EGU Gift workshop

Role of Organic Matter in Mineral Deposits Two case studies

Kliti Grice





Deposition of Organic Matter





and to determine ¹³C/¹²C of hydrocarbons





Stages of Petroleum Formation



EXPRESSION OF STABLE ISOTOPE COMPOSITION

• δ in ‰ (per mil) = (R sample - R standard) X 1000 (R standard)

R is the measured ratio of heavy to light isotope as determined from an isotope ratio mass spectrometer e.g. ¹³C/¹²C, relative to an international standard.



Habitat of Chlorobi PZE _cf. Present Day Black Sea Microbial Mats (Shark Bay)

280 million year old Kupferschiefer (Copper Shale, Germany) 1.6 Billion year old (Lead, Zinc, Silver Deposit, Australia) e.g. Grice et al., Science 2005; Brocks et al., Science 2005 3 major extinction events

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Chlorobi Biomarkers PZE



Grice *et al.,* 1996



Methyl Iso-Butyl maleimide Grice *et al.,* 1995

Radiolytic alteration of biopolymers in the Mulga Rock Uranium deposit

Caroline Jaraula, Lorenz Schwark, Xavier Moreau, Kliti Grice, Walter Pickel, & Leon Bagas

CSIRO Minerals Down under Flagship Organic Geochemistry of Mineral Systems

Study Area



alluvium and calcrete

(after Douglas et al., 2010)

Phanerozoic Stratigraphy

	AGE	Narnoo	Minz	EMA		
SEQ		Graph log	Unit		LITHOLOGY	
	Distates			Qa	Aeolian sand, <10 m (typically <3m).	
Upper Gunbarrel	Pleistocene	eee		K	Sandstone, rare granulestone <5 m.	
	Pliocene					
	Late Milocene			1	Lithic diamictite and conglomerate, rare claystone,<20m	
	Early-Mid Miocene			н	Claystone, sandy clay, sandstone, <25 m.	
	Late Eocene			G	Sandstone, siltstone and claystone (5-20 m) .SILCRETE CAP	
		0000000		F	Diamictite, claystone, sandstone, 2-40 m.	
			U+BM	E3 E2	Claystone (1-4 m), Lignite (2-30 m), Mulga Rock	
sin			BM-U	E1	Sandstone (Verv carbonaceous) (1-20m. tvpically <5m).	
rnoo Ba	Mid Eocene		BM-U	Dcb	Sandstone (carbonaceous), fining-up to claystone, rare lignite, 10-30 m	
					Claystone, grey, locally carb at top, 5-15 m	
20			U Dws	Dura	Sandstone (well sorted, finning up): 0-15 m	
-				Conclementer and conditions . Devinement at ten E 20 m		
			U-Au		Congiomerate and sandstone. Ravinement at top. 5-20 m.	
wer GB	Early-Mid Cretaceous	M	11	C2	Sandstone, Vy coase grained, sericite clasts 0-15 m.	
			0		Sandatana, grading to black alow siltatons 0, 152 m	
			U	C1	Sandstone, grading to black clay-sitistone 0-13? III.	
	Late			В	Diamictite and Shale. Very rare in Narnoo Basin.	
	Farly		U-Au	A5	Sandstone fine arkose (m?)	
	Permian		0710	Δ.4	Siltstone, very fine, arkose, <500 m ²	
	i onnan				Carb shale nyrtic <500m Thick?	
2	Late		A1/A2 Diamietite and shale			
	Carboniferous					
		Clay Sand Granule Pebble	U = Uranium, BM = Ni, Co, Cu (and REE in Unit E2-E3) Au = Gold			

Objective

1. Recognize biological sources of molecular markers.

2. Identify relationships between molecular markers and uranium accumulation.

3. Detect radiolytic effects on molecular marker composition.

Ambassador Prospect drill core 5766





Kerogen source and maturity



Total S correlation with [U]



Depositional Environment



complex shallow depositional systems ranging from lacustrine to deltaic, swampy wetland and even shallow lake (Douglas et al., 2011)

