Past, Present and Future Applications of Isotope Geochemistry in Resource Exploration and Environment

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The University of Queensland

QEC Technical Forum 2019
“Linking Industry with Research”

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THE UNIVERSITY OF QUEENSLAND
AUSTRALIA

Linking Industry with Research

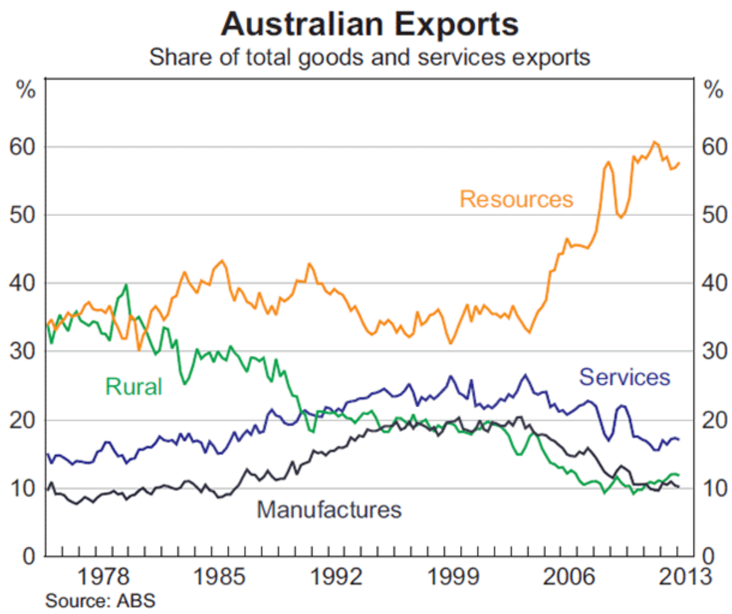
1970	1980	1990	2000	2010

Industry: Cu-Au, Au-U, ilmenite, coal

University-Industry research: Au, Cu-Au, Cu, Zn-Pb

University-Industry research: CBM, ME-CBM

University-Industry research: CCS



Applied Geochemistry

Hydrocarbon resources

- gas origins
- thermal maturity
- oil-source rock correlations
- thermochronology
- environmental studies
- new technologies (compound specific & clumped isotopes, noble gases)

Mineral resources

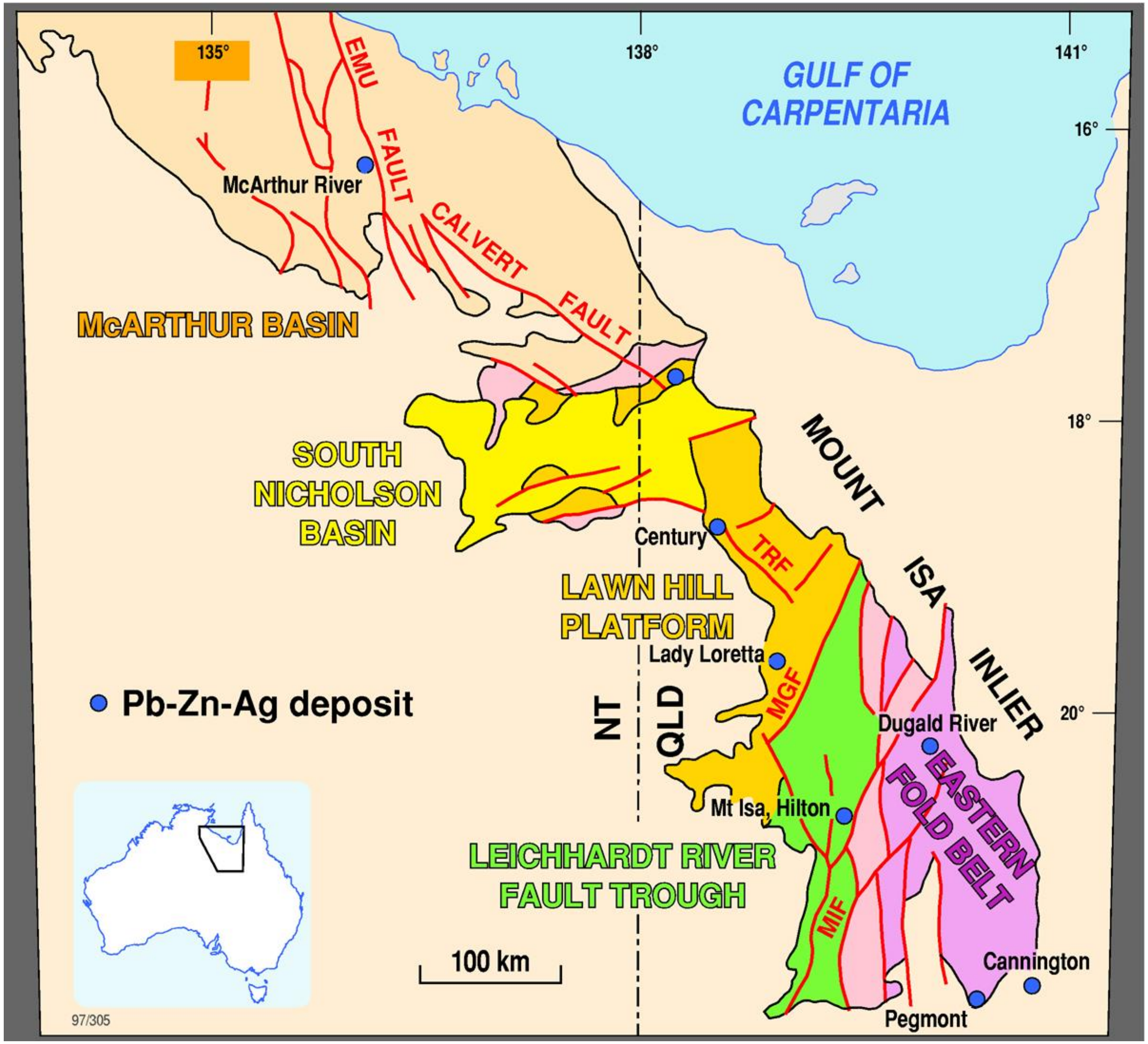
- ore forming processes
- mineral deposit classification
- mineral exploration
- minerals processing and metallurgy
- environmental studies
- new technologies (multiple sulfur & clumped isotopes, noble gases)

Mineral systems analysis

Hydrocarbon systems analysis

Carbon storage systems analysis

North-West Minerals Province

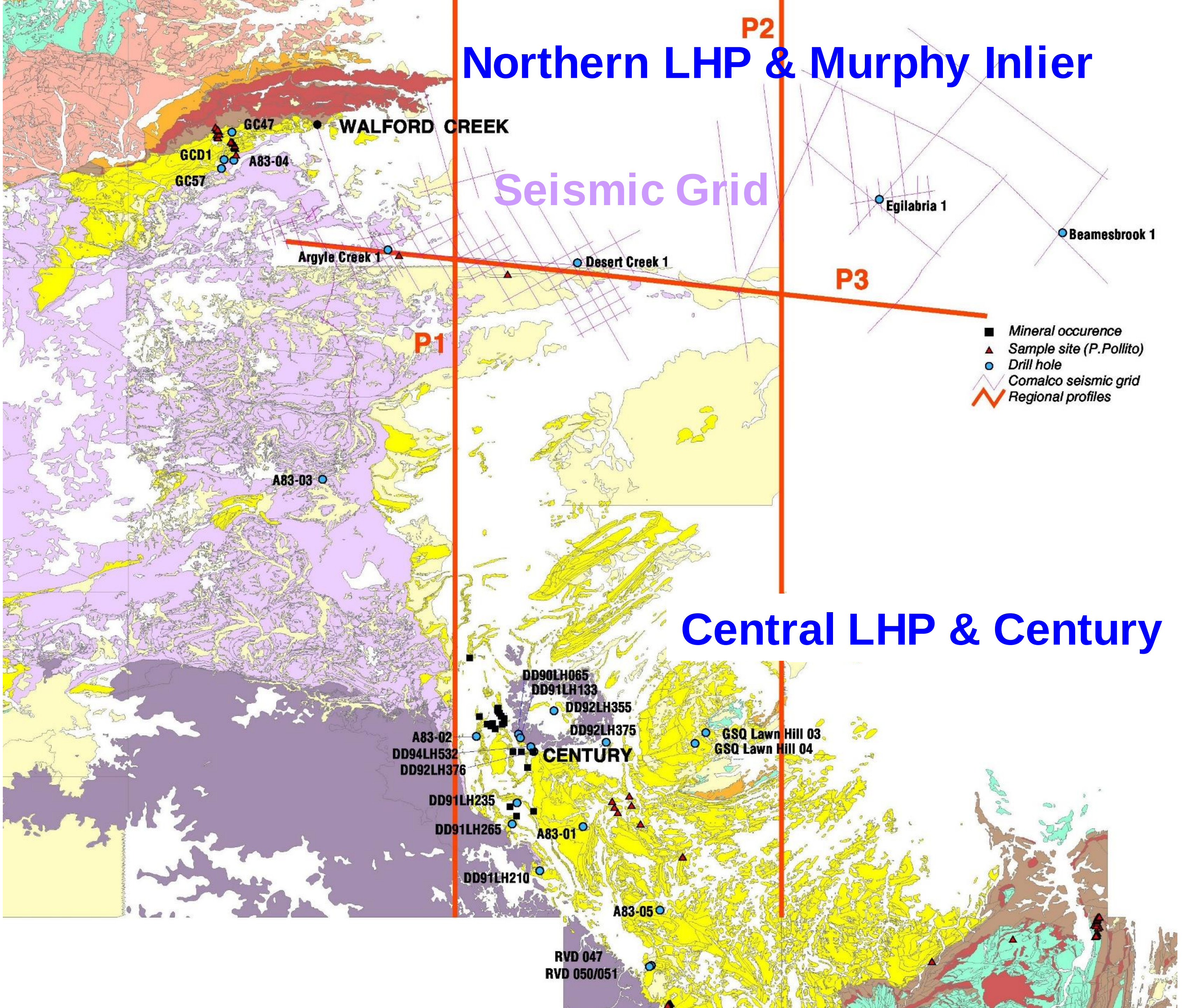


AMIRA P552: Integrated Mineral Systems Approach

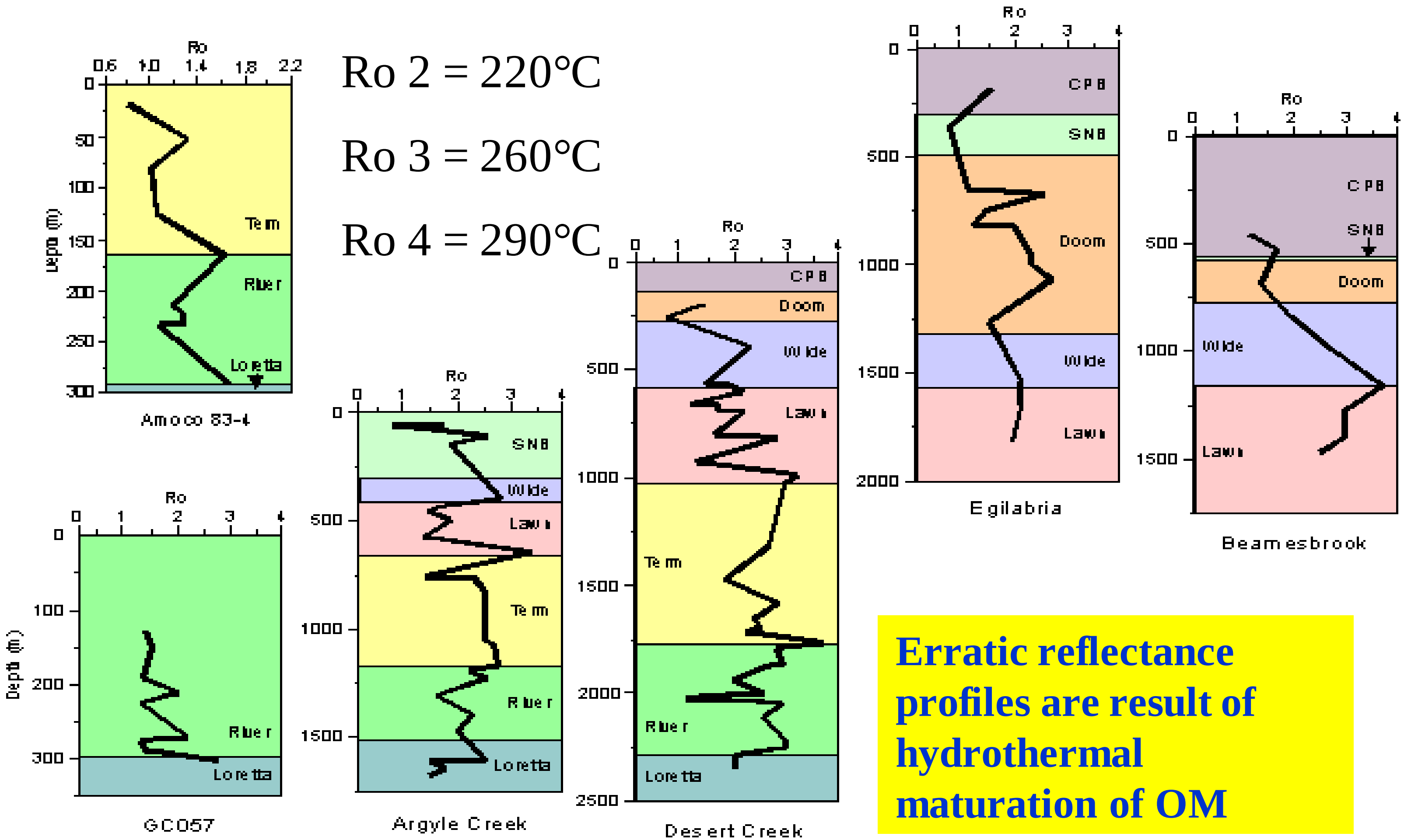
- Combine petroleum and mineral industry techniques
- Focus on mudrock and carbonate trap rock package in Lawn Hill Platform
  - determine thermal history from organic reflectance and clay mineralogy
  - regional fluid migration pathways (faults and sequence boundaries)
  - timing and chemistry of fluid migration events
  - link regional fluids to deposits through study of deposit haloes and orebody sulfides and carbonates

