditions (Figure 2; Boyle, 1982). The stability of these various complexes is poorly known. The sulphate and fluoride complexes are relatively stable below pH 5, the phosphate complexes have greatest stability between pH 5 and 8, and the hydroxide and carbonate complexes are stable above pH 7. The various natural organic complexes, including the natural citric, oxalic, fulvic, and other similar complexes have a broad and relatively marked stability between pH 4 and 8 (Boyle, 1982).

**THE PRECIPITATION OF THORIUM**

As thorium only exists in the tetravalent state in nature, reduction processes are not important in its geochemistry (Figure 2). Most precipitation reactions are hydrolytic. The carbonate complex is decomposed in acid solutions (pH < 5) and breaks down under highly alkaline conditions (pH > 10) resulting in the precipitation of hydroxide, hydrated oxide, or hydroxide gels. The sulphate and other similar salts are only stable under acidic conditions (pH < 3.5). At pH values greater than 3.5 they hydrolyse and precipitate hydroxide, hydrated oxide, or hydroxide gels. The hydroxide and positive colloid strongly absorb CO<sub>2</sub>, forming the insoluble oxycarbonate, or the positive colloid is neutralised by anions resulting in formation of ThO<sub>2</sub>, ThSiO<sub>4</sub>, Th(SiO<sub>4</sub>)<sub>1-x</sub>(OH)<sub>4x</sub>, or other more complex compounds. Also much of the thorium in the ionic or colloidal form is adsorbed and/or coprecipitated by clay minerals, silica-alumina gels, hydrous ferric oxide, hydrous manganese oxide, hydrous titania (titanium hydroxide), and organic matter in stream sediments and the sediments of lakes and oceans (Boyle, 1982).

The common salts of thorium are the nitrate, sulphate, and chloride. Also common are the soluble double carbonates of the type Na<sub>6</sub>(Th(CO<sub>3</sub>)<sub>5</sub>) which are formed when an excess of alkali carbonate is added to thorium solutions. The tetrafluoride is very insoluble in water as are the various phosphates, chromates, and molybdates. Thorium oxyhalides and thorium hydroxy-halides of the type ThOCl<sub>2</sub> and Th(OH)<sub>2</sub>Cl<sub>2</sub> are known, and there are a variety of halide double salts with alkali metals. Thorium oxalate is slightly soluble in water but the acetate, basic acetate, and tartrate are insoluble or only slightly soluble.



**Figure 2:** Cycle of Th<sup>4+</sup> interconversions in nature (modified from Boyle, 1982).

Some natural precipitates in springs or downstream from springs may carry above average amounts of thorium especially in the vicinity of rocks enriched in thorium. In this case, thorium enrichments are found in limonitic, manganiferous, jarositic, aluminous, and humic precipitates but less so in siliceous and carbonate sinters. Thorium concentrations ranging from 10 ppm to 3 % or more have been recorded in limonitic-jarositic and aluminous precipitates associated with cold springs while in hot springs thorium concentrations may range from 150 ppm to 1.23 %. Marine manganese nodules are commonly enriched in thorium (30 -125 ppm) and phosphate nodules may also exhibit similar enrichments (Boyle, 1982).

Uranium and thorium are chemically similar at high temperatures, which explains why they tend to occur together in igneous rocks and hydrothermal deposits. In the surficial environment, however, uranium is chemically more mobile. This is due to the limited stability of  $\text{Th}^{4+}$  complexes, especially those with carbonate, and the marked hydrolysis of  $\text{Th}^{4+}$  salts, compared with those of  $\text{U}^{4+}$  and  $\text{U}^{6+}$  at low temperatures. Uranium also has a stronger affinity to carbon.

### **Thorium Minerals**

The most important thorium minerals are monazite, thorianite, thorite, and thorogummite. Other minerals that contain lesser amounts of thorium are allanite, bastnäsite, pyrochlore, xenotime, fluorapatite and zircon.

Monazite  $[(\text{Ce}, \text{La}, \text{Nd}, \text{Th})\text{PO}_4]$  is the principal ore mineral of thorium. It is a complex phosphate of rare earths (principally Ce and La) and thorium. The thorium content typically ranges from a few percent to 10.6 % but can be as high as 26.4 %. Monazite is also an accessory mineral in many gneissic and granitic rocks and in calcareous metamorphic rocks and is a minor constituent of certain carbonate veins.

Thorianite  $[\text{ThO}_2]$  is isomorphous with uraninite ( $\text{UO}_2$ ) and is a very minor constituent of some igneous rocks and placer deposits.

Thorite  $[\text{ThSiO}_4]$  may contain from 25.2 to 64.1 % thorium and as much as 10.1 % uranium. It is typically a primary mineral of pegmatites, certain hydrothermal veins, and some fractionated I-type granites.

Thorogummite  $[\text{Th}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}]$  is a hydrated silicate of thorium and uranium containing 2.5 to 31.5 % uranium and 18.2 to 50.8 % thorium. It occurs in significant amounts in some veins and mineralised shear zones and has been found elsewhere in minor amounts associated with pegmatites and granitic rocks.

Allanite  $[(\text{Ce}, \text{Ca}, \text{Y}, \text{Th})_2(\text{Al}, \text{Fe}, \text{Mg})_3(\text{SiO}_4)_3(\text{OH})]$  is a complex silicate containing as much as 4.35 % thorium. Its characteristic occurrence is as an accessory mineral of plutonic igneous rocks and pegmatites. It is also found as a contact-metamorphic mineral associated with magnetite deposits. Allanite sometimes occurs in sufficient concentrations to be a viable source of thorium.

Bastnäsite  $[(\text{Ce}, \text{Th}, \text{La}, \text{Y}, \text{Ca})(\text{CO}_3)\text{F}]$  is a fluorocarbonate of the rare earth metals (principally Ce and La) containing up to 41 % thorium but less than 1 % uranium. Most bastnäsite deposits are in contact metamorphic zones that are rich in rare earths, barium,  $\text{CO}_2$ , and fluorine.

Xenotime  $[\text{YPO}_4]$  an yttrium phosphate, may contain as much as 2.2 % thorium. It characteristically occurs in pegmatites and as a minor accessory mineral in granites and gneisses. Xenotime is not known in sufficient concentrations to be a source of thorium but would contribute to the total obtainable resource from placers.

## **A Review of the Geochemical Processes Controlling the Distribution of Thorium in the Earth's Crust and Australia's Thorium Resources**

Fluorapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ] is a fluorine-bearing apatite, which sometimes contains rare earth metals and thorium. Fluorapatite occurs in a wide range of igneous rocks, pegmatites, and as detrital grains in some sediments.

A large variety of other minerals contain very minor amounts of thorium and a list of approximately 80 thorium-bearing minerals is given in [Appendix 1](#). The most effective host minerals for Th are compounds of U, Zr, or Ce that are isostructural with thorium compounds, such as zircon, uraninite, and monazite, or compounds in which mechanisms of coupled substitution are available for the housing of large, polyvalent ions, such as niobate-tantalates and monazite.

## **Part 2 – The Geology of Thorium-Bearing Mineral Deposits**

Thorium is widely distributed in nature and is usually associated with uranium and rare earth elements. At high temperatures, thorium commonly accompanies uranium and is deposited together with rare earths in a great variety of minerals, principally oxides, silicates, and phosphates, in pegmatites, skarn zones, and veins predominantly in or near granitic and syenitic intrusives. The presence of available silica and alkalis probably induces thorium (and uranium) to form highly mobile silicate complexes, and similarly, the presence of available mineralisers such as F, Cl, B, PO<sub>4</sub>, and CO<sub>2</sub> probably have a marked effect in increasing the mobility of thorium under high temperature and pressure conditions (Fron del, 1956).

However, at lower temperatures, when pitchblende (uraninite) veins are often deposited, thorium and rare earths are relatively immobile occurring in these veins in only trace to minor amounts. This restriction appears to be related to the limited stability of Th<sup>4+</sup> complexes, especially those with carbonate, and the marked hydrolysis (i.e. precipitation of oxides, gels, or insoluble colloids) of Th<sup>4+</sup> salts, compared with those of U<sup>4+</sup> and U<sup>6+</sup> at low temperatures.

In relation to supergene deposits, thorium is relatively immobile except under extremely acid conditions or where alkali carbonates are abundant in alkaline solution. In the first case, thorium may be leached from rocks principally as sulphate or sulphate complexes, and in some cases, as fluoride or phosphate complexes. Under alkaline conditions, some thorium may be leached from deposits as hydroxide, phosphate, carbonate (hydroxy-carbonate), or colloidal complexes. Most of the thorium in deposits is retained in the gossans and oxidised zones as a result of various hydrolytic reactions, ion exchange, adsorption, and/or coprecipitation by limonite, wad, and other oxidation products such as supergene phosphates, arsenates, jarosites, clay minerals and humic acid compounds (Boyle, 1982). Hydrolytic reactions precipitate thorumite and other undifferentiated, sols and gels.

Many of the thorium-bearing minerals (e.g. monazite, thorianite, thorite, and zircon) are remarkably resistant to oxidation and tend to become enriched in the oxidised zones of thorium-uranium deposits. Therefore, thorium tends to become enriched in the oxidised zones of most deposits as a result of the resistate nature of its minerals, the ready hydrolysis of its salts, and the marked adsorption and coprecipitation of the element by common oxidation products such as limonite and clay minerals. Hecht and Cuney (2000) have shown that hydrothermal alteration of monazite can lead to the formation of a Th-silicate phase in the primary alteration assemblage or to Ca-Th-phosphates in the regolith. Under highly acidic and favourable alkaline conditions thorium may be leached to varying degrees from the oxidised zones of its deposits. Most thorium deposits show relatively little enrichment in the zones of cementation. Exceptions are those where supergene clay minerals, chert, and other colloidal complexes occur in abundance and where there is development of secondary thorium minerals such as thorumite in association with other hydrous silicates and amorphous hydrous silicate-sulphate-phosphate complexes (Boyle, 1982).

The various types of thorium deposits are discussed in more detail below:

### **Placer Deposits**

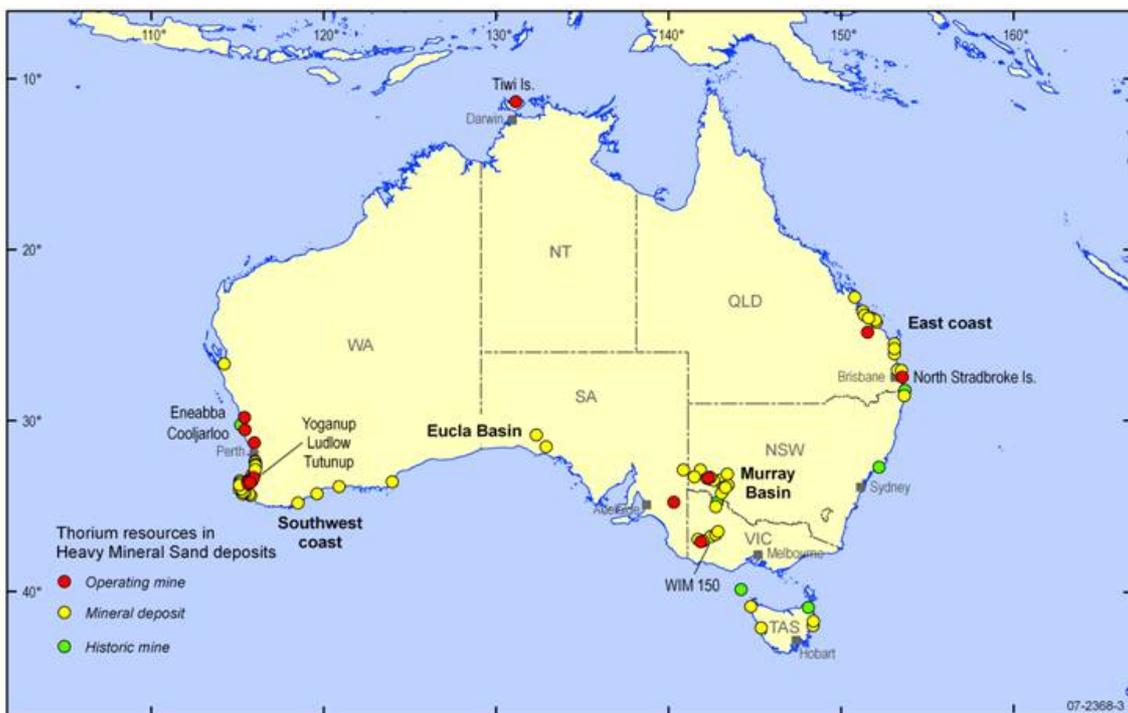
The placer deposits may be divided into two groups – unconsolidated and consolidated (fossil) placers. The majority of Australia's thorium is contained within unconsolidated "heavy mineral sands" deposits. These deposits contain varying proportions of monazite, xenotime, zircon, and titanium-bearing minerals such as ilmenite, rutile, and leucosene. Associated minerals, which are rarely of economic significance, can include garnet and kyanite.

## A Review of the Geochemical Processes Controlling the Distribution of Thorium in the Earth's Crust and Australia's Thorium Resources

Unconsolidated heavy mineral sand deposits can be formed as a result of concentration by water and /or wind. Placer deposits are found where water currents or waves have concentrated heavy mineral grains on a beach or in a river bar and these may occur in both modern and ancient shorelines, and in fluvial deposits. Many of the heavy mineral sand deposits are concentrated by wave action or wind-sorting (aeolian) in both parallel and transgressive dunes. Wind-sorted deposits generally are not comparable in heavy mineral grade or size to wave-concentrated beach or strandline deposits. However, large quantities of low-grade heavy mineral sand concentrations of economic importance do occur as extensive dune systems (e.g. North Stradbroke Island in Queensland).

Australian heavy mineral sand deposits (Figure 3) can be broadly grouped into four types of deposits; strand line or beach sand deposits, dune sand deposits, offshore mineral sand deposits, and a new type of heavy mineral deposit recently encountered in Western Australia – the channel type heavy mineral deposits. Almost all the deposits are Tertiary or Quaternary in age and are derived from source areas that include granitic rocks and /or high-grade metamorphic rocks (Towner et al., 1996).

Consolidated (fossil) thorium placers have a widespread distribution and range in age from Proterozoic to late Cainozoic. Examples of consolidated thorium placers occur in various sandstones, conglomerates, arkose, and their metamorphic and recrystallised equivalents, including migmatites, schists, gneisses and belts of pegmatites and aplites in schists and gneisses. Some of these mineralised units contain up to 1500 ppm Th or more although most have less than 100 ppm Th. The Th/U ratio varies widely, generally from 1:1 to 5:1 (Boyle, 1982). Examples include the Palaeozoic monazite-bearing sillimanite, staurolite, and kyanite schists, gneisses, and migmatites in the Piedmont of the eastern U.S.A. (Twenhofel and Buck, 1956) and the extensive Ordovician-Silurian quartzites of the Despenaperros zone in Spain in which the principal Th minerals are zircon and ilmenite (Alia, 1956).

