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Uranium Mineral Systems:

Processes, exploration criteria and a new deposit framework

Roger G. Skirrow, Subhash Jaireth, David L. Huston, Evgeniy N. Bastrakov, Anthony Schofield, Simon E. van der Wielen & Andrew C. Barnicoat

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APPLYING GEOSCIENCE TO AUSTRALIA'S MOST IMPORTANT CHALLENGES

Uranium mineral systems: Processes, exploration criteria and a new deposit framework

GEOSCIENCE AUSTRALIA RECORD 2009/20

by

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Abstract

Australia holds the world's largest resources of uranium recoverable at low cost, principally in the uranium-rich Olympic Dam iron oxide Cu-Au (IOCG) deposit together with the Ranger and Jabiluka unconformity-related deposits and Yeelirrie surface-related deposit. Despite this impressive inventory, resources of several other styles of uranium deposits appear to be under-represented in Australia relative to geologically similar regions elsewhere in the world. In particular, Australia has no known giant uranium deposits hosted by Mesozoic or younger sedimentary basins, although recent discoveries in the Frome Embayment have significantly increased total resources of 'sandstone' uranium in the region. Major deposits directly related to magmatic processes also appear to be under-represented, given the abundance of unusually uranium-rich igneous rocks in Australia. The Australian Government's Onshore Energy Security Program (OESP, 2006-2011) is providing pre-competitive geoscientific data and new area selection concepts to assist in reducing exploration risk and to support an assessment of onshore energy and uranium potential.

This report examines the key processes controlling where and how uranium mineralisation occurs in Australia and elsewhere. Based on this process understanding and on descriptions of well-documented systems, we develop generalised models of three distinct families of uranium mineral systems, including exploration criteria. The purpose of the report is to present a revised framework for a fresh assessment of Australia's uranium mineral potential. This systems-based approach, when combined with empirical data, provides a means of identifying previously unrecognised uranium provinces or districts.

The report has three parts. First, the fundamental chemical controls on uranium transport and deposition in aqueous geological systems are reviewed. Second, a new scheme of classification of uranium deposits is proposed (see below). Third, each of three families of uranium mineral systems, plus hybrid systems, is described in terms of ore-forming processes, essential components of the mineral system, and mappable criteria. Exploration models for key systems are presented in figures and tables.

Most current classification schemes for uranium deposits emphasise differences in host rock type, resulting in a plethora of apparently separate deposit styles. While this scheme has been useful in categorising uranium resource data, it has limitations when assessing greenfields regions for undiscovered or unrecognised styles of uranium deposits. We propose an alternative scheme that describes a continuum of possible deposit styles within and between three end-member uranium mineral systems. The scheme is based on the fundamental properties of uranium and its physico-chemical behaviour during earth processes.

Formation of almost all major uranium deposits involved aqueous fluids. Fluids of three distinctly different origin and composition are typically responsible for the transport and deposition of U^{6+} and U^{4+} : (1) magmatic-hydrothermal, (2) 'metamorphic' (including fluids reacted extensively with metamorphic rocks), and (3) hydrosphere-derived (meteoric waters, lake waters, seawater, groundwaters). Each end-member fluid is fundamental to one of three families of uranium mineralising systems: magmatic-hydrothermal-, metamorphic-, and sedimentary basin- and surface-related. These systems contain a range of deposit styles, reflecting the continuum in properties between end-member fluid types as well as differing geological settings.

Magmatic-related uranium systems include mineral systems directly related to magmatic-hydrothermal fluid, as well as 'orthomagmatic' uranium deposits formed directly from crystallising magmas. The latter are generally of low grade, although they may provide readily leached large-tonnage sources of uranium for secondary mineral systems.

Metamorphic-related uranium systems involve uranium deposition from fluids of true metamorphic origin (via dehydration, etc) or from fluids extensively reacted with metamorphic rocks at elevated temperatures. These 'metamorphic fluids' may acquire chemical and isotopic signatures that are indistinguishable from

true metamorphic fluids. 'Metasomatic' and some 'vein' deposits probably derive from a range of magmatic-hydrothermal to metamorphic fluids.

Sedimentary basin-related uranium systems contain a suite of deposit styles that share several fundamental characteristics and processes. One end-member fluid is oxidised water from the hydrosphere. Reaction with basin and/or basement rocks with leachable uranium may result in U-rich groundwaters, formation waters and connate brines. End-member metamorphic (including diagenetic) fluids may mix with these waters. Uranium is deposited via fluid-rock or fluid-fluid reactions predominantly involving reduction or evaporation. There is a growing recognition that 'sandstone-hosted', 'unconformity-related' and 'Westmoreland' type deposits are members of a continuum of styles within basin-related systems.

Hybrid deposit styles are a predicted consequence of the proposed scheme. Uranium-rich iron oxide Cu-Au deposits are a key example, and are proposed to have formed by the action of hydrosphere-derived fluids either mixing with deep-sourced high-temperature fluids of possible magmatic-hydrothermal or 'metamorphic' origin, or overprinting oxide and sulfide mineral assemblages that resulted from the deepsourced fluids. Uranium ore-forming systems

1. Introduction

Australia holds the world's largest share of uranium resources (983,000 t U, 34%) in the Reasonably Assured Resources category, 'recoverable at <USD\$80/kg U' (Geoscience Australia. 2008). Major resources include the Olympic Dam iron-oxide copper-uranium-gold deposit (South Australia), the Ranger, Jabiluka, Koongarra (Northern Territory) and Kintyre (Western Australia) unconformity-related deposits, the Yeelirrie surface-related deposit (Western Australia), and the Beverley, Four Mile and Honeymoon sandstone-hosted deposits (South Australia). Australia is the second largest uranium producer in the world after Canada. Globally, the largest uranium resources are contained in one IOCG deposit (Olympic Dam, the world's largest uranium resource), unconformity-related deposits (Canada and Australia), sandstone-hosted deposits (Kazakhstan), volcanic-hosted deposits in eastern Russia, and the 'alaskite'-hosted Rössing deposit (Namibia). However, no giant sandstone-hosted uranium deposits have yet been discovered in Australia, despite the presence of sedimentary basins with apparently favourable characteristics. Major deposits directly related to magmatic processes also appear to be underrepresented, given the abundance of unusually uranium-rich igneous rocks in Australia.

Low uranium commodity prices over many years up to the mid-2000s, and Australia's 'three mines policy' (overturned in 2007) contributed to low expenditure on uranium and a dearth of discoveries in Australia. The Athabasca Basin (Canada) was one of the few regions in which major uranium discoveries were made during the 1990s and early 2000s. In light of the significant advances over the past two decades in understanding how and where major mineral deposits form, it is timely to apply this knowledge to Australia's uranium resources and potential. In particular, the 'mineral systems' approach (Wyborn et al., 1994) adapted by the pmd*CRC (Walshe et al., 2005; Barnicoat, 2007) provides an effective framework for describing an entire ore-forming system at multiple scales, rather than focusing on deposit-scale attributes, as adopted in many previous economic geology studies. This approach is considered useful in assessing the potential of greenfields uranium provinces because the predictions are not reliant on the presence of known mineralisation.

Through the Commonwealth Government's \$59m Onshore Energy Security Program (OESP, 2006-11), Geoscience Australia is acquiring pre-competitive data in support of exploration for energy and uranium resources. A key part of the OESP is an assessment of the potential for undiscovered deposits, based on re-evaluation of the nature and distribution of uranium mineral resources in Australia.

The purposes of this report are threefold.

- 1) Identify the fundamental geological and geochemical processes operating in uranium mineral systems, that link the formation of diverse uranium deposit types in Australia and globally.
- 2) Apply the mineral systems approach to develop (a) a new classification scheme, and (b) revised exploration models of key uranium mineral systems.
- 3) Distil the essential characteristics of uranium ore-forming systems that are mappable and measurable using geoscientific datasets readily available to mineral explorers.

Application of this framework is currently underway in the OESP, to assess the uranium prospectivity of Australia, and to identify provinces and districts with potential to host undiscovered uranium deposits. One of these studies, reported by Schofield (2009), documents the uranium content of igneous rocks of Australia in a series of three maps, as a basis for assessing the potential for magmatic-related uranium deposits.

A mineral system is defined as follows (Wyborn et al., 1994): "all geological factors that control the generation and preservation of mineral deposits, and stress the processes that are involved in mobilising ore components from a source, transporting and accumulating them in more concentrated form, and then preserving them throughout the subsequent geological history".

2. Controls on uranium transport and deposition in aqueous systems

The following sections outline the key geochemical properties and behaviour of uranium in aqueous fluids. The formation of most major uranium deposits arguably involved fluids dominated by water. In building a better understanding of how and where uranium mineral systems develop, a foundation of knowledge of uranium hydrogeochemistry therefore is required. Favourable combinations of fluid properties, crustal architecture, metal depositional environments, and other factors, are necessary to form major uranium deposits, as discussed in later parts of this report.

Formation of uranium mineralisation directly from magmas is another fundamental process in some uranium mineral systems. The behaviour of uranium in magmatic processes is discussed in section 4.1 (magmatic-related uranium mineral systems).

The first four sections of this chapter focus on the physico-chemical conditions of uranium mobilisation and deposition in low- to high-temperature hydrothermal systems. In section 2.5 we discuss the critical geological and chemical parameters in the development of uranium mineral systems in general, and the observable manifestation of these parameters in the rock record.

2.1 VALENCE AND MINERALOGY

Uranium occurs in minerals predominantly in hexavalent (U^{+6}) and tetravalent (U^{+4}) states. The heterovalence of uranium determines its sensitivity to the oxidation state of the environment. In relatively reduced conditions, common in magmatic and metamorphic environments, tetravalent uranium predominates. In near-surface and low-temperature conditions where the conditions generally are more oxidised (e.g., air-saturated), U^{+6} is the dominant ion of uranium.

Uranium occurs in three groups of minerals: uranium ore minerals, accessory minerals, and complex ore minerals (Dahlkamp, 1993). The high charge and large size (0.8-1.01Å) of the U⁺⁶ and U⁺⁴ ions control the occurrence of uranium in these groups of minerals. Ore minerals of uranium include U⁺⁴-bearing uraninite and pitchblende (UO_{2+x}), coffinite (USiO₄), brannerite (UTi₂O₆), and U⁺⁶-bearing oxyhydroxides, phosphates, arsenates, vanadates (e.g. carnotite), and silicates. Major rock-forming silicates and oxides do not accommodate significant U⁺⁴ or U⁺⁶, although the low uranium abundances may be offset by the large quantities of the major minerals, and add significantly to the total uranium contents of rocks. Limited substitution of U⁺⁴ for Ca⁺² occurs in common accessory minerals such as apatite, titanite and fluorite (Table 1). Similar charge and radii of U⁺⁴, Zr⁺⁴, Th⁺⁴, and Ce⁺⁴ (and other REE) can result in high uranium concentrations in accessory minerals such as allanite, monazite, xenotime and zircon (Table 1). Similar substitutions by U⁺⁴ also occur in complex ore minerals such as davidite, euxenite, and samarskite (Dahlkamp, 1993).

MINERAL	COMMON RANGE (PPM, U)
Allanite (Ca,Ce) ₂ (Fe ⁺² ,Fe ⁺³)Al ₂ O.OH[Si ₂ O ₇][SiO ₄]	30-1000
Apatite Ca ₅ (PO ₄) ₃ (OH,F,CI)	5-100
Epidote (CaFe ⁺³)Al ₂ O.OH[Si ₂ O ₇][SiO ₄]	20-200
Garnet Ca ₃ Al ₂ Si ₃ O ₁₂	6-30
Ilmenite FeTiO ₃	1-50
Magnetite Fe ₃ O ₄	1-30
Monazite (Ce,La,Th)PO ₄	500-3000
Titanite CaTi[SiO ₄](O,OH,F)	10-700
Xenotime YPO ₄	300-35,000
Zircon ZrSiO ₄	100-6000

Table 1: Uranium content of accessory minerals (isomorphic substitution in crystal lattice)

After de Voto (1978)

2.2 URANIUM SPECIATION AND SOLUBILITY IN AQUEOUS FLUIDS

Pearson (1963) classified metal ions and ligands into acids (those which accept electrons) and bases (those with available electrons). The ions U^{+4} , U^{+6} and Th^{+4} are hard acids and hence tend to complex more readily with hard bases such as F⁻, OH⁻, NO₃⁻, CO₃⁻², HCO₃⁻, SO₄⁻², HSO₄⁻, PO₄⁻³, HPO₄⁻² and H₂PO₄⁻. In highly saline fluids with an excess of chloride ion U^{+4} also forms chloro complexes. A common association of uranium with manganese, cobalt, arsenic, vanadium, rhenium and other rare earth elements observed in many uranium ore deposits is possibly related to the fact that these elements form ions which also behave as hard acids. Important aqueous complexes of uranium (U^{+4} and U^{+6}) are shown in Table 2. In oxidised aqueous fluids U^{+6} readily forms the linear polar uranyl ion, UO_2^{+2} .

COMPLEX TYPE	URANIUM SPECIES
Simple and oxy and hydroxy	U ⁺³ , U ⁺⁴ , U(OH) ⁺³ , U(OH) ₂ ⁺² , U(OH) ₃ ⁺¹ , U(OH) ₄ , U(OH) ₅ ⁻¹ ,
	U ₂ (OH) ₅ ⁺³ , UO ₂ ⁺¹ , UO ₂ ⁺² , UO ₂ (OH) ⁺¹ , UO ₂ (OH) ₂ ,
	$UO_2(OH)_3$, $(UO_2)_2(OH)_2^{+2}$, $(UO_2)_3(OH)_5^{+1}$
Carbonate (uranyl)	UO ₂ CO ₃ , UO ₂ (CO ₃) ⁻² , UO ₂ (CO ₃) ⁻⁴
Phosphate (uranous and uranyl)	UHPO4 ⁺² , U(HPO4)2, U(HPO4)3 ⁻² , U(HPO4)4 ⁻⁴ , UO2(HPO4),
	UO ₂ (HPO ₄) ₂ ⁻² , UO ₂ (H ₂ PO ₄) ⁺ , UO ₂ (H ₂ PO ₄) ₂ , UO ₂ (H ₂ PO ₄) ₃ ⁻
Sulfate (uranous and uranyl)	U(SO ₄) ₂ , UO ₂ (SO ₄), UO ₂ (SO ₄) ₂ ⁺² , USO ₄ ⁺²
Fluoride	UF ⁺³ , UF ₂ ⁺² , UF ₃ ⁺ , UF ₄ , UF ₆ ⁻²
Chloride	UCI^{+3} , UO_2CI^+

Table 2: Aqueous complexes of uranium

Thermodynamic data constrained by experimental results are available for a wide range of uranium complexes at low temperatures (<100°C; see Murphy and Shock, 1999, and references therein). However, experimental data above 100°C are sparse and hence the prediction of uranium solubility and speciation at elevated temperature and pressure has relied upon theoretical estimation of thermodynamic properties of aqueous species, for example using the revised Helgeson-Kirkham-Flowers equation of state (Shock et al., 1997). The available thermodynamic data have been compiled and reviewed (Appendix Table A1) in order to construct a series of diagrams of uranium solubility and speciation at temperatures between 25° and 300°C, using the most reliable data.

Extrapolations of the thermodynamic data beyond 300°C are problematic. The experiments of Peiffert et al. (1994, 1996) and Zharikov et al. (1987) provide some semi-quantitative constraints on uranium solubility at 770°C and 500-600°C, respectively. It is clear that at these high temperature conditions very high uranium solubilities (up to 0.1%) are possible in aqueous chloride brines in equilibrium with

peralkaline melt and uraninite, and that fluoride complexes of uranium are significantly more stable than chloride complexes at equivalent molality and experimental conditions (Peiffert et al., 1996). The speciation of uranium complexes at these conditions is less clear, and may involve U^{+4} , U^{+5} and U^{+6} depending on the oxidation state of the system. By analogy with well understood halogen complexing of other metals, strong temperature and pH dependencies are expected for chloride and fluoride complexes of uranium. Decreasing temperature, fO₂ and/or increasing pH are likely to be major controls on uranium deposition at magmatic to sub-magmatic conditions where halogen complexes are dominant. These high-temperature constraints on uranium solubility have not been incorporated into estimations of thermodynamic properties of uranium species used in the present study.

The pH-logfO₂ diagrams in Figures 1 to 4 show the solubility and predominance fields of aqueous uranium species at temperatures between 25 and 300°C in relation to uraninite and Fe-S-O mineral stabilities. The uranium aqueous and solid phases used in the calculations are listed in Appendix Tables A1 and A2. A series of diagrams presented in the Appendix (Figs A1-A4) are temperature-logfO₂ cross sections through the pH-logfO₂ diagrams at pH values corresponding to the K-feldspar-muscovite and kaolinite-muscovite buffers, for pure water and 1 M NaCl solutions (~5.5 weight percent NaCl). Figures A3 and A4 represent the total solubility of uranium for redox conditions buffered by hematite-magnetite and $Mn_2O_4-Mn_2O_3$, for 1 M NaCl solutions at pH conditions buffered by K-feldspar-muscovite and kaolinite-muscovite. Note that aqueous P, S and C are included in Figures 1-4 and Figure A4, but are excluded from Figures A1-A3.

In general terms, these diagrams illustrate that high solubility of uranium is strongly favoured under very oxidising conditions (considerably more oxidised than those defined by the hematite/magnetite buffer). Oxy-hydroxide complexes and the concentration of ligands such as phosphate, carbonate, fluoride, sulfate and chloride determine the nature of dominant aqueous species of uranium. Uranium solubility generally increases with temperature for particular redox buffer conditions, except at extremely oxidised conditions (e.g., Mn_3O_4 - Mn_2O_3 buffer, Figs A3-A4). High solubilities are also possible at reducing conditions where pH is low or very low (<3) and chloride or fluoride concentrations are high, particularly at elevated temperatures. As noted above, however, speciation is problematic at these conditions due to uncertainties in the thermodynamic data.