AMIRA P552 Participants

- University of Queensland
  - Sue Golding, Miryam Glikson, Tonguc Uysal, Kim Baublys
- University of Tasmania
  - Ross Large, Jianwen Yang, Stuart Bull
- Queens University, Canada
  - Kurt Kyser, Paul Polito
- Geoscience Australia
  - Peter Southgate, Deb Scott, Jim Jackson
- CSIRO, Perth
  - Yanhua Zhang, Alison Ord
- GSQ
  - Paul Blake
- Funding sources
  - AMIRA P552
  - ARC Linkage Grant
  - Industry partners: Anglo American, Cameco Exploration, North Limited, Pasminco Exploration, Rio Tinto Exploration, Tech-Cominco, Western Metals, Xstrata


Northern LHP & Murphy Inlier
Seismic Grid
Central LHP & Century
P1
P2
P3
WALFORD CREEK
GC47
GCD1
A83-04
GC57
Egilabria 1
Beamesbrook 1
Argyle Creek 1
Desert Creek 1
A83-03
Mineral occurence
Sample site (P.Pollito)
Drill hole
Comalco seismic grid
Regional profiles
DD90LH065
DD91LH133
DD92LH355
DD92LH375
A83-02
DD94LH532
DD92LH376
CENTURY
GSQ Lawn Hill 03
GSQ Lawn Hill 04
DD91LH235
DD91LH265
A83-01
DD91LH210
A83-05
RVD 047
RVD 050/051

Northern Lawn Hill Platform Reflectance Profiles



Ro 2 = 220°C

Ro 3 = 260°C

Ro 4 = 290°C

Erratic reflectance profiles are result of hydrothermal maturation of OM

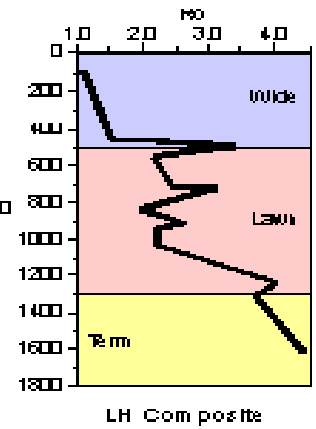
Glikson, M., Golding, S.D., Southgate, P.N., 2006. Thermal evolution of the ore-hosting Isa Superbasin: Central and Northern Lawn Hill Platform. *Economic Geology*, 101:1211-1229.

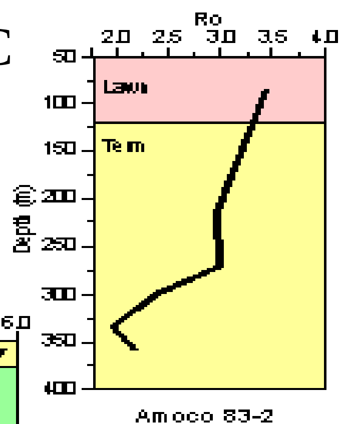
Central Lawn Hill Platform Reflectance Profiles

Ro 2 = 220°C

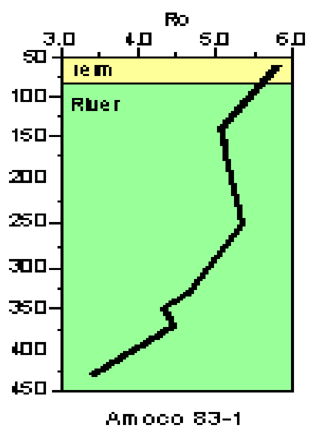
Ro 3 = 260°C

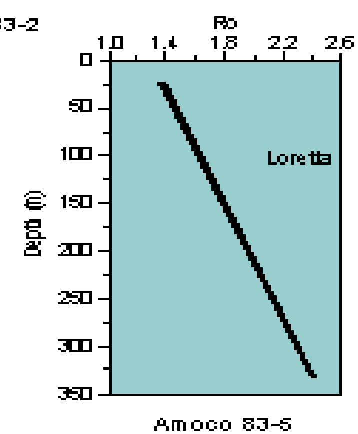
Ro 4 = 290°C

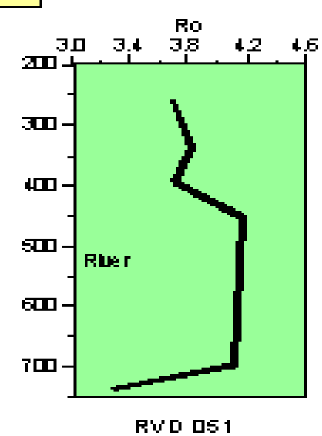


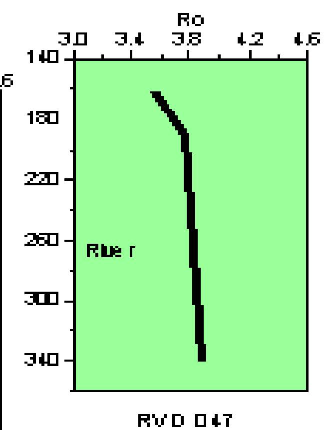


Inverted reflectance profiles indicate an overlying localized heat source.





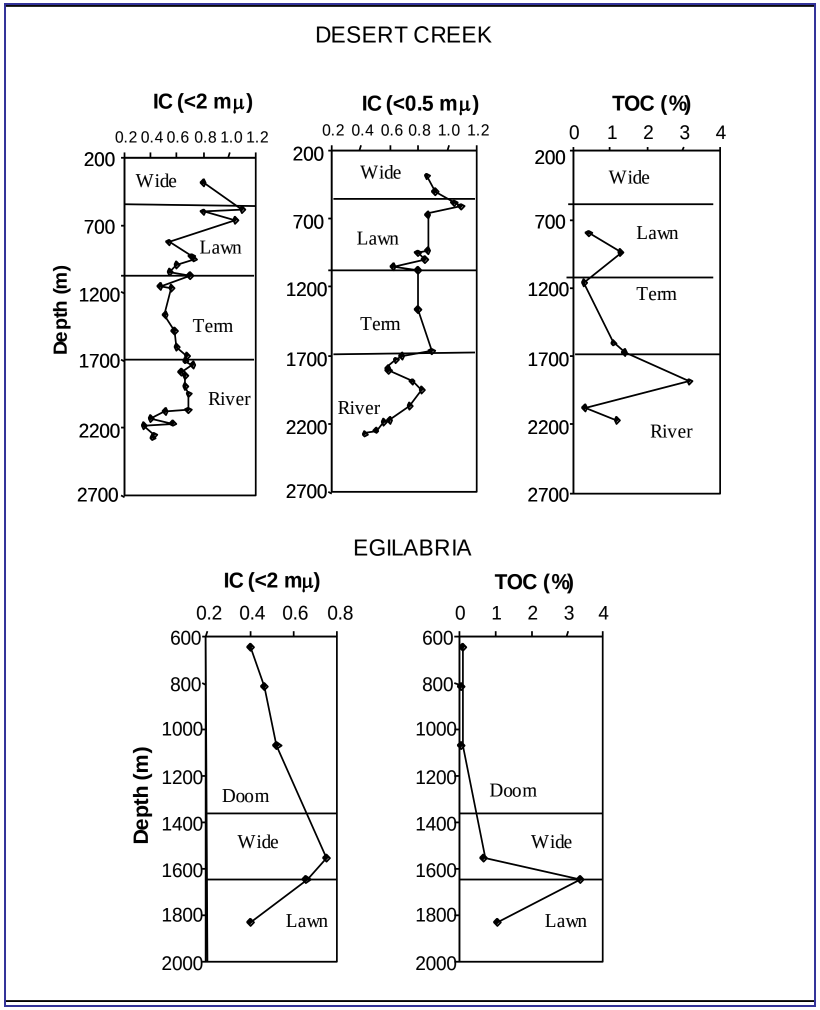




Organic maturation

Illite Crystallinity (IC) and TOC

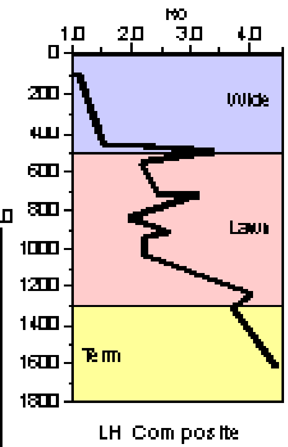
- IC values controlled mainly by temperature so expect a systematic decrease with depth.
- Perturbations due to variable fluid/rock ratio and temperatur during hydrothermal activity.
- Anomalous IC values locally coincide with high TOC and sequence boundaries.

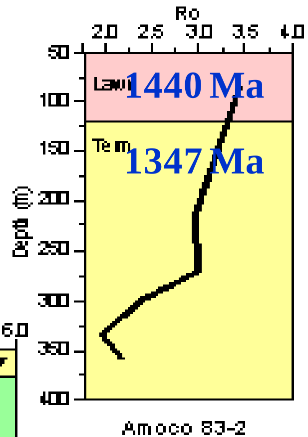


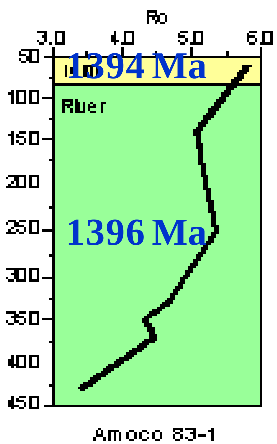
Golding, S.D., Uysal, I.T., Glikson, M., Baublys, K., Southgate, P.N., 2006. Timing and chemistry of fluid-flow events in the Lawn Hill Platform, Northern Australia. *Economic Geology*, 101:1231-1250.

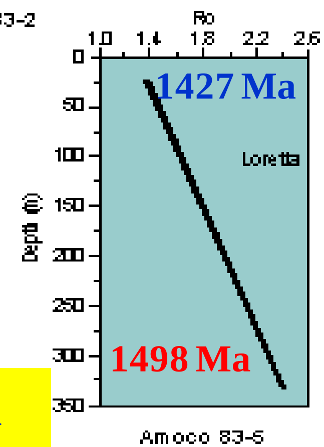
Central Lawn Hill Platform Illite K-Ar Age Distribution

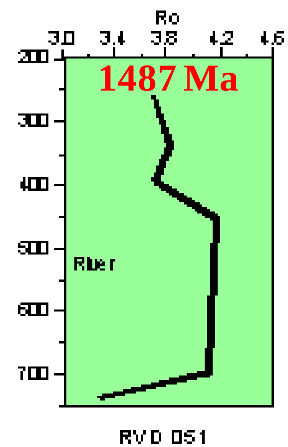
1400-1300 Ma cooling ages due to thermal relaxation and/or crustal exhumation