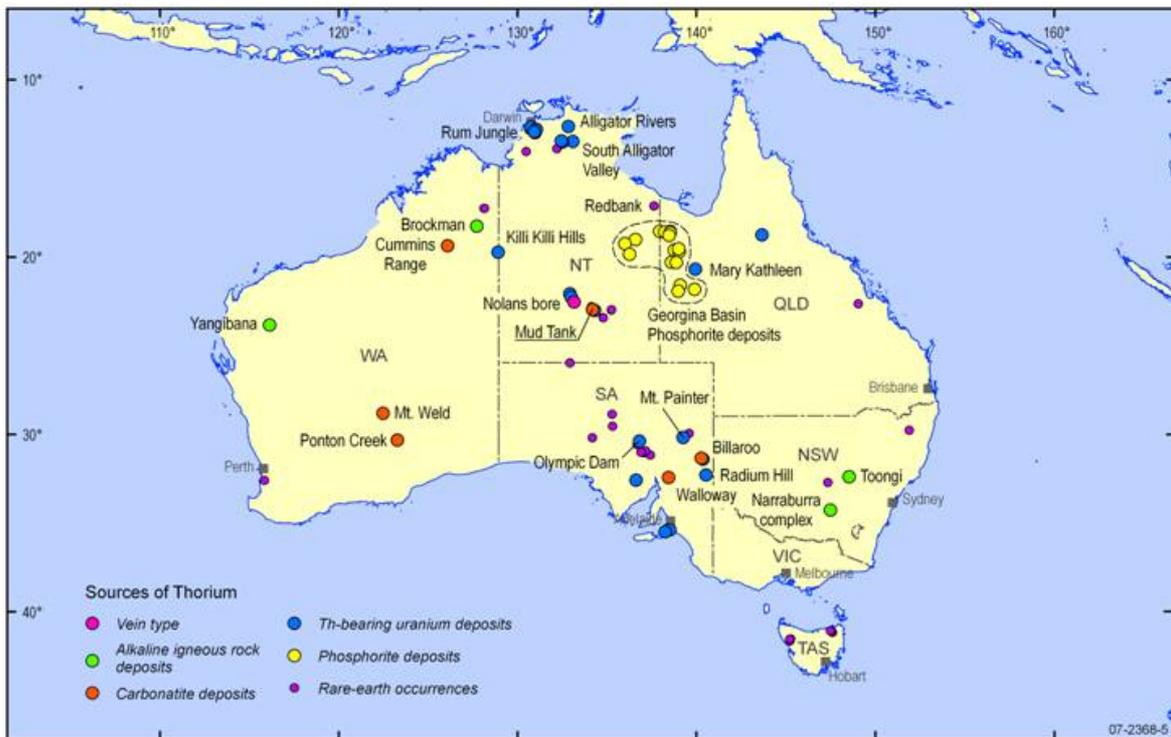


**Figure 3:** Location of Australia's mineral sand resources including the names of operating mines and selected historic mines. (Data is from [www.australianminesatlas.gov.au](http://www.australianminesatlas.gov.au))

**Carbonatites**

Comprehensive reviews of the currently known carbonatite occurrences in North and South America, the former USSR and Africa have been carried out by Woolley (1987), Kogarko et al., (1995), and Woolley (2001) respectively. Carbonatites generally contain <50 ppm thorium, however, some contain higher concentrations, for example the carbonatites from the Gardar Province in Greenland contain up to 843 ppm Th (Upton and Emeleus, 1987). The thorium is mainly within apatite, pyrochlore, monazite, perovskite, titanite, zircon and baddeleyite and also less frequently in thorianite, thorite, betafite, cerite, bastnäsite, xenotime, allanite and aeschynite. Carbonatites are not considered to be a commercial source of thorium at present, although thorium can probably be obtained from certain deposits as a byproduct. Most thorium-bearing carbonatites are indicated by their higher than normal radioactivity and by characteristic enrichments of one or more of the following elements: Li, Be, Sr, Ba, (Cu), (Pb), (Zn), Sc, Y, La, Ti, Zr, Nb, (Mo), P, F, and Cl (Boyle, 1982).

Carbonatite-related deposits can be sub-divided into deposits where primary and/or hydrothermal processes are important, and those where secondary processes such as supergene enrichment and laterisation predominate. The most important primary carbonatite-related deposit is the Bayan Obo deposit in Inner Mongolia, China. Bayan Obo is the world's largest known REE ore deposit and represents 70% of the world's REE resources. Although the origin of the deposit is still under debate, more than 30 carbonatite dykes occur within 3.5 km of the East ore body of the deposit (Yuan et al., 1992). The most abundant REE minerals at Bayan Obo are very fine-grained monazite and bastnäsite and coarser grained huanghoite [Ba(Ce,La,Nd)(CO<sub>3</sub>)<sub>2</sub>F]. Fine- to medium-grained bastnäsite also occurs in late-stage ore dominated by aegirine and aegirine augite, where it is associated with apatite and barite (Chao et al., 1997).



**Figure 4:** Location of Australia's thorium-bearing mineral deposits and occurrences excluding those related to heavy mineral sand deposits.

A number of carbonatite intrusions have been identified in Australia (see Jaques et al., 1991). The best known are Mount Weld, Cummins Range and Mud Tank. However, there are numerous others

such as Ponton Creek, Billaroo and Walloway (Figure 4). Most of the carbonatites in Australia are of late Proterozoic age and intrude either cratonised Proterozoic mobile belts or the margins of Archaean cratons. They all appear spatially related to deep-seated faults and are characterised on (and discovered by) the basis of marked magnetic anomalies.

Mount Weld is a large, high-grade Y, Nb, Ta, P, Zr, Ti and REE resource in the regolith of a large circular Proterozoic carbonatite, which intrudes Archaean greenstones of the Yilgarn craton (Duncan and Willett, 1990). The deposit formed as a result of supergene enrichment processes in the deep weathering profile of a large carbonatite complex. The weathered zone is rich in rare earth elements, niobium and tantalum whereas the unweathered carbonatite at depth contains these elements in lower amounts more typical of carbonatites. Long-term leaching and redeposition by groundwater is the preferred model for rare earth enrichment (Lottermoser, 1990). The central zone of rare earth mineralisation covers an area of one square kilometre of carbonatite regolith and varies systematically in thickness and grade. The rare earths are contained in the form of secondary monazite, which is particularly rich in light rare earth elements and the 'typical' thorium content is reported to be about 600 ppm (Carr Boyd Minerals Limited, Mt Weld project promotion brochure, April, 1991). The weathered monazite has only 0.07 weight % thorium and 0.003 weight % uranium. Significant yttrium and heavy rare earth elements are contained in secondary churchite.

Cummins Range is a large resource in the northeast corner of Western Australia, 130 km south-southwest of Halls Creek (Figure 4). The complex is a roughly circular body and is about 1400 m in diameter. It consists of a core of sövite, which is surrounded by pyroxenite (Andrew, 1990). Accessory minerals include apatite, monazite, zircon, zirkelite, ilmenite, pyrrhotite, chalcopyrite, pyrochlore, barite, bastnäsite, aeschynite, baddeleyite, pandaite, and thorianite (Richards, 1985). The complex is deeply weathered and covered by a thin layer of aeolian soil. Silicified limonitic collapse breccia mounds form the only surface expression of the complex. The weathered lithologies contain elevated Th, U, P, Sr, Zr, Nb, Ta, and light rare earth elements. The highest thorium contents were recorded in the jasperoidal ironstone breccia which contained up to 1160 ppm Th (Richards, 1985).

The Mud Tank carbonatite complex (Figure 4) comprises a series of lenses emplaced about 730 Ma ago along a 5 km segment of a ductile shear zone (Currie et al., 1992). Each lens consists of a carbonate core surrounded by mica-rich zones, emplaced into granitoid cataclasites, mafic granulites and rare lenses of aluminous rocks. Inclusions of unfoliated mafic granulites lack hypersthene, contain albitic plagioclase and Na-rich taramite to hastingsite amphiboles, and are enriched in Si, Na and Ba and depleted in Fe, Zr and Pb relative to similar granulites in the country rocks. Alkali-syenite inclusions contain riebeckite and aegirine. The complex contains magnesio-katophorite to magnesio-arfvedsonite amphibole, with late riebeckite and ferri-winchite, abundant phlogopitic mica and sparse acmitic pyroxene. Mineral thermobarometry suggests original emplacement at >650°C, 0.5 Gpa under high water and fluorine fugacities (Currie et al., 1992). Mud Tank yields fine gem quality zircons and also contains abundant detrital magnetite, apatite and vermiculite. The overall thorium content of the complex is not known but the gem zircons are characterised by very low Th and U (6 – 37 ppm U; Sutherland, 1996).

### **Alkaline Igneous Complexes**

Alkaline and peralkaline igneous rocks have a widespread distribution, some well known examples being the Illimaussaq intrusion in southern Greenland; the Lovozero and Khibini alkaline massifs in the Kola Peninsula USSR; the Red Wine-Letitia alkaline province in Canada; the Triassic alkaline laccolith at Poços de Caldas, Brazil; and the alkaline syenite body at Pilanesberg, South Africa (Woolley, 1987 & 2001; Kogarko et al., 1995). All these complexes are post orogenic, zoned or layered, enriched in Na and K, and contain a variety of relatively rare minerals including thorite, monazite, allanite, eudialyte, lovozerite, loparite, steenstrupine, rinkolite, pyrochlore, beryllite, ramsayite, baddeleyite, and zircon. Thorium is present in the rock-forming minerals, in zircon, and in the various rare earth accessory minerals such as rinkolite and loparite. Local thorium contents in

the above deposits may range up to 1500 ppm but overall they rarely contain in excess of 50 ppm Th (Boyle, 1982).

Reviews of the alkaline rocks of Australia have been carried out by Jaques et al. (1985) and Sutherland (1996). The majority of Australia's peralkaline rocks occur in the Yilgarn craton but their thorium contents are variable (Smithies and Champion, 1999). Other examples of Australian alkaline igneous complexes include the Brockman deposit, the Yangibana ironstones, Toongi, and the Narraburra Complex. The Brockman deposit is located 15 km south-east of Halls Creek in Western Australia (Figure 4). This is a complex, very large deposit containing niobium, zirconium, tantalum, gallium, hafnium and beryllium, plus yttrium and rare earths, in fine-grained particles. The mineralisation is hosted in a fluorite-bearing rhyolitic volcanoclastic unit informally termed the "Niobium Tuff". Drill hole intersections in the "tuff" have been reported to contain up to 371 ppm thorium (Ranstead, 1994). The tuff is the lowermost unit of a sequence of felsic lavas, subvolcanic rocks and volcanoclastic units within the Halls Creek Group (Taylor et al., 1995).

The Yangibana "ironstone" dykes occur 300 km east-northeast of Carnarvon in the Gascoyne Province of Western Australia (Figure 4). The ferrocarnatite-magnetite-rare earth-bearing dykes (termed 'ironstones') crop out over an area of 500 square kilometres (Pearson et al., 1996). The dykes are part of a carbonatitic episode that intrudes the Proterozoic Bangemall Group. This episode also includes pyrochlore-bearing sills (Spider Hill sills), limonitic intrusions (Bald Hill intrusions) and fluidisation breccias (Pearson et al., 1996). These intrusions collectively are part of the Gifford Creek Complex and comprise the largest area of alkaline metasomatic rock currently recognised in Australia. The ferrocarnatite-magnetite-rare earth-bearing dykes occur as lenses and pods from 2 to 25 m in width and traceable for up to 25 km (Pearson et al., 1996). They are typically the last stage of carbonatite fractionation and are enriched in REEs, fluorite and U-Th mineralisation. Whole rock chemical analyses of 21 ironstone samples collected from five prospects in the Yangibana area recorded thorium concentrations from 1062 ppm to 5230 ppm (Pooley, 1988) and it is interesting to note that host rocks such as the Dingo Granite and the Lyons River ultrabasic sills contain up to 150 ppm Th (Pearson et al., 1996). Surface samples also contain abundant monazite and bastnäsite and up to 40 % rare earth oxides.

The Toongi trachyte is one of a number of alkaline bodies which form part of a relatively extensive alkaline volcanic complex (Figure 4) in the Dubbo region (Cassidy et al., 1997). The Toongi trachyte is a roughly elliptical body with approximate dimensions of 850 metres east-west and 550 metres north-south and appears to be near vertical. The rock is comprised dominantly of K-feldspar, albite and aegerine microphenocrysts in a very fine-grained groundmass of similar composition. Overall the intrusive exhibits uniformly elevated grades for zirconium, hafnium, niobium, tantalum, yttrium and rare earth elements. The orebody also contains low level uranium and thorium (Ian Chalmers, Alkane Resources Ltd, pers. comm., 2007).

Three suites of alkaline granite have been recognised in the Narraburra Complex at the triple junction of the Tumut, Giralambone-Goonumbra and Wagga Zones in NSW (Figure 4). Compositionally, the Narraburra Complex is an intrusive equivalent of comendites and is only the second documented occurrence of peralkaline granite in the Lachlan orogen; the other being the Grampians granites in the western Lachlan orogen (Wormald et al., 2004). The peralkaline granites contain anomalous amounts of zirconium, rare earths and low concentrations of thorium (50g/t ThO<sub>2</sub>). Although granites of the Narraburra Complex have geochemical affinities with alkaline granites formed late in orogenic cycles, they post-date arc related magmatism by at least 75 Ma and they formed in a within-plate setting. Magmatism was related to localised reactivation of major faults in the region, and to partial melting involving both enriched mantle and Ordovician shoshonitic crustal components (Wormald et al., 2004).

## **Granites**

Granitic bodies that are greatly enriched in Th and their associated elements are generally the high level post-orogenic intrusive types. Most of the enriched granites are not of commercial importance at present but provide a large reserve of thorium and uranium for the future as some contain up to 240 ppm Th and 120 ppm U (Boyle, 1982). Such bodies are indicated by their higher than normal radioactivity, by their high alkali content resulting from initial crystallisation phenomena or later metasomatic processes, by enrichments of Th, U and rare earths, and by higher than normal amounts of P, F, and Zr (e.g. Adams et al., 1962).

Some granitic rocks in this category show two or more stages of mineralisation – an early magmatic stage during which thoriferous minerals such as monazite, thorite, allanite, titanite, epidote, and zircon were formed, and late stages punctuated by extensive fracturing, shattering, mylonitisation, hematization, albitisation, sericitisation and carbonatisation. These late stages are accompanied by or followed by precipitation of minerals such as uraninite, uranothorite, thorite, brannerite, monazite, fluorite, etc. in the microfractures. The elements most commonly enriched in these types of granitic rocks include Th, U, rare earths, Ti, Fe, Bi, Mo, P, F, S and less commonly Cu, Pb, Zn, and Ba.