Figure 1 shows the solubility and speciation at 25° C for fluids of low salinity (0.15m chloride or ~ 1 wt% NaCl). The topology is little changed at 50°C. The conditions are appropriate to low temperature near-surface environments of uranium mineralisation involving meteoric waters or groundwaters, such as 'sandstone' and 'calcrete' uranium systems. Key implications of uranium solubility and speciation at 25° C are as follows.

• For the conditions shown, uranyl sulphate dominates in acidic conditions (pH < 4) whereas uranyl phosphate is more important at pHs of 4-9. For conditions of lower aqueous phosphate or higher carbonate the predominance field of the uranyl carbonate complex will expand towards lower pH. This may be appropriate where waters contain appreciable Ca, such that aqueous phosphate is limited by apatite solubility.

• The addition of Si and V to the systems will result in a carnotite stability field (not shown) replacing parts of the aqueous phosphate and carbonate fields at near-neutral to high pH. In this case, pH increases may result in uranium (-vanadium) deposition.

Groundwaters of the Yilgarn Craton, Western Australia provide an example of the pH control on uranium solubility. Here, near-neutral pH low salinity waters carry up to \sim 20 ppb uranium whereas acidic (pH <3) saline groundwaters carry up to \sim 100 ppb uranium (D. Gray, written comm., 2008).

Thermodynamic data for the UCl_2^{+2} complex are considered unreliable above 50°C and therefore this complex is included only for the calculations below 50°C. The effect of UCl_2^{+2} in the calculations at 25°C is shown by comparing Figure 1. Tetravalent uranium as UCl_2^{+2} is stable at reduced very acidic conditions

(0.01ppm U for pH <3 and 3.65m Cl, equivalent to 25 weight percent NaCl). Under these restricted conditions pH becomes the dominant factor controlling uranium solubility:

$UO_2 + 4H^+ + 2CI^- = UCl_2^{+2} = 2H_2O$

Figures 2 and 3 show uranium solubility and speciation at temperatures of 100° C and 200° C for fluids of 1m and 3.65m chloride (equivalent to ~5.5 and 20 wt% NaCl). These diagrams are relevant to the behaviour of uranium in systems associated with heated waters in sedimentary basins, geothermal systems or in other low-moderate temperature hydrothermal systems. Such brines are known to be associated with unconformity-related uranium deposits and uranium-enriched zones in the Kupfershiefer deposits of Europe. Comparison of Figures 1, 2 and 3 shows the increasing stability of the HUO₄⁻ complex at the expense of the uranyl carbonate complex at high pH, and the increasing stability of the uranyl chloro complex relative to the sulfate complex at very low pH.

Uranium solubility at 300°C (Fig. 4) is dominated at the calculated conditions by phosphate complexes at oxidised conditions and pH ranging from ~8 to 4. However at pH <4 the stability of the U⁺⁴-bicarbonate complex results in solubilities of >1ppm U at both reduced and oxidised conditions. Increasing Cl⁻ from 1m to 3.65m has little effect on uranium solubility or speciation due to the omission of the UCl₂⁺² complex, as noted above. Its predominance field is partly replaced by that of the U⁺⁴-bicarbonate complex. These diagrams are appropriate for moderate to high temperature hydrothermal uranium systems such as those associated with low grade metamorphism or deep burial, deeper parts of some geothermal systems, and distal parts of magmatic-hydrothermal systems.



Figure 1: Log fO_2 -pH diagram at $25^{\circ}C$. Diagram calculated at [Cl] = 0.15m, [C] = 0.003m, [S] = 0.016m, $[P] = 4x10^{-6}m$, $[F] = 4x10^{-6}m$, $[SiO_2] = 8x10^{-5}m$. Stability fields of minerals in Fe-S-O system are shown in grey lines. Stability fields of sulphur species in blue dashed lines. The stability field of uraninite is shown for 0.01 ppm dissolved U (yellow) and for 1ppm U (orange+yellow). Two uranium oxides are stable (only uraninite has been labelled. Unlabeled oxide U_4O_9 is stable at relatively higher logfO₂ (two blue triangles adjoining the field of uraninite).



Figure 2a: Log fO_2 -pH diagram at 100°C. Diagram calculated at [Cl] = 1m, [C] = 0.001m, [S] = 0.001m, [P] = 1x10⁵m, [F] = 1x10⁴m. See Fig. 1 caption for other symbology.



Figure 2b: Log fO_2 -pH diagram at 100°C. Diagram calculated at [Cl] = 3.65m, [C] = 0.001m, [S] = 0.001m, [P] = $1x10^{-5}m$, [F] = $1x10^{-4}m$. See Fig. 1 caption for other symbology.



Figure 3a: Log fO_2 -pH diagram at 200°C. Diagram calculated at [Cl] = 1m, [C] = 0.001m, [S] = 0.001m, [P] = 1x10⁻⁵m, [F] = 1x10⁻⁴m. See Fig. 1 caption for other symbology.



Figure 3b: Log fO_2 -pH diagram at 200°C. Diagram calculated at [Cl] = 3.65m, [C] = 0.001m, [S] = 0.001m, [P] = $1x10^{-5}m$, [F] = $1x10^{-4}m$. See Fig. 1 caption for other symbology.



Figure 4a: Log fO_2 -pH diagram at 300°C. Diagram calculated at [Cl] = 1m, [C] = 0.001m, [S] = 0.001m, [P] = $1x10^5m$, [F] = $1x10^4m$. See Fig. 1 caption for other symbology.



Figure 4b: Log fO_2 -pH diagram at 300°C. Diagram calculated at [Cl] = 3.65m, [C] = 0.001m, [S] = 0.001m, [P] = $1x10^5m$, [F] = $1x10^4m$. See Fig. 1 caption for other symbology.

2.3 URANIUM TRANSPORT - SUMMARY

The speciation and solubility relationships described above permit the following generalisations regarding favourable conditions of uranium transport in hydrothermal systems.

- At low to moderate temperatures (<200°C) geologically significant concentrations of uranium (>0.01-1ppm) can be carried only in highly oxidised fluids, where fO₂ is well above hematite-magnetite buffer conditions. This observation places significant constraints on the nature, origins and flow paths of uranium ore-forming fluids.
- Uranium solubility is generally enhanced with increasing fO₂, decreasing pH in the acidic regime, increasing temperature (except at very high fO₂), and increasing concentrations of aqueous phosphate, bicarbonate, sulfate, chloride and fluoride ions.
- At intermediate pH conditions (~4-8) and temperatures up to at least 300°C uranyl phosphate complexes are most stable. However, uranium transport may be dominated by bicarbonate or oxy-hydroxide or sulfate complexes where aqueous phosphate concentrations are low relative to other ligands (e.g., due to elevated Ca²⁺).
- At 200-300°C chloride and fluoride complexes of U⁶⁺ and U⁴⁺ become important at low pH, at both oxidised and reduced conditions.
- In high temperature experimental analogues of magmatic-hydrothermal brines, chloride and fluoride complexes may transport up to ~0.1% uranium at oxidised as well as reduced conditions.
- Limitations with thermodynamic data for chloride and fluoride complexes at elevated temperatures (>300°C) prevent quantitative prediction of uranium solubilities at these conditions.

2.4 URANIUM DEPOSITION

The major controls on deposition of uranium from aqueous fluids are redox, pH, ligand concentration, and temperature. Other important processes include adsorption and bacteria-mediated deposition at low temperatures (Lovley et al., 1991; Waite et al., 1994; Fredrickson et al., 2000; Sherman et al., 2008).

At high temperatures where chloride and fluoride complexes of U^{6+} and U^{4+} are significant, cooling and/or pH increases may result in uranium deposition, whether the fluids are oxidised or reduced. In some cases these processes will be linked to changes in ligand activity, for example where acidic and Frich magmatic-hydrothermal brines are neutralised through reaction with carbonate rocks to produce fluorite. Fluoride complexes of U^{6+} or U^{4+} will be destabilised to precipitate uranium minerals, with or without a redox step. The common occurrence of brannerite ((U,Ca,Ce)(Ti,Fe)₃O₆) in some moderate to high temperature uranium deposits associated with Na-metasomatism (e.g., Valhalla, Polito et al., 2007; Ukraine, Cuney and Kyser, 2008; Crocker Well, McKay and Miezitis, 2001) may be related to the mobility of both U and Ti in F-rich fluids (Gieré, 1990).

In oxidising conditions where aqueous uranium species are dominantly uranyl complexes, ore minerals containing tetravalent uranium (such as uraninite, coffinite, and brannerite) require reduction of the uranium-bearing oxidised fluids. Reductants may be present in rocks or fluids in the form of reduced carbon (organic matter, hydrocarbons including CH₄, graphite), iron in Fe²⁺-bearing minerals or aqueous species, and reduced sulfur in sulfide minerals, H₂S gas and aqueous H₂S. Fluid-rock reaction and fluid mixing are two of the key processes involved in uranium deposition. The products of these processes are commonly preserved in the rock record as zoned alteration mineral assemblages centred on the gradient between oxidised and reduced parts of the mineral system. Zones recording the passage of oxidised fluids may contain combinations of: hematite or goethite replacing magnetite or sulfides; sulfate minerals; high Fe^{3+}/Fe^{2+} ratios in silicates such as chlorite or amphibole; high CO₂/CH₄ ratios in fluid inclusions; negative δ^{34} S ratios in sulfide minerals (although not uniquely the result of oxidation); Mn oxides; Cu oxides; or rutile replacing ilmenite. The destabilisation of aqueous uranyl complexes may result in characteristic minerals associated with the uranium minerals. For example, bicarbonate-rich fluids carrying uranyl bicarbonate complexes may react to form carbonate alteration minerals; or phosphate minerals may occur with uranium minerals where uranyl phosphate complexes were destabilised; and fluorite may indicate the former presence of F-rich fluids in which uranium-fluoride complexes were important.

The kinetics of oxidation-reduction reactions may determine the effectiveness of reduction of U^{6+} to U^{4+} (e.g., Nakashima et al., 1999).

The deposition of hexavalent uranium bearing minerals such as the uranyl vanadates carnotite and tyuyamunite will be caused by destabilisation of uranyl aqueous complexes through changes in pH, and/or increase in the concentration of other ions such as calcium, potassium and vanadium. A redox step is not involved, although mixing of oxidised U^{6+} -bearing and reduced V^{4+} -bearing waters has been proposed for the formation of carnotite in calcrete-hosted uranium deposits (Butt et al., 1984).

Non-equilibrium precipitation of uranium may occur by adsorption on Fe-oxide and oxyhydroxide minerals. This is a potentially important process in retarding the aqueous transport of uranium in the formation and weathering of uranium deposits, as well as in the redistribution of uranium in radioactive waste repositories (e.g., Sherman et al., 2008). Sorption of U on goethite is strongly controlled by pH, with the consequence that desorption will occur via a decrease in pH around values of 4-5 (Sherman et al., 2008). Ferrihydrite was found to be one of the most significant U-sorbing phases in weathering of the Koongarra uranium deposit, Northern Territory (Payne and Airey, 2006). Hematite and goethite have much lower uranium sorbing ability than ferrihydrite, and hence transformation of ferrihydrite to the more crystalline iron minerals may result in partial incorporation of uranium in these phases as well as release of some uranium to the external environment (Payne and Airey, 2006). It is possible that such processes play an important role in the mobilisation of uranium in some redbed sedimentary settings, where Fe oxyhydroxides transform to hematite during early diagenesis. Copper and uranium released from Fe-oxides during the reddening process may be transported in groundwaters or diagenetic fluids to form mineral deposits downstream (Brown, 2006).

The importance of bacteria in controlling uranium deposition in low-temperature environments should not be underestimated (Ewing, 1999). Some bacteria produce reduced compounds (e.g., H₂S) for inorganic reduction of U⁶⁺. However a more direct role has been identified for several species of anaerobic bacteria that are known to catalyse the reduction of aqueous U⁶⁺ species to insoluble U⁴⁺ forms, coupled with the oxidation of organic substrates or H₂ (Fredrickson et al., 2000). These dissimilatory metal reducing bacteria obtain energy for growth by electron transfer to U⁶⁺ (Lovely et al., 1991). Such processes have been suggested in the formation of some sandstone-hosted uranium deposits, as documented in northwestern China where fungi and bacteria are replaced by uraninite and coffinite (Min et al., 2005). The organic matter in the host sediments (e.g., fossilised wood) provided the substrate and nourishment for bacteria colonies that mediated uranium deposition. This depositional mechanism may be capable of extracting uranium from waters undersaturated with respect to uranium minerals.

2.5 PARAMETERS GOVERNING URANIUM SYSTEMS DEVELOPMENT

Figure 5 illustrates the relative importance of key variables or parameters in forming low- to hightemperature hydrothermal uranium mineralisation. The cross-plots qualitatively represent positive and negative influences in uranium ore formation. The selection of parameters is based on the *mineral systems* paradigm of source-transport-deposition (Wyborn et al., 1994). We have extended this concept to include additional parameters controlling the mineral system such as the drivers of fluid flow, and fluid volume. Together, these parameters represent most of the '5 Questions' in the mineral system approach developed by the pmd*CRC (Walshe et al., 2005; Barnicoat, 2007). However, the architecture of uranium mineralising systems and geodynamic evolution (Questions 1 and 2) are not easily represented in the parameter spaces shown in Figure 5. Aspects of geodynamic setting and architecture are covered for particular mineral systems in section 4. Other parameters shown in Figure 5 map approximately to the remaining three of the '5 Questions', namely fluid characteristics and sources/reservoirs (Q3), fluid flow drivers and pathways (Q4), and transport and depositional processes (Q5).

2.5.1 Fluid source parameters (Fig. 5a)

Fluids of differing origins including surface-derived, metamorphic and magmatic fluids, are compared in terms of their intrinsic redox characteristics and ligand concentrations (OH^- , PO_4^{2-} , CO_3^{2-} , SO_4^{2-} , F^- , CI^-).

These characteristics may be modified during subsequent fluid-rock reaction, as illustrated in the diagram of 'fluid pathway parameters' (Fig. 5e). Note that high concentrations of U^{4+} are possible under reduced conditions (contours in Fig. 5a relate to U^{6+} only). Surface-derived waters saturated with atmospheric oxygen and magmatic-hydrothermal fluids buffered to high oxidation states (e.g., by SO₂) and containing abundant F or Cl are capable of transporting high concentrations of uranium, as discussed above. The oxidation state of groundwaters, connate basinal brines or diagenetic/metamorphic fluids will be influenced strongly by the mineralogy and bulk composition of the host rocks through which the fluids pass, although in general their oxidation state will be lower than that of surface-derived waters.

2.5.2 Uranium source parameters (Fig. 5b)

The uranium content of potential sources is only one factor in generating a U-bearing ore fluid. In hydrothermal systems where uranium is scavenged from rock sources, a critical factor in the effectiveness of the mineral system is the 'leachability' or availability of U for possible transfer from mineral to fluid. Aspects of leachability are discussed in section 4.1.4 in relation to igneous rocks. In general, felsic igneous and derived sedimentary and metamorphic rocks contain higher concentrations of U, Pb and Th than mafic or ultramafic rocks, whereas intermediate to mafic rocks contain higher levels of Cu, Au and Zn (Wedepohl, 1969-1974). Whether a sedimentary basin hosts major U or Cu mineralising systems may relate partly to the metal contents of source rocks (e.g., U/Cu ratios of mafic igneous-derived versus felsic igneous-derived detritus) as well as the oxidation state of the fluids (Brown, 2006; Jaireth et al., 2009).

Maximum availability of uranium is likely to be in felsic igneous rocks where uraninite has crystallised, either through orthomagmatic or magmatic-hydrothermal processes (see section 2.1). Particular peraluminous magmas are most favourable. Alternatively, peralkaline felsic igneous rocks with metamict U-rich accessory minerals, and especially the volcanic representatives, are potentially excellent sources of leachable uranium. Felsic igneous rocks with moderate or high U contents locked in zircon or other minerals resistant to metamictisation or chemical reaction are less favourable sources of leachable uranium.

Sediments eroded from U-rich igneous sources may be viable sources of uranium, with similar caveats as for the igneous rocks. Igneous uraninite is very unlikely to have survived the erosion process in most post-Archean settings because of the oxygenated atmosphere and its solubility in oxidised fluids. Hence the role of detrital uraninite as a secondary, sediment-hosted, uranium source is minimal after the oxygenation of the atmosphere. Uranium-rich accessory minerals with high resistance to physical transport but vulnerability to metamictisation, such as monazite and allanite, may represent favourable secondary sources of leachable uranium.

Whether or not the source minerals are effectively leached clearly is dependant on the presence of fluids with suitably high uranium solubility, which in turn is a function of permeability evolution, fluid/rock ratios, etc.



Figure 5: Critical parameters governing development of uranium mineralising systems, with emphasis on basin-related systems. Diagonal lines represent qualitative contours across gradients from low to high values or small to large deposits, e.g. low versus high concentrations of aqueous U, or small versus large uranium deposits. Most favourable conditions of ore formation at upper-right of each plot. Dashed-line ellipse represents conditions for the example of sandstone-hosted style of basin-related uranium system.