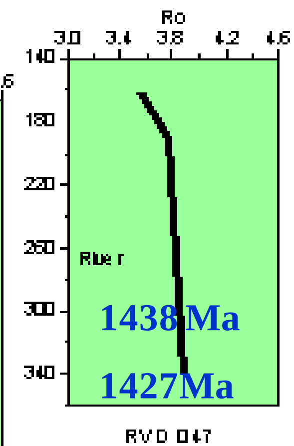












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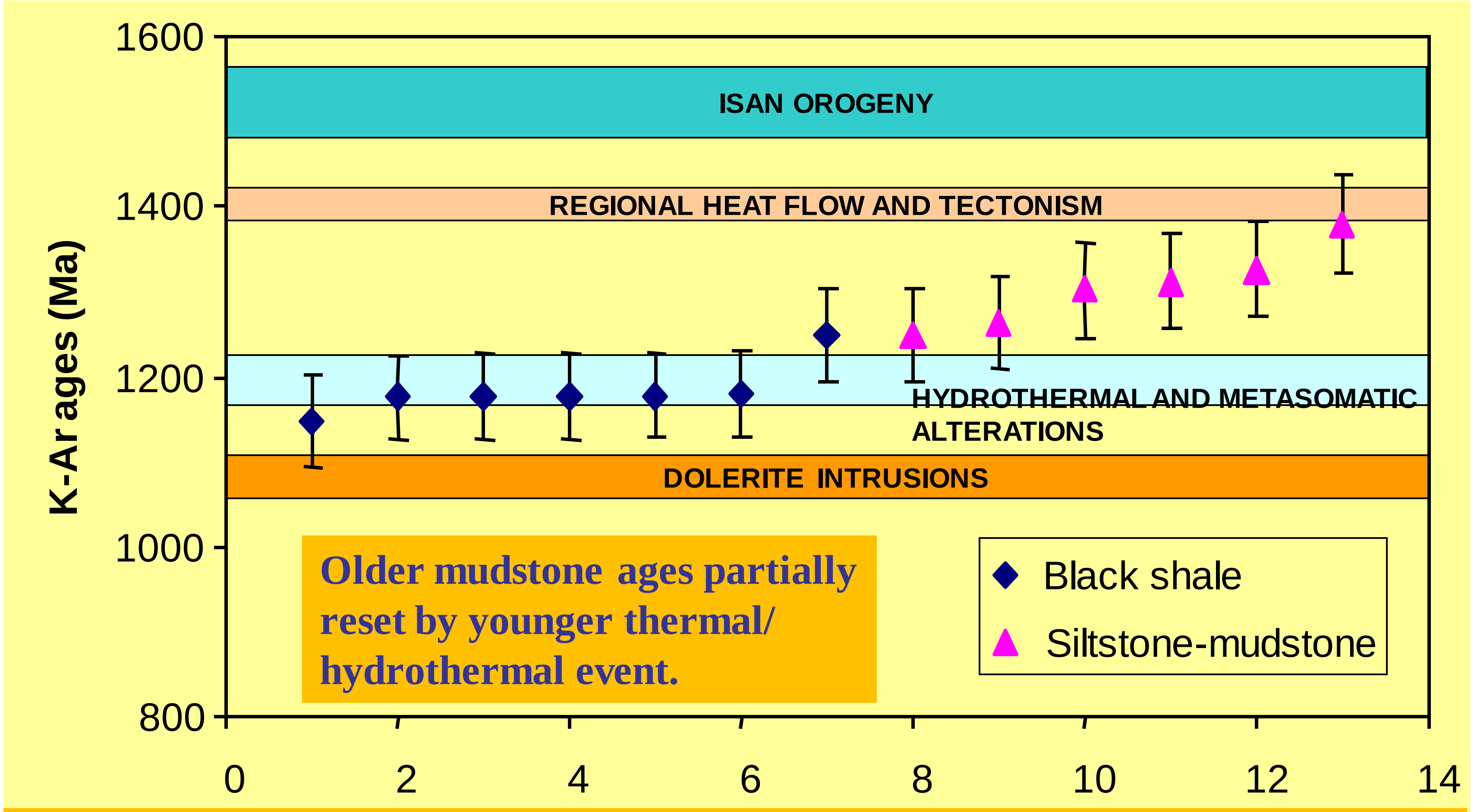
Ro 4 = 290°C

Organic maturation

Inverted reflectance profiles and illite K-Ar ages indicate a 1440-1400 Ma thermal event

Late Isan 1500 Ma ages in southern boreholes

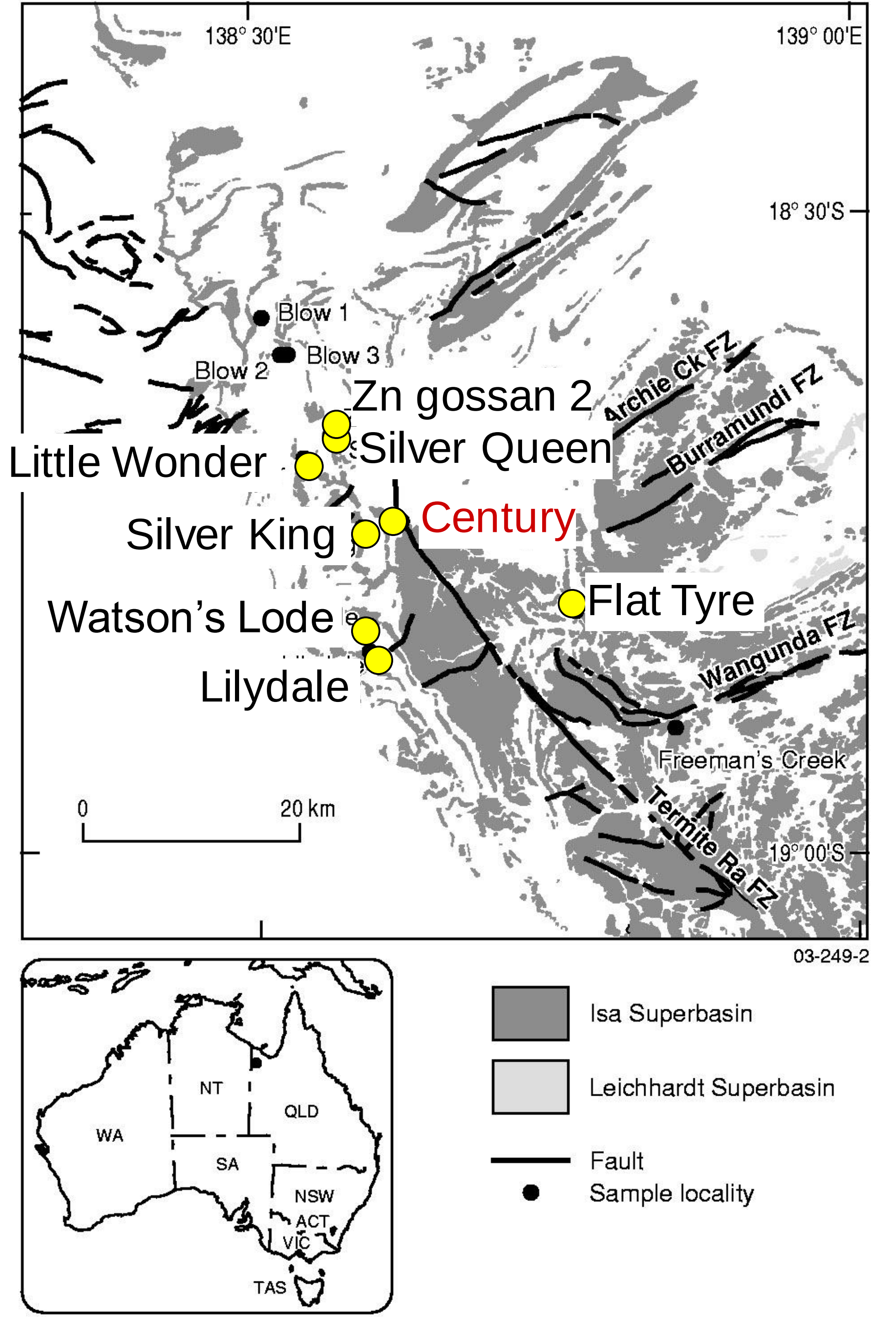
Northern Lawn Hill Platform Illite K-Ar ages



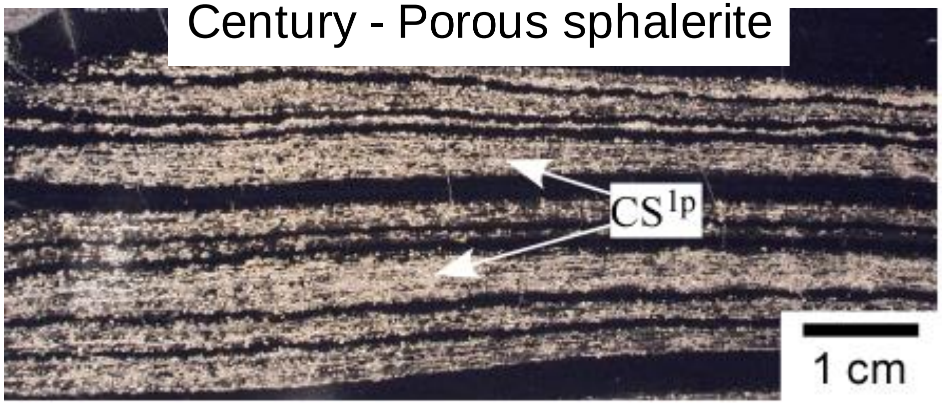
Youngest hydrothermal event in NLHP at some 1200 Ma mainly effects organic-rich shales; their permeability was enhanced by hydrocarbon generation.

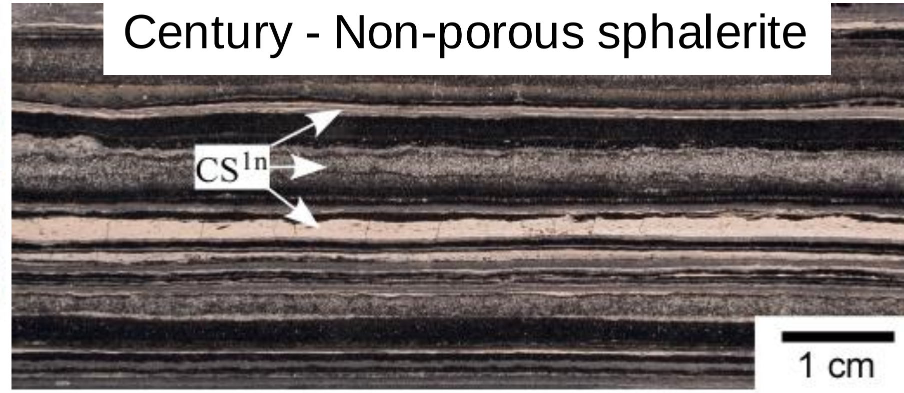
Burketown Mineral Field

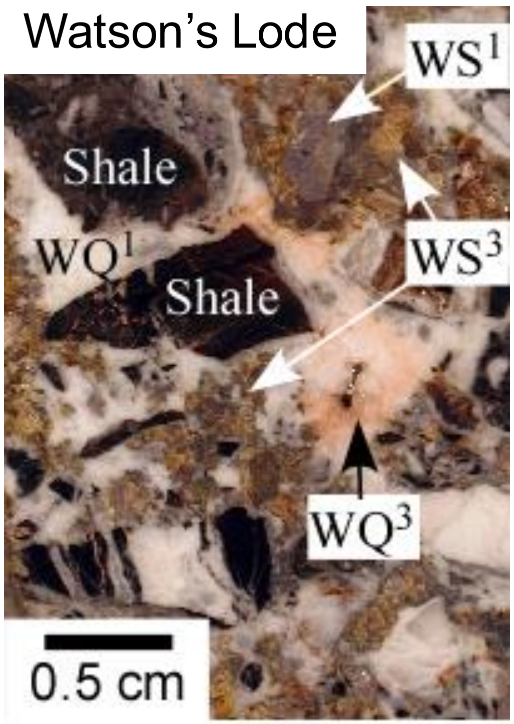
- The Burketown Mineral Field covers 14 x 38 km.
- Zn, Pb and Ag are the predominant commodities in this area that includes the world class Century deposit and > 47 Zn lode deposits
- Watson's Lode, Silver King, Silver Queen, Little Wonder, Coghlan's, Mended Hill, Bell's Lode, Anglo American, Little Banner, McGregor, Axis Hill, Edith and Lilydale
- Mineralization is not significantly overprinted by the 1610 – 1500 Ma Isan Orogeny