Thorium- and uranium-bearing leucocratic granitic rock and pegmatite-aplite complexes are known to occur in the Bancroft area of Ontario, in the Namib desert of South West Africa, in the Charlebois Lake area of northern Saskatchewan, and on the north shore of the St. Lawrence River in Quebec. Somewhat similar occurrences of this type occur at Crocker's Well in South Australia where thorian-brannerite mineralisation occurs in sodic granitic rocks and associated sodic felsic gneisses (Ashley, 1984). The sodic granitic rocks are largely peraluminous, containing high Na<sub>2</sub>O, low K<sub>2</sub>O, CaO, Rb, Ba, Sr and ferromagnesian elements. Contents of U, Th, Nb, Ce, Y and F are variable, but tend to high values (e.g. Th ≤ 153 ppm). Many geochemical parameters are inherited from the compositionally similar sodic felsic gneisses, which are interpreted to be metamorphosed analcime-rich volcano-sedimentary rocks of original intermediate-felsic (alkaline) affinities. Significant U-Th mineralisation is restricted to fractures and local breccia bodies which contain a mineral assemblage rich in quartz, F-bearing phlogopite and minor fluorapatite, sodic plagioclase, niobian rutile, thorian brannerite, monazite, muscovite, chlorite, tourmaline and fluorite (Ashley, 1984).

The best examples of Archaean allanite-bearing granites occur in the Yilgarn craton with thorium concentrations up to 100 ppm (Smithies and Champion, 1999). Proterozoic, allanite-bearing granites occur in the Arunta Region. Prominent examples include the Gum Tree and Ennugan Mountains Granites. A phase of the Wuluma Granite also contains probable allanite. The Ennugan Mountains Granite, in particular, is seen as prospective for U-Th-REE because Otter Exploration found several small U, Th, Ta and Nb occurrences in narrow biotite shears (Stewart et al., 1980). These authors also mapped a hematitic porphyry in the Wangala Granite with an average of 55 ppm Th. The calcisilicate rocks near the Wangala Granite may also potentially host Th-U-REE mineralisation (eg Mary Kathleen-style Th-U-REE see below).

## **Pegmatites**

Examples of Th-bearing pegmatites are known in many parts of the world and most commonly occur in or near granitic or syenitic bodies or in high-grade metamorphic zones near their contacts with granitic stocks or batholiths. The principal radioactive minerals in these deposits are uraninite, thorite, brannerite, uranothorite, betafite, monazite, tantalite-columbite, euxenite, pyrochlore, fergusonite, allanite, epidote, samarskite, blomstrandite, gadolinite, yttrifluorite, xenotime, thortveitite, gagarinite, wiikite, thalenite, cyrtolite, zircon, djalmaite, and pyrobitumen. Two general types can be recognised – granite pegmatites and syenite pegmatites. The former are well known and the latter often contain considerable amounts of nepheline and are generally marked by the presence of mainly rare earth-, thorium-, and zirconium-bearing minerals, including thorite, thorianite, pyrochlore, allanite, and zircon.

The Archaean North Pilbara Craton contains at least 120 pegmatite deposits in over 27 pegmatite groups and fields, including the giant Mount Cassiterite tantalum orebody in the Wodgina pegmatite district. Pegmatites in the Cooglegong and Abydos districts are relatively enriched in REE and U-Th-bearing minerals, including tautauxenite, gadolinite, ytrotantalite, fergusonite, monazite, and samarskite (Sweetapple and Collins, 2002). A number of pegmatites are also known to occur in the Archaean Yilgarn Craton (Partington, 1987) and the most significant of these is the Greenbushes rare earth deposit, which occurs within a large pegmatite body that intrudes Archaean metasediments and includes half the world's tantalum resource. This pegmatite was intruded and crystallized synchronously with deformation and has a medium- to high-temperature and medium-pressure metamorphic setting. The main ore shoots occur exclusively in the albite zones in the pegmatite and generally within tourmaline-rich subzones. The ore zones at Greenbushes contain low levels of uranium and thorium with average grades in the range 6 – 20 ppm U and 3 – 25 ppm Th (Partington et al., 1995).

Proterozoic pegmatite swarms and associated granites occur in the Arunta Region and Blueys Folly, and numerous other allanite-bearing pegmatites occur between Alice Springs and Ruby Gap in the Northern Territory. Pegmatites in the Harts Range region, informally named the Entia pegmatite field, contain Th-bearing minerals such as samarskite, monazite, allanite, fergusonite, formanite, euxenite, xenotime and others (Hussey, 2003). Descriptions of them appear to be analogous to the Nb-Ta, Y, REE, Sc, Ti, Be, Th, U, F (NYF)-type pegmatite and associated granitic suite of Černý (1991).

The Olary district in South Australia also contains several areas of uranium mineralisation related to the metamorphism and anatexis of Proterozoic volcano-sedimentary sequences. The REE minerals variously occur in pegmatites or as disseminated fissure fillings within granitoids and migmatites. REE-bearing minerals in these occurrences are allanite, betafite, brannerite, davidite, euxenite, fergusonite, florencite, monazite, polycrase, samarskite, synchysite, brannerite-(thorium), thorite, xenotime and ytrocraite (Robertson et al., 1998). The Radium Hill deposit is located within shear zones of Precambrian gneisses, aplitic gneisses and schists, intruded by mafic and felsic bodies. The principal ore mineral at Radium Hill is davidite. Tailings from the Radium Hill mine, which are located at Port Pirie in South Australia, are reported to contain large amounts of rare earth oxides (Cassidy et al., 1997).

### **Iron Oxide Copper-Gold-(Uranium) and Breccia Deposits**

Iron oxide copper-gold (IOCG) deposits generally form in extensional environments and range in age from the present at least back into the Late Archaean. According to Williams et al. (2005) they occur in crustal settings with very extensive and pervasive alkali metasomatism, and many are enriched in a distinctive, geochemically diverse suite of minor elements including F, P, Co, Ni, As, Mo, Ag, Ba, LREE, Th and U. The largest deposits include Salobo, Cristallino, Sossego, and Alemão (Carajás), Olympic Dam (Gawler craton) Ernest Henry (Cloncurry district), and Candelaria-Punta del Cobre and Manto Verde (Chile). IOCG deposits often contain significant amounts of fluorocarbonates, phosphates, and elevated amounts of Th and Zr. Groves and Vielreicher (2001) have suggested that the striking geochemical similarities between the Phalabowra carbonatite-hosted Cu deposit and Olympic Dam imply that the former should be regarded as an end member of the IOCG family. However, Williams et al. (2005) conclude that contributions from alkaline-carbonatite magmas could explain features of some IOCG deposits, but presently, they cannot be invoked as essential although fundamentally different types of IOCG deposits may exist.

The Olympic Dam Cu-U-Au-Ag deposit is located approximately 520 km north-northwest of Adelaide in South Australia (Figure 4) and contains a very large resource of rare earths (in excess of 45 Mt based on a total resource of 7.7 Gt, BHP Billiton Annual Report, 2007). The deposit is mainly hosted by hematite-rich breccias in Proterozoic mafic to intermediate granitoid basement of the Stuart Shelf region. Most of the ore is breccia that contains 40 – 90 % hematite along with quartz, sericite, fluorite, barite, sulphides and rare earth minerals. Typically there is about 0.59 % total rare

earth oxide in the orebody (Roberts and Hudson, 1983). Known minerals in the deposit are as follows: bornite, chalcopyrite, chalcocite, roxbyite, carollite, digenite, covellite, a Cu-Ni-Co arsenate, native copper, uraninite, coffinite, brannerite, native gold, silver, argentite, silver tellurides and copper sulphides. The deposit also contains anomalous concentrations of iron, barium, fluorine and rare earth elements (REE). Abundances of ~2000 ppm La and 3000 ppm Ce are common for the mineralised breccias and the lithologies have pronounced light rare earth element (LREE) enrichments. Bastnäsite is the dominant host for LREE, followed by fluorencite and synchysite. Monazite and xenotime and heavy rare earth element (HREE) bearing zircon are also present but are much less abundant than bastnäsite and fluorencite. REE concentrations are correlated with the hematite content of the host rocks and higher values occur in hematite breccias in the centre of the deposit (Oreskes and Einaudi, 1990). Sm-Nd systematics at Olympic Dam suggest a mantle source for the highly enriched REE values (Johnson and McCulloch, 1995).

Lottermoser (1995) reported thorium concentrations up to 0.23 wt. % in bastnäsite but commented that the analyses were only semi-quantitative due to the very small grain size and/or porous nature of the specimens. The REE resource at Olympic Dam is not being recovered in the current mining operation and the thorium content of the ore is estimated to be between 40 and 50 ppm (Jane Belcher, BHP Billiton Limited, pers. comm., 2007). Olympic Dam is currently processing approximately 10 Mt of ore per year (BHP Billiton Annual Report, 2007) and this is estimated to contain around 400 to 500 tonnes of thorium. This figure will increase to around 2000 tonnes per annum if the planned expansion of the mine proceeds and production reaches the target of 40 Mt of ore per year.

The Mount Painter U-REE-bearing granite breccia deposits are located in the Mount Painter and Mount Babbage Inliers at the northern edge of the Adelaide Geosyncline in South Australia (Figure 4). The inliers comprise Proterozoic granitoids, metasedimentary rocks and volcanic rocks (the Mount Painter Complex) that have been intruded by Paleozoic granitoids. Large bodies of breccia, the Radium Ridge breccias, occur in the Mount Painter Complex and the Paleozoic granitoids and most consist of clasts of granitoid and metamorphic rocks, with some massive hematitic breccia (Drexel and Major, 1990). The hematitic breccias contain base metal sulphides, uraninite, monazite, chlorite, carbonate, fluorite and quartz in addition to hematite and magnetite. Rare earth elements are relatively abundant throughout the hematitic breccias and the Mount Gee Sinter. Similarities between the hematitic breccias at Olympic Dam and Mount Painter have been noted by several workers, thus implying that these breccias also contain thorium.

### **Thorium-bearing veins and lodes**

These deposits are widely distributed throughout the world but are relatively rare. They are localised in shear zones, faults, fractures, breccia zones, and diatremes in meta-sedimentary and meta-volcanic rocks, and are often, but not always, associated with alkalic rock complexes and carbonatites. The principal thorium-bearing minerals in the deposits are thorite, thorigummite, monazite, and brockite and they are associated with various rare earth minerals including allanite, bastnäsite, xenotime, cenosite, fluorencite, and synchysite. Quartz, hematite and/or magnetite, feldspar, micas, carbonates, barite, apatite, fluorite, and rutile are present as gangue minerals. Titanite, pyrite, chalcopyrite, and other base metal sulphides occur in minor amounts in some of the veins. Examples of these deposits include Lemhi Pass (thorite) in Idaho, USA; Steenkampskraal (monazite), Vanrhynsdorp Division, in South Africa; Mountain Pass (bastnäsite and thorite), California, USA; and the Eskisehir deposit, Turkey (bastnäsite) (Boyle, 1982; Gultekin et al., 2003). The U/Th ratio is generally less than 1 in these deposits. There is also a strong Mo-Cu-Th-U association and a Th-U-F affinity in many of these deposits.

A sub-type of this category includes certain thorium-uranium and uranium-thorium veins and lodes localised in shear zones, faults, fractures, stockworks, breccia zones, and irregular segregations in tuffs, conglomerates and other favourable lithologies and permeable zones in or near alkali syenite stocks, laccoliths, and dyke swarms. The Nolans Bore deposit in the Northern Territory (Figure 4)

may be an example of this style of mineralisation. Nolans Bore has world-class characteristics in terms of size and grade of rare earth elements, phosphate, uranium, and thorium. The prospect occurs in two zones over a strike length of about 2 km within variably deformed and altered granitic gneiss and pegmatite, and minor calc-silicate rocks. Four styles of REE mineralisation have been recognised at Nolans Bore ([http://www.arafuraresources.com.au/nol\\_geo.html](http://www.arafuraresources.com.au/nol_geo.html)):

- Massive fluorapatite dykes with 4-6% REE.
- Very high grade REE mineralisation of 10-20% REE found in cheralitic apatite-poor rocks.
- Calc-silicate hosted apatite-allanite-epidote REE mineralisation
- Zones of low grade REE mineralisation in gneisses and kaolinite-altered rocks adjacent to the fluorapatite dykes and adjacent to mylonite zones.

Observations, based on a limited number of thin sections of surface samples collected from Nolans Bore (Hussey, 2003), suggest that brecciation is present and that several generations of fluorapatite are present in these veins. REE mineralisation is not restricted to fluorapatite. It is also present in altered country rock (deformed granite and pegmatite) and occurs in other REE phases, but apart from one region, these appear to be subordinate. The REE are possibly derived from late-stage hydrothermal fluids and alteration systems related to pegmatite emplacement. Thevissen (1995) suggested that the Nolans Bore fluorapatite was deposited as a low-temperature hydrothermal vein system. The Th content of Nolans Bore fluorapatite generally ranges from 0.067-0.593% and averages 0.233% Th (11 analyses; Hussey, 2003). Thevissen (1995) reported a similarly high Th content (averaging 0.483% Th). This high Th content suggests that the Nolans Bore fluorapatite is not related to a carbonatite, or to fluids derived from them, but is more likely to be related to hydrothermal fluids associated with an NYF-type pegmatite (Cerný P., 1991). Current plans for processing the ore indicate that the thorium will be extracted during processing of the rare earths and placed into storage ([http://www.arafuraresources.com.au/nol\\_met.html](http://www.arafuraresources.com.au/nol_met.html)).

It is also interesting to note that in the Arunta, at least several shear zones, which are interpreted as being related to the Alice Springs Orogeny, show elevated Th signatures in radiometric images. It has been suggested that these shear zones were flushed with Th-enriched fluids from contemporaneous pegmatites during the Alice Springs Orogeny (Hussey, 2003). Prominent examples of shear zones with elevated Th signatures include the Peaked Hill Shear Zone, unnamed shear zones to the south of Pine Hill, and the parts of the West Bore Shear Zone near Alice Springs in the Northern Territory.

The nature and extent of secondary oxidation in the various types of thoriferous vein and lode deposits depends on a number of factors including the nature of the wall rocks, and nature of the gangue and associated minerals. In oxidised zones where the primary mineralisation is siliceous and largely carbonate free, and where pyrite and chalcopyrite are abundant, the conditions tend to be acidic and much of the thorium is leached leaving oxidised rubble composed mainly of limonite, wad, and disintegrated wall rock. In oxidised zones where the mineralisation is rich in carbonates, various nickel-cobalt arsenides, arsenopyrite, chalcopyrite, galena, sphalerite and pyrite, the leached and oxidised zones are commonly composed of sooty masses of manganese oxides and hydroxides (wad), limonite, and highly decomposed wall rocks (Boyle, 1982). The radioactivity of these zones is usually high mainly because of the presence of compounds such as radium wad and limonite, radium opal and clay complexes, radiobarite, and supergene radiocarbonates.