2.5.3 Fluid flow drivers (Fig. 5c)

Figure 5c attempts to show the effects of two principle drivers of fluid flow: gravity, and tectonic processes. Fluid flow is maximised in the regime represented at upper right in the diagram, where deformational drivers of fluid flow such as extension reinforce gravitational drivers such as topography. However, this qualitative diagram does not portray the scale of hydrologic systems – a large system in which fluids are driven purely by topography could, for example, drive more fluid than in a small system in which both extension and topography contributed to driving fluids. Although convective systems involve a complex interplay of multiple parameters including heat flow, the variation in fluid density (buoyancy) is a major parameter controlling fluid flow. High geothermal gradients (e.g., related to high-heat-producing granites) are favourable for strong convection, whereas compressive deformation appears to have negative effects on convection (Oliver et al., 2006). For this reason, convection is shown only along the left side of the diagram. Extension generally will result in downwards migration of surface-derived fluids (Oliver et al., 2006). Compressional deformation processes may result in tectonic loading which ultimately can drive buried fluids upwards and outwards towards foreland settings. The tectonic and geodynamic settings of the uranium provinces will strongly influence topography and hence hydraulic heads.

Gravity-driven flow in the absence of topography-induced hydraulic head includes downflow of dense saline fluids, for example bittern brines.

2.5.4 Fluid flux over time (fluid volume) (Fig. 5d)

Major uranium deposits formed by deposition from fluids require large volumes of ore fluid (upper right, Fig. 5d). This is possible in regimes of very high fluid flux over short periods of time, or lesser fluid flux over longer time intervals. Paleochannels with highly permeable fill or transient fault/fracture networks are examples of the former, whereas sheet sand aquifers may provide a medium for large volumes of fluid flow when integrated over long time periods, if permeability and a hydraulic head (among other characteristics) are maintained.

2.5.5 Fluid pathway parameters (Fig. 5e)

Hydrothermal uranium deposits develop generally through acquisition of uranium by fluids from source rocks, and transport along permeable pathways to the depositional environment. Alteration mineral assemblages along fluid pathways mark the passage of the fluids, and vary greatly according to the physical and chemical properties of the fluid and rock.

Two characteristics of the pathway rocks that are critical for productive uranium mineralising systems are their oxidation state and the presence or absence of minerals that may inhibit or enhance the transport of uranium in solution. The slope of qualitative contours in the diagram illustrates the competing effects of these variables, with U^{6+} transport maintained in pathways where the oxidation is maintained at high levels and where there are low abundances of reductants such as Fe²⁺-bearing minerals, sulfides, or reduced carbon. Uranium transport may be inhibited by the presence of Fe-oxyhydroxides such as ferrihydrite and goethite, which effectively adsorb uranium (see section 2.4). Phosphate-bearing rocks and evaporites may enhance U^{6+} transport, due to PO₄²⁻, SO₄²⁻ or CO₃²⁻ complexing of U^{6+} ions. A key question is whether sulfate-bearing evaporite sequences and/or the presence of Fe³⁺-bearing iron oxides can sufficiently raise or maintain the oxidation state of migrating fluids at levels required to transport oreforming concentrations of uranium. Chemical modelling of air-saturated meteoric waters reacting with sulfate-hematite-bearing rock then mafic mineral-bearing sandstone analogues demonstrates that very high oxidation states can be maintained within the sandstone if fluid/rock ratios are high (e.g., >5000, E. Bastrakov and S. Jaireth, unpublished data, 2008).

Understanding these roles of Fe oxides is important because they are readily identified in rock sequences and may provide clues on the passage or otherwise of uranium-bearing fluids.

2.5.6 Depositional parameters (Fig. 5f)

Two major parameters controlling the grade and tonnage of uranium deposits are the physico-chemical gradient in the depositional environment, and the mass of the rocks, minerals or fluids participating in uranium deposition. The qualitative contours in the diagram illustrate that deposits with greater amounts of contained metal are favoured by large masses of rocks, minerals or fluids that can simultaneously produce a steep chemical or physical gradient in 3D space. Examples of physico-chemical gradients include: reductants for U^{6+} ; oxidants for U^{4+} ; P_{CO2} or activity of V^{4+} for carnotite deposition in 'calcrete' deposits; and temperature decrease for some magmatic-hydrothermal deposits. Greatly concentrated reactants have enhanced potential to produce higher uranium grades. For example, carbonaceous matter, coal, oil, massive sulfides or iron oxides may provide efficient reactant for extracting uranium from solution (e.g., Moore, 1954), whereas disseminated sulfides may be less efficient in terms of uranium grade. Additionally, adsorption of uranium by Fe-oxides (Waite et al., 1994) potentially could result in sequestration of uranium from fluids undersaturated with respect to uranium minerals.

2.6 OBSERVABLE EFFECTS OF MINERAL SYSTEM PARAMETERS

How can the generalised parameters described above be applied to specific natural uranium mineral systems? The observable or measurable effects in the rock record are listed in Table 3 against each parameter, along with the geological, geochemical, geophysical methods that may be used to map and document the parameters. For example, it is clear from earlier sections and as shown in Figures 5a and 5e that high oxidation state of fluids is required to mobilise and maintain significant quantities of uranium in solution as U^{+6} . The observable or mappable features representing oxidised fluid sources in magmatic environments include mineral compositional indicators, and igneous rock composition. We would use petrography and electron microprobe analysis of Fe-Ti-oxides, biotite, etc, and whole rock geochemistry (e.g., FeO/Fe₂O₃ ratios, U depletion/enrichment, etc) to establish the primary and secondary oxidation states of the igneous rocks involved in the fluid source regions or along fluid flow paths. In this way, field and laboratory observations may be used to map potential fluid source regions and fluid flow paths in the uranium mineral system in question. This approach may be useful in 'greenfields' regions where few if any uranium deposits are known yet the observations of potential sources and pathways may indicate that a uranium mineral system was active in the region.

Table 3: Parameters controlling development of uranium mineralising systems (based on Fig. 5), their observable effects in the rock record, and methods of mapping and measuring these effects.

PARAMETER	OBSERVABLES (MAPPABLE)	METHODS
Fluid source		
Oxidation state	For magmatic & metamorphic fluids: mineral compositional indicators; igneous rock composition (e.g. I- vs. S- vs A-type granitoids)	Petrography of Fe-oxides; microprobe analysis of biotite, Fe-Ti oxides, etc; mineral assemblage modelling
Oxidation state	For basin-related fluids: diagenetic mineral assemblages; presence of paleoregolith; bulk Fe^{2^+}/Fe^{3^+} , reduced-C content	Petrography; whole rock & mineral chemical analysis
Ligand availability	Source rocks rich in phosphate-, carbonate-, sulfate-, fluorine- or chlorine-bearing minerals	Mineralogy; lithogeochemistry
U metal source		
U content	Proportion of felsic vs mafic material in potential source regime; distribution of U-rich igneous rocks; anomalous mantle compositions?	Stratigraphy; whole rock geochemistry; radiometrics+ surface geology/regolith mapping; mantle Pb isotope variations?
'Leachability'	Abundance and nature of potential source minerals; evidence for leaching	Whole rock & mineral geochemistry; petrography; radiometric signatures e.g. low U/Th
Fluid flow drivers		
Hydraulic head / buoyancy	Effects of palaeotopography, eg proximal immature sediments; effects of high geothermal gradient, eg shallow magmatism & hydrothermal activity, HPLT metamorphism	Basin architecture (seismic; AEM, etc); sequence stratigraphy; geological mapping & reconstruction; petrology of metamorphic & hydrothermal rocks
Deformation	structures; age of diagenetic/alteration minerals in aquifers in relation to deformation	structural geology; petrography; geochronology of diagenetic/ hydrothermal phases recording fluid flow; pressure-temperature history
Fluid volume		
Fluid flux	Permeability and its connectivity & temporal evolution; intensity & scale of alteration (regional vs district vs deposit scale)	Basin/aquifer architecture (seismic, AEM, etc); petrography; stable isotope estimates of W/R ratios
Duration	Evidence for multiple fluid flow and/or tectonic events related to mineralisation	Mapping; petrography; dating of fluid flow events including weathering in relation to timing of U deposition
Fluid pathways		
Oxidation state	Magmatic & metamorphic fluids: mineral compositional indicators	Petrography of Fe-oxides; EMP analysis of biotite, Fe-Ti oxides, etc; mineral assemblage modelling
Oxidation state	Basin-related fluids: diagenetic mineral assemblages; palaeoregolith; bulk Fe ²⁺ /Fe ³⁺ , org C	Petrography; WR & mineral chem. analysis
U transport enhancers	Presence of ligand-bearing minerals – sulfates, phosphates, carbonates, or fluoride- or chloride-bearing minerals	Mineralogy; geological maps
Inhibitors to U transport	Presence & abundance of Fe ²⁺ –bearing minerals, sulfides, reduced C, phosphates, Fe- oxyhydroxides	Petrography; whole rock geochemistry; aeromagnetics may detect magnetite, pyrrhotite; AEM may detect reduced C, sulfides if connected conductivity; IP may detect disseminated sulfides
U depositional		
parameters		
Pressure- temperature- compositional (PTX) gradients	Reductant concentration: e.g. plant matter, coal, oil, gas, Fe ²⁺ -bearing minerals, sulfides, graphite; Temperature gradient: e.g. evidence for paleosurface; shallow magmatism & hydrothermal activity Phosphates: evaporites	Petrography; WR geochemistry; aeromagnetics may detect magnetite, pyrrhotite; AEM may detect reduced C, sulfides if connected conductivity; induced polarisation may detect disseminated sulfides
Scale of PTX gradient	Volumetric extent (mass) of reductant; dimensions of contact metamorphic aureole	Geological & geophysical mapping / basin analysis

3. Scheme of uranium mineral systems and deposit styles

Classifications of uranium deposits have previously followed two alternative approaches, focusing either on descriptive features of the mineralisation such as host rock type and orebody morphology, or on genetic aspects (e.g., see discussion by Dahlkamp, 1993; Cuney, 2009). The former approach was adopted by the IAEA in their widely used classification published bi-annually in the OECD/NEA Red Book. Fifteen uranium deposit types have been distinguished, and are listed below in order of their approximate economic importance in Australia (McKay and Miezitis, 2001): (1) breccia complex, (2) unconformity-related, (3) sandstone, (4) surficial, (5) metasomatite, (6) metamorphic, (7) volcanic, (8) intrusive, (9) vein, (10) quartz-pebble conglomerate, (11) collapse breccia pipe, (12) phosphorite, (13) lignite, (14) black shale, (15) other types. Dahlkamp (1993) subdivided 15 deposit types into 30 subtypes and thence into classes. Plant et al. (1999) re-grouped the types listed by the IAEA within three associations in recognition of the shared geological settings among groups of uranium deposits: igneous plutonic and volcanic, metamorphic, and sediment/sedimentary basin associations. Cunev (2009) proposed a genetic classification based on uranium deposit formation conditions through the geological cycle, including deposits related to surface processes, synsedimentary deposits, deposits related to hydrothermal processes, and deposits related to partial melting and crystal fractionation.

The OECD/NEA Red Book classification has served a useful purpose particularly in assigning uranium resource data to deposit categories. However, there are limitations in the application of this and other empirically-based classification schemes where there is a need to *predict* the location of undiscovered resources. Such a need exists in greenfields exploration; Geoscience Australia's Onshore Energy Security Program is supporting this exploration by providing pre-competitive data and new concepts for area selection at the continental to regional scales.

An alternative classification approach is proposed below, that emphasises the *similarities* in the *processes* of formation of uranium deposits and takes account of the crustal- to deposit-scales of the mineralising processes – a 'mineral systems' approach. This scheme builds on the concepts presented by Skirrow et al. (2008). Underpinning the new classification scheme is the concept of redistribution of uranium from the mantle to the crust and its progressive concentration and recycling via igneous, metamorphic, sedimentary and fluid processes, illustrated in Figure 6.

We suggest that the large number of known uranium deposit styles listed in previous schemes may be simplified to fit within and between three families of uranium mineralising systems, illustrated in Figure 7: (1) magmatic-related, (2) metamorphic-related, and (3) basin- and surface-related. In addition to accommodating known deposit styles, this new scheme predicts a *continuum* of deposit styles between the three end-member mineralising systems. It is built on the concept that each of the three end-member uranium mineral systems is the product of one of three fundamentally different fluids that transported uranium - magmatic-hydrothermal, metamorphic, and hydrosphere-derived (meteoric water, lake water, seawater). The differing geological settings in which these three fluids are generated and through which they migrate gives rise to the diversity of uranium deposit types. Involvement of more than one of the end-member fluids results in hybrid styles of uranium mineralisation.

Magmatic-related uranium systems are defined here as those that involve uranium deposition directly from magmas ('orthomagmatic' systems) or from fluids exsolved from magmas (magmatic-hydrothermal systems). Uranium in magmatic-related systems may be derived from the magma or from crystallised igneous or even non-igneous host rocks, and deposited either within the crystallising igneous body or externally in any rock type. Mixing of magmatic-hydrothermal fluids with other fluids or extensive reaction with wall rock may lead to formation of hybrid styles of uranium mineralisation (Fig. 7). Analogues of magmatic-related uranium systems occur in the spectrum of porphyry to epithermal Cu-Au deposit styles. Magmas are considered to be part of the



Figure 6: Scheme relating uranium mineral systems to earth processes.

magmatic-related system, because there is a continuum in the behaviour of uranium between solid phases, melt and fluids in magmas. Mantle-derived fluids may represent a separate, fourth, fluid end-member but the behaviour of uranium in such fluids is unknown and hence we focus here on the crustally-derived and hydrosphere-derived fluids.

'Volcanic' uranium deposits are viewed by Plant et al. (1999) as the product of magmatic-hydrothermal fluids reacting with volcanic rocks, and can be considered a type of magmatic-related uranium system where this process has occurred. Alternatively, some 'volcanic' uranium deposits may involve leaching of uranium from igneous or other rocks by *non-magmatic* fluids and deposition of uranium in volcanic rocks. Due to the differing architecture and fluid characteristics of this scenario compared with magmatic-related uranium systems as defined herein, we consider these non-magmatic fluid systems to be hybrids, or basin-related or metamorphic-related systems.

Metamorphic-related uranium systems involve uranium deposition from fluids of true metamorphic origin (via dehydration, etc) or from fluids extensively reacted with metamorphic rocks at elevated temperatures. These 'metamorphic fluids' may acquire chemical and isotopic signatures that are indistinguishable from true metamorphic fluids.



Figure 7: Scheme of three families of uranium mineralising systems, and three end-member fluid types. A continuum of deposit styles may exist between these end-members, represented by hybrid styles of uranium mineralisation such as IOCGU deposits. For reference, uranium deposit types from the IAEA Red Book classification are numbered, in order of economic importance in Australia (McKay & Miezitis, 2001): (1) breccia complex (IOCGU), (2) unconformity-related, (3) sandstone, (4) surficial (including calcrete), (5) metasomatite, (6) metamorphic, (7) volcanic, (8) intrusive, (9) vein, (10) quartz-pebble conglomerate, (11) collapse breccia pipe, (12) phosphorite, (13) lignite, (14) black shale.

We propose that there is a continuum of deposit styles in basin-related uranium systems between those formed from surficial waters or groundwaters (e.g. 'surficial' or 'calcrete' deposits, 'sandstone-hosted' deposits) to those formed in deeper parts of basins including 'Westmoreland' style and 'unconformity-related' styles (Fig. 7). Mixing of fluids derived via dehydration reactions during metamorphism/diagenesis and surface-derived fluids is one possible process resulting in the spectrum of deposit styles in basin-related uranium mineralising systems. 'Syngenetic' sedimentary uranium deposits (e.g., 'quartz pebble conglomerate' style; lignite, phosphorite, black shale hosted deposit styles) are suggested here to be members of the basin-related family of uranium systems because uranium is transported physically (as detrital grains) or chemically by meteoric waters or seawater prior to deposition with the sediments.

Descriptions of the three end-member families of uranium mineral systems, and a major type of hybrid system (uranium-bearing iron oxide copper-gold deposits), are given in the final four sections of this report. However, for detailed descriptions of individual uranium deposits, the reader is referred to other sources such as Dahlkamp (1993), McKay and Miezitis (2001), Cuney and Kyser (2008), and references therein.

4. Uranium mineral systems

4.1 MAGMATIC-RELATED URANIUM MINERAL SYSTEMS

4.1.1 Introduction – uranium in magmatic processes

Large highly charged ions including U and Th generally behave incompatibly during magmatic processes. These properties are largely responsible for the fact that the average uranium content of felsic igneous rocks (4.0 ppm, Rogers and Adams, 1969) is significantly higher than that of upper continental crust (2.5 ppm, Rogers and Adams, 1969), and is almost two orders of magnitude higher than typical uranium contents of mantle-derived mafic rocks such as N-MORB (0.047 ppm, Sun and McDonough, 1989). The disparity between mafic and felsic igneous rocks reflects the progressive partitioning of uranium into the lithosphere during crustal growth.

Based on the well known behaviour of incompatible elements in magmatic systems, critical factors in determining the uranium content of igneous rocks are:

- bulk rock composition of the source, including uranium content;
- degree of partial melting and residual mineralogy;
- extent of fractional crystallisation and mineralogy of fractionating assemblage;
- pressure-temperature conditions during melting and ascent; and
- extent of assimilation of wall rock or of magma mixing.

These factors will largely determine the bulk composition of the resultant melts, and are therefore the primary control on uranium content. Extreme concentration of uranium by particular magmatic processes may lead to orthomagmatic uranium mineralisation, as discussed below.

Processes of magmatic fluid exsolution may further modify the uranium content of the melt, and in some circumstances results in magmatic-hydrothermal uranium mineralisation. The major controls on this process are discussed in section 4.1.3.

Igneous rocks are a key source of uranium in the formation of many low- to high-temperature hydrothermal uranium deposits. Although magmatic processes rarely produce economic grades of uranium mineralisation, the mineralogy of U-bearing minerals in igneous rocks is critical to the processes of leaching and remobilising uranium to form non-magmatic mineralisation. Favourable scenarios for such secondary processes are discussed in section 4.1.4.