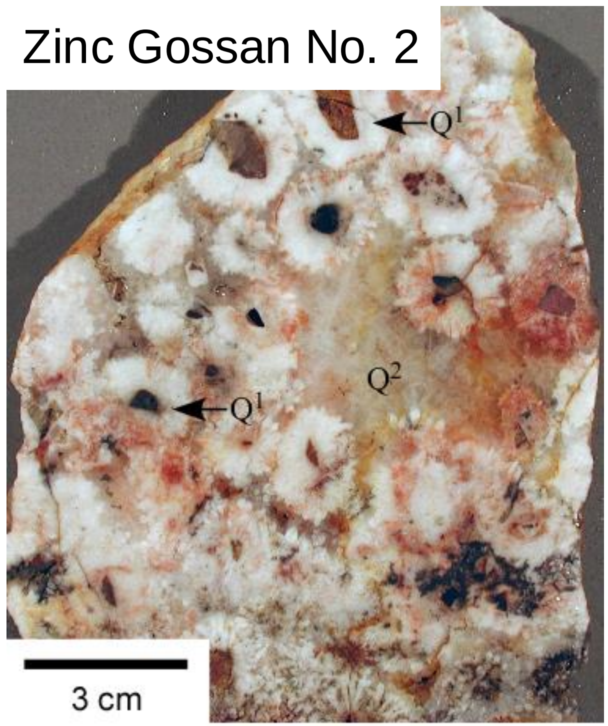


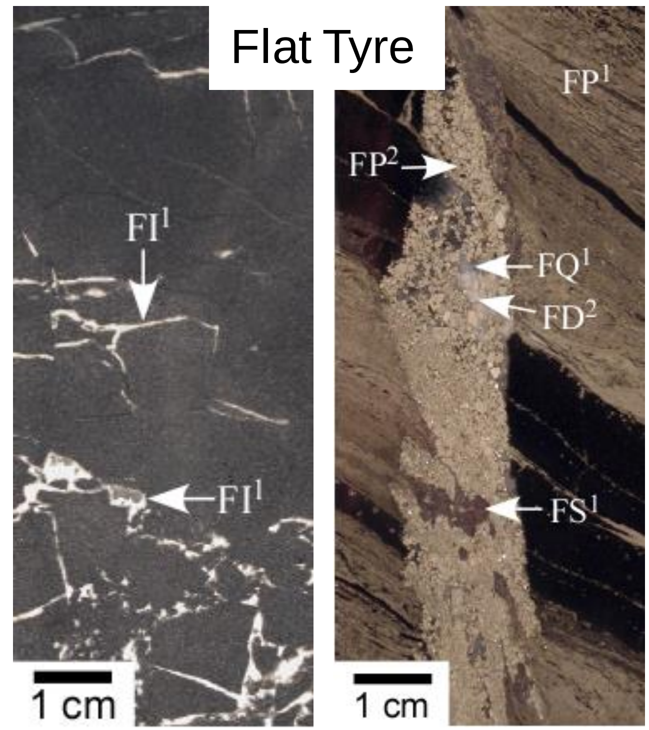
Mineral Assemblages





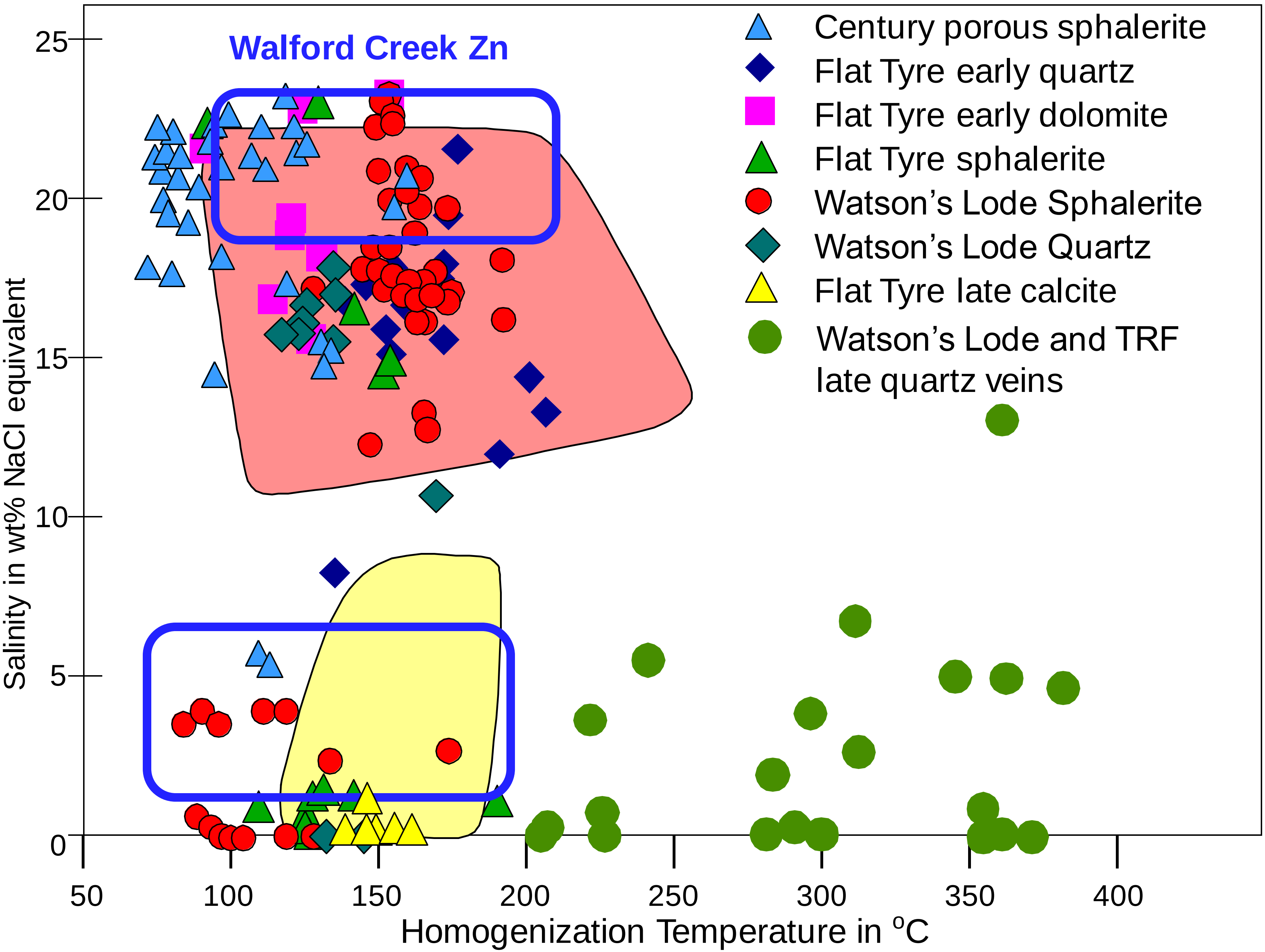




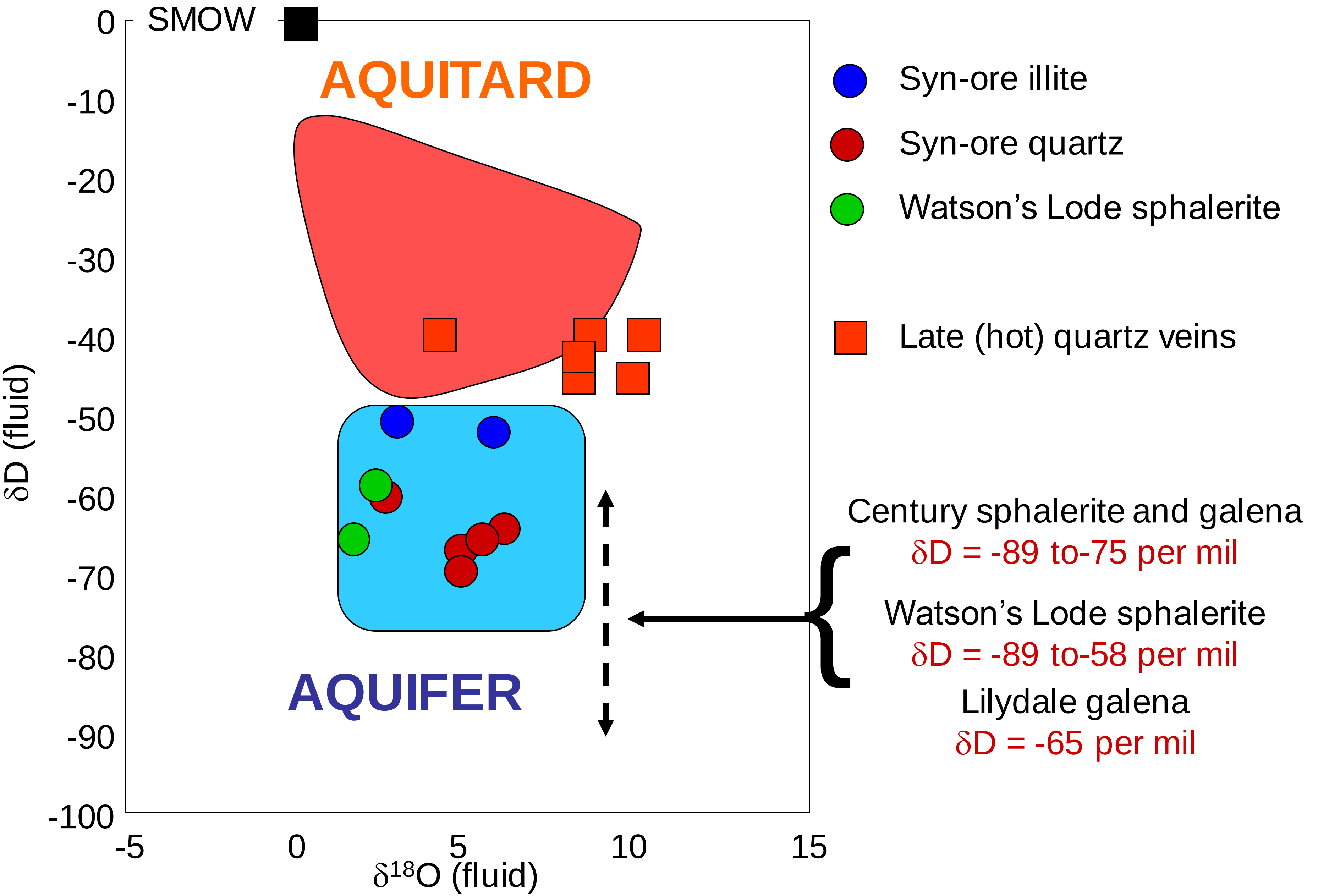


Polito, P.A., Kyser, T.K, Golding, S.D., Southgate, P.N., 2006. Zinc deposits and related mineralization of the Burketown Mineral Field, including the world-class Century deposit, Northern Australia: Fluid inclusion and stable isotope evidence for basin fluid sources. *Economic Geology*, 101:1251-1273.

Fluid inclusion data from the deposits on the Lawn Hill Platform



Stable isotopic compositions of fluids recorded in the BMF



Fluid Composition Comparisons

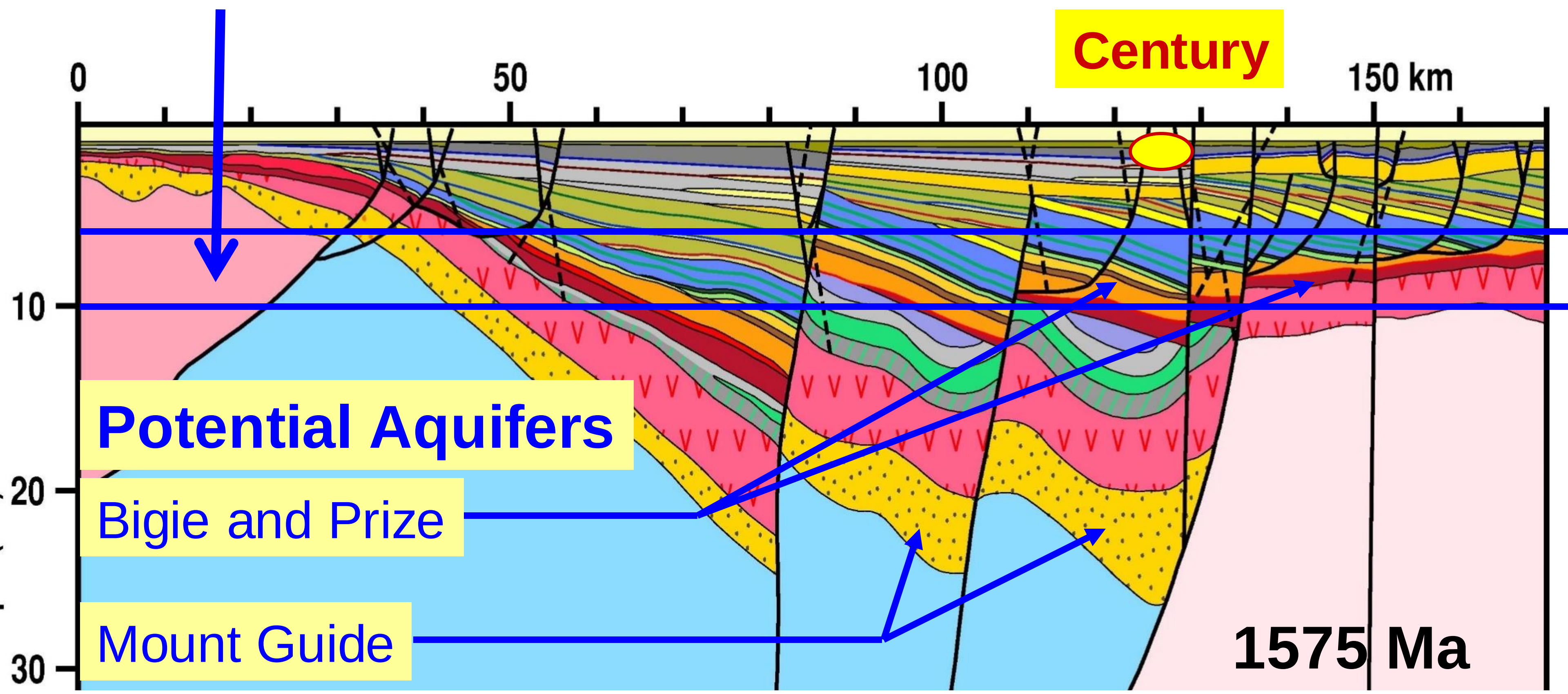
	Diagenetic aquifers	Aquitards	Century Zn ore	Mt Isa Cu Ore
Salinities (wt.% NaCl)	15-25	5-10	11-23	10-20
Compositions	Na-Ca-Mg-Cl	Na-K-Cl	Na-Ca-Mg-Cl	Na-Ca-Mg-Cl
Temperatures	200 to 260^{o}C	250^{o}C	150 to 200^{o}C	300^{o}C
δ^{18}O	2-8‰	0-9‰	1-7‰	2-6‰
δD	-75 to -58‰	-40 to -20‰	-89 to -50‰	-70 to -40‰
Ages	1780-1510Ma	1600-1500Ma	1575 Ma	1530 Ma

Polito, P.A., Kyser, T.K, Southgate, P.N., Jackson. M.J., 2006. Sandstone diagenesis in the Mount Isa Basin: An isotopic and fluid inclusion perspective in relationship to district-wide Zn, Pb, and Cu mineralization. *Economic Geology*, 101:1159-1188.