#### **Pitchblende (uraninite) veins, lodes, and disseminated bodies in or near major faults, shear zones, or unconformities.**

These may be subdivided into two general types – those with relatively simple mineralogy versus those with a complex mineral assemblage. Both are probably gradational in respects to their mineralogy, and both may occur in the same fault system or in the same uriferous province.

Deposits with a simple mineralogy contain essentially pitchblende (uraninite) and/or coffinite with minor amounts of pyrite, chalcopyrite, molybdenite, umangite, and other selenides, and traces of

sulphides, arsenides, antimonides, tellurides and other minerals mentioned in the more complex type below. Certain deposits contain native gold. Some deposits contain davidite as an important ore mineral and brannerite is present in other deposits. Quartz, calcite, chlorite and hematite are the principal gangue minerals. Certain deposits exhibit slight enrichments of Sc, Y, rare earths and pegmatitic elements such as Li, Rb, Cs, Be, B, and Nb. Thorium generally only occurs in trace amounts and the U/Th ratio is invariably greater than 1. Uraninite (the most common uranium mineral in unconformity-type uranium deposits) is a chemically active mineral and readily exchanges elements or recrystallizes when subject to hydrothermal events, and as a result can contain variable amounts of thorium, rare earth elements, calcium, and radiogenic elements such as lead, radium, and polonium (Alexandre and Kyser, 2004).

The best-known Australian examples of unconformity-type uranium deposits are those of the Alligator Rivers and South Alligator Valley uranium fields (Figure 4). There are over one hundred uranium-bearing occurrences in this region, of which over seventy are in the Alligator Rivers field including Ranger, Koongarra and Jabiluka. In the South Alligator Valley uranium field, the Pul Pul Hill area and the area north of El Sherana both have pronounced thorium anomalies in the airborne radiometric data and contain high levels of REE and zirconium. Ayres and Eadington (1975) reported that rocks of the Edith River Group contain between 12 and 56 ppm Th. These deposits are also similar to the unconformity-related uranium deposits in the Athabasca basin where Hecht and Cuney (2002) have shown that the average thorium content of 116 basement samples was  $51 \pm 66$  (1 SD) ppm. These authors also reported that replacement of monazite by a Th-silicate phase (containing an average of  $47 \pm 4$  wt% Th) occurred in most lithologies down to at least 200m below the unconformity.

The Killi Killi Hills area of the Granites-Tanami Block near the border of Western Australia and the Northern Territory (Figure 4) also has pronounced thorium radiometric anomalies and contains a number of thorium-uranium prospects (Blake et al., 1979). In this region the mineralisation is confined to conglomerates at the base of the Gardiner Sandstone, which unconformably overlies steeply dipping basement shales and greywackes of the Killi Killi beds. The mineralogy includes xenotime and fluorencite, indicating that uranium, thorium and HREE should be present. Geoscience Australia conducted an airborne radiometric survey over the West Tanami region in 2002 and the stronger radiometric anomalies were attributed to local thin zones of heavy mineral concentrations carrying anomalous uranium and thorium values.

The second type of these deposits comprises veins and lodes of a second generation of minerals consisting of Ni-Co-Fe arsenides, sulphides, and antimonides and various sulphosalts and selenides. In some deposits, native silver, native bismuth, native arsenic, gold and other tellurides also occur. Thorium is generally only present in trace amounts in the ores and is usually present in minerals such as allanite and epidote. The rare earth content of the uraninite and pitchblende rarely exceeds 2%. Typical examples of these deposits include Jáchymov in the Czech Republic, Great Bear Lake in Canada, the Black Hawk district in New Mexico and Shinkolobwe in Zaire (Boyle, 1982). A similar style of U-Cu-Co-Ni-Pb mineralisation occurs in the Rum Jungle Complex in the Northern Territory (Figure 4, McCready et al., 2004). Three thorium prospects have been recorded in the Rum Jungle Complex (Crohn, 1968). These are the Crater prospect, situated along the southeastern margin of the Rum Jungle Dome, and two prospects in the Manton Dam area. Morlock and England (1971) reported that the source of radioactivity in the Crater prospect was an amorphous or metamict phosphate of Th, Ca and Fe, containing small amounts of Si, Ti and Ce. McCready et al. (2004) reported that unmineralised rocks near the Brown's deposit contained 13.33 – 20.83 ppm Th, while mineralised rocks contained 10.6 – 18.3 ppm Th and altered samples contained 6.4 – 14.87 ppm Th. Heier and Rhodes (1966) analysed the granites and gneisses of the basement complex for thorium, uranium and potassium and reported thorium concentrations up to 129 ppm and an average concentration across all the basement units of 45.7 ppm Th and 10.3 ppm U. They concluded that thorium and uranium were leached from the basement complex with concentration of uranium in structurally favourable zones occurring during a period of low-grade metamorphism.

### **Pyritic quartz-pebble conglomerates**

The best known examples of these are the Blind River-Elliot Lake deposits in Ontario, Canada and the Witwatersrand deposits in South Africa. The former contain essentially thorium, uranium, and rare earths and the latter contain gold and uranium. The orebodies constituting these deposits occur mainly in pyrite-bearing oligomictic conglomerates but interbedded pyritic quartzites may also contain orebodies as in the Witwatersrand and in the Koli area of Finland.

In the Blind River-Elliot Lake deposits the uranium, thorium, and rare earths occur mainly in a brannerite-uraninite-monazite mineral assemblage and the yttrium group of rare earths predominates in the deposits. The Witwatersrand reefs are not only extremely rich in gold but also are one of the world's largest uranium depositories. The principal uranium minerals are uraninite, brannerite and leucocoxene and the uraninite is reported to have high thorium contents (average 3.9 wt% Th, Barnicoat et al., 1998; Frimmel, 2005). In the Koli deposits the principal uranium minerals are pitchblende and/or uraninite with secondary uranophane near the surface. Most of the pyritic quartz-pebble conglomerate deposits exhibit enrichments of U, Th, Sc, Y, rare earths, Ti, Fe, As, P, and S with major concentrations of Au and Ag and minor platinoids. The typical uranium content of the ores ranges between 500 – 1500 ppm (Boyle, 1982).

The oxidised zones of these deposits are generally leached of most of their uranium and some of their thorium. They typically contain a large amount of primary pyrite which when oxidised yields acidic conditions often with the formation of jarosite and ultimately limonite. The gossanous rubble may, however, be marked by considerable radioactivity because of the coprecipitation and adsorption of some uranium and thorium and their various daughter elements. Resistate minerals such as brannerite, monazite, and zircon may be concentrated in some gossans, thus increasing their Th and U contents.

### **Skarns and hornfels deposits**

These deposits are large and relatively thorium-rich but are also quite rare worldwide. The thorium- and uranium-bearing minerals in these deposits are mainly uraninite, coffinite, stillwellite, uranothorianite, rinkite, epidote, allanite, and monazite and occasionally pyrobitumen. The main Australian example of this style of deposit is the Mary Kathleen deposit in Queensland (Figure 4). It contains an irregular cluster of steeply dipping uraniferous lenses in a garnetite zone developed in a granulite-skarn-marble environment. The rare earth content of this deposit is about 4 % and the commonly occurring REE minerals are stillwellite and allanite while other REE-bearing minerals include apatite, titanite and garnet (Scott and Scott, 1985). The mineralisation is reported to contain about 0.025% thorium oxide (<http://www.uic.com.au/fmine.htm>). It is interesting to note that the presence of REE- and uranium- (and possibly thorium-) bearing minerals in fluid inclusions from the Mary Kathleen deposit has been reported by Kwak and Abeyasinghe (1987) which suggests that these elements can be strongly concentrated in high temperature hydrothermal fluids.

Skarn deposits carrying uraninite, thorite, uranothorite, uranothorianite, pyrochlore, and minerals such as monazite, apatite, fluorite, titanite, tourmaline, pyrite, pyrrhotite and molybdenite occur as disseminations or irregular zones in skarnifield marble, skarn, and metamorphic pyroxenites and amphibolites in many parts of the Grenville province of Ontario and elsewhere in the world in granulite and gneissic terranes containing marbles or calcareous schists. The grade of many of these deposits is low ranging from <10 to 200 ppm Th but the tonnage is often large (Boyle, 1982).

Some magnetite-hematite skarn deposits also contain thorium and uranium. For example, Walker and Osterwald (1956) have described the Prince Mine, Lincoln County in New Mexico as a magnetite-hematite skarn deposit. The deposit is composed of mainly magnetite with lesser amounts of hematite, hydrated iron oxide, pyrite, gypsum, chalcocopyrite, metatorbernite, covellite, quartz, marcasite, and uranium-bearing minerals. It is surrounded by an aureole of recrystallised limestone, gypsum, epidote, and actinolite with minor amounts of phlogopite, fluorite, pyrite, and chalcocopyrite.

### **Phosphates**

The thorium content of igneous and hydrothermal phosphate deposits is highly variable. Some deposits contain up to 200 ppm Th or more, whereas others contain less than 30 ppm. Marine phosphorites are composed mainly of carbonate-fluorapatite. They commonly contain 20 – 300 ppm U and up to 50 ppm Th and are also enriched in a great variety of other elements including rare earths, V, Zr, Cr, Mo, Nb, As, Ag, Pb, Zn and Cu (Boyle, 1982). The Georgina Basin of northern Australia (Figure 4) contains a number of marine phosphorite deposits of Middle Cambrian age (Howard and Hough, 1979). The phosphorite lenses in the Georgina Basin range in thickness from 1 to 19 metres and the indicated and inferred reserves are estimated to be about 4000 Mt of phosphorite ore (Lottermoser, 1991). Total REE grade in the phosphorite ores is typically less than 1000 ppm (Howard and Hough, 1979). The Th and REE occur as cation substitutions within the fluorapatite or are present within REE secondary minerals.

### **Coal, Peat, and Carbonaceous Material**

The thorium content of coal typically ranges from 1 – 10 ppm but up to 100 ppm has been reported. Th<sup>4+</sup> is also strongly absorbed on peat but the normal thorium content of most peat bogs is low (~10 ppm) but can increase from 2 to 10 fold in the vicinity of thorium-rich rocks (Boyle, 1982). Thorium, like uranium and rare earths, is generally also found as a constituent of petroleum and bitumen and in solid hydrocarbons variously called thucolite, carburant and radioactive anthraxolite. Thorium also forms numerous water insoluble complex compounds with organic acids such as gallic, tannic, oxalic, and aspartic acid. Some such as tannic acid, are probably present in peat, humus, and perhaps in organic sediments. Some of these may act as important precipitants for thorium and others as solubilisers.

### **Conclusions about Thorium Mineral Deposits**

From the above examples it can be seen that thorium can occur in a large variety of rock and deposit types. The elements associated with thorium are numerous and differ with the type of deposit and frequently from deposit to deposit, but there is a nearly universal association of the elements Th and U, Cu, Mo, P, and F in deposits. This reflects the fact that thorium is a minor to trace component of a large number of rare earth and other minerals such as monazite, zircon, uraninite, fergusonite, pyrochlore-microlite, betafite, xenotime, allanite, etc. The elements Ra and Rn and certain isotopes of He, Kr, and Xe are of radiogenic origin, and therefore, also have a universal association with thorium and uranium. Titanium is also very commonly associated with thorium as shown by the fact that titanite in rocks and deposits is often enriched in thorium and uranium.

The paragenetic relationships of the thorium (and uranium) minerals in the different types of deposits are varied, but some generalities are evident. In most granitic, pegmatitic, and vein-type deposits the thorianite, thorite, uraninite, pitchblende, and coffinite are preceded by quartz, pyrite, chalcopyrite, etc. and are generally followed by various arsenide and precious metal minerals. In other deposits the paragenesis of the various thorium minerals is complex and not entirely clear.

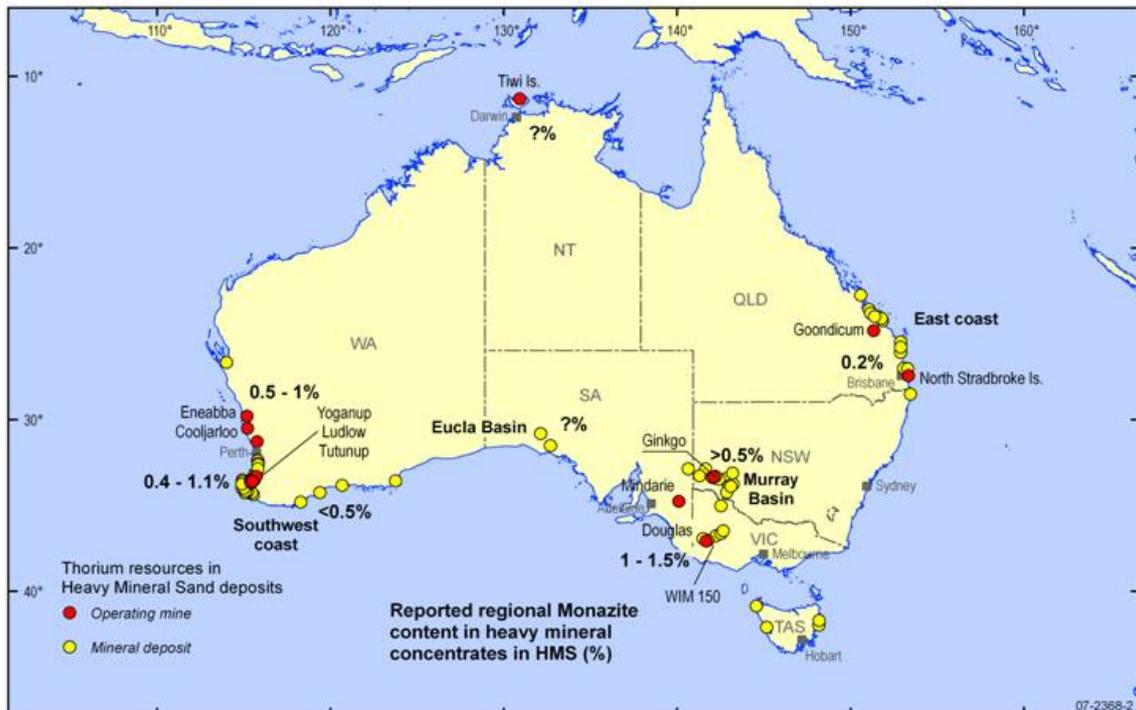
The deposits of thorium and uranium are very similar but at lower temperatures, during which pitchblende (uraninite) veins are deposited, thorium and rare earths are relatively immobile and occur in only trace to minor amounts. Furthermore, a number of thorium deposits (e.g. pegmatites, iron oxide copper-gold deposits, quartz-pebble conglomerates, and certain veins) contain appreciable quantities of Be, Sc, rare earths, Sn, Zr, Bi, Nb, and Ta.