4.1.2 Effect of melt bulk composition

A fundamental control on the solubility of incompatible elements such as uranium in silicates melts is the extent of polymerisation (linking between Si-O tetrahedra) of the melt (Mysen, 1988). Key variables are temperature, the [K+Na]/Al ratio and fluorine (F) content of the melt (Mysen et al., 2004). Dissolved F acts to break bridging oxygen bonds, causing melt depolymerisation and thereby increasing uranium solubility in the magma (Fig. 8; Peiffert et al., 1996; Mysen et al., 2004). A similar effect on incompatible element solubility is produced at high concentrations of $Na_2O + K_2O$ (Peiffert et al., 1994; Peiffert et al., 1996), and especially in magmas with high Na/K (Dominé and Velde, 1985; Peiffert et al., 1996). The solubility of uranium in peralkaline melts ([K+Na]/Al >1.0) as well as F-rich peraluminous or peralkaline melts may exceed percent levels. As a consequence, even though peralkaline melts may contain high uranium contents they are almost always undersaturated with respect to uranium minerals such as uraninite. Instead, uranium is incorporated as a minor element in a wide range of accessory minerals along with Zr, REE, Th, Nb and Ta. Uranium is more soluble in Na-rich melts as compared to K-rich melts (Dominé and Velde, 1985). Given that CO₂ shifts the granite eutectic towards sodic compositions, an association may be expected between Na-CO₂-rich melts and related uranium mineralisation. The redox state of the melt has a subordinate role in controlling uranium contents, relative to the [K+Na]/Al ratio and F content of the melt. Melts buffered to high oxidation states by hematitemagnetite or Cu₂O-CuO may carry up to 3 times more uranium (as U^{6+}) than corresponding reduced Ni-NiO-buffered melts in which uranium is in the U^{4+} state (Fig. 8; Peiffert et al., 1994, 1996).



Figure 8: Experimentally determined uranium solubility in silicate melt as a function of (Na+K)/Al ratio of the melt, oxygen fugacity, and different aqueous fluid compositions (redrawn from Cuney and Kyser, 2008, based on data from Peiffert et al., 1994, 1996). Shading of symbols represents different fluid compositions (HF, HCl, NaF, NaCl, Na₂CO₃) in equilibrium with melt in the experiments.

Peralkaline melts generally derive from high-temperature partial melting of lower crust or upper mantle which in some cases results in the formation of carbonatites. Extreme fractionation may lead to high concentrations of uranium, although this process alone does not appear to result in economic grades. In well documented examples of uranium mineralisation associated with peralkaline igneous rocks, higher grade mineralisation is related to magmatic fluid exsolution, and hence is considered separately (section 4.1.3).

Metaluminous magmas and corresponding I-type calc-alkaline magma compositions generally have the lowest concentrations of uranium, due to their derivation generally from mafic protoliths. However, high-temperature K-rich variants and some A-type magmas may contain moderate to high concentrations of uranium, particularly more evolved members. The Ca content of the magmas strongly controls the mineralogy of U-bearing phases. Early crystallisation of Ca minerals such as allanite and titanite in high-Ca melts extracts REE and results in increasing Th/REE ratios. Crystallisation of uranium-bearing thorite is favoured in these circumstances, and minor uraninite may form in some highly fractionated, high-K calc-alkaline granites (Cuney and Kyser, 2008). These minerals may become available as uranium sources for later fluids.

At elevated temperatures, melt generation is facilitated by the breakdown of biotite or phlogopite, progressing to amphibole breakdown at temperatures exceeding $\sim 1000^{\circ}$. The breakdown of such phases may release significant amounts of F into the melt, which has important consequences for the enrichment of uranium (see below). This may give rise to the high HF/H₂O ratios commonly observed in A-type granitoids (Loiselle and Wones, 1979). Hot H₂O-poor magmas can reach higher levels of emplacement compared to hydrous magmas, and will do so under extensional tectonic conditions, with consequences

for development of shallow-crustal hydrothermal uranium systems (Plant et al., 1999). High-temperature I-type or A-type granitoids are widespread in the Australian Proterozoic (Wyborn et al., 1998), the most uranium enriched igneous rocks of any geological period in Australia (Lambert et al., 2005). While it is evident that many of these magmas were generated within the crust at depths of <35 km, based on Sr-depleted, Y-undepleted trace element patterns (Wyborn et al., 1998), the geodynamic environment for the granite, and in particular the cause of the highly elevated thermal gradients, remains poorly understood.

Calc-alkaline granites may become peraluminous through extreme fractionation, assimilation of crustal material, and/or magmatic-fluid related processes. These magmas, and peraluminous S-type granites generated by partial melting of sedimentary sources, will become mildly enriched in uranium through crystal fractionation. As potential uranium sources, however, Cuney and Kyser (2008) suggest the most important peraluminous magmas are those resulting from low degrees of partial melting of quartzo-feldspathic sources such as arkose or felsic volcanics. Melt extraction and crystal fractionation can lead to uraninite crystallisation at only a few tens of ppm uranium, due to the low solubility of uranium, zircon and monazite in low-temperature peraluminous melts (Cuney and Friedrich, 1987; Peiffert et al., 1994, 1996). Uranium concentration is particularly favoured in low-Ca peraluminous magmas with high F, resulting in a delay in uraninite saturation until high levels of uranium are attained (Peiffert et al., 1996).

4.1.3 Uranium in magmatic fluids and magmatic-related uranium deposits

A fundamental control in the development of magmatic-related uranium mineralisation is the partitioning behaviour of uranium between melt and coexisting magmatic fluid. In experimental systems the uranium partition coefficient between fluid and melt $(D(U)^{fluid-melt} = ratio of uranium concentration in each phase)$ increases with decreasing Na+K/Al ratio of the melt (Fig. 8). Chloride-bearing experimental systems exhibit partition coefficients 1.5-2.5 orders of magnitude higher than in fluoride and CO₃-bearing systems with equivalent Na+K/Al ratios. This implies that in Cl-bearing peraluminous systems exsolved hydrous fluids may have uranium concentrations more than 10 times those of the melt. The experimental data also indicate that fluids exsolved from peralkaline melts may contain low uranium concentrations relative to melt (Fig. 9), despite the potentially high uranium content of the melt (Fig. 8). For example, in the Streltsovka uranium district, eastern Russia, Chabiron et al. (2003) estimated that magmatic-hydrothermal fluids exsolved from peralkaline rhyolites had quite low uranium contents of ~1ppm.

At oxidising conditions (hematite-magnetite, or Cu₂O-CuO buffers; Fig. 9), solubilities of up to 970 ppm uranium are indicated for the fluid, carried as chloride or hydroxyl-chloride complexes (Peiffert et al., 1994, 1996). The presence of fluoride suppresses the partition coefficient but this is counterbalanced by greater stability of aqueous uranium-fluoride complexes relative to chloride complexes (Peiffert et al., 1996). Thus, fluids exsolved from peraluminous melts potentially may carry high concentrations of uranium, in the U^{6+} state where the melt is oxidised and Cl-or F-rich, or in the U^{4+} state where the melt is reduced and F-rich.

Few data are available from natural magmatic-hydrothermal systems of the uranium contents of fluids. Audétat et al. (2008) reported concentrations of up to 20 ppm U, 390 ppm Ce and 270 ppm La in brine fluid inclusions from granophyre and from the Mina Tiro Estrella Th-U-REE prospect within the Capitan pluton, New Mexico.

As noted above, the processes of partial melting and fractional crystallisation very rarely result in uranium concentrations of economic grades and tonnages. True 'orthomagmatic' uranium deposits of high grade are probably exceedingly rare. Most if not all of the well documented uranium deposits closely associated with peralkaline and peraluminous igneous rocks appear to be the product of either exsolved magmatic fluids or of separate later hydrothermal fluids that interacted with the U-rich igneous rocks. Magmatic fluids may remain within the igneous body, evolving through reaction with the parent intrusion, or may escape the intrusion and continue to evolve as magmatic-hydrothermal fluids.

Better known examples of magmatic-related uranium mineralisation are the giant Rössing deposit in Namibia, associated with peraluminous F-rich magmas ('alaskite'), the Kvanefjeld uranium deposit hosted by the Ilimaussaq peralkaline intrusive complex in Greenland, and the Ross Adams deposit hosted

by the Bokan Mountain peralkaline igneous complex in southeastern Alaska (Cuney & Kyser, 2008, and references therein). The geology and mineralogy of mineralisation at the Kvanefjeld and Ross Adams deposits indicate that uranium mineralisation is related to exsolved magmatic-hydrothermal fluids. Although the origin of the Rössing deposit continues to be debated, most proposed models involve a fluid phase in uranium transport and deposition, whether the fluid was exsolved from the magma (Cuney and Kyser, 2008) or was of external origin (Plant et al., 1999). The role of magmatic-hydrothermal fluids in iron oxide copper-gold (uranium) deposits has been debated since the first recognition of this class of deposit (Hitzman et al., 1992). At the world's largest uranium deposit, Olympic Dam, Haynes et al. (1995) proposed a two-fluid mixing model involving evolved meteoric waters and deep-sourced fluids of undefined but conceivably magmatic-hydrothermal origin. Reynolds (2000) and Hayward (2008) alluded to a magmatic-hydrothermal origin of Cu-U-Au mineralisation. Based on work in the region by Geoscience Australia (Skirrow et al., 2007; Bastrakov et al., 2007; Skirrow, 2008), a hybrid model is proposed for IOCGU systems in the Gawler Craton, largely supporting the proposal of Haynes et al. (1995). This model is discussed in section 4.4.1.

Figure 9: Experimentally determined uranium partition coefficient (D(U)) between granitic melts and different fluid compositions at equilibrium, as a function of (Na+K)/Al ratio of the melt and oxygen fugacity (redrawn from Cuney and Kyser, 2008, based on data from Peiffert et al., 1994, 1996). Shading of symbols represents different fluid compositions (HF, HCl, NaF, NaCl, Na₂CO₃) in equilibrium with melt in the experiments.

4.1.4 Suitability of igneous rocks as a uranium source

A spatial association has long been recognised between uranium mineral deposits and U-rich igneous rocks, as shown in recent data compilations for Australia (Lambert et al., 2005; Schofield, 2009). This empirical association is apparent even where uranium mineralisation postdates emplacement of the igneous rocks by millions or even billions of years (Lambert et al., 2005). It is widely assumed that the igneous rocks were the sources of uranium, either directly or indirectly via sedimentary and hydrothermal processes. Two of the factors controlling the potential of an igneous rock as a suitable source of uranium in the formation of mineralisation are:

- (a) The initial magma must be enriched in uranium. The criteria for this have been addressed above.
- (b) The crystallised igneous rock must have the uranium available for transfer from mineral to fluid (leaching).

Uranium is present in uraninite in the +4 oxidation state, and hence is highly susceptible to remobilisation by oxidising fluids of a variety of origins (see section 2.2). As discussed above, high-F low-Ca peraluminous magma compositions are some of the most favourable for crystallisation of uraninite. In peralkaline and metaluminous igneous rocks where primary uraninite is rare, uranium is dispersed in other accessory minerals that generally have low solubilities in post-magmatic fluids. Nevertheless, other processes can result in significant uranium availability to post-magmatic fluids. For example, metamictisation of U and/or Th-rich phases such as monazite, thorite, allanite and zircon may provide fluid access to crystal interiors, given sufficient passage of time. Additionally, the wide range of processes that increase the permeability of igneous rocks may enhance transfer of uranium from mineral to fluid. Weathering processes may be particularly effective in leaching uranium, due to the high oxidation state of meteoric waters.

The Streltsovka uranium district in eastern Russia is an example of the interplay between magmatic and hydrothermal processes leading to formation of a major uranium resource. More than 280,000 tonnes of U_3O_8 (in cost category <USD\$80/tonne) is distributed in 20 deposits, hosted by peralkaline rhyolites (Laverov et al., 1992). Petrological studies and mass-balance calculations using melt/fluid partition coefficients indicate that magmatic-hydrothermal fluids exsolved from the Jurassic peralkaline magmas could have contributed only a minor portion of the U and F in the known uranium deposits (Chabiron et al., 2003). It is argued that the bulk of the uranium was leached by hydrothermal fluids from both the volcanic rocks and U-rich subalkaline granitoids in Paleozoic basement beneath the rhyolites. Metamict accessory minerals in the granitoids such as allanite, thorite, zircon and apatite were evidently partially leached of uranium. Chabiron et al. (2003) suggested that leaching, mobilisation and deposition of uranium mineralisation in the rhyolites took place within a convective hydrothermal system driven by heat from the Jurassic magmatism. The origins of the hydrothermal fluids and uranium depositional mechanisms are less clear, but may have involved oxidised meteoric waters as well as acidic magmatic-hydrothermal fluids (Chabiron et al., 2003).

A key conclusion from the study of the Streltsovka district is that peralkaline volcanic rocks may be excellent sources of uranium. Fine grained or glassy groundmass hosting uranium may be susceptible to alteration and release of uranium to hydrothermal fluids or groundwaters. For similar reasons the volcanic products of high-temperature K-rich I-type and A-type magmas may represent important sources of uranium.

High Th/U ratios (>>4 in felsic rocks) in comparison to crustal averages may indicate that uranium leaching has occurred, and may suggest the presence of downstream secondary uranium mineralisation.

4.1.5 Summary and model of magmatic-related uranium systems

The key processes of uranium concentration and mobilisation in magmatic-related uranium systems are illustrated in Figure 10, for plutonic to volcanic crustal settings. The settings of selected magmatic-related uranium deposits are depicted (e.g., Rössing, Namibia).

Four sets of processes may lead to the extreme concentration of uranium required to form uranium mineralisation directly related to magmatic activity or spatially associated with igneous rocks:

• <u>Uranium-rich source and high-temperature melting</u>: metasomatised mantle for peralkaline magmas, U-rich metasedimentary rocks (e.g., terrestrial rather than marine sediments) for peraluminous magmas; U-rich felsic igneous rocks as sources of metaluminous magmas.

• <u>Extensive fractional crystallisation with elevated F</u>: peralkaline and high-K I- and A-type felsic rocks may contain high uranium contents hosted by chemically stable minerals (plutonic rocks) or by glass (volcanic rocks); peraluminous magmas may crystallise minor uraninite; however, economic U grades are rarely attained during fractional crystallisation.

• Exsolution of uranium-rich magmatic-hydrothermal fluids: highest uranium contents will be in fluids exsolved from Cl-rich peralkaline magmas and Cl- and/or F-rich peraluminous melts. Aqueous chloride and fluoride complexes are important at magmatic conditions, with uranium transported either as U^{4+} in reduced magmatic systems or as U^{6+} or U^{5+} in oxidised systems. Magmatic-hydrothermal uranium deposition may occur within or external to the igneous body, controlled by gradients in temperature, pH, F activity, fO₂, CO₂ or Ca activity.

• <u>Leaching and remobilisation of uranium</u>: high-U volcanic rocks of high-F peralkaline, peraluminous or high-K metaluminous composition are especially susceptible to reaction with reduced or oxidised fluids of magmatic-hydrothermal origin or with oxidised fluids of meteoric or other non-magmatic origin. Peralkaline and high-K I- and A-type plutonic rocks with metamict U-bearing minerals will be susceptible to uranium leaching, as will uraninite-bearing strongly fractionated peraluminous rocks.

MAGMATIC-RELATED URANIUM SYSTEMS: PERALUMINOUS and PERALKALINE MAGMAS

Figure 10: Model of uranium mineral systems related to peraluminous and peralkaline magmas (pink and dark plum ellipses, respectively), at depths ranging from volcanic to plutonic environments. Example uranium deposits and districts shown abbreviated as follows: MC - Massif Central deposits, France; K - Kvanefjeld deposit, Illimausaq Complex, Greenland; RA - Ross Adams deposit, Bokan Mountain complex, Alaska; CW - Crocker Well deposits, New South Wales; S - Streltsovka deposits, Russia.

Table A3 summarises the characteristics of magmatic-related uranium mineral systems in terms of the 'Five Questions' framework. The key 'ingredients' and processes are listed for each question, as well as the reason for the 'ingredient' or process and its relative importance for ore formation (essential, desirable, etc). For each 'ingredient' the <u>mappable or measureable</u> geological, geophysical and geochemical features are listed along with the scale at which the ingredient is important in the mineral system (continental, district, deposit, etc). Thus the table provides a practical guide to the field identification of magmatic-related uranium systems, which can assist in assessing the uranium potential of regions of interest.

Fundamental in the 'answers' to all five 'Questions' are the processes of uranium enrichment in magmas and related fluids, as discussed above. The geodynamic and pressure-temperature evolution of magmaticrelated uranium systems (Q1) and architecture (Q2) are those of terranes where either fractionated peralkaline or peraluminous magmas were generated. Favourable settings are suggested in Table A3, although these geodynamic and tectonic settings are not unique to uranium provinces and many questions remain.

The fluid characteristics, sources of uranium and fluids (Q3) and uranium transport and depositional processes (Q5) are determined largely by the melt bulk composition, fractionation processes, and nature of fluid exsolution from peralkaline and peraluminous magmas, as discussed in sections 4.1.2 and 4.1.3. Three separate scenarios of magmatic-related uranium systems are distinguished here: (a) orthomagmatic uranium concentration, (b) uranium sourced from magmas and transported within or out of the magma by fluids exsolved from the magma (magmatic-hydrothermal fluids), and (c) magmatic-hydrothermal fluids leaching uranium from igneous rocks external to the magma, and then deposited either within igneous or non-igneous host rocks. In Table A3, each of these three source (Q3) scenarios are listed.