Metal leaching window **?**

5 - 10 km, 25°C thermal gradient

~200°C fluid



Southgate, P.N., Kyser, T.K., Scott, D.L., Large. R.R., Golding, S.D., Polito, P.A., 2006. A basin system and fluid-flow analysis of the Zn-Pb-Ag Mount Isa-type deposits of Northern Australia: Identifying metal source, basinal brine reservoirs, times of fluid expulsion, and organic matter reactions. *Economic Geology*, 101:1103-1115.

Summary Findings LHP Mineralisation

~1575 Ma

- The earliest mineralisation formed at Century and Flat Tyre.
- The mineralising brines were saline (18-23 wt.% NaCl eq), 120 to 160^{o}C and had depleted δD values (-89 to -75 per mil) suggesting formation from meteoric fluids.
- The most likely source for the fertile brine is the Big and Prize Supersequences.

~1575 to 1485 Ma

- The discordant Zn lodes, and the crackle veins at Century form.
- The dominant fluid was the same saline brine (high salinity, meteoric origin), but another fluid with lower salinities (10 wt. % NaCl eq) and higher δD values (toward -40 per mil) was also involved.
- The second fluid may have been derived from thin sandstone units in the Isan Superbasin with seawater dominated fluids.

Summary Findings LHP Mineralisation

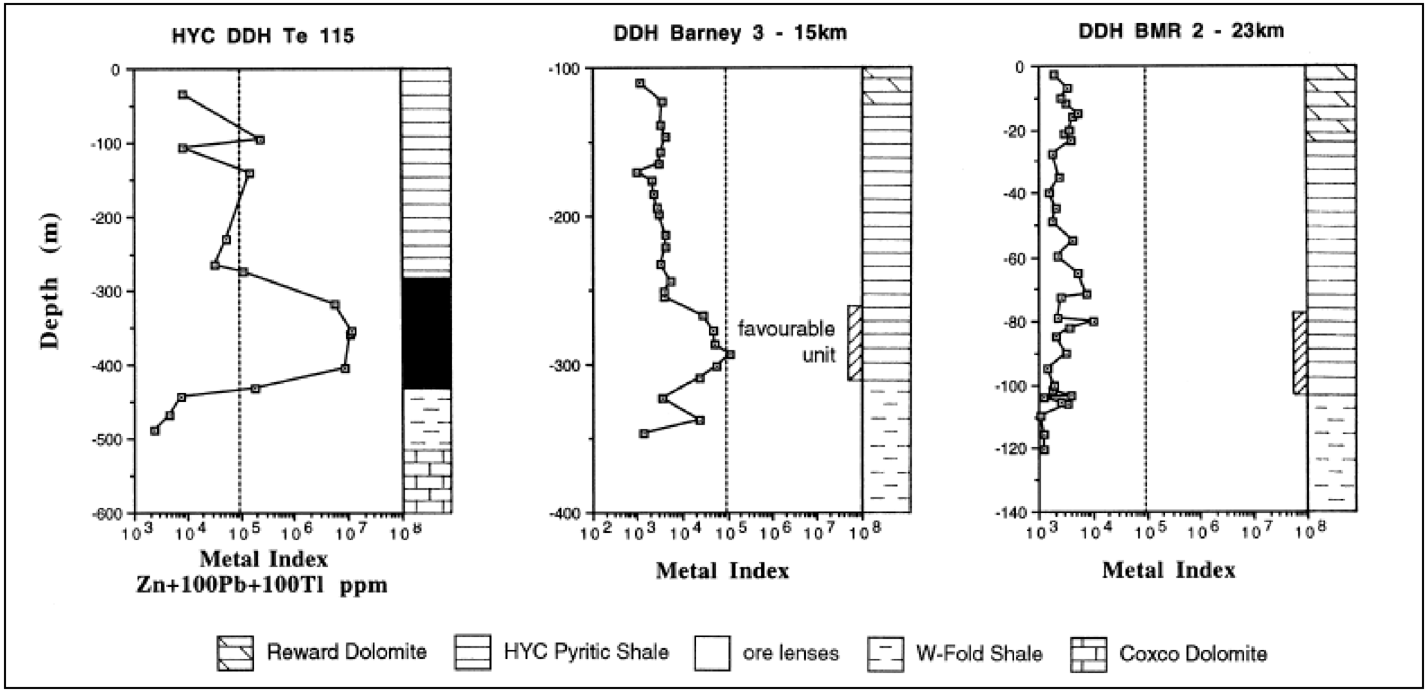
~1485 to 1300 Ma

- Minor sphalerite, quartz and calcite veins form throughout the Burketown Mineral Field.
- Fluid inclusion geochemistry indicate precipitation from 140 ± 30ºC fluids with low salinities (0 and 6 wt. % NaCl).
- This event may represent waning mineralization in the area, but numerous Pb-Pb model ages from the deposits and K-Ar ages from LHP illite record ages of 1400 to 1300 Ma.
- These fluids and ages could represent downward percolation of brine through the overlying sediments of the Roper Superbasin.

~1300 to 1100 Ma

- Large druzy quartz veins cross-cut mineralisation and occur in the Termite Range Fault.
- Fluid inclusions indicate precipitation from low salinity, ~300ºC fluids. O and H isotopes indicate a metamorphic fluid may have been involved.
- K-Ar ages between 1300 and 1100 Ma are common across the LHP and coincide with regional hydrothermal activity associated with the emplacement of the Lakeview Dolerite.

Metal index for Mt Isa-type (MIT) deposits



Metal Index values (MIT Metal Index = Zn + 100 Pb + Tl) was first defined at Lady Loretta and shows a regular increase in the FW sediments towards the deposit (Large and McGoldrick, 1998).

Values greater than 10^4 characterise HW and FW strata of the HYC deposit and the favourable stratigraphy some 15 km west of HYC (Large et al., 2000).

At Mt Isa, values in excess of 10^4 occur in Zn-Pb ore equivalent horizons up to 5.5 km north of Mt Isa mine; values in excess of 10^5 are associated with visible sphalerite mineralisation (Painter, 2003).

Mn carbonate halo – MIT deposits

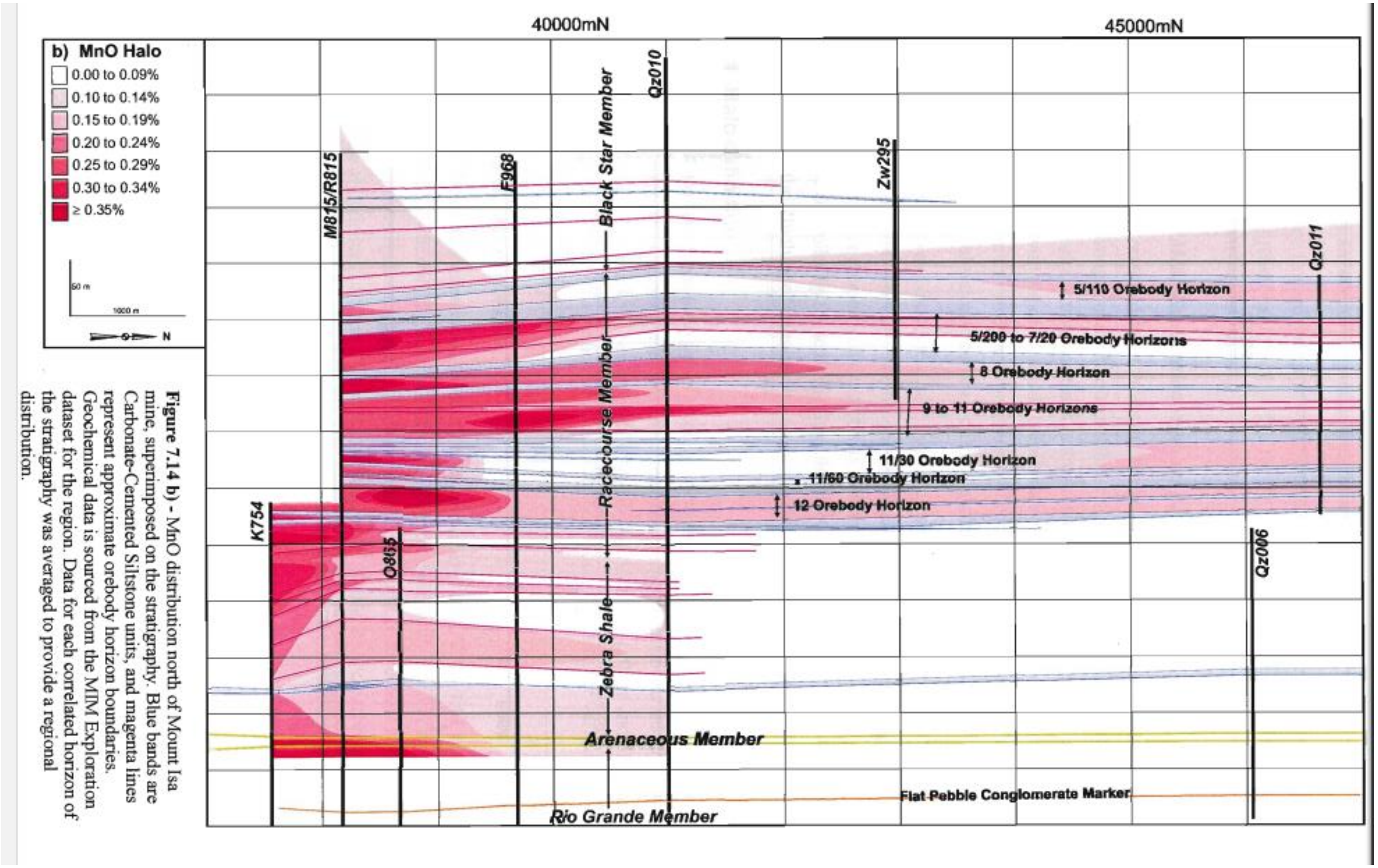


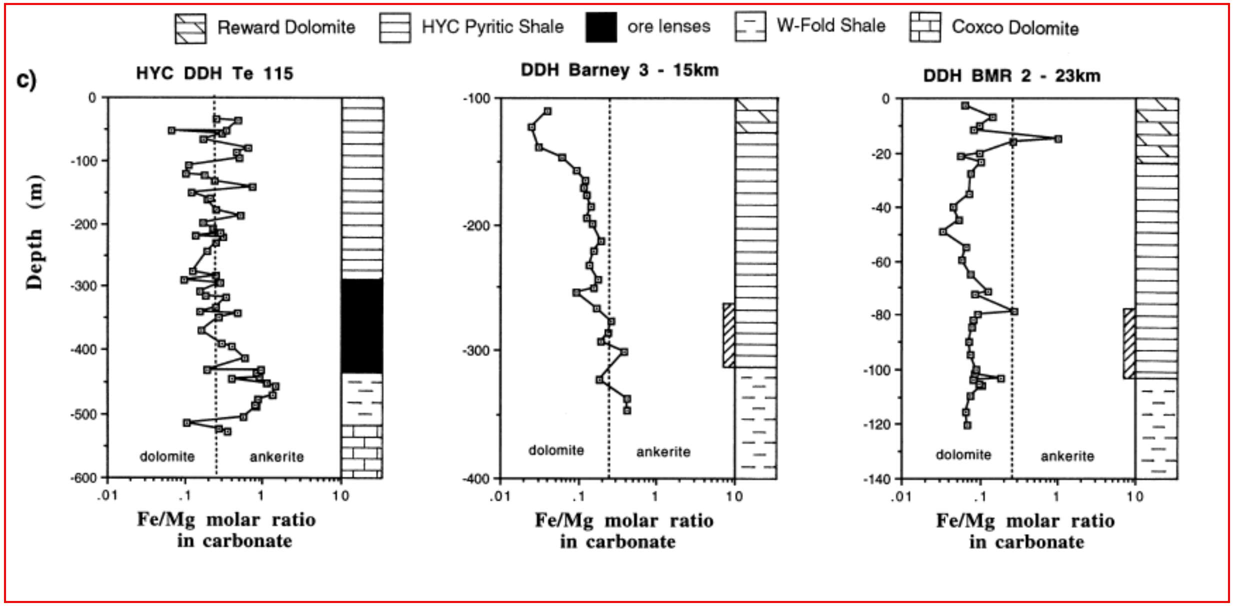
Figure 7.14 b) - MnO distribution north of Mount Isa mine, superimposed on the stratigraphy. Blue bands are Carbonate-Cemented Siltstone units, and magenta lines represent approximate orebody horizon boundaries. Geochemical data is sourced from the MIM Exploration dataset for the region. Data for each correlated horizon of the stratigraphy was averaged to provide a regional distribution.

Strong Mn enrichment in the dolomitic FW of the HYC deposit and its lateral equivalent some 15 km from deposit (Large et al., 2000).

Siderite at Century in the FW and HW and early siderite in the deposit is variably enriched in Mn up to 20 atomic % towards the deposit (Broadbent et al., 1998).

Mt Isa exhibits a strong manganese carbonate halo that extends up to 5 km north of the mine in ore equivalent horizons (Painter, 2003).