## Part 3 – Australia's Thorium Resources

### DISTRIBUTION OF AUSTRALIA'S THORIUM RESOURCES BY DEPOSIT TYPE

All of Australia's thorium resources occur in multi-commodity deposits, dominantly the heavy mineral sands and rare earth deposits where the extraction cost would be shared with, if not totally supported by, the other commodities in the deposit.

As there is no established large scale demand and associated costing information for thorium, there is insufficient information to determine how much of Australia's thorium resources are economic for the purposes of electricity power generation in thorium nuclear reactors



**Figure 5:** Reported regional monazite content (in weight %) in heavy mineral concentrates.  
(Data is from [www.australianminesatlas.gov.au](http://www.australianminesatlas.gov.au))

### Placer deposits

Most of the known thorium resources in Australia are held in the monazite component of heavy mineral sand deposits, which are mined for their ilmenite, rutile, leucoxene and zircon content. There are no comprehensive detailed records on Australia's thorium resources in heavy mineral sands because of the lack of large-scale commercial demand for thorium and a paucity of required data. The monazite content of heavy mineral resources is seldom recorded by mining companies in published reports. Publicly available analyses of monazite for their thorium content are very rare and analyses of samples for calculation of thorium resources of individual deposits are virtually non-existent. In order to estimate Australia's thorium resources in the heavy mineral sand deposits, Geoscience Australia has used the following sources of information,

- In cases where analyses for monazite for individual heavy mineral sand deposits is not available, Geoscience Australia has applied publicly available monazite grades characteristic for the particular region to calculate the volume of monazite in the heavy mineral deposit (Figure 5).



**A Review of the Geochemical Processes Controlling the Distribution of Thorium in the Earth's Crust and Australia's Thorium Resources**

- The world wide thorium content in monazite was considered by the OECD/NEA & IAEA (2006a) to be of the order of 8-10% Th.
- For the purpose of an initial estimate of Australia's thorium resources, Geoscience Australia adopted an average of 7% Th for all Australian heavy mineral sand deposits. Geoscience Australia is currently engaged in compilation of all available information on the monazite and thorium content in Australia's heavy mineral sand deposits and will conduct limited analyses of monazite to determine its thorium content which will be used to calculate the thorium resources for individual deposits or for groups of deposits.

Australia's monazite resources are estimated from available information by Geoscience Australia to be of the order of 5.2 million tonnes. Assuming an average thorium content in monazite of about 7%, Australia's inferred thorium resources in heavy mineral sand deposits could amount to about 364,000 tonnes. The distribution of the inferred resources of thorium in both heavy mineral sands as well as in the hard rock deposits is shown in [Figure 7](#).

**Table 6** Types of heavy mineral sand deposits in Australia

Type of Deposit	Possible Thorium Tonnage	Selected deposits and comments
<b>Strand Line</b>		
○ <i>Present Day Shore Line Deposits</i>	small	Initially on east coast, northern NSW and southern Queensland and southwest WA. Most available resources mined out. Remaining resources are in national parks, built up areas – these are not available for mining.
○ <i>Tertiary Fossil Shoreline Deposits</i>	27,000t Th in NSW 74,000t Th in WA	Main sources of production in southwest WA including Eneabba and Cooljarloo north of Perth and the Yoganup south of Perth. The Murray Basin is a major new heavy mineral sand province in NSW, Victoria and South Australia with Ginkgo (NSW) and Douglas (Vic) mines and Mindarie (SA) starting up recently. Variable monazite content. Another new province of fossil shore line deposits is the Eucla Basin in South Australia and Western Australia.
<b>Dune Sand Deposits</b>	25,000t Th in Queensland	All of the heavy mineral sand resources in dune sand deposits are in Queensland and virtually all are in various types of national parks or conservation areas. Monazite content is generally low at around 0.2 – 0.3% of the heavy mineral fraction. North Stradbroke Island is the only operating mine.
<b>Offshore Deposits</b>		
○ <i>Present Day Offshore Deposits</i>	No Data	Offshore heavy mineral sand deposits are known to occur off the southern Queensland and northern NSW coast.
○ <i>Fossil Offshore Deposits</i>	232,000t Th in Victoria 6,000t Th in South Australia?	Mainly in the Murray Basin in western Victoria in the 'WIM' type deposits formed in an offshore environment (Williams, 1990). Monazite grades are around 1-1.5%.
<b>Channel Deposits</b>	No data on Th	Heavy mineral exploration in the Cooljarloo region in Western Australia, have encountered thick high grade intersections of heavy mineral concentrations of the order of 40m at 4.4% heavy minerals which the company believes to be a channel type rather than strand line or dune sand heavy mineral deposit.

### **Types of heavy mineral sand deposits**

Australian heavy mineral sand deposits can be broadly grouped into four types of deposits as shown in Table 6 which are further subdivided into current day depositional environments and preserved fossil environments. The four main groups are strand line or beach sand deposits, dune sand deposits, offshore mineral sand deposits, and a new type of heavy mineral deposit recently encountered in Western Australia – the channel type heavy mineral deposits. Most of the inferred thorium resources are in the fine-grained flat-lying tabular fossil offshore heavy mineral sand deposits in western Victoria (Figure 7).

### **Thorium deposits and occurrences in igneous and metamorphic rocks**

Apart from heavy mineral sand deposits, Australian thorium resources are present in other geological settings, in veins and dykes, and in alkaline complexes (Figure 4, Table 7).

#### ***Vein-type thorium deposits***

Substantial thorium resources are present in the Nolans Bore rare earth, phosphate uranium deposit, hosted in fluorapatite veins and dykes. The deposit has a thorium resource of about 60,600 tonnes of ThO<sub>2</sub> (53,300 tonnes of Th) in 18.6 million tonnes of indicated and inferred ore grading at 3.1% rare earth oxides, 14% P<sub>2</sub>O<sub>5</sub>, 0.021% U<sub>3</sub>O<sub>8</sub> (Arafura Resources NL, Annual Report 2006) and 0.326% ThO<sub>2</sub> (personal communication Alistair Stephens, Arafura Resources NL, August 2006). The Nolans Bore project is currently undergoing pre-feasibility studies.

#### ***Alkaline and peralkaline igneous complexes***

Alkaline rocks are known from all major tectonic provinces in Australia except for the Precambrian Pilbara Block in north Western Australia and range in age from Archaean to Holocene (Jaques et al, 1985). Thorium resources have been published for at least two of the alkaline complexes.

In New South Wales, an alkaline trachyte plug is located 30 km south of Dubbo and hosts a measured resource of 35.7 million tonnes and 37.5 million tonnes of inferred resources grading 1.96% ZrO<sub>2</sub>, 0.04% HfO<sub>2</sub>, 0.46% Nb<sub>2</sub>O<sub>5</sub>, 0.03% Ta<sub>2</sub>O<sub>5</sub>, 0.14% Y<sub>2</sub>O<sub>3</sub>, 0.745% total REO, 0.014% U<sub>3</sub>O<sub>8</sub> (Alkane Resources Ltd, Annual Report, 2004), and 0.0478% Th giving a total tonnage of about 35,000 t of Th (personal communication Ian Chalmers, Alkane Resources Ltd, August 2007). The company is currently setting up a demonstration pilot plant to develop a process for treating the ore.

Similarly the peralkaline granitic intrusions of the Narraburra Complex 177km northwest of Canberra contain anomalous amounts of zirconium, REO and low concentrations of thorium (55 Mt at 1000g/t ZrO<sub>2</sub>, 60g/t Y<sub>2</sub>O<sub>3</sub>, 300g/t REO, 40g/t HfO<sub>2</sub>, 80g/t NbO<sub>2</sub>, and 50g/t ThO<sub>2</sub>, Capital Mining Limited Prospectus 2006). The ThO<sub>2</sub> content amounts to 2750 t (2420 t Th).

Other alkaline complexes with known rare earth and thorium mineralisation include Brockman, Western Australia; a large low-grade, Zr-Nb-REE deposit hosted in altered trachytic tuff of Palaeoproterozoic age containing mineralised material of 50 Mt at 4,400 ppm niobium, 270 ppm tantalum, 1.04% zirconium, 1240 ppm yttrium, 350 ppm hafnium, 110 ppm gallium and 900 ppm rare earths (Aztec Resources Ltd, 2004 Annual Report). Historic company reports show analyses for Th in six separate drill hole intersections (in tuffs) of 16m to 28m averaging from 259 to 371 ppm Th (Ranstead, 1994).

The Yangibana ferrocarnatite-magnetite-rare earth-bearing dykes (termed 'ironstones') crop out over an area of 500 square kilometres and forms part of the Gifford Creek Complex. (Pearson et al., 1996). The Yangibana prospect has a recorded resource of 3.5 Mt at 1.7% REO (Taylor, 1991). The rare earths are contained in coarse grained monazite containing up to 20% Nd<sub>2</sub>O<sub>5</sub> and 1600 ppm Eu<sub>2</sub>O<sub>3</sub> (Western Rare Earths N.L., 1990). Whole rock chemical analyses of 21 ironstone samples collected from five prospects in the Yangibana area recorded more than 1000 ppm Th for ten of the samples (1062 ppm to 5230 ppm Th, Pooley, 1988).

**Table 7** Thorium deposits and occurrences in igneous and metamorphic rocks, and phosphorites.

<b>Type of Deposit</b>	<b>Possible Thorium Tonnage or Th content</b>	<b>Selected deposits and comments</b>
<b>Vein-type deposits</b>		
○ <i>Veins</i>	53,000t Th	Nolans Bore, Northern Territory, REO-P-U-Th deposit in fluoroapatite veins and dykes. Anticipated to commence production in 2010.
○ <i>Pegmatite</i>	Very low grade Th 3-25 ppm Th	Greenbushes, Western Australia, giant pegmatite dyke of Archaean age with Li-Sn-Ta mineralisation. Operating mine.
<b>Alkaline and per-alkaline igneous complexes</b>		
	35,000t Th	Toongi, New South Wales; REO, U, and Th in an alkaline trachyte plug.
	Very low grade Th (<50 ppm Th)	Narraburra, New South Wales; Zr, Y, REO, Hf, Nb, and Th in peralkaline granitic intrusions,
	Drill hole intervals in tuffs averaging 259 ppm to 371 ppm Th	Brockman, Western Australia; a large low-grade Zr-Nb-REE deposit hosted in altered fluorite-bearing trachytic tuff.
	Up to 5230 ppm Th	Yangibana, Western Australia: REO (Nd, Eu) ferrocarnatite-magnetite-rare earth-bearing dykes ('ironstones'), part of the Gifford Creek Complex, the largest area of alkaline metasomatic rocks in Australia.
<b>Carbonatites</b>		
	Very low grade Th (~600 ppm Th)	Mt Weld carbonatite, Western Australia, REO, Ta, Nb (~0.069% ThO <sub>2</sub> – Carr Boyd Minerals Limited, Mt Weld project promotion brochure, April, 1991) – production of rare earths anticipated in second half of 2008.
	~ 500 ppm Th in the top 48 m of weathered zone in one drill hole	Cummins Range carbonatite, Western Australia, REO, U, P, Nb, Ta, Sc, Zr, Y .
<b>Occurrences of thorium in other types of deposits</b>		
○ <i>Iron oxide copper gold uranium deposits</i>	Very low Th content (~40 - 50 ppm Th)	Olympic Dam, South Australia; Cu, Au, U, REE, Ag
○ <i>Other uranium deposits</i>	No data available	Ranger, Jabiluka, Mary Kathleen, Radium Hill
○ <i>Phosphorites</i>	Very low Th content (5 - 47 ppm Th)	Australian phosphate deposits

### ***Carbonatites***

Mount Weld and Cummins Range have the most significant rare earth resources reported for carbonatites in Australia to date.

The Mount Weld deposit occurs within the regolith profile developed over the carbonatite and has a resource of 273 Mt at 0.9% Nb<sub>2</sub>O<sub>5</sub> and 12.24 Mt at 9.67% REO (Lynas Corporation Ltd announcement 3 March 2008). Tantalum is usually, but not always, associated with niobium, and the estimated resource amounts to 145 Mt at 0.034% Ta<sub>2</sub>O<sub>5</sub>. The 'typical' thorium content is reported to be about 600 ppm Th (~0.069% ThO<sub>2</sub> – Carr Boyd Minerals Limited, Mt Weld project promotion brochure, April, 1991).

Cummings Range has an inferred resource of 6.3 Mt at a grade of 0.5-1.0% rare earth oxides that was reported in 1978. However, current exploration by Navigator Resources Ltd is returning much higher grades that include 48 m at 3.5% REO and 64 m at 3.3% REO. Preliminary uranium intersections include 44 m at 881 ppm U<sub>3</sub>O<sub>8</sub> and 24 m at 798 ppm U<sub>3</sub>O<sub>8</sub> (Navigator Resources Ltd, June Quarterly Report, 2007). Historic sample analyses recorded about 500 ppm Th in the top 48 m of weathered zone in one drill hole with thorium values generally less than 400 ppm below the weathered zone (Richards, 1985).

### **Occurrences of thorium in other types of deposits**

#### ***Iron oxide copper gold (uranium) IOCG deposits***

In their 2007 Annual Report, BHP Billiton Limited reported total measured, indicated and inferred resources for their Olympic Dam deposit as being 7.738 billion tonnes at 0.87% Cu, 0.029% U<sub>3</sub>O<sub>8</sub>, 0.3g/t Au and 1.61g/t Ag. Olympic Dam also contains about 0.59% rare earths, which are not recovered in current mining operation. The thorium content in the ore is reportedly low at 40-50 ppm Th (Jane Belcher, pers. comm. BHP Billiton Limited, August 2007).

#### ***Thorium content in other uranium deposits***

Thorium is known to be present in other uranium deposits in Australia including unconformity type uranium deposits (e.g. Ranger, Jabiluka, Rum Jungle), metamorphic uranium deposits (e.g. the Mary Kathleen deposit - metamorphic skarn hosted), and intrusive uranium deposits (e.g. Radium Hill, Crockers Well). The available information suggests that in general, the thorium content in these deposits is low.

### **EXPLORATION**

There has been no widespread exploration for thorium in Australia apart from two exploration licences that have been reportedly acquired primarily for thorium exploration in Queensland.

Thorium however is a significant component of some deposits being explored for other commodities. As mentioned above, thorium is present in the Nolans Bore deposit and in the Narraburra Complex. Heavy mineral concentrations within the King Leopold Sandstone and the Warton Sandstone, which constitute the Durack Range Uranium project in the East Kimberley region in north-west Western Australia, also contain up to 2% thorium in the heavy mineral concentrate (Northern Mining Limited – announcement to the Australian Stock Exchange 21 March, 2007).