* Berner RA, Raisewell R, 1984 - C/S method

Localised uranium enrichment



1 - pollen2 - spores3 - woody materialThe predicament in Mulga Rock: rare occurrence of discrete mineral or
crystal phases hosting uranium as uraninite $[UO_2]$ and coffinite $[U(SiO_4)_{1-x}(OH)_{4x}]$ (Energy & Minerals Australia, Pty Ltd,)

Aliphatic fraction



 $\delta^{13}C$ (‰, VPDB): average of *n*-C₂₅ to *n*-C₂₉; average of *n*-C₁₇ to *n*-C₂₂;

Aliphatic fraction



average of $n-C_{25}$ to $n-C_{29}$; average of $n-C_{17}$ to $n-C_{22}$; $\Delta = \delta^{13}C_{25 \text{ to } 29} - \delta^{13}C_{17 \text{ to } 22}$

Links between uranium and organics

Lines of evidence



Organic matter source/type



1. Highly aliphatic biopolymers are closely associated with uranium:

2. Provide a chemical trap for uranium

Mechanism

	Aliphatic components		Indicators & mechanism
			X Thermal cracking
<i>TS</i> (%) <u>U</u> (ррт)	$20 \Delta = +0.4$	MR 49	 X Change in Temperature regime/ burial history Microbial source No isoprenoidal components
3.1 5280 Selative aprindance	$\Delta = +0.2$	MR 53	 Microbial degradation No UCM Radiolytic cracking
1.3 <u>1161</u>	$\Delta = 0.0$	MR 51	plant waxes aliphatic biopolymer spores & pollen algal, fungi & bacterial cysts
			radiolytic cracking

Alkanone distribution



n-pentacosanone isomers



n-alkan-2-one relative abundance



Radiolytic alkanone formation



Conclusions & Implications

- Radiolytic cracking of aliphatic biopolymers in Ambassador deposits
- pollen and spores as possible sources of highly aliphatic biopolymers are recalcitrant & likely have a close spatial relationship with U, perhaps serving as a chemical trap.
- Radiolysis and the cascade of secondary and tertiary reactions (*i.e.* cracking, radioysis of water to produce OH- radicals, cabonylation) produced the suite of alkanones
- Low pH and high S inhibit alkene isomerization such that alkan-2-ones become the predominant isomer in samples with high U and S contents.
- Identification of radiolytic molecular markers provide applications to mineral exploration, initiation of petroleum products, environmental applications in tracking radiolysis in organic matter

A depositional model of the Paleoproterozoic Here's Your Chance Pb-Zn-Ag deposit from novel organic and inorganic geochemical techniques

Alex Holman, Kliti Grice, Paul Greenwood, Katy Evans



CSIRO





Here's Your Chance (HYC)

- Hosted in the Barney Creek Formation (BCF), McArthur Basin, NT
- Host rocks dated at 1.64 billion years old¹
- Part of the Proterozoic Mt.
 Isa / McArthur Pb-Zn province
- One of the world's largest sediment-hosted Pb/Zn/Ag deposits (30 Mt Pb + Zn)²



Modified from Ireland et al. 2004. Miner. Deposita 39, 143

1 Page & Sweet 1998. *Aus. J. Earth Sci.* **45**, 219 2 Huston *et al.*2006. *Econ Geol.* **101**, 1117

Formation of HYC – current model



Modified from Greenwood et al. 2013. Ore Geol. Rev. 50, 1

Formation of HYC – unanswered questions

- Redox conditions of McArthur Basin?
 - Recent evidence suggests ferruginous basin (Fe²⁺ rich)¹
- Microbial ecosystem of basin?
 - Previous studies hindered by alteration/overprinting ²⁻⁴
 - Possible influence on redox conditions?