Fe carbonate halo – MIT deposits

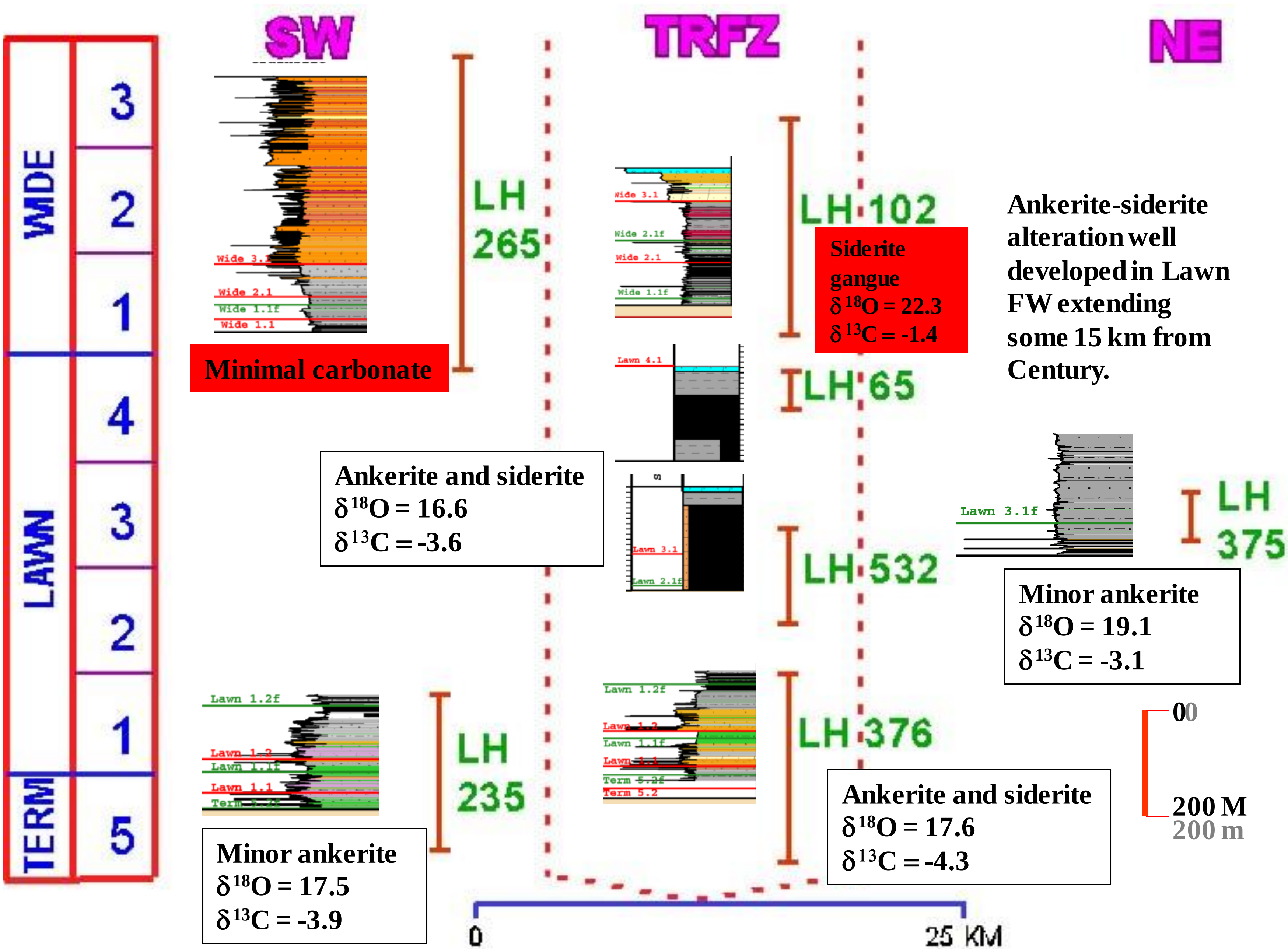


The Fe-dolomite and Mn-carbonate halos at HYC broadly coincide; however, the Fe-dolomite halo extends further into the HW than the Mn-carbonate halo (Large et al., 2000).

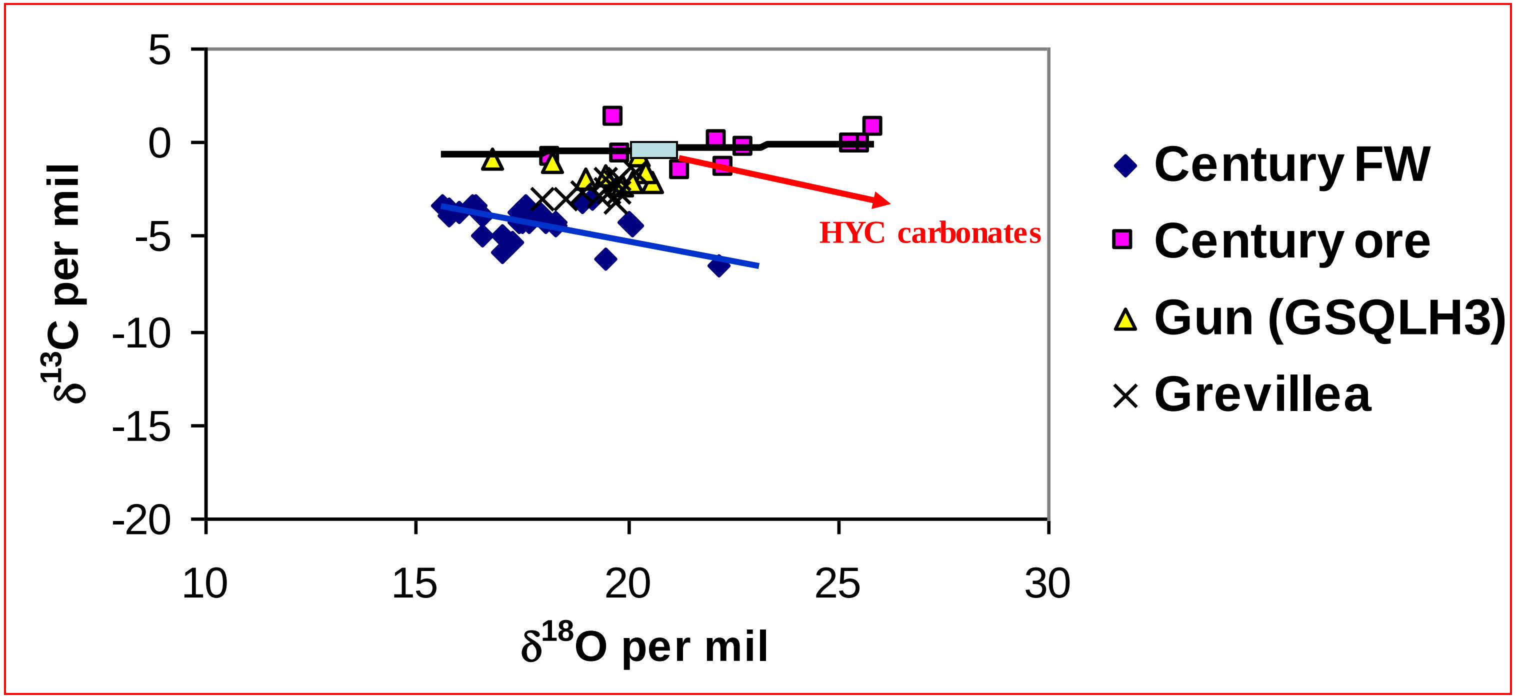
An inner siderite halo at Lady Loretta extends 50 m across strike and 1 km along strike; an ankerite and ferroan dolomite halo extends a further 100 m into the HW (Large and McGoldrick, 1998).

Mt Isa exhibits a strong ferroan dolomite halo that extends up to 9.5 km north of the mine in the rhythmite facies (Painter, 2003).

Century Ferroan Carbonate Alteration Halo

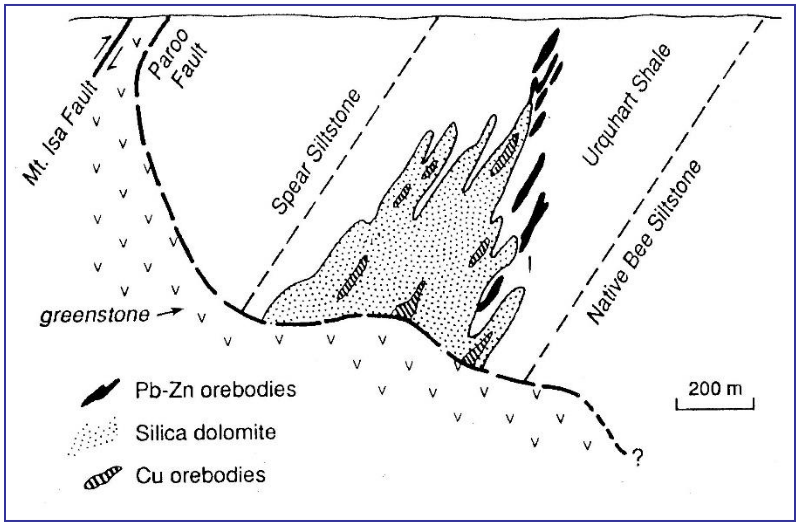


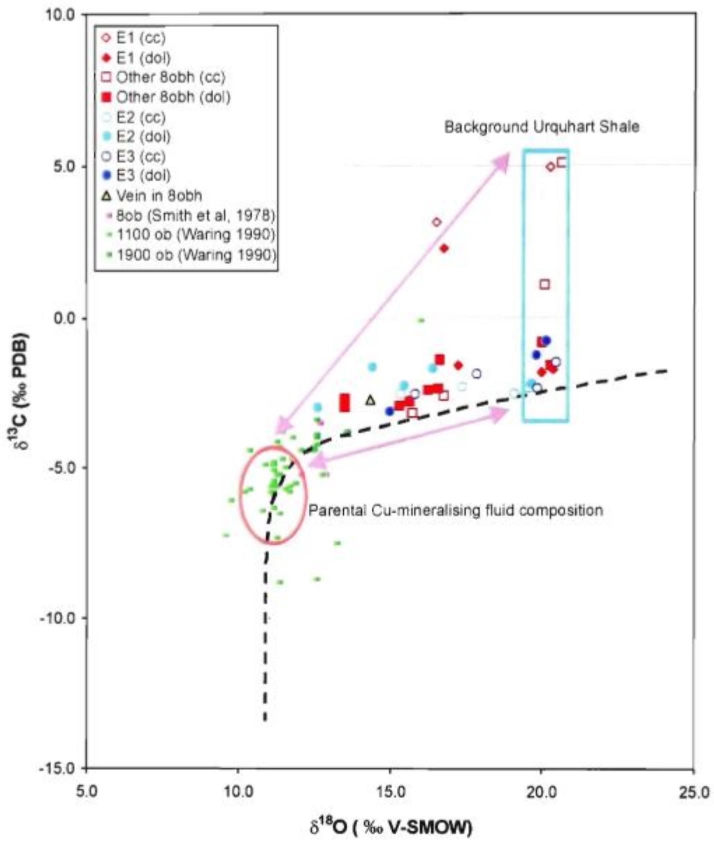
Century Carbonate C- and O-isotopes



Heavy carbonate $\delta^{18}O$ values in the alteration halo are a useful ore vector that reflect the relatively low mineralisation temperatures of MIT deposits and are also found in proximal carbonates at HYC and Lady Loretta (Golding et al., 2006).