All mineral exploration in Australia is carried out by the private companies of the minerals industry. The Australian Government, State and Northern Territory Government participation is limited to provision of geoscientific data ('pre-competitive data') and in provision of geoscientific research support for the exploration industry to reduce exploration risk. Some State Governments provide limited funding for drilling programs.

Geoscience Australia's Onshore Energy and Minerals Division is currently engaged in the Australian Government's Onshore Energy Security Program (OESP), which commenced in August 2006 as part

of a broader package of energy exploration initiatives. The program has been developed in consultation with state and Northern Territory geological surveys and peak minerals and petroleum industry bodies, including the Australian Petroleum Production and Exploration Association and the Association of Mining and Exploration Companies. The five year program will deliver pre-competitive data packages and scientifically based assessments of the potential for onshore energy resources such as oil, gas, uranium, thorium and geothermal energy.

#### **PRODUCTION**

There is no current production of thorium in Australia. Thorium is present in monazite in heavy mineral beach sand deposits including in those that are currently being mined.

During the period 1980 to 1995, a total of about 165,000 t of monazite was produced from heavy mineral sand operations and exported for extraction of rare earths. About 159,500 t was produced from deposits in Western Australia and the remaining 5,500 t from New South Wales and Queensland. However, monazite is no longer considered to be a commercially viable source of rare earths because of the cost of disposal of radioactive material containing thorium.

In current heavy mineral sand operations in Australia, the monazite is generally dispersed back through the original host sand (to avoid the concentration of radioactivity) which is used in returning the mine site to an agreed land use. In doing so, the rare earths and thorium present in the monazite are negated as a resource as it would not be economic to recover the dispersed monazite for its rare earth and thorium content.

## Part 4 – Exploration Guidelines

There has been no widespread exploration for thorium in Australia apart from two exploration licences that have been reportedly acquired primarily for thorium exploration in Queensland. However, thorium is known to be widely distributed across Australia in a number of different geological settings but most of these have not been properly evaluated for their thorium content. The most important of these are heavy mineral sand deposits, carbonatites, (per)alkaline igneous complexes, granites and pegmatites, and iron oxide Cu-U-Au-REE deposits.

### **CARBONATITES**

There has been little exploration for carbonatites in Australia. Considering the presence of numerous tectonic settings favourable to the formation of carbonatites (cratonic regions, rifts) and the small number of known carbonatites in Australia the prospects for finding more carbonatite complexes appears good. Australia is underexplored for carbonatite-associated primary magmatic and, especially, supergene-enriched ore deposits.

Current exploration guidelines for carbonatite-associated deposits (Richardson and Birkett, 1996) include the following:

1. Carbonatites occur as irregular, centrally located rounded masses or continuous to semicontinuous concentric rings and dykes, commonly within more extensive alkali-silicate complexes. They are notable for their relatively small size with the carbonatites being typically only a few kilometres in diameter and the surface area of the complexes generally less than 50 km<sup>2</sup>. However, extrusive pyroclastic carbonatites can be laterally extensive (e.g. the Mount Grace extrusive carbonatite in Canada can be traced for at least 100 km).
2. Because carbonatite deposits are commonly contained in plug-like intrusive bodies or ring structures, many are associated with annular topographic features. However, in Australia the deep weathering of much of the Australian continent has destroyed primary rock lithologies, making recognition of weathered carbonatite exceptionally difficult.
3. The presence of the characteristic fenite facies may prove useful as a general guide in the detection of carbonatites and associated mineralisation. Fenitisation is generally characterised by desilification; however, in certain REE-rich magnesiocarbonatites and ferrocyanatites (e.g. Mountain Pass, California) mineralisation is associated with enrichment in silica.
4. Elements associated with carbonatite deposits (i.e. Nb, Ta, Ba, Sr, U, Th, LREEs, Ti, F, and P) are usually contained in distinct chemically resistant minerals (e.g. pyrochlore, monazite, perovskite) that can be detected through regional studies of heavy mineral suites from unconsolidated sediments.
5. Magnetic, radiometric, and gravimetric techniques can all be applied to exploration for carbonatite deposits. Since carbonatites commonly contain appreciable magnetite, they generally have a higher magnetic susceptibility than their host rocks and appear on aeromagnetic maps as small-diameter (~ 5 km) high-intensity, circular to elliptical positive magnetic anomalies. Exposed carbonatites that contain radioactive minerals (e.g. thorian pyrochlore, monazite, etc.) have positive radiometric responses. However, the lack of penetration of the conventionally measured (K, U, Th) radiation detracts from the usefulness of this method in areas of thick cover.

Nevertheless, the chance of finding new carbonatite occurrences remains high. For example, in 1996 (Rugless and Pirajno, 1996) reported the discovery of the Copperhead carbonatite complex 70 km north of Halls Creek in Western Australia. Possible carbonatite dykes have also been reported near Arltunga and Mount Bleechmore in the Northern Territory (Hussey, 2003).

### **PERALKALINE AND ALKALINE ROCKS**

The majority of Australia's peralkaline rocks occur in the Yilgarn craton but alkaline rocks are known from all major tectonic provinces except for the Pilbara Block (Jaques et al., 1985). Current exploration guidelines for peralkaline rock-associated deposits (Richardson and Birkett, 1996) include the following:

1. Tectonic setting: The deposits typically occur in anorogenic tectonic settings in which magma generation and intrusion are associated with crustal extension.
2. Mineralogy: Undersaturated peralkaline intrusions are characterised by quartz, fluorite and colourful but relatively rare, alkali-rich minerals such as sodalite (dark blue), eudialyte (pink/red), acmite (brown/green), alkali-amphiboles (blue/black), rinkolite (red/brown/yellow brown), and gadolinite (green/brown-black). The presence of U and Th in these deposits commonly results in the fluorite being purple.
3. Geochemistry: Peralkaline rocks associated with mineralisation typically have high Rb/Sr values and are anomalously enriched in Zr, Zn, Nb, Y, Th, U, LREE and HREE, F, Be, and Pb. These elements provide strong contrasts to regional background concentrations. Indicator minerals in heavy mineral concentrates from stream sediments include pyrochlore, chrysoberyl, helvite, and euclase.
4. Geophysics: Because most REE(Th) ores are somewhat radioactive, due to the presence of Th, and to a lesser extent U, radiometric surveys may be useful for identifying parent granites and other features associated with mineralisation (e.g. alteration, structural controls, etc.). In Canada and Greenland, airborne radiometric surveys at 1 km line-spacing have proven effective in delineating peralkaline intrusions and their mineral deposits (Batterson and LeGrow, 1986; Steenfelt, 1991). Gravity surveys can also be used to outline REE(Th) deposits in host rocks of contrasting density.

### **PEGMATITES**

U-Th-REE-bearing pegmatites are common throughout Australia (Lottermoser, 1991). In the past, most pegmatite deposits were believed to be either too small or too low grade to be economically mined (Lottermoser, 1991). However, pegmatites enriched in REE were mined on a small scale at Coolegong and Wodgina in Western Australia at the turn of the last century (Hill, 1975; Sweetapple and Collins, 2002), and the Greenbushes pegmatite deposit is the world's largest hard rock tantalum resource.

The North Pilbara Craton contains at least 120 pegmatite deposits and many more are known to occur in the Yilgarn Craton. Another prospect located 100 km northeast of Alice Springs contains a number of allanite-rich coarsely crystalline pegmatites with a reported resource of 1 Mt grading at 4 % allanite. Detailed studies have shown that the allanite contains up to 1.5 wt.% thorium (O'Driscoll, 1988). Numerous other pegmatites, with appreciable accessory allanite and monazite, also intrude the Harts Range Group gneisses of the Arunta Block in the Northern Territory (Hussey, 2003). Thus, chances of discovering other pegmatite-associated deposits remain high.

Current exploration guidelines for rare earth pegmatites (Trueman and Černý, 1982) include the following:

1. Geological setting: rare earth pegmatites typically occur in rock suites of medium grade metamorphic facies, along fault systems and lithological boundaries, or closely associated with anorogenic granitoid plutons.
2. Regional zoning: identification of zonal patterns of pegmatite distribution can help isolate specific areas of interest.
3. Fractionation: mineral assemblages and chemistry of individual minerals in pegmatites indicate fractionation levels and economic potential.
4. Geochemistry: primary dispersion aureoles in host rocks (e.g. Li, Rb, Cs, Be, B), secondary dispersion halos in overburden, and light plus heavy minerals in stream sediments help identify target areas at both regional and local scales.

5. Geophysics: Radiometric surveys may be useful for identifying parent granites and/or associated pegmatites that are enriched in U and Th. Gravity surveys or worms can be used to outline pegmatites in host rocks of contrasting density.

#### **OTHER THORIUM RESOURCES**

Although the bulk of Australia's thorium resources may reside in heavy mineral sand deposits, there is also considerable thorium associated with the other styles of mineralisation reported above.

World-class iron oxide Cu-U-Au-Ag deposits occur in the Gawler Craton and the Mount Isa Inlier and they are known to contain thorium-bearing bastnäsite, fluorencite, monazite, xenotime, etc., but there are no publicly available estimates of their thorium resources. Some skarn deposits (e.g. Mary Kathleen) also contain significant U-Th-REE mineralisation. Pronounced thorium anomalies are also known to be associated with the unconformity-style uranium deposits in the Pine Creek Geosyncline but little is known about the thorium resources of these deposits.

Furthermore, an estimated 4000 million tonnes of phosphorite ore, with potentially up to 50 ppm Th, is reported to lie within the Georgina Basin in northern Australia (Lottermoser, 1991). Thorium-bearing apatite also occurs in the Redbank breccia pipes in the MacArthur Basin and the volcanic host rocks in this region show evidence of intense potassium metasomatism within many hundreds of kilometres of the Redbank area (Jaques et al., 1985). In other regions, U-Th bearing veins and lodes are known to occur in faults and shear zones in meta-sedimentary and meta-volcanic rocks (Robertson et al., 1998).

Geophysical surveys involving radiometric, magnetic, and gravimetric techniques can all be applied to the search for Th-bearing deposits. However; the lack of penetration of radiometric surveys limits the usefulness of this method in areas of thick cover that are typical of many parts of Australia. In many places, the deep weathering of the Australian continent has destroyed primary rock lithologies, making recognition of mineralised areas exceptionally difficult. Thus, stream sediment and other geochemical surveys may also be used to help identify target areas at both regional and local scales.

It is clear that Australia has a wide variety of deposits that contain thorium but the geochemical processes that lead to thorium-enrichment are poorly understood at present. Much more work is required to better understand the paragenesis of thorium in the different deposit types and to more comprehensively evaluate Australia's total identified thorium resources.

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## Appendix 1

Compilation of thorium-bearing minerals after (1982), with supplements from (Fron del, 1956).

MINERAL	FORMULA	Th content (up to percentage shown)	U content (up to percentage shown)
<b><u>OXIDES</u></b>			
Uraninite	$(U^{4+}_{1-x}U^{6+}_x)O^{2+}_x$	45.3	88.1
Davidite	$(Fe^{2+}, La, U, Ca)_6(Ti, Fe^{3+})_{15}(O, OH)_{36}$	0.12	4.4
Broggerite	$(U, Th)O_2$	12	
Thorianite	$(Th, U)O_2$	88	44.6
Cerianite	$(Ce, Th)O_2$	4.5	
Clarkeite	$(Na, Ca, Pb, Th)_2U_2(O, OH)$	2.2	68.0
Fergusonite	$(Y, Ce, Fe, U)(Nb, Ta, Ti)O_4$	6.0	7.2
Formanite	$(Y, U, Th, Ca)(Ta, Nb, Ti)O_4$	1.1	1.1
Fourmarierite	$Pb(UO_2)_4O_3(OH)_4 \cdot 4H_2O$		
Vandendriesscheite	$Pb_{1.5}(UO_2)_{10}O_6(OH)_{11} \cdot 11H_2O$		
Fersmite	$(Ca, Ce, Na)(Nb, Ta, Ti)_2(O, OH, F)_6$	<1	
Pyrochlore / microlite	$(Na, Ca, Ce, U)_2(Nb, Ta, Ti)_2(O, OH, F)_7$	5.5	17.1
Irinite	$(Na, Ce, Th)(Ti, Nb)(O, OH)_3$		
Betafite	$(Ca, Na, U)_2(Nb, Ta, Ti)_2O_6(OH)$	1.1	24.5
Obruchevite (yttropyrochlore)	$(Y, Na, Ca, U)_{1-2}(Nb, Ta, Ti)_2(O, OH)_7$	0.2	10.9
Zirkelite	$(Ca, Th, U, Ce)Zr(Ti, Nb)_2O_7$	6.4	1.4
Loparite	$(Ce, Th, Na, Ca)_2(Ti, Nb)_2O_6$	11.4	0.17
Euxenite	$(Y, Ca, Ce, U, Th)(Nb, Ta, Ti)_2O_6$	14.2	12.45
Polycrase	$(Y, Ca, Ce, U, Th)(Ti, Nb, Ta)_2O_6$	4.7	12.4
Kobeite	$(Y, U)(Ti, Nb, Ta)_2(O, OH)_6$	1.0	10.7
Aeschynite	$(Ce, Y, Ca, Fe, Th)(Ti, Nb)_2(O, OH)_6$	4.7	12.4
Samarskite	$(Y, Ce, U, Ca, Pb)(Nb, Ti, Ta, Sn)_2O_6$	3.7	16.6
Yttrotantalite	$(Y, U, Fe)(Ta, Nb)O_4$	2.2	4.8
Ishikawaite	$(U, Fe, Y, Ca)(Nb, Ta)O_4$		19.3
Brannerite/thorutite	$(U, Ca, Ce, Th)(Ti, Fe)_2(O, OH)_6$	47.5	43.6
Yttrocra site	$(Y, Th, U, Ca)(Ti, Fe)_2(O, OH)_6$	7.3	3.3
Polymignite	$(Ca, Fe, Y, Th)(Nb, Ti, Ta, Zr)O_4$	3.4	
Zirconolite	$(Ca, Fe, Y, Th)_2Fe(Ti, Nb)_3Zr_2O_{14}$		
Thorutite	$(Th, U, Ca)Ti_2(O, OH)_6$		
<b><u>CARBONATES</u></b>			
Bastnäs site	$(Ce, Th, La, Y, Ca)(CO_3)F$	41.0	0.09
Cordylite	$NaBaCe_2(CO_3)_4F$	<1	
Thorbastnasite	$Th(Ca, Ce)(CO_3)_2F_2 \cdot 3H_2O$		
Mckelveyite	$Ba_3Na(Ca, U)Y(CO_3)_6 \cdot 3H_2O$	3.9	0.09
Kukharenkoite	$Ba_2(La, Ce, Th)(CO_3)_3F$		
Tengerite	$Y_2(CO_3)_3 \cdot nH_2O$	<1	
Tuliokite	$BaNa_6Th(CO_3)_6 \cdot 6H_2O$		