Scenario (c) is considered in section 4.1.4 (suitability of igneous rocks as a uranium source). It relates to both Questions 3 and 4 (fluid flow drivers and pathways) because leaching of uranium from igneous rocks may take place along fluid flow pathways *en route* from fluid source via metal source to metal depositional settings. Although scenario (c) describes a magmatic-related uranium system according to our definition (section 3), similar scenarios involving leaching of uranium from igneous rocks by non-magmatic fluids can be envisaged. It may be difficult to distinguish uranium systems involving magmatic-hydrothermal from those with non-magmatic fluids. However, in either case the key 'ingredients' of the system include the presence of suitable igneous source rocks and availability of fluids capable of leaching and transporting uranium to a favourable depositional environment. Differing architecture and alteration assemblages may help to distinguish magmatic-related from other uranium systems.

The processes of uranium deposition (Q5) in magmatic-related systems are not well understood, except for those in orthomagmatic systems where uranium deposition is related to crystallisation of U-bearing rock-forming minerals and U-minerals directly from melt. General aspects of uranium deposition in hydrothermal systems were discussed in sections 2.4 and 2.5.6. Based on the low abundances of reduced carbon, sulfur or iron mineral phases reported in published descriptions of most magmatic-related uranium systems, chemical reduction processes appear to be less important than in other uranium mineral systems. Changes in temperature, pH or ligand concentration may be more important in controlling uranium deposition in magmatic-hydrothermal systems, but our understanding is currently limited by the paucity of thermodynamic data for uranium complexes at high temperature-pressure conditions.

4.2 METAMORPHIC-RELATED URANIUM MINERAL SYSTEMS

4.2.1 General characteristics

Uranium deposits formed from fluids of metamorphic-dehydration origin appear to be rare and of low grade and tonnage (Plant et al., 1999). However, a diverse group of significant deposits including so-called 'metasomatic' uranium deposits occur within metamorphic or igneous rocks and formed at high temperature (i.e., 350-500°C) during deformation in synorogenic settings. Metasomatism or alteration associated with such deposits is commonly sodic with desilicification, and uranium mineralisation

generally includes brannerite, uraninite and/or uranothorianite (Dahlkamp, 1993; Cuney and Kyser, 2008). Examples described by Cuney and Kyser (2008; and references therein) include the Krivoy Rog region (Ukraine), Lagoa Real district (Brazil), Mt Isa district (Queensland), and the Tranomaro district (Madagascar).

Some of the characteristics of 'metasomatic' uranium deposits are shared by a number of deposits previously classified as 'vein' type (e.g., 'episyenite' hosted deposits in France), although the 'vein' class of Dahlkamp (1993) also includes a range of other hydrothermal uranium deposits in 'granite-related' and 'non-granite related' settings. Yet other deposits ascribed by some authors to intrusion- or magmatic-related systems share similar alteration characteristics to 'metasomatic' deposits (e.g., Ross Adams deposit, Dahlkamp, 1993; Plant et al., 1999).

Issues of classification of these diverse deposit types can be reconciled if we consider them within the tripartite mineral systems framework of Figure 7. We suggest that 'metasomatic' uranium deposits formed from fluids that reacted extensively with metamorphic rocks at elevated temperatures, termed 'metamorphic' fluids here. These metamorphic-related systems are discussed in detail below. Intrusion-centred hydrothermal uranium systems with sodic alteration and disseminated or vein mineralisation (e.g., Ross Adams deposit) are viewed as variants of magmatic-related systems because they involved magmatic-hydrothermal fluids. Some 'vein' deposits hosted by albitised and desilicified felsic intrusive rocks appear to have formed through the reaction of deeply circulated basinal brines with pre-existing high-U igneous rocks (Cuney and Kyser, 2008), and we therefore view them as hybrids between metamorphic rocks (e.g., Schwarzwalder, USA; Bohemian massif; Beaverlodge, Saskatchewan; Dahlkamp, 1993; Plant et al., 1999) are also probably hybrids with varying contributions of 'metamorphic' and basinal fluids.

4.2.2 Sodic alteration (Q3, Q4, Q5)

As noted above, a key characteristic of many uranium deposits within metamorphic-related uranium systems is the presence of sodic alteration that formed in high-temperature syn-deformational settings. Insights on where and how these uranium systems formed may be gained from an understanding of possible processes of sodic alteration, as follows.

The sodic minerals are dominantly albite accompanied in places by Na-rich calc-silicates (clinopyroxene, amphibole, scapolite), as well as anhydrous minerals such as garnet, oxides and carbonates. Sodic alteration is not unique to uranium mineral systems, and occurs as regional alteration zones in some IOCG districts (commonly Na-Ca alteration), volcanic-associated massive sulphide (VAMS) districts, in the Broken Hill region stratigraphically beneath Pb-Ag-Zn mineralisation, in deeper parts of some porphyry copper systems, and associated with some alkaline igneous complexes (Na-fenitisation). The oxidation state of fluids involved in some of these systems is relatively low (e.g., VAMS, Broken Hill), perhaps explaining why sodic alteration in such systems is not associated with significant uranium mineralisation.

The origins of sodic metasomatism have long been debated. In higher temperature settings (>350-500°C), the principal processes resulting in sodic metasomatism are:

- Increasing temperature, such as in prograde domains of convecting hydrothermal systems, where albite stability is favoured due to the strong temperature dependence of alkali feldspar equilibria (Orville, 1962);
- Involvement of exceptionally Na-Cl-rich fluids, derived by evaporitic mineral dissolution (e.g., Barton and Johnson, 1996), absorption of water by melt or anhydrous rocks (Markl and Bucher, 1998), or by other processes;
- Decreasing CO₂ content of Na-K-bearing fluids buffered by Na-K silicates (Iiyama, 1965), via phase separation (e.g., Pollard, 2000) or carbonate-forming reactions;
- Fluid-mediated Na-Ca cation exchange across lithological boundaries, with or without CO₂ phase separation (e.g., Schmulovich and Graham, 2004).

The role of phase separation in sodic(-calcic) alteration was discussed by Pollard (2000), who used the results of Iiyama (1965) to conclude that unmixing of H₂O-CO₂-NaCl ±CaCl₂-KCl magmatic fluids could account for regional sodic(-calcic) alteration in IOCG systems such as those in the Cloncurry district. However, the applicability of Iiyama's (1965) studies of single phase systems at 600°C and 1 kb to Na-K partitioning in two-phase CO₂-bearing systems is unclear. Whereas the loss of CO₂ from a single-phase fluid will favour sodic metasomatism, phase separation in the system alkali feldspars-NaCl-KCl-H₂O will favour potassic alteration of feldspars (Lagache and Weisbrod, 1977). In high temperature H₂O-CO₂ systems may be focussed on lithological boundaries between packages of calcic (e.g., basic or carbonate) rocks and quartzo-feldspathic or pelitic rocks (Schmulovich and Graham, 2004). Possible consequences are albitisation of plagioclase, carbonate and quartz dissolution, and CO₂ release accompanied by brecciation. Some or all of these characteristics have been reported in Na(-Ca) alteration in IOCG and metamorphic-related uranium mineral systems. Further studies are required to test whether the processes proposed by Schmulovich and Graham (2004) have wide application in these mineral systems.

4.2.3 Uranium transport and deposition in metamorphic-related systems (Q5)

The transport and deposition of uranium in metamorphic-related systems is problematic, due to the dearth of relevant high-temperature thermodynamic data. Fluorine-rich apatite and riebeckite at the Valhalla deposit led Polito et al. (2007) to infer fluoride complexing of uranium. Similarly, in U-Th-REE mineralisation of the Tranomaro district of Madagascar hydroxyl-bearing minerals in high temperature alteration are fluorine-rich, suggesting metal-fluoride complexing (Cuney and Kyser, 2008). The high levels of F and/or CO₂ may also account for Ti mobility in forming brannerite in some metamorphicrelated uranium systems. Based on the experimental results of Peiffert et al. (1996), chloride complexing of uranium also may be important in high temperature highly saline brines, particularly where low water activities suppress the stability of oxy-hydroxide complexes. A redox step may or may not be involved in destablising either fluoride or chloride complexes of uranium, depending on the predominance of U^{4+} or U^{6+} in the hydrothermal fluids (see sections 2.2 and 4.1.3). In high-temperature reduced F-rich metamorphic-related systems, the activity of calcium and pH may be more important than redox in controlling uranium deposition due to the low solubility of fluorite (CaF₂) and fluorapatite. Reactive Cabearing host rocks such as mafic-intermediate rocks or carbonates may represent favourable uranium depositional environments in such systems. Uranium transported by F- and/or Cl-rich oxidised fluids in metamorphic-related systems, however, may be deposited via reduction reactions. The ranges of hydrothermal mineralogy of documented metamorphic-related uranium deposits appear to represent a spectrum from reduced to oxidised styles.

4.2.4 Regional settings (Q1, Q2)

The high temperature fluids implicated in metamorphic-related uranium systems were generated in terranes that attained medium or higher grade metamorphism, although the timing of mineralisation relative to this metamorphism is not well constrained in most documented systems. Brannerite and riebeckite in the Valhalla deposit yielded U-Pb/Pb-Pb and 40 Ar/³⁹Ar ages, respectively, of 1555 to 1510 Ma, interpreted to correspond to the Isan Orogeny (Polito et al., 2007). A strong structural control is evident in most metamorphic-related uranium systems, with mineralisation commonly hosted by ductile to brittle-ductile shear and fault zones that in some cases were reactivated (Cuney and Kyser, 2008). The geodynamic and tectonic settings and crustal architecture of metamorphic-related uranium systems are not sufficiently understood to present a unified model. However, we suggest that a key requirement is synorogenic generation of highly saline Na(-Ca) brines that were in places F-rich and CO₂-bearing. Such compositions are atypical of most metamorphic fluids and may indicate unusual contributions of cations and halides from syn-orogenic magmas or from halide-rich crustal rocks such as earlier rift basins. Fluid pathways in the mid-crustal settings of the metamorphic-related uranium systems were shear and fault zones, not unlike the architecture of orogenic gold systems and magnetite-dominated IOCG systems. Fluid unmixing involving CO₂, perhaps triggered by pressure fluctuations in faults and/or contrasts in

bulk rock composition, may have locally enhanced permeability via breccia formation and led to characteristic sodic(-calcic) alteration associated with uranium deposition.

4.2.5 Model of metamorphic-related uranium systems

Figure 11 illustrates syn- to post-orogenic regional settings for a range of metamorphic uranium systems. Examples in five representative settings are based on descriptions by Dahlkamp (1993), Plant et al. (1999) and Cuney and Kyser (2008) and references therein. Setting (1) depicts deposition of uranium (a) from reduced or oxidised ore fluids within metacarbonate units possibly via change in F activity, and/or CO₂ phase separation (e.g., Tranomaro, Madagascar; ?Mary Kathleen, Queensland), and (b) along the basal contact of a reduced mafic igneous rock unit via reduction of oxidised ore fluid. Setting (2) represents uranium deposition from oxidised ore fluids mixing with reduced fluids in permeable sedimentary units within reduced mafic igneous rocks (e.g., Valhalla, Queensland). Setting (3) is a dilatant jog adjacent to a competent rock body along a terrane boundary between chemically contrasting rock packages (e.g., Krivoy Rog U district, Ukraine). Setting (4) is a dilatant jog adjacent to or within a U-rich felsic igneous body, favourable for U leaching by metamorphic or magmatic-hydrothermal fluids (e.g., Lagoa Real, Brazil). The setting is also favourable for mixing of reduced metamorphic and oxidised magmatichydrothermal fluids in a hybrid uranium system. Finally, setting 5 represents a hybrid of metamorphicand basin-related uranium systems in which 'vein' deposits are hosted by metamorphic or igneous rocks, with or without sodic alteration. Fluids were oxidised surface- or basin-derived, deeply circulated and reacted at elevated temperatures with metamorphic or igneous rocks to result in fluids of 'metamorphic' Fluid pathways are post-orogenic extensional faults, with oxidative alteration (e.g., character. hematisation) and leaching of uranium. Syn-deformational ore deposition occurred via reduction within suitable reduced units in the metamorphic basement or in the upper sedimentary basin sequence. Possible examples include some 'vein' type deposits in the Variscan of Europe, and Beaverlodge district (Saskatchewan). There may be links between setting 5 and some 'unconformity-related' uranium systems hosted by shear zones in reduced basement units.

Figure 11: Model of metamorphic-related uranium mineral systems. Syn-to post-orogenic settings are shown for uranium mineralisation and associated sodic(-calcic) alteration. Dilatent zones in fault and shear zones such as jogs at lithological contacts are favoured sites, in some cases associated with terrane boundaries. Five settings of metamorphic-related uranium mineralisation are numbered: (1) carbonate or mafic-rock hosted uranium, (2) clastic metasedimentary rock-hosted uranium within mafic volcanic sequence, (2) dilatant jog along major shear/fault zone adjacent to mafic igneous body, (4) dilatant jog adjacent to felsic pluton, with or without magmatic-hydrothermal fluid input, (5) hybrid fluid system with deeply circulated surface-derived fluids.

4.3 BASIN-AND SURFACE-RELATED URANIUM MINERAL SYSTEMS

4.3.1 Model of basin- and surface-related uranium systems

Figure 12 illustrates a hypothetical basin with a range of settings for uranium mineral systems and deposit styles. It should be noted that not all deposit styles necessarily would form simultaneously within the basin. A uranium mineral system in this context is envisaged as a volume of crust through which fluids of surface or basin origin passed to form one or more uranium deposits, possibly of different styles within or adjacent to the basin. For example, meteoric waters sourced outside the basin may leach uranium from basement rocks or basin sediments, and carry the uranium in ground waters to depositional sites within paleochannels or tabular sandstone units to produce 'roll front' or 'tabular' mineralisation styles. Calcrete hosted 'surficial' uranium deposits may be a variant where near-surface processes within the weathering

zone, such as evaporation, resulted in uranium deposition at or above the water table. The same groundwaters in deeper basin aquifers may mix with mobile reductants in fault zones to produce a different, fault-controlled style of deposit. This family of deposit styles all may form within a single uranium mineral system.

Deeper penetration of meteoric or ground waters generally will result in heating and chemical modification of fluid chemistry, and the role of formation waters, diagenetic fluids and ultimately metamorphic fluids will increase. This mid- to deep-basin setting requires particular architectures to maintain the high oxidation state of fluids necessary to transport significant uranium. For example, coarse clastic sediment aprons adjacent to basin margin growth faults may provide pathways connecting oxidised surface waters with aquifers deep within the basin. Alternatively, trapped formation waters may be buffered and/or maintained at high oxidation states by the presence of Fe³⁺-bearing minerals such as hematite and goethite, or by sulfate minerals, provided that reductants are in low abundance. Redbed-evaporite sequences may be favourable 'reservoirs' for storage of oxidised fluids deep within basins.

Migration or expulsion of these deep-basin oxidised uraniferous fluids may be driven by gravity (topography or salinity-related density controls), compaction, convection, or tectonic processes (e.g. 'seismic pumping' Sibson et al., 1975). The formation of major deposits in basin-related uranium systems requires focussing of fluid flow into settings with steep physico-chemical gradients. Favourable environments are fault zones intersecting reductants either within the basin (e.g. 'Westmoreland' style, associated with mafic volcanics, Fig. 12) or in basement (e.g., possibly some basement-hosted 'unconformity-related' deposits). The extensional scenario, illustrated in Figure 12, shows fluid down-draw into a basement-hosted 'unconformity-related' uranium system ('ingress' style, Quirt, 1989).

During basin inversion, fluid flow patterns will be significantly different and in some cases reversed relative to directions during extension. Switches in fluid flow direction may be partly responsible for the variations in local settings and characteristics of basement-hosted versus basin-hosted styles of 'unconformity-related' uranium deposits. Additionally, the role of basement-reacted fluids in 'unconformity-related' uranium systems (Cuney et al., 2003) may vary in importance with switches in fluid flow direction. Thus, some 'unconformity-related' mineralisation may represent hybrids of basin-related and metamorphic-related uranium systems.

Tables A5 and A6 summarise the key components of two of the most important members of basin-related uranium mineral systems, 'sandstone-hosted' and 'unconformity-related' uranium deposits. The tables are arranged in terms of the 'Five Questions' framework, along with corresponding 'ingredients' and processes considered to be important. Observable geological, geophysical and geochemical features are listed against each 'ingredient' or process.

Figure 12: Model of basin-related uranium mineralising systems, during the extensional stage of basin evolution. A range of uranium depositional sites and deposit styles are represented in this district- to deposit-scale mineral systems model (see text).

4.4 HYBRID URANIUM MINERAL SYSTEMS

4.4.1 Uranium in IOCG systems

Hybrids of uranium mineral systems involve input of fluids from two or more end-member sources (Fig. 7). Uranium-bearing iron oxide copper-gold (IOCGU) systems are arguably the most important type of hybrid uranium system. Whereas uranium is present in anomalous concentrations in many IOCG deposits, only the hematite-rich Olympic Dam deposit contains currently economic quantities of uranium, and indeed is the world's largest resource (BHP Billiton, 2008). Models for uranium mineralisation in IOCG systems are therefore based primarily on models for the Olympic Dam deposit (Haynes et al., 1995; Hitzman and Valenta, 2005; Skirrow, 2008).