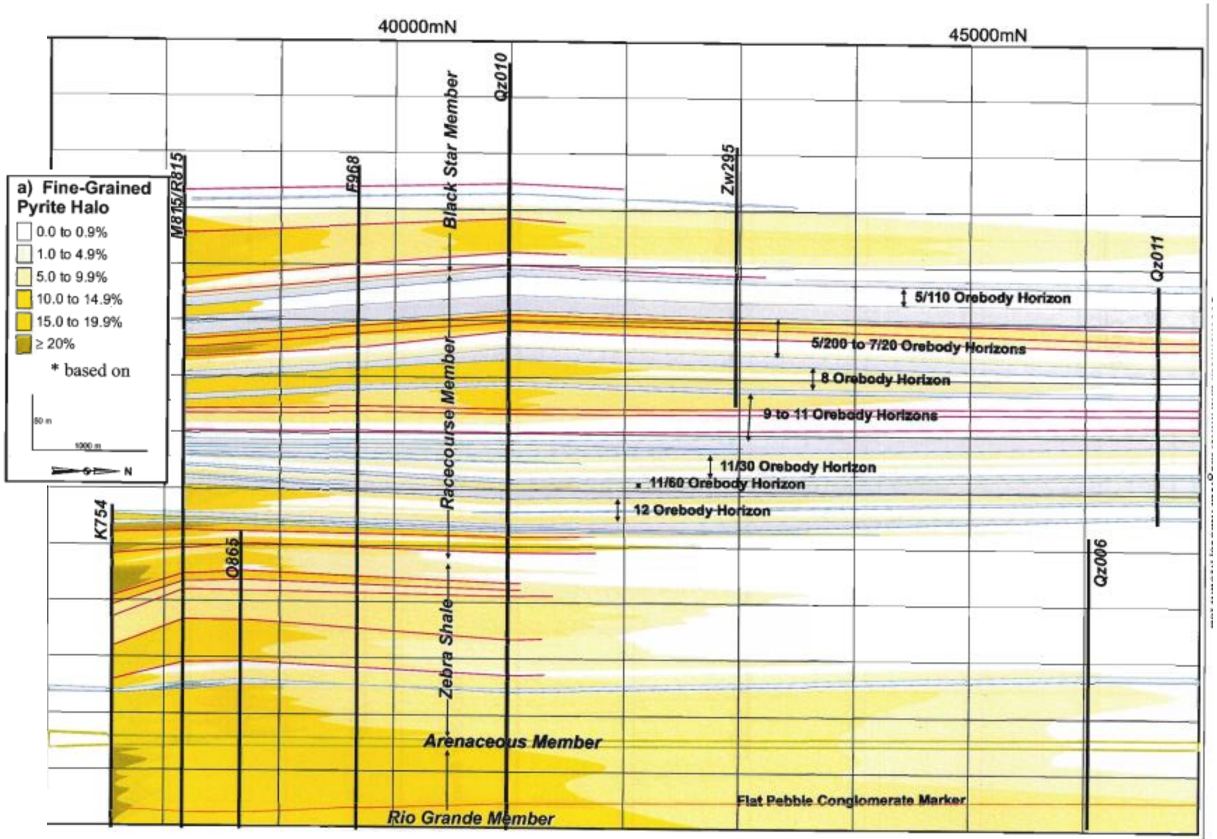
Mt Isa Zn-Pb and Cu Orebody Haloes

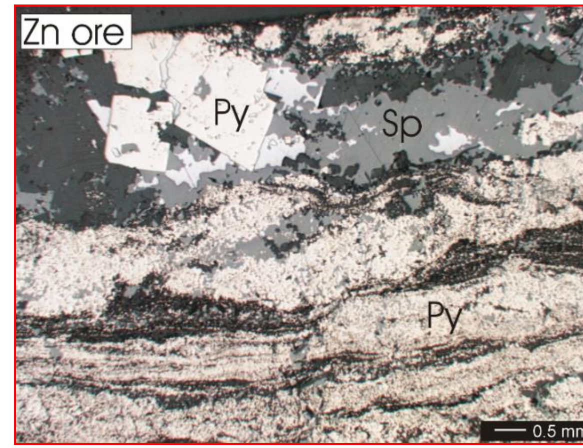




Heavy carbonate O isotopes not evident at Mt Isa because of the C and O isotope depletion trend related to emplacement of the Mt Isa Cu orebodies (Painter 2003; Waring, 1990).

Fine-grained Pyrite Halo, Mt Isa

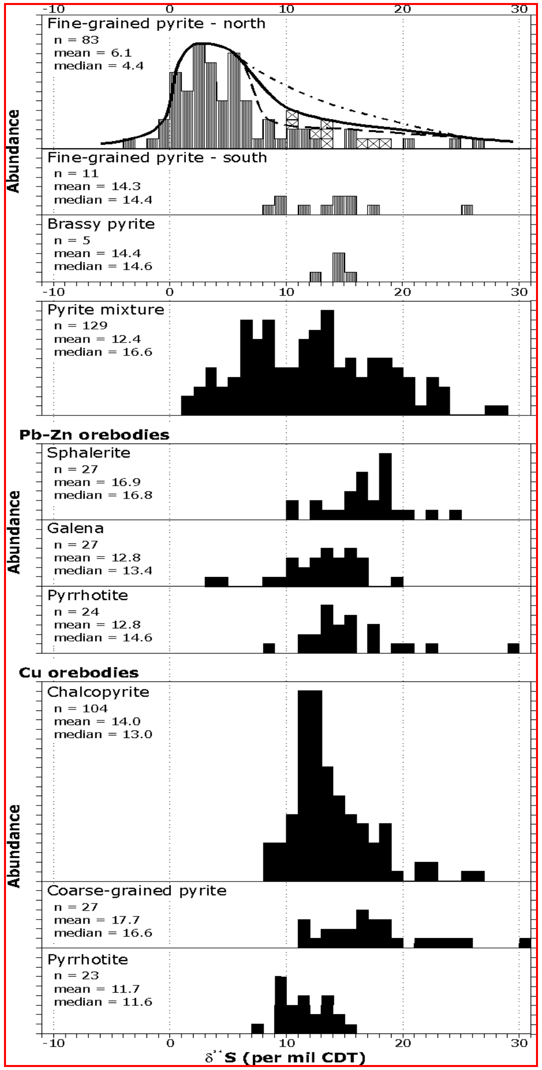




Coarse-grained sphalerite-pyrite mineralisation overprints fine-grained pyrite mineralisation, Mt Isa mine

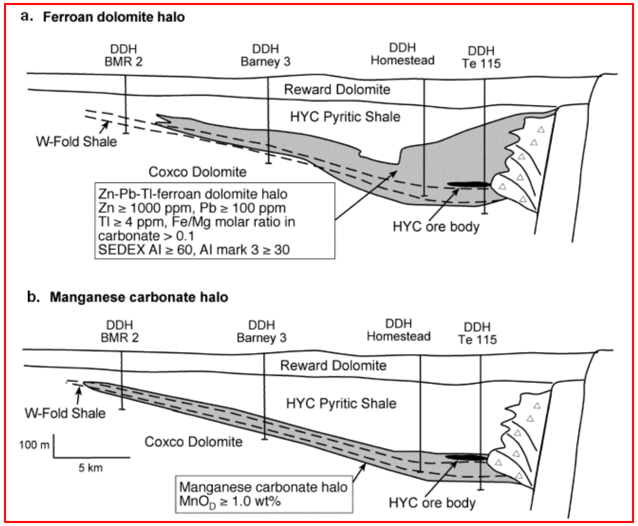
Fine-grained pyrite distribution north of Mt Isa mine; concordant fine-grained pyrite is more extensive than the Zn-Pb mineralization that overprints it in the Zn-Pb orebodies.

Sulfur Isotopes – MIT deposits



- MIT deposits (Mt Isa, Lady Loretta, Century, McArthur River) are characterised by variably enriched $\delta^{34}S$ values consistent with an ultimate seawater sulfur source.
- Main stage ore sulfides have the lowest $\delta^{34}S$ values with more enriched sulfur isotope compositions at the margins of the mineralisation (Mt Isa) and in late stage veins (e.g., LHP lodes).
- BHT deposits exhibit a much smaller range of $\delta^{34}S$ values around zero per mil consistent with magmatic sulfur sources.

Summary MIT Lithogeochemistry



Whole rock and carbonate chemistry together with stable isotopes of carbonates and sulfides have most potential in exploration for MIT deposits

– MIT (SEDEX) Metal Index
– MIT (SEDEX) Alteration Indices 1, 2 and 4
– Ferroan carbonate alteration halos
– Manganese content of dolomite/siderite
– Enriched carbonate oxygen isotopes
– Enriched sulfide sulfur isotopes

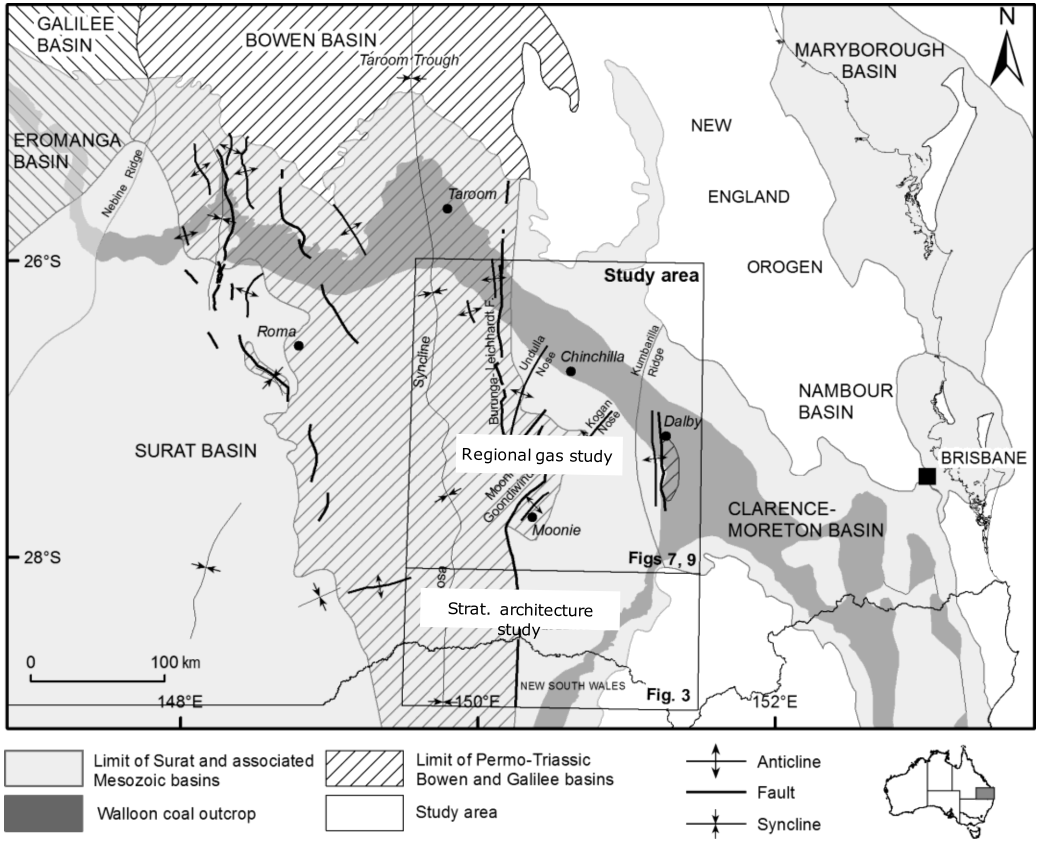
Can we use carbonate clumped isotopes as an additional tracer of ore-forming processes and a vector to mineralisation in MIT Zn-Pb (and Cu) systems?

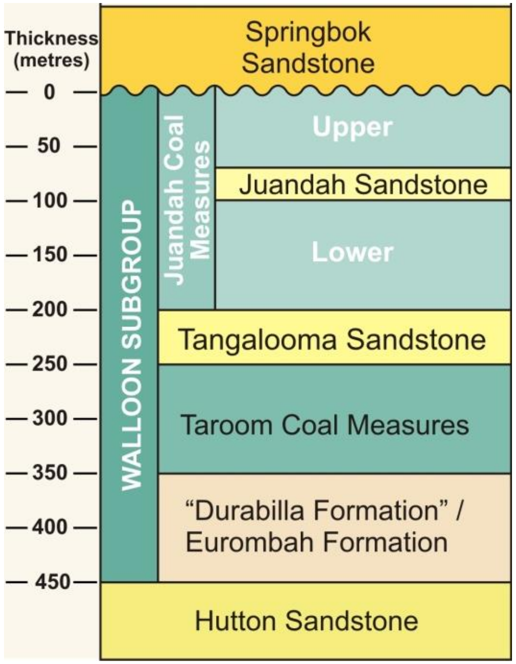
Coals as Methane Bioreactors

- Earth Sciences (UQ)
  - Sue Golding, Joan Esterle, Gordon Southam, Huiling Xing, Sandra Rodrigues, Stephanie Hamilton, Maija Raudsepp, Kim Baublys, Astrid Hentschel
- Chemical Engineering (UQ)
  - Victor Rudolph, Hang Zeng, Andy Chen
- Australian Centre for Ecogenomics (UQ)
  - Gene Tyson, Paul Evans, Donovan Parks, Steven Robbins
- Chemical Engineering (SDSMT)
  - Patrick Gilcrease, Sam Papendick, Sam Lane

- Funding sources
  - ARC Linkage Grant
  - Queensland State Government Smart Futures Project Grant
  - Industry partners - BG-QGC, Santos, TOTAL, Vale

Surat Desktop Study – Present Day Gas Distribution



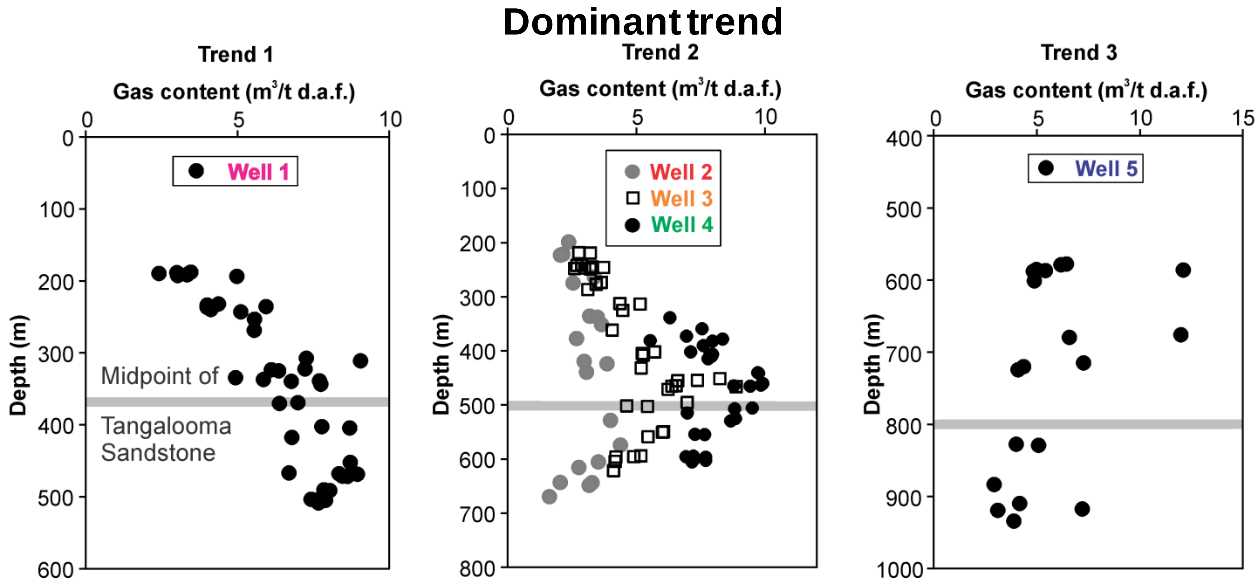


Hamilton, S.K., Esterle, J.S., Golding, S.D., 2012. Geological interpretation of gas content trends, Walloon Subgroup, eastern Surat Basin, Queensland, Australia. *International Journal of Coal Geology,* 101:21-31.