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<b>MINERAL</b>	<b>FORMULA</b>	<b>Th content (up to percentage shown)</b>	<b>U content (up to percentage shown)</b>
<b><u>SILICATES</u></b>			
Coffinite	$U(SiO_4)_{1-x}(OH)_{4x}$		60.2
Ekanite	$(Th, U)(Ca, Fe, Pb)_2Si_8O_{20}$	24.0	1.8
Cheralite	$(Th, Ca, Ce, La, U, Pb)(P, Si)O_4$	27.7	5.5
Cappelenite	$(Ba, Ca, Na)(Y, La)_6B_6Si_3(O, OH)_{27}$	0.7	
Thorite	$ThSiO_4$	64.1	10.1
Huttonite	$ThSiO_4$	71.6	
Thorogummite	$Th(SiO_4)_{1-x}(OH)_{4x}$	50.8	31.5
Saryarkite	$Ca(Y, Th)Al_5(SiO_4)_2(PO_4, SO_4)_2(OH)_7 \cdot 6H_2O$	8.0	
Abukamalite	$(Ca, Y, Th)_5(Si, P, AlO_4)_3(O, F)$	<1	
Perrierite	$(Ca, Ce, Th)_4(Mg, Fe)_2(Ti, Fe^{3+})_3Si_4O_{22}$	3.6	
Britholite	$(Ca, Ce)_5(SiO_4, PO_4)_3(OH, F)$	17.0	1.9
Allanite	$(Ce, Ca, Y, Th)_2(Al, Fe, Mg)_3(SiO_4)_3(OH)$	4.35	2.95
Melanocerite	$(Ce, Th, Ca)_5(Si, B)_3O_{12}(OH, F) \cdot nH_2O$	12.0	
Mosandrite	$Na_2Ca_4(Ce, Y)(Ti, Zr)(Si_2O_7)_2OF_3$	<1	
Lovozerite	$Na_2CaZrSi_6O_{18}(OH, O)_6 \cdot H_2O$	<1	
Rinkite	$Na(Na, Ca)_2(Ca, Ce)_4(Ti, Nb)(Si_2O_7)_2(O, F)_2$	<1	
Thalenite	$Y_3Si_3O_{10}$	10.5	4.0
Tritomite	$(Y, Ca, La, Fe)_5(Si, B, Al)_3(O, OH, F)_{13}(?)$	8.3	
Chevkinite	$(Ca, Ce, Y, U, Th)_4(Fe, Mg)_2(Ti, Fe)_3Si_4O_{22}$	18.4	2.3
Steenstrupine	$(Ce, La, Th, Na, Mn)_6(Si, P)_6O_{18}(OH)$	9.96	0.18
Arapovite <sup>1</sup>	$(U, Th)(Ca, Na)_2(K_{1-x}[X])Si_8O_{20} \cdot H_2O$ (x=0,5)		
Ciprianiite <sup>1</sup>	$Ca_4[(Th, U)REE]_2Al[Si_4B_4O_{22}](OH, F)_2$		
Coutinhoite	$(Th, Ba)0,5(UO_2)_2Si_5O_{13} \cdot 1-3,5H_2O$		
Clinglusite	$(Na, K)_4(Mn, Ca)_5(Ti, Zr)_3Si_{14}O_{41} \cdot 9H_2O$	<1	
Dissakisite	$Ca(La, Ce, Th)(Mg, Fe^{2+})(Al, Fe^{3+}, Cr)_2(SiO_4)(Si_2O_7)O(OH)$		
Eylettersite	$(Th, Pb)_{1-x}Al_3(PO_4, SiO_4)_2(OH)_6$ (?)		
Iraqite	$K(La, Ce, Th)_2(Ca, Na)_4(Si, Al)_{16}O_{40}$		
Phosinaite	$Na_{13}Ca_2(Ce, La, Th, Nd, Pr)(Si_4O_{12})(PO_4)_4$		
Stacyite	$Th(Ca, Na)_2K_{1-x}Si_8O_{20}$		
Thomasite	$Na_{12}Th_3(Si_8O_{19})_4 \cdot 18H_2O$		
Turkestanite <sup>1</sup>	$Th(Ca, Na)_2(K_{1-x}[X])Si_8O_{20} \cdot nH_2O$		
Umbozerite	$Na_3Sr_4ThSi_8(O, OH)_{24}$		
Vicanite	$(Ca, REE, Th)_{15}Fe^{3+}(SiO_4)_3(Si_3B_3O_{18})(BO_3)(As^{5+}O_4)(As^{3+}O_3)_x(NaF_3)_{1-x}F_7 \cdot 0.2H_2O$ (x=0 - 4)		
Karnasurtite	$(Ce, La, Th)(Ti, Nb)(Al, Fe^{3+})(Si, P)_2O_7(OH)_4 \cdot 3H_2O$ (?)		
Uranophane	$Ca(UO_2)_2SiO_3(OH)_2 \cdot 5H_2O$	1	
Yttrialite	$(Y, Th)_2Si_2O_7$	7.7	
Zircon	$ZrSiO_4$	13.1	2.7
<b><u>PHOSPHATES</u></b>			
Grayite/brockite	$(Th, Pb, Ca, Ce)PO_4 \cdot H_2O$	36.8	
Xenotime	$YPO_4$	2.2	3.6
Lermontovite	$(U, Ca, Ce)_3(PO_4)_4 \cdot 6H_2O$ (?)		44.3
Ningyoite	$(U, Ca, Ce)_2(PO_4)_2 \cdot 1-2H_2O$		20.4

**A Review of the Geochemical Processes Controlling the Distribution of Thorium in the Earth's Crust and Australia's Thorium Resources**

<b>MINERAL</b>	<b>FORMULA</b>	<b>Th content (up to percentage shown)</b>	<b>U content (up to percentage shown)</b>
<b><u>PHOSPHATES (cont.)</u></b>			
Monazite	(Ce, La, Nd, Th)PO <sub>4</sub>	26.4	0.1
Althupite	ThAl(UO <sub>2</sub> ) <sub>7</sub> (PO <sub>4</sub> ) <sub>4</sub> (OH) <sub>5</sub> · 15H <sub>2</sub> O		
Brockite	(Ca, Th, Ce)(PO <sub>4</sub> ) · H <sub>2</sub> O		
Kivuite	(Th,Ca,Pb)H <sub>2</sub> (UO <sub>2</sub> ) <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>8</sub> · 7H <sub>2</sub> O (?)		

<sup>1</sup> [] = vacancy

## Glossary

**Accessory mineral** Any mineral the presence of which is not essential to the classification of the rock. Accessory minerals generally occur in minor amounts; in sedimentary rocks they are mostly heavy minerals.

**Acid** A solution of pH less than 7.0 at 25 degrees C.

**Actinide series** A group of chemical elements of increasing atomic number, starting with actinium (atomic number 89) and extending through atomic number 103. These elements occupy one single place in the extended periodic table, in the same group into which the rare-earth elements (lanthanides) are classified.

**Adsorption** Adherence of gas molecules, or of ions or molecules in solution, to the surface of solids with which they are in contact.

**Albitisation** Introduction of, or replacement by, albite, usually replacing a more calcic plagioclase.

**Alkali** Any substance having marked basic properties; i.e., being capable of furnishing to its solution or other substances the hydroxyl ion, OH<sup>-</sup>.

**Alkalic** Said of an igneous rock that contains more alkali metals than is considered average for the group of rocks to which it belongs.

**Alkaline earth** One of a group of elements (Group II) forming divalent cations; esp. calcium, strontium, and barium, but also includes beryllium, magnesium, and radium.

**Anatexis** Melting of pre-existing rock. This term is commonly modified by terms such as intergranular, partial, differential, selective, or complete.

**Anorogenic** A geologic feature that forms during a period of quiescence between orogenic periods.

**Aplite** A light-colored igneous rock characterized by a fine-grained saccharoidal (i.e., aplitic) texture. Aplites may range in composition from granitic to gabbroic, but the term aplite with no modifier is generally understood to mean granitic aplite, consisting essentially of quartz, potassium feldspar, and acid plagioclase.

**Argillaceous** Pertaining to, largely composed of, or containing clay-size particles or clay minerals, such as an argillaceous ore in which the gangue is mainly clay; esp. said of a sediment (such as marl) or a sedimentary rock (such as shale) containing an appreciable amount of clay.

**Atomic number** The number of protons in the nucleus of an atom.

**Aureole** A circular or crescentic distribution pattern about the source or origin of a mineral, ore, mineral association, or petrographic feature. It is encountered principally in magnetic and geochemical surveys.

**Basalt** A general term for dark-coloured mafic igneous rocks, commonly extrusive but locally intrusive (e.g., as dikes), composed chiefly of calcic plagioclase and clinopyroxene; the fine-grained equivalent of gabbro. Nepheline, olivine, orthopyroxene, or quartz may be present.

**Basic** A basic substance is most commonly thought of as a substance that can accept protons. This refers to the Brønsted-Lowry theory of acids and bases.

**Batholith** A discordant pluton that increases in size downwards, has no determinable floor, and shows an area of surface exposure exceeding 100 km<sup>2</sup>.

**Bauxite** An off-white, grayish, brown, yellow, or reddish brown rock composed of amorphous or microcrystalline aluminum oxides and oxyhydroxides, mainly gibbsite Al(OH)<sub>3</sub>, bayerite Al(OH)<sub>3</sub>, boehmite AlO(OH), and diaspore AlO(OH) admixed with free silica, silt, iron hydroxides, and esp. clay minerals; a highly aluminous "laterite." It is massive, pisolitic, earthy; occurs as weathered surface deposits after prolonged leaching of silica from aluminous rocks under tropical to subtropical weathering, also transported deposits. Bauxite is the chief ore of aluminum.

**Biophile** Those elements that are concentrated in and by living plants and animals.

- Bond character** The attractive interactions between atoms and molecules, and that which confers stability to diatomic and polyatomic chemical compounds.
- Breccia** A coarse-grained clastic rock, composed of angular broken rock fragments held together by a mineral cement or in a fine-grained matrix; it differs from conglomerate in that the fragments have sharp edges and unworn corners. Breccia may originate as a result of talus accumulation, explosive igneous processes, collapse of rock material, or faulting.
- Breeder reactors** A nuclear reactor that manufactures more fissionable isotopes than it consumes. Breeder reactors use the widely available, nonfissionable uranium isotope  $^{238}\text{U}$ , together with small amounts of fissionable  $^{235}\text{U}$ , to produce a fissionable isotope of plutonium,  $^{239}\text{Pu}$ .
- Carbonatite** A carbonate rock of apparent magmatic origin, generally associated with kimberlites and alkalic rocks. Carbonatites have been variously explained as derived from magmatic melt, solid flow, hydrothermal solution, and gaseous transfer.
- Carbonatisation** Introduction of, or replacement by, carbonates.
- Catalyst** A substance capable of changing the rate of a reaction without itself undergoing any net change.
- Chelate** A substance that contains two or more electron donor groups and will combine with a metal ion so that one or more rings are formed.
- Chondrites** are stony meteorites that have not been modified due to melting or differentiation of the parent body. They formed when various types of dust and small grains that were present in the early solar system accreted to form primitive asteroids.
- Cogenetic** Formed in the same event or at the same time.
- Colloidal** A substance composed of extremely small particles, ranging from 0.2 to 0.005  $\mu\text{m}$ , which when mixed with a liquid will not settle, but remain permanently suspended; the colloidal suspension thus formed has properties that are quite different from those of the simple, solid-liquid mixture or a solution.
- Comendite** A sodic rhyolite containing alkalic amphibole and/or pyroxene.
- Contact metamorphism** A process whereby rocks undergo physical or chemical changes or both at or very near contact between magma and rock during intrusion.
- Coordination number** This is the total number of neighbors of a central atom in a chemical compound.
- Crystal chemistry** The study of the relations among chemical composition, internal structure, and the physical properties of crystalline matter.
- Deuteric** Referring to reactions between primary magmatic minerals and the water-rich solutions that separate from the same body of magma at a late stage in its cooling history.
- Diatreme** A breccia-filled volcanic pipe that was formed by a gaseous explosion.
- Differentiation** See magmatic differentiation.
- Dyke** A long mass of minerals, usually an intrusion of igneous rocks, filling up rents or fissures in the original strata.
- Electron configuration** the arrangement of electrons in an atom, molecule, or other physical structure (e.g., a crystal).
- Fenite** A quartzo-feldspathic rock that has been altered by alkali metasomatism at the contact of a carbonatite intrusive complex. The process is called fenitization. Fenite is mostly alkalic feldspar, with some aegirine, subordinate alkali-hornblende, and accessory sphene and apatite.
- Fission** The process by which atomic nucleus breaks down to form nuclei of lighter atoms.
- Fractionation** The process whereby crystals that formed early from magma have time to settle appreciably before the temperature drops much further. They are thus effectively removed from environment in which they formed.
- Gel** A colloidal system in which a porous network of interconnected nanoparticles that spans the volume of a liquid medium. Both by weight and volume, gels are mostly liquid in

composition and thus exhibit densities similar to liquids, however have the structural coherence of a solid.

**Gneiss** Metamorphic rock with close cleavage a few hundredths of a millimeter to a centimeter or more apart.. Commonly formed by metamorphism of granite.

**Granite** Coarse-grained igneous rock dominated by light-coloured minerals, consisting of about 50 percent orthoclase, 25 percent quartz, and balance of plagioclase feldspars and ferromagnesian silicates.

**Granodiorite** A group of coarse-grained plutonic rocks intermediate in composition between quartz diorite and quartz monzonite, containing quartz, plagioclase (oligoclase or andesine), and potassium feldspar, with biotite, hornblende, or, more rarely, pyroxene, as the mafic components; also, any member of that group; the approximate intrusive equivalent of rhyodacite. The ratio of plagioclase to total feldspar is at least 2: 1 but less than 9: 10. With less alkali feldspar it grades into quartz diorite, and with more alkali feldspar, into granite or quartz monzonite.

**Granulite facies** Gneissic rocks produced by deep-seated, high-grade regional metamorphism.

**Greenschist facies** Assemblage of minerals formed between 150 and 250° C during regional metamorphism.

**Greenstone** A field term applied to any compact dark-green altered or metamorphosed basic igneous rock (e.g., spilite, basalt, gabbro, diabase) that owes its colour to the presence of chlorite, actinolite, or epidote.

**Half life** The time in which the quantity of a particular radioactive isotope is reduced to one-half of its initial value.

**Heavy rare earth elements (HREE)** The rare earth elements from Europium to Lutetium.

**Hornfels** A fine-grained rock composed of a mosaic of equidimensional grains without preferred orientation and typically formed by contact metamorphism. Porphyroblasts or relict phenocrysts may be present in the granoblastic matrix.