Uranium occurs in the Olympic Dam deposit principally in uraninite, coffinite and brannerite, and is distributed at low grade throughout the mineralized hematitic breccias (Reeve et al., 1990). Higher grade uranium is weakly correlated with bornite-chalcocite zones (Reynolds, 2000). Higher grade gold zones occur between the uraniferous bornite-chalcocite mineralization and the "barren hematite-quartz" core of the deposit (Reynolds, 2000). By comparison, the Prominent Hill deposit in the northern Olympic Cu-Au province is far less endowed with uranium, although narrow high grade zones are present (e.g., up to 5000 ppm U; Belperio et al., 2007). Unlike at Olympic Dam, the higher grade uranium is associated with chalcopyrite rather than bornite-chalcocite. Hitzman and Valenta (2005) noted that host rocks at Prominent Hill (andesite; felsic and mafic dykes) are different (and of lower uranium content) to those at Olympic Dam (Hiltaba Suite granite). The sub-economic Oak Dam East Cu-U (Au) deposit in the Olympic Dam district contains significant uranium enrichment within the main chalcopyrite-pyrite mineralized zone (Davidson et al., 2007). The granitic host rock at Oak Dam East is assigned to the \sim 1850 Ma Donington Suite, which is less uraniferous than the Hiltaba Suite (Creaser, 1989). It is interesting to note that the recently discovered Carrapateena deposit appears to have low uranium grades (Fairclough, 2005), and occurs in an area interpreted as Donington Suite granite (Direen and Lyons, 2002). Most other IOCG prospects in the Olympic Cu-Au-U province that are hosted by metasedimentary units have insignificant reported uranium, whether magnetite- or hematite-rich.

IOCGU mineral system component

Geodynamic and tectonic setting

- Pre-IOCG continental margin, metasomatised mantle wedge, extensional basins along margin;
- 'Far-field' continental back-arc or intracontinental settings at IOCG time, where pre-IOCG orogenesis has produced over-thickened crust & mantle lithosphere;
- Destabilisation of mantle lithosphere triggered by plate margin processes (e.g. collision);
- Mantle and high-T crustal melting, compressional tectonism and HTLP metamorphism followed by extension, uplift and exhumation.

Observable proxies: Large-volume high-T crustal melts emplaced during compression & HTLP metamorphism, followed by extension, exhumation and volcanismplutonism; mafic/ultramafic rocks of metasomatised mantle origin; clastic sediments coeval with exhumation.

Architecture

- Belts of repeated orogenesis at margins of cratons;
- Terrane boundary zones and crustal-scale orogen-parallel & conjugate fault/shear zones;
- Sedimentary basin sources of Fe, Cl, Cu, Au, U, S;
- Igneous rock / magma sources of Fe, CI, Cu, Au, U, S

Observable proxies: syn-orogenic I-type intrusive suites & tectonic events associated with multiple pre-IOCG orogenies; terrane boundaries marking major changes in PTt evolution; crustal sutures & fault networks in seismic, MT, gravity & magnetic datasets; igneous products of pre-IOCG continental margin arcs; continental or shallow marine basins along cratonic margins - siliciclastic-dominated, mostly oxidised, may contain iron formations, evaporites, volcanics.

Fluid flow drivers and pathways

Drivers of IOCG hydrothermal activity:

- Mantle-driven high-T melting of crust leading to high-T I & A-type & mafic magmas emplaced in upper crust;
- IOCG districts best developed above & within felsic-mafic magmatic complexes;

• U-rich IOCGs require preservation of high-U shallow-crustal igneous rocks.

Observable proxies: coeval mafic & high-T I- or A-type high-level intrusions and volcanics.

- Fluid flow pathways:
- Reactivated orogen-parallel & conjugate
- fault/shear zones, near or above suture zones between major crustal blocks, e.g. Archean & Proterozoic.
 - **Observable proxies:** regional-scale magnetite-, Na-Ca and hematite-bearing alteration along major shears/faults; syn-compressional magnetite alteration overprinted by syn-extensional hematite alteration.

Cu-Au-U ore deposition

Single fluid systems: Cooling & phase separation of fluid A brine; deeper magnetite and shallower hematite alteration at time 1 (t1), followed by thermal collapse at time 2 (t2).
Two-fluid systems: Mixing & reduction of oxidised U-bearing fluid B with brine & vapour products of fluid A phase separation, or reaction of fluid B with magnetite alteration. **Observable proxies:** hematite-bearing alteration with bornite-chalcocite-U overprinting magnetite-bearing alteration; highest Cu-Au-U grades near interface between these alteration zones (see map).

Example: Gawler Craton

Exhumation of magnetite system during IOCG hydrothermal activity results in settings where U-bearing fluid B mixes with fluid A or reacts with alteration products of fluid A. **Observable proxies:** volcanic rocks overlying exhumed metamorphic basement; low-T alteration overprinting higher temperature-pressure assemblages.

Figure 13: Uranium-bearing IOCG mineral system model, based on the Olympic Dam system in the Gawler Craton.

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Uranium is locally enriched in some magnetite-dominated IOCG deposits, for example the Juno Au-Bi deposit in the Tennant Creek district, Northern Territory (Large, 1975), and several deposits in the Carajás district of Brazil and in the Cloncurry district of Queensland (Hitzman and Valenta, 2005). Zoning of uranium distribution generally has not been reported in these deposits, although at Juno the uranium is spatially closely related to gold distribution (Large, 1975). In the Andean IOCG province, uranium as well as gold contents tend to be lower than in the Australian and Brazilian Precambrian IOCG deposits (Sillitoe, 2003). Nevertheless, hematite-rich deposits in the Andes generally have higher uranium contents than their magnetite-rich counterparts (Sillitoe, 2003).

4.4.2 Model of uranium-bearing IOCG systems

We consider Olympic Dam to be a hybrid system in the context of Figure 7 because fluids of multiple origins were involved in Cu-U-Au mineralisation. It has been proposed that oxidised fluids of surficial origin leached uranium from felsic igneous rocks including the host granite, and transported the uranium to depositional settings within the hematite-rich Olympic Dam Breccia Complex (Haynes et al., 1995; Hitzman and Valenta, 2005). On the other hand, magnetite-bearing alteration assemblages observed regionally and at Olympic Dam appear to have formed from less oxidised magnetite-stable hightemperature brines (Bastrakov et al., 2007). The high-temperature brines and related magnetite alteration have chemical and isotopic signatures indicating extensive reaction with metasedimentary and/or igneous rocks, although input of magmatic-hydrothermal fluids cannot be ruled out (Bastrakov et al., 2007; Skirrow et al., 2007). We support the model of Haynes et al. (1995) involving mixing of less oxidised high-temperature brines with oxidised uraniferous waters. However, magmatic-hydrothermal models for Olympic Dam have also been proposed in which the role of non-magmatic fluids presumably was minimal (e.g., Reynolds, 2000; Hayward, 2008).

Figure 13 illustrates key components of IOCGU mineral systems, using Olympic Dam and the Gawler Craton as the example. Appendix Table A7 and Figure 13 also list the principal 'ingredients', processes and observable geological, geophysical and geochemical features of uranium-bearing IOCG systems.

In summary, a conjunction of tectonic and geological factors or criteria is necessary to allow efficient large-scale uranium mass transfer and to form a major hematite-group IOCG(U) deposit (Skirrow, 2008).

- 1. Tectonic settings yielding voluminous U-rich (e.g. A-type) subaerial felsic volcanic and/or high-level felsic intrusive rocks, and allowing subsequent preservation of shallow crustal levels. Permissive settings include continental back-arc or intracontinental settings with evidence of a switch from compressive to extensional deformation, with crustal melting possibly driven by mantle lithosphere removal (convective, or delamination, etc).
- 2. Crustal-scale magma and fluid pathways, e.g. earlier orogenic belt at a cratonic margin.
- 3. Pre-IOCG basins lacking major reduced sections (Haynes, 2000) and commonly with evidence for evaporites.
- 4. High to extreme paleogeothermal gradients, that resulted in regional-scale uppermost crustal fluid flow and magnetite-rich hydrothermal alteration zones; mafic/ultramafic intrusive magmatism may mark the locus of crustal-scale thermal anomalies, and may contribute ore metals or sulfur to IOCG systems.
- 5. Exhumation of an active magnetite-forming hydrothermal regime, allowing telescoping of this alteration with oxidized surface-derived fluids in an environment favourable for fluid mixing.
- 6. Hydrological setting in which large volumes of oxidized groundwaters or basinal waters were mobilized to sites of upflow of magnetite-forming fluids, e.g. basins related to tectonism, calderas or maar volcanic centres (Reeve et al., 1990; Haynes et al., 1995).
- Near-surface exposure of U-rich source rocks in this hydrological setting.
 Reducing agents to precipitate U⁶⁺ as U⁴⁺ minerals, for example mixing of reduced deep-sourced fluids with oxidized surface-derived fluids (Haynes et al., 1995), or reaction of oxidized fluids with Fe^{2+} or S^2 -bearing or reduced-C minerals. Variants of unconformity-related U deposits may exist in some IOCG (U) districts (Davidson et al., 2007).
- 9. Hydrothermal assemblages associated with uranium mineralization in IOCG deposits typically contain combinations of hematite, chlorite, sericite, carbonate, pyrite, chalcopyrite, bornite, chalcocite, barite and various REE and phosphate minerals.
- 10. Hematite-rich zones may be lateral to or above magnetite-bearing zones; higher grade uranium mineralization is generally associated with gold-rich and/or more oxidized parts of IOCG deposits.

5. Conclusions

1) At low to moderate temperatures (<200°C) geologically significant concentrations of uranium (>0.01-1ppm) can be carried only in highly oxidised fluids, where fO_2 is well above hematite-magnetite buffer conditions. This observation places significant constraints on the nature, origins and flow paths of uranium ore-forming fluids.

2) At 200-300°C chloride and fluoride complexes of U^{6+} and U^{4+} become important at low pH, at both oxidised and reduced conditions.

3) New thermodynamic data are required for uranium complexes at >300°C to estimate uranium solubilities at these conditions. Regardless, experiments simulating magmatic-hydrothermal systems indicate solubilities of up to ~0.1% uranium in fluids at oxidised as well as reduced conditions, probably as chloride and/or fluoride complexes.

4) The major controls on deposition of uranium from aqueous fluids are reduction of oxidised fluids, pH increase, changes in ligand concentration, and decreases in temperature. Other important processes include adsorption and bacteria-mediated deposition of uranium at low temperatures.

5) Formation of almost all major uranium deposits arguably involved aqueous fluids, although preconcentration via magmatic processes clearly was important in some uranium systems.

6) Fluids of three fundamentally different origins and compositions are important in formation of uranium deposits: surface-derived waters (meteoric, seawater, lakewater), magmatic-hydrothermal fluids, and 'metamorphic' fluids including those reacted with metamorphic rocks at elevated temperatures.

7) A new and simplified classification scheme is proposed, based on the three end-member fluid types. The ternary scheme comprises three families of uranium mineral systems: (1) basin- and surface-related, (2) magmatic-related, and (3) metamorphic-related. This scheme accommodates all major known deposit styles, and predicts a *continuum* of deposit styles among and between the three families of uranium mineralising systems.

8) *Hybrid* uranium mineral systems involve more than one end-member fluid. For example, uraniumbearing iron oxide Cu-Au deposits are suggested to have formed in systems with both modified surfacederived fluids as well as deep-sourced fluids of magmatic-hydrothermal and/or 'metamorphic' origin.

9) Relative to similar geological environments globally, giant deposits of several different types appear to be under-represented in Australia. These include 'sandstone-hosted' deposits (similar to those in Kazakhstan) and magmatic-related deposits (similar to the Rössing deposit, Namibia, and volcanic-hosted deposits in eastern Russia).

10) Application of the mineral systems approach and the exploration criteria presented in this report is recommended as a framework for assessing Australia's potential for undiscovered uranium resources.

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APPENDIX

Table A1: Aqueous uranium species used in calculations. For hydroxide complexes, conventional hydroxide complex representation is shown in the second column.

SPECIES		VALENCY	MODEL	REFERENCE	COMMENT
U+++		Ш	MHKF	Shock,97a	
UOH++		III	MHKF	Shock,97b	
UO+	U(OH)2+	III	MHKF	Shock,97b	
HUO2 (aq)	U(OH)3 (aq)	III	MHKF	Shock,97b	
UO2-	U(OH)4-	III	MHKF	Shock,97b	
U++++		IV	MHKF	Shock,97a	
UOH+++		IV	MHKF	Shock,97b	
UO++	U(OH)++	IV	MHKF	Shock,97b	
HUO2+	U(OH)3+	IV	MHKF	Shock,97b	
UO2 (aq)	U(OH)4 (aq)	IV	MHKF	NEA; Shock,97b; *	
HUO3-	U(OH)5-	IV	MHKF	Shock,97b	excluded
UF+++		IV	mrb	NEA; *	
UF2++		IV	mrb	NEA; *	
UF3+		IV	mrb	NEA; *	
UF4		IV	mrb	NEA; *	
UF5-		IV	mrb	BB2003	
UF6		IV	mrb	BB2003	
UCI+++		IV	MHKF	NEA; *	
UCI2++		IV	MHKF	BB2003; *	excluded
UHCO3+++		IV	MHKF	BB2003; *	
U(HCO3)2++		IV	MHKF	BB2003; *	
U(CO3)5		IV	MHKF	NEA; *	
UHPO4++		IV	MHKF	BB2003; *	
U(HPO4)2		IV	MHKF	BB2003; *	
U(HPO4)3		IV	MHKF	BB2003; *	
U(HPO4)4		IV	MHKF	BB2003; *	
USO4++		IV	MHKF	NEA; *	
U(SO4)2 (aq)		IV	MHKF	NEA; *	
UO2+		V	MHKF	Shock,97a	
UO2OH (aq)		V	MHKF	Shock,97b	
UO3-	UO2(OH)2-	V	MHKF	Shock,97b	
UO2CI (aq)		V	MHKF	BB2003; *	
UO2CI2-		V	MHKF	BB2003; *	
UO2HCO3		V	MHKF	BB2003; *	
UO2(HCO3)2-		V	MHKF	BB2003; *	
UO2++		VI	MHKF	Shock,97a	
UO2OH+		VI	MHKF	Shock,97b	
UO3 (ag)	UO2(OH)2	VI	MHKE	NEA: Shock 97h: *	
		VI	MHKE	Shock 97h	
11004				Shock 97b	
(UO2)20H+++	002(011)4		mrb	PG1004: *	evoluded
(UO2)2OH++			mrb	PG1005: *	excluded
$(UO2)^{2}(OH)^{2++}$			mrb	PG1006: *	evoluded
(UO2)3(OH)5+			mrb	PG1007·*	CACIUUEU
(UO2)3(OH)3+			mrb	PG1008·*	
(UO2)3(OH)7+			mrb	PG1000·*	
			mrb	ΝΕΔ·*	
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SPECIES	VALENCY	MODEL	REFERENCE	COMMENT
UO2F2	VI	mrb	NEA; *	
UO2F3-	VI	mrb	NEA; *	
UO2F4	VI	mrb	NEA; *	
UO2CI+	VI	mrb	NEA; *	
UO2CI2	VI	mrb	NEA; *	
UO2CO3	VI	mrb	NEA; *	
UO2(CO3)2	VI	mrb	NEA; *	
UO2(CO3)3	VI	mrb	NEA; *	
(UO2)3(CO3)6-6	VI	mrb	NEA; *	
UO2H2PO4+	VI	mrb	BB2003; *	
UO2(H2PO4)2	VI	mrb	BB2003; *	
UO2(H2PO4)3-	VI	mrb	BB2003; *	
UO2HPO4	VI	mrb	BB2003; *	
UO2(HPO4)2	VI	mrb	BB2003; *	
UO2SO4	VI	mrb	BB2003; *	
UO2(SO4)2	VI	mrb	BB2003; *	

Models: MHKF – modified Helgeson-Kirkham-Flowers (Helgeson, 1981); mrb – modified Rhyzhenko-Bryzgalin model (Borisov, 1992). References: BB2003 – (Barsukov, 2003); NEA – (Guillaumont, 2003); PG1994 – (Plyasunov, 1994); SSB97 – (Shock, 1997); SSWS97 – (Shock, 1997); * – Bastrakov and Jaireth, in prep. (re-fitted or adjusted data).

Table A2: Uranium solid phases used in calculations.

SPECIES	FORMULA	REFERENCE
Uranium	U	SBGB99
Uraninite	UO2	NEA
UO3 (cr)	UO3	SBGB99
U3O8 (cr)	U3O8	SBGB99
U4O9 (cr)	U4O9	SBGB99
Rutherfordine	UO2CO3(cr)	*
Coffinite		*

References: NEA - (Guillaumont, 2003); SBGB99 - (Shvarov, 1999); * - Bastrakov and Jaireth, in prep.

Figure A1: Total uranium solubility and speciation in 1M total chloride solution at 25 and 100°C in equilibrium with quartz-muscovite-K-feldspar-albite and quartz-kaolinite-muscovite assemblages. Only uranium species contributing more than 1 mol% are shown.

Figure A2: Total uranium solubility and speciation in 1M total chloride solution at 200 and 300°C in equilibrium with quartz-muscovite-K-feldspar-albite and quartz-kaolinite-muscovite assemblages. Only uranium species contributing more than 1 mol% are shown.

Figure A3: Total uranium solubility and speciation in 1M total chloride solution with additional ligands in equilibrium with quartz-muscovite-K-feldspar-albite and quartz-kaolinite-muscovite assemblages along Mn_3O_4 - Mn_2O_3 and hematite-magnetite redox buffers as a function of temperature.

Figure A4: Total uranium solubility and speciation in 1M total chloride solution with additional ligands in equilibrium with quartz-muscovite-K-feldspar-albite and quartz-kaolinite-muscovite assemblages along Mn_3O_4 - Mn_2O_3 and hematite-magnetite redox buffers as a function of temperarature.