Poulton *et al.* 2010. *Nat. Geosci.* 3, 486
 Logan *et al.* 2001. *Geochim. Cosmochim. Acta* 65, 1345
 Chen *et al.* 2003. *Earth Planet. Sci. Lett.* 210, 467

4 Williford *et al.* 2011. *Earth Planet. Sci. Lett.* **301**, 382 5 Dick *et al.* 2014. *Geo Res J* **3-4**, 19

This study





- Received samples analysed by Williford, Grice *et al.*
- Five samples taken along the estimated flow path of mineralising fluid
- Novel organic and inorganic techniques were applied to answer the previouslymentioned questions

Williford et al. 2011. Earth Planet. Sci. Lett. 301, 382

Bitumen II – background

- Freely-extractable OM vulnerable to overprinting and alteration
- Removal of silicate minerals with HF exposes Bitumen II from within mineral matrix
- Bitumen II believed to be shielded from overprinting and alteration ^{1,2}



1 Nabbefeld *et al.* 2010. *Org. Geochem.* **41**, 78 2 Sherman *et al.* 2007. *Org. Geochem.* **38**, 1987

Bitumen II – saturated hydrocarbons



 Bitumen II *n*-alkane distribution suggests contribution from sulfate-reducing and sulfide-oxidising bacteria (Melendez et al. 2013. Geology 40, 123)

Bitumen II – $\delta^{13}C$



- Bitumen II appears indigenous to HYC
- Low ¹³C depleted contribution from SRB
- Bitumen I possibly a later overprint
- Evidence of SRB and SOB suggest that HYC was deposited under euxinic conditions

$\delta^{34}S$ – inorganic sulfur

- Sulfur sourced from seawater sulfate or evaporitic deposits
- Sulfate reduced to sulfide by sulfate-reducing bacteria
 - Significant depletion in ³⁴S (¹)

$$2 H^{+} + SO_{4}^{-2} + 4 H_{2} \rightarrow H_{2}S + 4 H_{2}O(^{2})$$

$$SO_{4}^{-2} + 2 CH_{2}O \rightarrow H_{2}S + 2 HCO_{3}^{-}(^{2})$$

- Sulfide reacts with metal ions to precipitate sulfide minerals
 - Almost no isotopic fractionation (³)

Brunner & Bernasconi 2005. *Geochim. Cosmochim. Acta* 69, 4759
 Canfield 2001. *Rev. Mineral. Geochem.* 43, 607
 Seal 2006. *Rev. Mineral. Geochem.* 61, 633

$\delta^{34}S$ – organic and elemental sulfur

 Sulfide can be oxidised to elemental sulfur (S⁰) and polysulfides (S_x⁻²), with slight ³⁴S enrichment

2 HS⁻ + O₂
$$\rightarrow$$
 2 S⁰ + 2 OH⁻ (¹)
HS⁻ + (1-x) S⁰ \rightarrow H⁺ + S_x⁻² (x = 2 to 5) (²)

 Polysulfides can incorporate into functionalised organic matter during diagenesis (³)



Living cells also incorporate sulfate (biosynthetic sulfur)

1 Steudel 1996. *Ind. Eng. Chem. Res.* **35**, 1417 2 Chen & Morris 1972. *Env. Sci. Technol.* **6**, 529 3 Aizenshtat *et al.* 1995. *ACS Symposium Series* **612**, 16

$\delta^{34}S$ – results



- Organic and elemental S similar to sulfide minerals
- Sulfur source distinct from non-mineralised Barney Creek

Eldridge et al. 1993. Econ. Geol. 88, 1
 Ireland et al. 2004. Econ. Geol. 99, 1687
 Johnston et al. 2008. Geochim. Cosmochim. Acta 72, 4278

Conclusions - HYC depositional model

- External source of sulfate derived from McArthur Basin evaporitic units ¹
 - Possibly carried with mineralising fluid
- Sulfate entered HYC sub-basin, was reduced to sulfide by sulfate-reducing bacteria ^{1,2,3}
 - Euxinic conditions created in sub-basin

Holman *et al.* 2014. *Chem. Geol.* **387**, 126
 Holman *et al.* 2012. *Org. Geochem.* **52**, 81
 Holman *et al.* 2014. *Geochim. Cosmochim. Acta* **139**, 98

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