**Hydrolysis** The formation of an acid and a base from a salt by interaction with water, caused by the ionic dissociation of water.

**Igneous rock** These are formed by the solidification of molten material that originated within the earth.

**Incompatible element** This is an element that is unsuitable in size and/or charge to the cation sites of the minerals, and is defined by the partition coefficient between rock-forming minerals and melt being much smaller than 1.

**Intrusive** Rock solidified from mass of magma that invaded Earth's crust but did not reach surface.

**Ion Exchange** Reversible exchange of ions contained in a crystal for different ions in solution without destruction of crystal structure or disturbance of electrical neutrality. The process is accomplished by diffusion and occurs typically in crystals possessing one- or two-dimensional channelways where ions are relatively weakly bonded. Also occurs in resins consisting of three-dimensional hydrocarbon networks to which many ionizable groups are attached.

**Ionic size** Average distance from center to outermost electron of an ion.

**Isostructural compounds** Compounds or minerals that have the same ionic or molecular crystal structure. Isostructure is more rigorous than isomorphism; the latter requires similar crystal forms, the former a one-to-one correspondence of atomic particles. Isostructural minerals may differ markedly in chemical composition and physical properties, e.g., fluorite and uraninite, or may be closely similar, e.g., the calcite group of carbonates.

**Isotope** Alternative form of an element produced by variations in number of neutrons in nucleus.

**I-type granite** Granite with an igneous protolith. These cover a broad spectrum of compositions from felsic to mafic and have relatively high Na<sub>2</sub>O normally greater than 3.2% in felsic varieties, decreasing to >2.2% in more mafic types. Mol. Al<sub>2</sub>O<sub>3</sub>/(Na<sub>2</sub>O+K<sub>2</sub>O+CaO)<1.1.

**Jarosite** A trigonal mineral,  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ; alunite group; amber yellow to dark brown; forms druses of minute crystals, crusts, and coatings; may be fibrous or fine-grained and massive; associated with volcanic rocks; thought to form under solfataric conditions at elevated temperatures and pressures; in some places with alunite.

**Juvenile** A term applied to rock, water and gases that are known to have been derived directly from magma and are thought to have come to the Earth's surface for the first time.

**Kimberlite** A highly serpentinised porphyritic peridotite, commonly brecciated, which occurs in vertical pipes, dikes, and sills. It is the principal original environment of diamond, but only a small percentage of the known kimberlite occurrences are diamondiferous.

**Laccolith** A concordant igneous intrusion with a known or assumed flat floor and a postulated, dike-like feeder commonly thought to be beneath its thickest point. It is generally plano-convex in form and roughly circular in plan, less than 5 miles (8 km) in diameter, and from a few feet to several hundred feet in thickness.

**Lamproite** A group name for dark-coloured hypabyssal or extrusive rocks rich in potassium and magnesium; also, any rock in that group, such as madupite, orendite, fitzroyite, verite, cedricite, or wyomingite.

**Lamprophyre** A group of dark-coloured, porphyritic, hypabyssal igneous rocks characterized by panidiomorphic texture, a high percentage of mafic minerals (esp. biotite, hornblende, and pyroxene), which form the phenocrysts, and a fine-grained groundmass with the same mafic minerals in addition to feldspars and/or feldspathoids; also, any rock in that group. Most lamprophyres are highly altered. They are commonly associated with carbonatites.

**Laterite** Red residual soil developed in humid, tropical, and subtropical regions of good drainage. It is leached of silica and contains concentrations particularly of iron oxides and hydroxides and aluminum hydroxides. It may be an ore of iron, aluminum, manganese, or nickel.

**Leucocratic** Light-colored; applied to igneous rocks that are relatively poor in mafic minerals. The percentage of mafic minerals necessary for a rock to be classified as leucocratic varies among petrologists, but is usually given as less than 30% to 37.5%.

**Light rare earth elements (LREE)** The rare earth elements from Lanthanum to Samarium.

**Limonite** A rock composed of cryptocrystalline and amorphous hydrated iron oxyhydroxides, generally predominantly goethite with or without adsorbed water, but also akaganeite, ferrosityte, or lepidocrocite; may be yellow, red, brown, or black; hardness variable; an oxidation product of iron (rust) or iron-bearing minerals and may be pseudomorphous after them; as a precipitate, both inorganic and biogenic, in bogs, lakes, springs, or marine deposits; and as a variety of stalactitic, reniform, botryoidal, or mammillary deposits. It colors many yellow clays and soils and is a minor ore of iron. See also: iron ore; brown hematite; brown umber.

**Lithophile** An element that is concentrated in the silicate rather than in the metal or sulfide phases of meteorites. Such elements concentrate in the Earth's silicate crust in Goldschmidt's tripartite division of elements in the solid Earth.

**Mafic** Pertaining to or composed dominantly of the ferromagnesian rock-forming silicates.

**Magmatic differentiation** The process by which more than one rock type is derived from a parent magma.

**Metamorphic rock** Any rock derived from pre-existing rocks by mineralogical, chemical, and/or structural changes, essentially in the solid state, in response to marked changes in temperature, pressure, shearing stress, and chemical environment, generally at depth in the Earth's crust.

**Migmatite** A composite rock composed of igneous or igneous-appearing and/or metamorphic materials that are generally distinguishable megascopically.

**Moho** Short name for the Mohorovicic discontinuity separating the Earth's crust from the mantle

- Monomer** This is a small molecule that may become chemically bonded to other monomers to form a polymer.
- Mylonite** A compact, chertlike rock without cleavage, but with a streaky or banded structure, produced by the extreme granulation and shearing of rocks that have been pulverized and rolled during overthrusting or intense dynamic metamorphism. Mylonite may also be described as a microbreccia with flow texture.
- Mylonitisation** Deformation of a rock by extreme microbrecciation, due to mechanical forces applied in a definite direction, without noteworthy chemical reconstitution of granulated minerals. Characteristically the mylonites thus produced have a flinty, banded, or streaked appearance, and undestroyed augen and lenses of the parent rock in a granulated matrix.
- NYF pegmatites** (Niobium, yttrium, fluorine) – These pegmatites carry accessory mineralisation with Nb>Ta, Y, REE, Ti, Zr, Be, U, Th, and F while the contents of P, B, and rare alkalis are commonly negligible. They are typically associated with subalkaline to peralkaline granites.
- Oligomer** This consists of a finite number of monomer units in contrast to a polymer which, at least in principle, consists of an unbounded number of monomers.
- Oxidation state** An indicator of the degree of oxidation of an atom in a chemical compound. The formal oxidation state is the hypothetical charge that an atom would have if all bonds to atoms of different elements were 100% ionic.
- Oxyions** These are negatively charged polyatomic ions that contain oxide. Oxyions can be viewed as the conjugate base of a corresponding oxyacid, although both components are not necessarily stable.
- Oxyphile** A term used to describe elements that have a greater free energy of oxidation per gram of oxygen than iron.
- Pegmatite** An exceptionally coarse-grained igneous rock, with interlocking crystals, usually found as irregular dikes, lenses, or veins, especially at the margins of batholiths. Most grains are 1 cm or more in diameter. Although pegmatites having gross compositions similar to other rock types are known, their composition is generally that of granite; the composition may be simple or complex and may include rare minerals rich in such elements as lithium, boron, fluorine, niobium, tantalum, uranium, thorium and rare earths. Pegmatites represent the last and most hydrous portion of a magma to crystallize and hence contain high concentrations of minerals present only in trace amounts in granitic rocks.
- Peralkaline rocks** Igneous rocks characterised by a molar excess of alkali elements ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) over aluminium ( $\text{Al}_2\text{O}$ ). Mineralogically, this chemical distinction is commonly manifested in the presence of alkali amphiboles and pyroxenes.
- Peridotite** A general term for a coarse-grained plutonic rock composed chiefly of olivine with or without other mafic minerals such as pyroxenes, amphiboles, or micas, and containing little or no feldspar. Accessory minerals of the spinel group are commonly present.
- Perovskite** An orthorhombic mineral,  $\text{CaTiO}_3$ ; may have Ca replaced by rare earths and Ti replaced by niobium and tantalum; pseudocubic; massive or in cubic crystals; yellow, brown, or grayish black; occurs in silica-deficient metamorphic and igneous environments such as skarns; also occurs in mafic and alkaline igneous rocks.
- pH** The negative logarithm (base 10) of the hydrogen-ion activity. It denotes the degree of acidity or of basicity of a solution. At 25 °C, 7 is the neutral value. Acidity increases with decreasing values below 7, and basicity increases with increasing values above 7.
- Phenocryst** A crystal significantly larger than crystals of surrounding minerals.
- Plutonic igneous rock** A rock formed by slow crystallization, which yields coarse texture. Once believed to be typical of crystallization at great depth, but not a necessary condition.
- Polymer** This is a substance composed of molecules with large molecular mass composed of repeating structural units, or monomers, connected by covalent chemical bonds.

**Polyvalent** This is a synonym for multivalent and an ion or molecule that has more than one valence state.

**Protolith** refers to the precursor lithology of a metamorphic rock.

**Psammitic** A term formerly used for a fine-grained, fissile, clayey sandstone.

**Rare earth elements (REE)** A series of 15 metallic elements, from lanthanum (atomic number 57) to lutetium (71), and of two other elements; yttrium (39), and scandium (21). These elements are not especially rare in the Earth's crust, but concentrations are. The rare earth metals resemble one another very closely in chemical and physical properties, thus making it most difficult to separate them. The rare earths are constituents of certain minerals, esp. monazite, bastnaesite, and xenotime.

**Resistate** A sediment consisting of minerals that are chemically resistant and are enriched in the residues of weathering processes.

**Rhyolite** A group of extrusive igneous rocks, typically porphyritic and commonly exhibiting flow texture, with phenocrysts of quartz and alkali feldspar in a glassy to cryptocrystalline groundmass; also, any rock in that group; the extrusive equivalent of granite. Rhyolite grades into rhyodacite with decreasing alkali feldspar content and into trachyte with a decrease in quartz.

**Schist** A strongly foliated crystalline rock, formed by dynamic metamorphism, that can be readily split into thin flakes or slabs due to the well developed parallelism of more than 50% of the minerals present, particularly those of lamellar or elongate prismatic habit, e.g., mica and hornblende. The mineral composition is not an essential factor in its definition unless specifically included in the rock name, e.g., quartz-muscovite schist. Varieties may also be based on general composition, e.g., calc-silicate schist, amphibole schist; or on texture, e.g., spotted schist.

**Sedimentary rocks** Rocks formed by the accumulation of sediment in water (aqueous deposits) or from air (eolian deposits). The sediment may consist of rock fragments or particles of various sizes (conglomerate sandstone, shale); of the remains or products of animals or plants (certain limestones and coal); of the product of chemical action or of evaporation (salt, gypsum, etc.); or of mixtures of these materials. Some sedimentary deposits (tuffs) are composed of fragments blown from volcanoes and deposited on land or in water. A characteristic feature of sedimentary deposits is a layered structure known as bedding or stratification. Each layer is a bed or stratum. Sedimentary beds as deposited lie flat or nearly flat.

**Sericitisation** A hydrothermal, deuteric, or metamorphic process involving the introduction of, alteration to, or replacement by sericitic muscovite.

**Shoshonite** A trachyandesite composed of olivine and augite phenocrysts in a groundmass of labradorite with alkali feldspar rims, olivine, augite, a small amount of leucite, and some dark-colored glass. Shoshonite grades into absarokite with an increase in olivine and into banakite with more sanidine. Its name, given by Iddings in 1895, is derived from the Shoshone River, Wyoming.

**Sill** A concordant pluton that is substantially wider than it is thick. Sills form within a few kilometers of the Earth's surface.

**Skarn** An old Swedish mining term for silicate gangue (amphibole, pyroxene, garnet, etc.) of certain iron ore and sulfide deposits of Archean age, particularly those that have replaced limestone and dolomite. Its meaning has been generally expanded to include lime-bearing silicates, of any geologic age, derived from nearly pure limestone and dolomite with the introduction of large amounts of Si, Al, Fe, and Mg.

**Sol** A homogeneous suspension or dispersion of colloidal matter in a fluid (liquid or gas).

**Stock** A discordant pluton that increases in size downward, has no determinable floor, and shows area of surface exposure less than 100 km<sup>2</sup>.

**S-type granite** Granite with a sedimentary protolith. These are relatively restricted in composition to high SiO<sub>2</sub> types and have relatively low Na<sub>2</sub>O, normally <3.2% in rocks with ~5% K<sub>2</sub>O decreasing to <2.2% in rocks with ~2% K<sub>2</sub>O. Mol. Al<sub>2</sub>O<sub>3</sub>/(Na<sub>2</sub>O+K<sub>2</sub>O+CaO)>1.1.

**Subduction** The process of one lithospheric plate descending beneath another.

**Supergene** A mineral deposit or enrichment formed near the surface, commonly by descending solutions.

**Syenite** A group of plutonic rocks containing alkali feldspar (usually orthoclase, microcline, or perthite), a small amount of plagioclase (less than in "monzonite"), one or more mafic minerals (esp. hornblende), and quartz, if present, only as an accessory; also, any rock in that group; the intrusive equivalent of "trachyte." With an increase in the quartz content, syenite grades into "granite."

**Trachyte** A group of fine-grained, generally porphyritic, extrusive rocks having alkali feldspar and minor mafic minerals (biotite, hornblende, or pyroxene) as the main components, and possibly a small amount of sodic plagioclase; also, any member of that group; the extrusive equivalent of syenite. Trachyte grades into latite as the alkali feldspar content decreases, and into rhyolite with an increase in quartz.

**Transuranic elements** These are the chemical elements with atomic numbers greater than 92 (the atomic number of uranium).

**Tuff** Rock consolidated from volcanic ash.

**Ultramafic** An igneous rock composed chiefly of mafic minerals, e.g., monomineralic rocks composed of hypersthene, augite, or olivine.

**Valence** also known as valency or valency number, is a measure of the number of chemical bonds formed by the atoms of a given element.

**VVER** (*Vodo-Vodyanoi Energetichesky Reactor* or WWER) A series of pressurised water reactors that were developed from around 1970 onwards and used by the former Soviet Union and its satellites, as well as the present-day Russian Federation.

**Wad** An earthy, dark brown to black mineral material consisting chiefly of an impure mixture of manganese oxides and oxyhydroxides with variable amounts of copper, cobalt, and iron oxides and oxyhydroxides and silica plus 10% to 20% adsorbed water. It is commonly soft (soiling hands), but may be hard and compact, and has a low density. Wad results from the decomposition of other manganese minerals and accumulates in marshy areas or other zones of ground-water emission where it is an ore of manganese. See also: asbolan earthy manganese; manganese hydrate.

**WIM-type deposits** Large resources of fine-grained, heavy mineral sands deposits (referred to as WIM-type deposits) that occur in the Horsham region of Victoria.