Table A3: Magmatic-related uranium mineralising systems

System component [#]	Ingredient / process	Reason	Importance	Mappable/measurable characteristics	Outstanding questions	Scale
Q1. Geodynamic setting Q.3 Source	Metasomatised mantle, eg via subduction	Fertile source for U-rich peralkaline magma generation	Unknown	Mafic rock isotopic compositional variation at craton/province scale	Do provinces with magmatic-related U have distinctive mantle?	Continental to terrane
Q1. Geodynamic setting Q.3 Source	U-rich crustal source, e.g., sediments, earlier felsic igneous rocks	Fertile source for U-rich peraluminous or high-T I-type crustal magma generation	Unknown	Mafic rock isotopic compositional variation at craton/province scale	Do provinces with magmatic-related U have distinctive mantle?	Continental to terrane
Q1. Geodynamic setting	Low degree partial melting of upper mantle or crust, and extensive fractional crystallisation	Magmatic concentration of U and other incompatible elements	Highly desirable	Igneous fractionation geochemical trends; highly fractionated granitoids identified in WR geochemistry	How much magmatic concentration is required? Or are magmatic-hydrothermal processes sufficient to yield U ore fluid?	
Q1. Geodynamic setting	Orogenesis followed by magmatism assoc with 'extensional collapse' or delamination	May result in shallow emplacement of HFSE-enriched magmas including volcanics	Desirable	peralkaline or A- or I-type HFSE- enriched igneous complexes assoc with late- or post-orogenic basins	Not relevant to intracontinental rift-related alkaline magmatism (?)	
Q1. Geodynamic setting	Major (mantle-driven?) thermal anomaly, eg related to plume, back-arc extension, intracontinental rifting, lithosphere removal, etc	Generates mantle melting thence crustal melts of alkaline composition rich in HFSE, which are a source of U; crustal melting at low p_{H2O} , high p_{CO2} , and/or high p_F ?	Essential	Alkaline igneous complexes with elevated HFSE compositions; A-type & high-temp I-type suites; intracontinental rift packages	Is crustal melting at low p_{H20} , high p_{C02} , and/or high p_F the key process in generating HFSE-enriched melts?	Continental to district (camp)
Q2. Architecture Q4. Fluid pathways	Crust-penetrating shear/fault zones separating crustal blocks or orogens	Magma & fluid pathways from mantle & lower crust to near- surface	Unknown	PTt variations across crustal block boundaries; geophysical responses of deep crustal fault/shear zones	Not clear if this is necessary	Terrane to district (camp)
Q2. Architecture Q4. Fluid pathways	Regional to deposit scale flow of high- to moderate-T fluids	Large U deposits require very large volumes of fluid	Highly desirable	Regional to deposit scale albitic or carbonate alteration zones ¹		District (camp) to deposit
Q3. Sources	Highly fractionated peralkaline magma	High solubility of U in magma, but held in refractory minerals; magmatic-hydrothermal fluids with elevated U	Highly desirable	High (Na+K)/Al and fractionation trends in WR geochem; high K, U, Th in radiometrics		
Q3. Sources	Highly fractionated high- temp I- or A-type magmas	High solubility of U in magmas, but may be held in refractory minerals; magmatic- hydrothermal fluids with elevated U	Highly desirable	High (Na+K)/Al and fractionation trends in WR geochem; high K, U, Th in radiometrics		
Q3. Sources	Highly fractionated F-rich peraluminous magma	Uraninite may occur as accessory mineral; magmatic- hydrothermal fluids with elevated U	Highly desirable	Low (Na+K)/AI and fractionation trends in WR geochem		
Q3. Sources	Leaching of U from HFSE- rich igneous rocks by fluids derived external to igneous rocks	Generates hydrothermal U ore fluid via leaching of pre-existing U-rich igneous rocks	Desirable	??	Magma vs host rock sources of U? Magmatic vs external source of fluid?	
Q3. Sources	Leaching of U from U-rich wall rocks by magmatic- hydrothermal fluids	Generates hydrothermal U ore fluid via leaching of pre-existing U-rich wall rocks	Desirable	??	Magma vs host rock sources of U? Magmatic vs external source of fluid?	
Q5. Transport & deposition	Moderate to high temperature (~300-700°C?) CO ₂ -rich Na-dominated magmatic-hydrothermal fluids	Carries U ⁶⁺ and/or U ⁶⁺ depending on redox of melt	Essential	Presence of fossil mod-high-T CO ₂ - rich fluids trapped in hydrothermal minerals		District (camp) to deposit
Q5. Transport & deposition	High fluid/melt partition coeff e.g. in Cl-rich peraluminous magmas	Partitioning of U and other HFSE from magma to co-existing fluid generates magmatic- hydrothermal U ore fluid	Desirable	??	Magma vs host rock sources of U? Magmatic vs external source of fluid?	District (camp) to deposit
Q5. Transport & deposition	U^{6+} deposition via fluid-rock reaction (reduction, pH change, activity of ligands, etc): • Fe ²⁺ oxides, silicates, carbonates • And/or sulfides, H ₂ S • And/or reduced C, CH ₄ • a_{Ca2+}	Fe ²⁺ -bearing oxides, silicates, carbonates, sulfides or reduced gases may act as reductants for U ⁶⁺ ; deposition of U from U ⁴⁺ -F complexes via fluorite formation	Desirable	Presence of Fe ²⁺ -bearing oxides, silicates, sulfides, carbonates; presence of fluorite; reactants for U deposition may be within igneous host itself or external, in wall rocks proximal to distal from intrusion/volcanic rocks		District (camp) to deposit
Q5. Transport & deposition	U ^{•+} or U ⁺⁺ deposition via cooling, eg by fluid mixing		Desirable	Evidence for cooling, fluid mixing		District (camp) to deposit
Q6	?					

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[#]Q1: What is the geodynamic and P-T-t history of the system? Q2: What is the architecture of the system? Q3: What are the characteristics and the sources (reservoirs) of water, metals, ligands and sulphur? Q4: What are the fluid flow drivers and pathways? Q5: What are the transport and depositional processes for metals, ligands and sulphur? Q6: How and where do later geological processes allow preservation of deposits?

Table A4: Metamorphic-related uranium mineralising systems

System component [#]	Ingredient / process	Reason	Importance	Mappable/measurable characteristics	Outstanding questions	Scale
Q1. Geodynamic setting	Orogen with medium or high grade metamorphism, with or without syn-orogenic felsic magmatism	Fluids in metamorphic-related U systems are 'metamorphic' and syn-deformational	Essential	Metamorphic belt with major crustal scale shear/fault zones	Type of orogen unclear; importance of collisional style orogen unclear.	Province
Q1. Geodynamic setting	Continental or shallow marine basin	Oxidised sediments to buffer trapped fluids or infiltrating fluids to high oxidation state	Highly desirable	Subaerial to shallow aqueous sedimentary / felsic volcanic rocks, eg redbeds, evaporites, oxidised volcanics		Province
Q1. Geodynamic setting	First cycle metamorphism of basins	Greater fluid volumes available (e.g. connate waters) than in previously metamorphosed basin rocks	Highly desirable	Geochronology of metamorphic events in relation to basin formation.		Province
Q2. Architecture Q4. Fluid pathways	Crustal scale shear/fault zones separating crustal blocks or orogens	District scale alteration indicates very large fluid volumes, controlled by permeable/active major shears	Essential	PTt variations across crustal block boundaries; geophysical responses of deep crustal fault/shear zones		Province
Q2. Architecture Q4. Fluid pathways	Regional to deposit scale high-moderate-T alteration	Large U deposits require very large volumes of fluid, producing extensive hydrothermal alteration	Highly desirable	Regional to deposit scale sodic(-calcic) (e.g. hydrothermal albite, Na-amphibole, Na-scapolite, Na-clinopyroxene) alteration zones		Regional to deposit
Q3. Sources	Leaching of U from igneous rocks by 'metamorphic' fluids	Generates hydrothermal U ore fluid via leaching of pre-existing U-rich igneous rocks	Highly desirable	U-depleted alteration zones in igneous rocks	Are U-rich source rocks necessary?	District
Q3. Sources	Leaching of U from U-rich metamorphic rocks by 'metamorphic' fluids	Generates hydrothermal U ore fluid via leaching of pre-existing U-rich metamorphic rocks	Highly desirable	U-depleted alteration zones in metamorphic rocks	Are U-rich source rocks necessary?	District
Q5. Transport & deposition	Moderate to high temperature (~300-700°C?) oxidised or reduced CO ₂ -Na- F-rich hydrothermal fluids	Carries U ⁶⁺ and/or U ⁶⁺ depending on redox of fluid	Essential	Presence sodic alteration (albite & other Na-silicates); presence of fossil mod-high- T CO ₂ -rich fluids trapped in hydrothermal minerals; presence of F-rich alteration minerals (fluor-apatite, fluorite, F- amphiboles, F-micas, etc)		District (camp) to deposit
Q4. Drivers and fluid pathways	Fold-and-thrust belt	Tectonic loading induces fluid expulsion from core or orogen	Highly desirable	Mapping of fold-and-thrust belt geology; Na-alteration along active thrusts		Province
Q4. Drivers and fluid pathways	Post-orogenic extension	High-U granitoids commonly emplaced during extensional collapse; extensional faults control downflow of oxidised surface- or basin-derived fluids into metamorphic basement	Desirable	Normal fault reactivation of thrusts at cessation of orogenesis; high-U granitoids with evidence of U leaching; oxidative alteration along normal faults	May be important for hybrid systems involving 'metamorphic'- and surface-derived fluids	Regional to district
Q5. Transport & deposition	U ⁶⁺ deposition via fluid-rock reaction (reduction, pH change, activity of ligands, etc): • Fe ²⁺ oxides, silicates, carbonates • And/or sulfides, H ₂ S • And/or reduced C, CH ₄ • a _{Ca2+}	Fe ²⁺ -bearing oxides, silicates, carbonates, sulfides or reduced gases may act as reductants for U ⁶⁺ ; deposition of U from U ⁴⁺ -F complexes via fluorite or other F- rich mineral formation	Highly desirable	Presence of abundant Fe ²⁺ -bearing oxide, silicate, sulfide, carbonate minerals; presence of fluorite or other F-bearing minerals, phosphates;		District (camp) to deposit
Q5. Transport & deposition	U ⁶⁺ or U ⁴⁺ deposition via cooling, eg by fluid mixing		Desirable	Evidence for cooling, fluid mixing in fluid inclusions and hydrothermal mineral assemblages		District (camp) to deposit

[#]Q1: What is the geodynamic and P-T-t history of the system? Q2: What is the architecture of the system? Q3: What are the characteristics and the sources (reservoirs) of water, metals, ligands and sulphur? Q4: What are the fluid flow drivers and pathways? Q5: What are the transport and depositional processes for metals, ligands and sulphur? Q6: How and where do later geological processes allow preservation of deposits?

Question [#] Q1,Q2	Ingredients Intracratonic, continental or intermontane	Reasons Preferred basin type (see	Importance Essential	Mappable/measurable features Basement of continental crust; paleogeography	Outstanding questions Nomenclature of basin types?	Scale Continental
Q1	Deposition of host sandstone in continental fluvial and/or mixed fluvial-marine environment	Generate rocks of high permeability	Essential	Sedimentary facies assemblages and distribution; sequence stratigraphy		Terrane (basin)
Q1	Age of basin and mineralisation younger than atmosphere inversion at ~2.4 Ga; mostly younger than late Devonian	Younger than 2.4 Ga for oxidising atmospheric conditions; younger than Devonian to ensure presence reactive organic reductant	Essential	Ages of host basin and mineralisation	Are paleoclimates important in producing suitable ore fluids?	Continental
Q1-Q5	Evidence of uranium (and related) mineral system activity	Evidence that mineralising process has taken place	Desirable	Distribution of mineral occurrences (U, Cu, V, Co, Pb-Zn, etc)	What is relationship between U and other mineral systems?	Continental to terrane (basin)
Q2	 Topographic gradient (preferably 5-10°) at time of mineralisation, for instance: Primary depositional dip Tilting of sequence due to reactivation of basin margin faults Change in continental stress fields (e.g. compression or extension) Basinal subsidence Doming 	Topography of basin providing hydraulic head and fluid flow towards an outflow zone	Essential	Geometry of basin, at time of mineralisation, as determined from field mapping, sedimentary facies, structural measurements, depth-to-basement (Euler deconvolution and/or drill hole data), seismic, gravity, MT and AEM data. Structural/movement history, including neotectonics		District (camp)
Q2,Q4	Embayments of basin into basement	Focus of ore fluids into district??	Desirable	Geometry of basin	What is importance: fault control; proximity to granite; facies variations?	District (camp)
Q3	Low temperature (<50°C), highly oxidised (initially air-saturated) fluid	Fluids most suitable for high U solubilities	Essential	Fluid inclusion data; other methods of estimating temperature, modern hydrochemistry (?), diagenetic history, alteration assemblages ¹	Are there any other fluid types that could transport U in this setting? Is silica content of fluids important?	District (camp) and deposit
Q3	 Source of highly oxidised fluids Recharge zone in hydrologic upland area Other sources 	Chemistry allowing high U solubility	Essential	O-H isotopes; alteration assemblages' (e.g. hematite-stable); upland areas at time of mineralisation for hydrologic recharge	Are paleoclimates important in producing suitable fluids? Are there other ways to get highly oxidised fluids?	District (camp)
Q3,Q4	Preservation of redox state of fluids during migration controlled by fluid flow rates sufficient to move the redox roll front	Chemistry maintaining high U solubility	Essential	Alteration assemblages ¹ , hydrology of fluid flow at time ofmineralisation	Are evaporites important in maintaining redox state of fluids?	District (camp)
Q3	 Leachable U-enriched source, fitting one or more of the following: U-rich felsic rocks rimming and/or underlying the basin. Lithic fragments of felsic rocks (including volcanic ash) in the sandstone aquifer. Leachable detrital U-rich minerals (zircon, monazite, allanite, apatite etc) in sandstone Felsic volcanics in and/or close proximity to the sandstone aquifer Uranium occurrences in hinterland 	Uranium source	Leachable U: essential; U enrichement: highly desirable	U enrichment indicated by γ-ray spectrometric data and geochemical analyses of potential sources	Which are more important U sources: basement rocks or sediments eroded from basement rocks? If basement U is important source, how do fluids from basement get into sandstone aquifer? Can you make a U deposit from a garden variety source?	Terrane (basin)
Q3	Leaching of potential U sources	Uranium source	Desirable	U depletion zones as indicated by γ-ray spectrometric data, wire-line logs and geochemical analyses; oxidised paleoweathering profiles		District (camp) and terrane (basin)
Q4, Q2	Hydrologically connected, highly permeable, unlithified, immature (feldspathic-arkosic) sandstone (less commonly pebble conglomerate or eolian siltstone/sandstone) as aquifer and ore host	Fluid pathway and redox buffer at time of mineralisation	Essential	Lithostratigraphy, sequence stratigraphy, permeability and diagenetic and cement history of potential host		District (camp)
Q4	Lateral and vertical variations in permeability focussing fluid flow in aquifer	Fluid conduit	Essential	Litho- and sequence stratigraphy; facies distribution; structural mapping; mapping of shales/siltstone and other impermeable rocks	How important are silcretes as aquicludes? How important are aquicludes, paleochannels, etc in determining size and grade of deposits?	District (camp)
Q4,Q5	Regional gradation from oxidized (upstream) to reduced conditions (downstream) in host sandstone	Redox boundary in plumbing/trap system	Essential	Mineral occurrences and regional mapping of alteration assemblages ¹ and geochemistry ² in host sandstone; mapping of hydrochemical gradients ³ in groundwater from regional aquifers		Terrane (basin) to deposit
Q5	 Presence of reductants, including: Solid carbonaceous material (e.g. woody material, coal, humic/humate components Hydrocarbons and/or H₂S (derived from reservoir or coal seams) that are focussed into deposition site along pathways including local structures and permeable facies Inorganic reductants (e.g., Fe²⁺-rich rocks, sulphides (particularly pyrite) and/or H₂S) 	Reduction of uranium-carrying fluids and deposition of uranium	Essential	EM contrasts/conductors; drill hole logs from water and exploration drill holes; sedimentary facies analysis; structural mapping (including distribution and history of movement of second and third order structures, potential field data); hydrocarbon shows; alteration facies along permeable pathways; C-O and S isotopes of ore-related minerals		District (camp)
Q5	Uranium deposition caused by water-rock interaction and fluid mixing from • Reduction (the major factor) • pH changes • changes in silica saturation • changes in vanadium saturation	Chemical trap for uranium (and vanadium)	Essential	Mineral occurrences. Zoning about ore as follows: Oxidized (brown/red) sandstone with total oxidation of pre-existing sulphide minerals \rightarrow Se enrichment \rightarrow U ores±silcrete \rightarrow Mo and sulphide mineral enrichment/replacement of Fe- bearing silicates and silicates \rightarrow reduced (green/gray) sandstone± silcrete. Groundwater zonation from upstream to downstream as follows: high (oxidized) Eh \rightarrow ore \rightarrow low (reduced) Eh. Redox and related reactions may also be reflected in δD , $\delta^{13}C$, $\delta^{18}O$, $\delta^{34}S$ and U-series disequilibria variations in rock and in groundwater.	What is the relation between silcrete, silica saturation, coffinite and ore depositional processes?	District (camp) and deposit
Q6	Insulation of ores from reaction with oxidised groundwater flows	Preservation of ore deposit	Essential	Regional redox and chemical gradients in aquifers; post-mineralisation tectonic and climate history		Terrane (basin), District (camp) and deposit
[#] Questions are Q1 Q2 Q3 Q4 Q5	e as follows: : What is the geodynamic and P-T-t history of the system? : What is the architecture of the system? : What are the characteristics and sources (reservoirs : What are the fluid flow drivers and pathways? : What are the transport and depositional processes for : How and where do later geological processes allow	stem?) of water, metals, lagands and sulphur? or metals, ligands and sulphur? preservation of deposits?			<u>.</u>	

Question [#]	Ingredients / process	Reasons	Importance	Mappable/measurable features	Outstanding questions	Scale
Q1,Q2	Intracratonic, epicontinental or foreland basin	Preferred basin type (see	Essential	Unconformity between reduced basement and overlying oxidising	Are foreland basins important?	Continental
	rocks (e.g., granite-gneissic domes and/or			aquifer/basin; paleogeography		
02 04	inliers and/or felsic (meta)sediments)	Possible source & conduit for	Essential	Distribution of oxidised sandstone:	What is diagenetic history of	Terrane (basin)
Q2, Q4	sandstones that overlie the unconformity	(buffered) oxidised, U-bearing fluids	LSSCILLA	distribution; sequence stratigraphy;	basal sandstone of basin? Effect of diagenesis on permechility? How "clean"?	and district (camp)
				variations; permeability		
Q1	Age of basin and mineralisation younger than ~2.4 to 1.8 Ga	Completion of atmospheric inversion producing highly oxidising atmosphere	Essential	Ages of host basin and mineralisation	Why is main age of known mineralisation between 1.74 Ma 1.39 Ma? Do these deposits form outside of this range? How important is percent.	Continental
Q1-Q5	Evidence of uranium (and related) mineral	Evidence that mineralising	Desirable	Distribution of mineral occurrences (U,	What is relationship between U	Continental to
Q1	system activity Clock-wise P-T-t path to metamorphism of	process has taken place Unknown	Unknown	Cu, V, Co, Pb-Zn, etc) Determination of metamorphic P-T-t	and other mineral systems? Is this important (or a furphy)? If	terrane (basin) Continental to
Q1	the basement rocks External changes in plate stress	Initiate fluid flow	Highly	paths in basement Major changes to apparent polar	so, why? What other mechanisms	terrane (basin) Continental
Q2, Q4	Major disconformity (generally unconformity)	Juxtaposes oxidised & reduced	desirable	Spatial distributions and ages of major	initiated fluid flow (e.g. convection, compaction)? How do we map these effects? Can low-angle thrusts or detachments serve same	Terrane (basin)
				and geophysical data sets (e.g. gravity, aeromagnetics and land seismic)	purpose as unconformity? Is unconformity a fluid pathway? Can unconformity U deposits form if discontinuity has been folded?	
Q2	Periodic reactivation of basement faults during and after basin development,	Control of (sub)-basin accommodation, palaeo-relief, architecture and later fluid flow	Essential	Relative and absolute timing of fault movement relative to units in basin and basement: changes in unit thickness	Role of extension vs compression? Are all deposits in reverse faults?	Terrane (basin) to district (camp)
Q2	Close association of deposits with gravity highs and/or ridges	Unknown; possible basement highs or major structures?	Unknown	Variations in the gravity field; deep seismic	What are sources of gravity anomalies?	Terrane (basin)
Q2	Onlapping relationship between basin and	Unknown	Unknown	Sequence strat	Is role of onlap the juxtaposition	Basin
Q3	Moderate temperature (~150-200°C), saline	Fluids most suitable for high U	Essential	Fluid inclusion data; other methods of	Are there any other fluid types	District (camp)
	oxidised fluid derived through diagenesis in overlying basin	solubilities		estimating temperature, diagenetic history, alteration assemblages ¹	that could transport U in this setting? Is silica content of fluids important? Importance of Na vs. Ca in brines?	and deposit
Q3	Source of highly oxidised fluids, e.g.: • Diagenetic fluids buffered by evaporites • Connate brines • Evolved meteoric waters • Seawater	Chemistry allowing high U solubility	Essential	O-H isotopes; alteration assemblages ¹ (e.g. hematite-stable); distribution of evaporites (particularly gypsum, anhydrite) in basin	Are there other ways to get highly oxidised fluids?	District (camp)
Q3,Q4	Preservation of redox state of fluids during migration controlled; low abundance of reductants	Chemistry maintaining high U solubility	Essential	Alteration assemblages ¹ , hydrology of fluid flow at time of mineralisation, distribution of reductants (e.g. FeO and organic matter) in sandstone above unconformity	Are evaporites important in maintaining redox state of fluids?	District (camp)
Q3	 Leachable U-enriched source, fitting one or more of the following: U-rich felsic rocks rimming and/or underlying the basin. Lithic fragments of felsic rocks (including volcanic ash) in aquifer. Leachable detrital U-rich minerals (zircon, monazite, allanite, apatite etc) in sandstone Felsic volcanics within and/or close entroirerspine provimity to the agrifer 	Uranium source	Leachable U: essential; U enrichment: highly desirable	U enrichment indicated by γ-ray spectrometric data and geochemical analyses of potential sources	Which are more important U sources: basement rocks or sediments eroded from basement rocks? If basement U is important source, how do fluids from basement get into aquifer? Can you make a U deposit from a garden variety source?	District (camp) and terrane (basin)
Q3	Leaching of potential U sources	Uranium source	Desirable	U depletion zones as indicated by γ-ray spectrometric data, wire-line logs and geochemical analyses; oxidised paleoweathering profiles	Is thermoluminescence of qtz useful to estimate U abundances? Can we use Cu, Co, V as proxies for U?	District (camp) and terrane (basin)
Q4	Lateral and vertical variations in permeability focussing fluid flow in aquifer: • Lithological variations.	Fluid conduits and aquicludes / aquitards	Essential	Litho- and sequence stratigraphy; facies distribution; structural mapping; mapping of shales/siltstone and other importantly and shales service compart	How important are aquicludes, etc in determining size and grade of deposits?	District (camp)
	 Diagenetic destruction or creation of porosity/permeability. 			history		
Q4,Q5	 Regional to district alteration: in basal sandstone aquifer, including regional illite-kaolin alteration, silicification and oxidation along basement penetrating faults 	Record of passage of uraniferous fluids through sandstone aquifer and into basement	Essential	Mineral occurrences and regional mapping of alteration assemblages ¹ (particularly Fe-chlorite-sericite assemblages) and geochemistry ² in basal sandstone & basement	Is this alteration zoned?	Terrane (basin) to deposit
Q5	including chlorite, illite-kaolinite Zones of faulting and brecciation, particularly in basement	Facilitate mixing, permeability & fluid-rock interaction	Desirable	Trace of faults as determined from geological, aeromagnetic and gravity	What other mechanisms can produce secondary	Deposit
Q5,Q4	Presence of reductants, including:	Reduction of uranium-carrying	Essential	EM contrasts/conductors; drill hole logs	Is graphite really effective as a	District (camp)
	Carbonaceous material (e.g. graphitic shale)	fluids and deposition of uranium		from water and exploration drill holes; sedimentary facies analysis; structural	reductant at 150-200°C?	
	 Hydrocarbons and/or H₂S in reduced 			mapping (including distribution and		
	 fluids Inorganic reductants (e.g., Fe²⁺-rich rocks, sulphides and/or H₂S) 			third order structures, potential field data); alteration facies along permeable pathways; C-O and S isotopes of ore-		
05	Association of calcareous rocks with roduced	nH neutraliser of the basing!	Linknown	related minerals		Denosit
~	rocks in basement	fluids				
Q5	Uranium deposition caused by water-rock interaction and fluid mixing from • Reduction (the major factor) • pH changes	Chemical gradient for uranium (and copper, gold and PGEs)	Essential	Mineral occurrences. Zoning of alteration assemblages from ore as follows: Ingress-type (basement-hosted ores):		District (camp) and deposit
				Fe-Mg chlorite \rightarrow biotite±sudoite \rightarrow sudoite±illite \rightarrow illite±sudoite Egress-type (sandstone-hosted ores): biotite±sudoite Fe-Mg chlorite \rightarrow sudoite±illite \rightarrow illite±sudoite. Redox and related reactions may also be reflected in 8D \overline{A}^{13} C \overline{A}^{18} O and \overline{A}^{34} S		
Q6	Presence of thick (~3-5km?) cover sequence above unconformity at time of mineralisation	Better chance of preservation; allows temps of ~150-200°C to be reached in aquifor/course	Desirable	Thickness of cover sequence		Terrane (basin)
Q6	Preservation of sandstone above basement, particularly for ingress-type deposits	Preservation of ores	Essential	Distribution of preserved sandstone above unconformity		District (camp) to deposit
Q	2: What is the architecture of the system?					
Q. O	3: What are the characteristics and sources (reservoirs) 4: What are the fluid flow drivers and pathways?) of water, metals, lagands and sulphur?	,			
Q Q	5: What are the transport and depositional processes for 6: How and where do later geological processes allow	or metals, ligands and sulphur? preservation of deposits?				

Question	Ingredient / process	Reason	Importance	Mappable/measurable	Outstanding questions	Scale
Q1	Passive margin or intracontinental extension (pre-IOCG)	Sedimentary-volcanic rocks in subaerial to shallow water basin settings provide sources of metals and salinity, and maintain fluid redox at intermediate to	Unknown	Passive margin or intracontinental extensional basins; (meta)evaporite sequences	Importance of pre-IOCGU setting? Can other settings provide similar sources & buffering?	Continental to terrane
Q1	Pre- to syn-IOCGU orogenesis on margin of craton; terrane accretion; multiple pre-IOCGU magmatic events	high levels Pre-IOCGU orogenesis and/or terrane accretion provides crustal-scale fluid pathways; pre- IOCGU magmatism provides source for U-rich A-type syn- IOCGU magmas	Desirable	Syn-orogenic pre-IOCGU granitoids; metamorphic belts; crustal-scale faults/shears	Tectonic setting of orogenesis and A-type magmatism not well understood	Continental to terrane
Q1, Q4	Major (mantle-driven?) thermal anomaly at IOCGU time; LPHT metamorphism	High geothermal gradients; formation of A-type U-rich melts including volcanics; mantle melts are source of some metals; LPHT indicative of high geothermal gradients regionally, needed to maintain high temps of fluids in near-surface; drives convection of brines deep into basement	Essential	A-type U-rich crustal melts emplaced at shallow levels; alkaline mafic magmatism; region may also have high-T I-type crustal melts & co- magmatic volcanics; LPHT metamorphic assemblages in syn- IOCGU orogens but not necessarily in shallow-crustal IOCGU districts	Tectonic setting of orogenesis and A-type magmatism not well understood; are U- bearing IOCG systems found only distally from regions of exposed highest grade LPHT metamorphism? Are thermal anomalies mantle-derived or radiogenic in origin? Not clear if convection was necessary, or if single-pass systems	Continental to district (camp)
Q1 Q1	Presence of shallow U-rich A- type granitoids and/or volcs immediately pre- to syn-IOCGU Age of mineralisation younger than atmosphere inversion at ~2 5 Ga	Exposure of U-rich sources to shallow oxidised fluids Oxidising atmosphere	Essential Essential	Cooling ages of exhumed basement same as intrusions & mineralisation (unless reset) Age of mineralisation & associated magmatism	Exhumation of granites less important if volcanics or cover sandstones are source of U (?) Is 2.5Ga the earliest that IOCG deposits formed (or could form)? Is <2.5Ga age required for U-rich IOCG?	Terrane to district (camp) Continental
Q2, Q4	Crust-penetrating shear/fault zones separating crustal blocks	Magma & fluid pathways from mantle & lower crust to near-	Highly desirable	PTt variations across crustal block boundaries; geophysical responses	Is crustal block boundary universal to IOCGUs, or just Olympic Dam? (Mt Isa ,	Terrane to district (camp)
Q2	of orogens; district scale fault networks reactivated during IOCGU Close association of deposits with gradients of major gravity	flow of deep-sourced and possibly meteoric fluids Gradients represent crustal block boundaries (major fluid	Desirable	Gravity data (upward continued); worms	strike-slip?	Terrane
Q2	Brecciation at high crustal level; diatreme / maar volcanic setting	High permeability fluid pathways; maar volcanism indicative of high geothermal gradient & presence of groundwaters	Essential	Breccias of hydrothermal, and/or tectonic and/or phreato-magmatic origins; volcanological evidence for maar / diatreme setting	Not clear if breccias are essential for U- rich IOCG (OD cf. Wirrda Well, Oak Dam); drivers of hydrothermal brecciation unclear $- CO_2$ driven? Is diatreme/maar essential, or simply represents a thermal centre and topographic low in the bydrologic system?	District (camp) to deposit
Q2	Cover sequence of permeable, oxidised, U-rich sediments or volcanics, overlying basement with IOCG deposits/alteration	Source of U; pathways for meteoric fluid flow	Desirable	Clastic red beds; hematitic altered felsic volcanics /volcaniclastics; U- depleted where leached; U-rich where least altered; evidence of high permeability	Role of cover sequence versus basement as source of U unclear; potential for "unconformity-related" U hybrids?	Terrane to district (camp)
Q3, Q4	Moderate to high temperature (300-550°C) Fe-rich (hyper)saline brine, magnetite- (to ?hematite-) stable	Carries Fe (±S, Cu) to form Fe ²⁺ - bearing oxides, silicates, carbonate & sulfides, which may act as reductants for U ⁶⁺	Essential	Presence of fossil mod-high-T brines trapped in hydrothermal minerals	Is magnetite-stable brine necessary, or is the high-T brine only hematite-stable in some systems? Are U and REE carried in this brine? Magmatic versus non- magmatic contributions? Role of alkaline mafic sources of U, REE, Cu, Au?	District (camp) to deposit
Q3, Q4	Low-moderate temperature (150-250°C) oxidised brines of variable salinity, hematite-stable; evolved meteoric waters	Assumed to transport U ⁶⁺	Essential	Presence of fossil low-mod-T brines trapped in hydrothermal minerals; evidence for preserved palaeosurface (IOCG time) close to current surface	Are these fluids what differentiate IOCGU from IOCGs? Could sandstones overlying basement be U source, in a post-IOCG U model?	District (camp) to deposit
Q3	Evaporite or ex-evaporite bearing sequences in basement and/or cover	Sources of Cl ⁻ for complexing of Fe, Cu; source of CO_3^- and $SO_4^{2^-}$ for complexing of U; buffered redox state of fluids to moderate to oxidised levels	Unknown	Presence, extent and distribution of evaporite or ex-evaporite minerals (e.g. scapolite) and related rocks; fluid inclusion evidence (e.g. Br/Cl) suggestive of interaction of fluids with evaporites	Source of salts in either high- or low- moderate T brines poorly constrained; however, a non-magmatic contribution is present	Terrane (basin) to district (camp)
Q3	U-enriched granites or gneisses in basement or U-rich volcanic rocks and/or sandstones in cover	Sources of U	Essential	U enrichment indicated by γ-ray spectrometric data and geochemical analyses of potential sources	Not clear if source(s) of U are syn-IOCG granites and/or volcanics (syn-IOCG model) and/or overlying sandstones (post- IOCG model)	Terrane (basin) to district (camp)
Q3	Leachable U source, e.g. uraninite, metamict/altered monazite, allanite, etc.	U must be available for leaching, not locked in resistant minerals	Essential	Mineralogy and leaching characteristics of U sources	Mineralogy of U sources unknown; magmatic-hydrothermal vs host rock sources of U?	Terrane (basin) to district (camp)
Q3	Leaching of potential U sources	Indicates removal and uptake of U by fluids	Desirable	Loss of U associated with regional alteration of and/or palaeo-regolith development on potential source rocks; evidence of alteration of monazite and other U-bearing minerals in potential U source	Magmatic-hydrothermal vs host rock sources of U?	District (camp) to deposit
Q4	Topography	Drives flow of meteoric waters towards IOCG depositional zones, and possibly contributes	Unknown	Palaeogeographic evidence for hydrological head, or evidence for deeper circulation	Essential if U introduced by (evolved) meteoric waters	Terrane to district (camp)
Q2, Q4	Regional flow of high-T brines	Large IOCGU deposits require very large volumes of fluid	Essential	Mapping of regional magnetite- bearing albite or K-feldspar		District (camp) to deposit
Q2, Q4	Regional flow of low-T evolved meteoric waters towards IOCG	Large IOCGU deposits require very large volumes of fluid	Essential	Mapping of proximal hematite- sericite-chlorite-carbonate alteration ¹ ; hematitic zones with U may be above or lateral to any magnetite-bearing zones		District (camp) to deposit
Q5	Reductant: • Fe ²⁺ oxides, silicates, carbonates • And/or sulfides • And/or reduced C	Fe ²⁺ -bearing oxides, silicates, carbonate & sulfides may act as reductants for U ⁶⁺	Essential	Presence of Fe ²⁺ -bearing oxides, silicates, sulfides, carbonates; presence of alkali feldspars (albite in deeper zones, K-feldspar in shallower zones)	Is minor U introduced in early Fe oxide stage? Was U transported as F ⁻ or other complexes in magnetite-stable brine?	District (camp) to deposit
Q5	Late stage oxidation of earlier alteration assemblages	Indicates influx of oxidised fluids, possibly carrying U ⁶⁺ ; deposition by fluid-rock reaction	Essential	Late stage overprint of hematitic alteration & U mineralisation; associated with chlorite, sericite, carbonate	What U complexes were critical, and how oxidised were fluids? How do (evolved) meteoric waters maintain high oxidation state? Significance of evaporites?	District (camp) to deposit
Q5	Fluid mixing	U deposition by reduction of U ⁶⁺ via mixing with reduced fluid; can produce high grades	Desirable	Evidence for two fluids, e.g. barite, fluid inclusion evidence, isotopic evidence	Role of mixing versus two-stage fluid-rock reaction unresolved; can either produce ore-grade U?	Deposit
Q6	Cratonisation during or before IOCGU formation	Preserves near-surface setting of U-bearing IOCG systems, without excessive erosion	Essential	Lack of evidence for major tectonothermal events post-IOCG (i.e. require minimal erosion of IOCG sotting)	If deeper IOCG systems also contain U (present answer is no), then this criterion is non-essential.	Continental to terrane
Q6	Basin formation over basement- hosted U-bearing IOCG	Minimises effects of weathering and erosion of IOCGU deposit	Desirable	Presence of basin not much younger than IOCGU systems	Is the basin an active part of U-bearing IOCG system, or a preserving blanket?	Terrane (basin) to district (camp)