What Factors control Methane Distribution in the Walloon Subgroup?

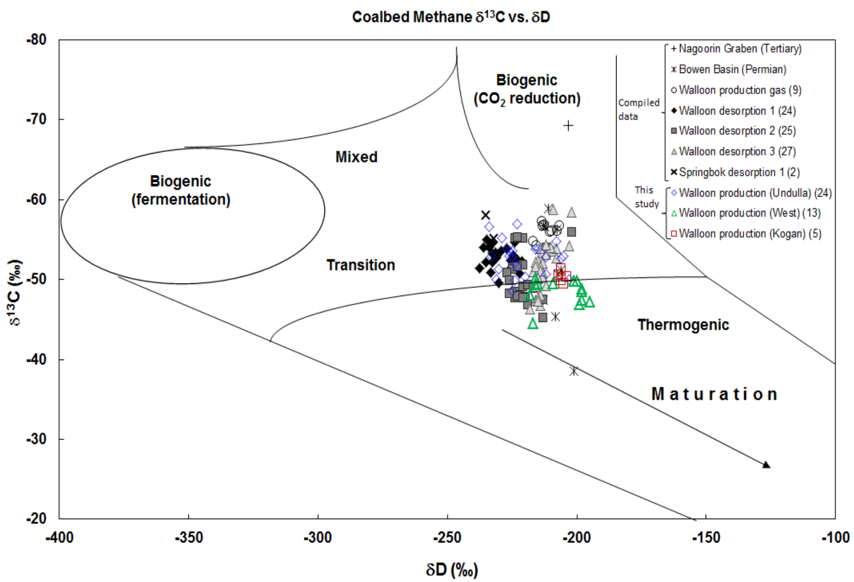
❖ Results of desktop study provided a platform for geochemical data collection and regional synthesis aimed towards understanding the *in situ* bioreactor potential of the Surat Basin.

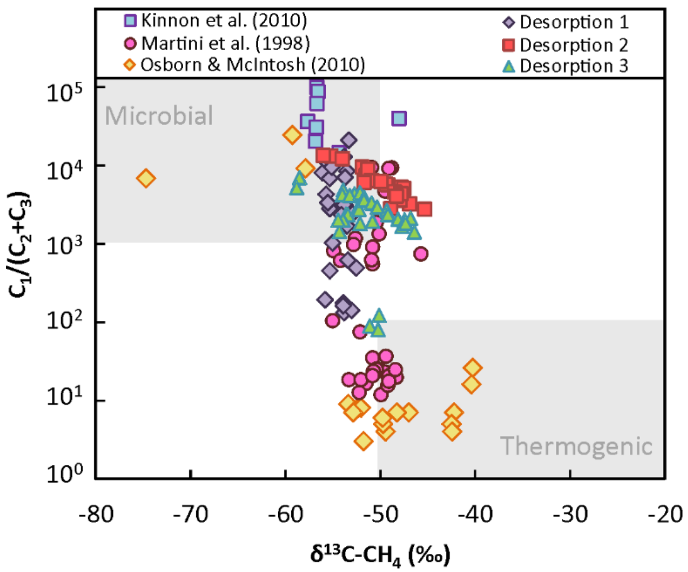
- 3 down-hole gas content trends
- Parabolic wells inflect around the Tangalooma Sandstone, regardless of depth



Hamilton, S.K., Esterle, J.S., Golding, S.D., 2012. Geological interpretation of gas content trends, Walloon Subgroup, eastern Surat Basin, Queensland, Australia. *International Journal of Coal Geology,* 101:21-31.

Methane Isotopes and Gas Origins





- Intermediate $\delta^{13}C\text{-}CH_4$ compositions of desorbed and production gases consistent with mixed biogenic-thermogenic origins.
- $\delta D\text{-}CH_4$ values and dry gas compositions indicate that the Walloon Subgroup CSG is dominated by secondary biogenic methane formed by reduction of CO_2 rather than acetoclastic reactions.

Hamilton, S.K., Golding, S.D., Baublys, K.A., Esterle, J.S., 2014. Stable isotopic and molecular composition of desorbed coal seam gases from the Walloon Subgroup, eastern Surat Basin, Australia. *International Journal of Coal Geology,* 122:21-36.

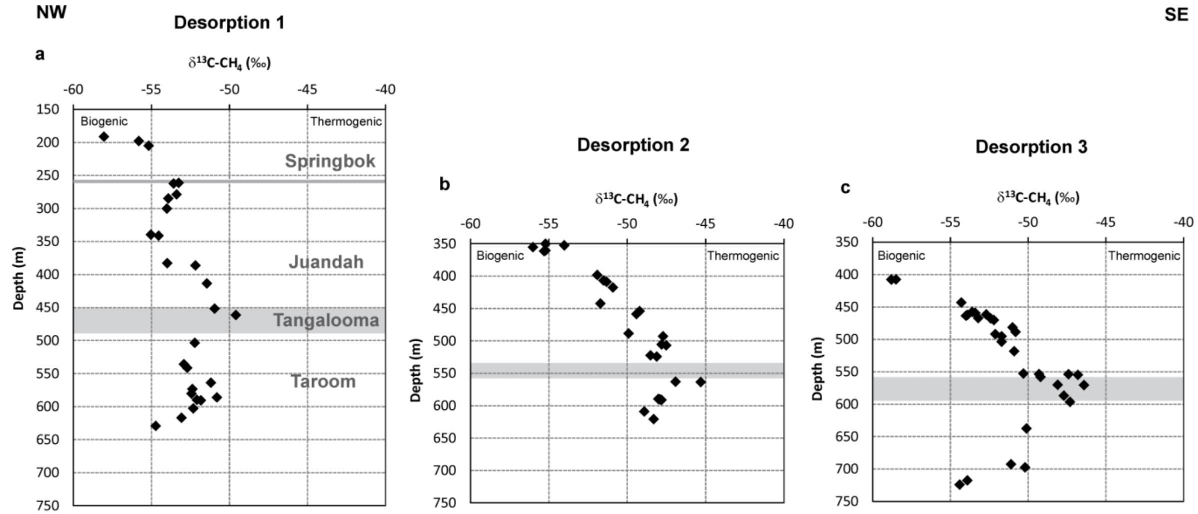
Baublys, K.A., Hamilton, S.K, Golding, S.D., Vink, S., Esterle, J., 2015. Microbial controls on the origin and evolution of coal seam gases and production waters of the Walloon Subgroup, Surat Basin, Australia. *International Journal of Coal Geology*, 147-148:85-104.

Down-hole Methane Isotope Profiles

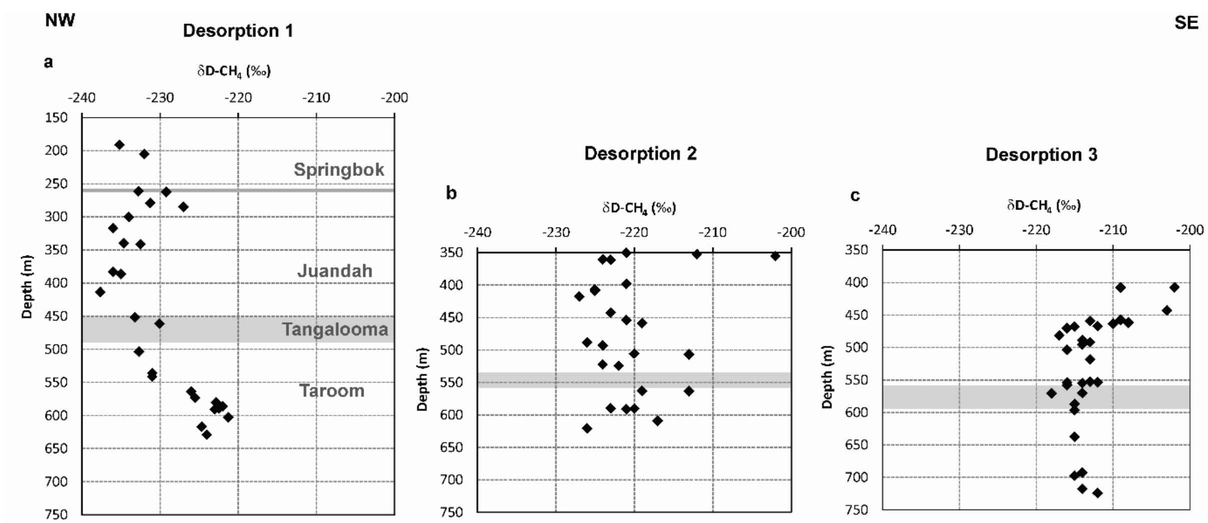
All 3 wells display positively parabolic down-hole $\delta^{13}C\text{-}CH_4$ trends, with maxima at the Tangalooma Sandstone level.

These trends track gas content for 2 of the wells. Desorption 1 displays lower variance of $\delta^{13}C\text{-}CH_4$ and gas content increases uniformly with depth.

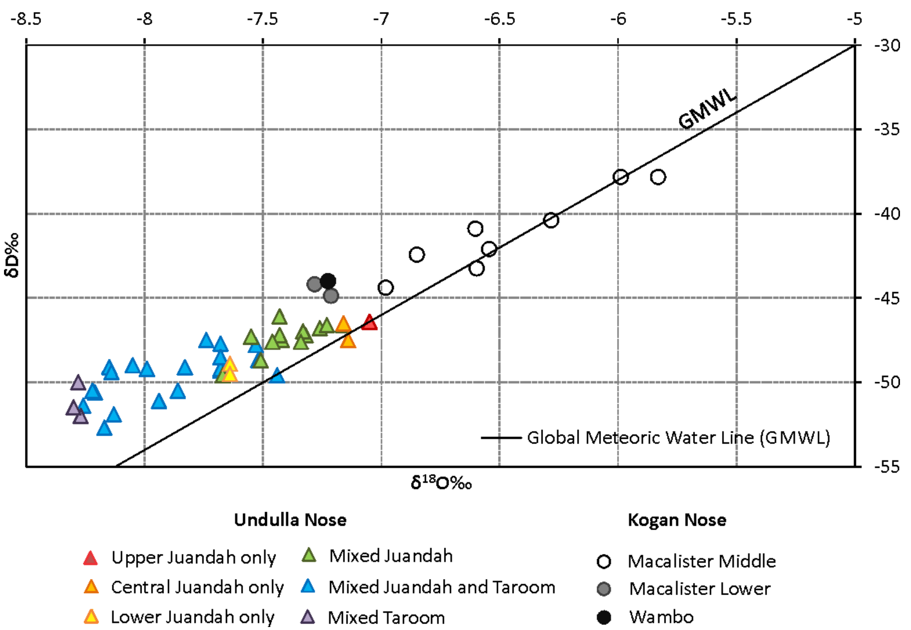
Methane δ13C

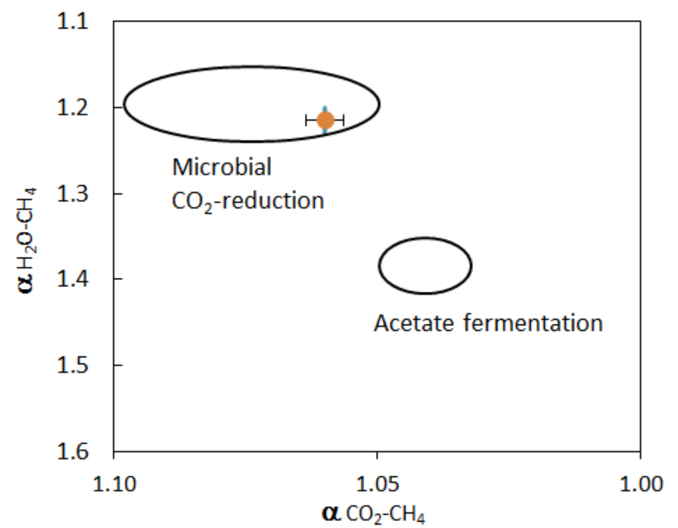


Methane δD



Production water and gas isotopes





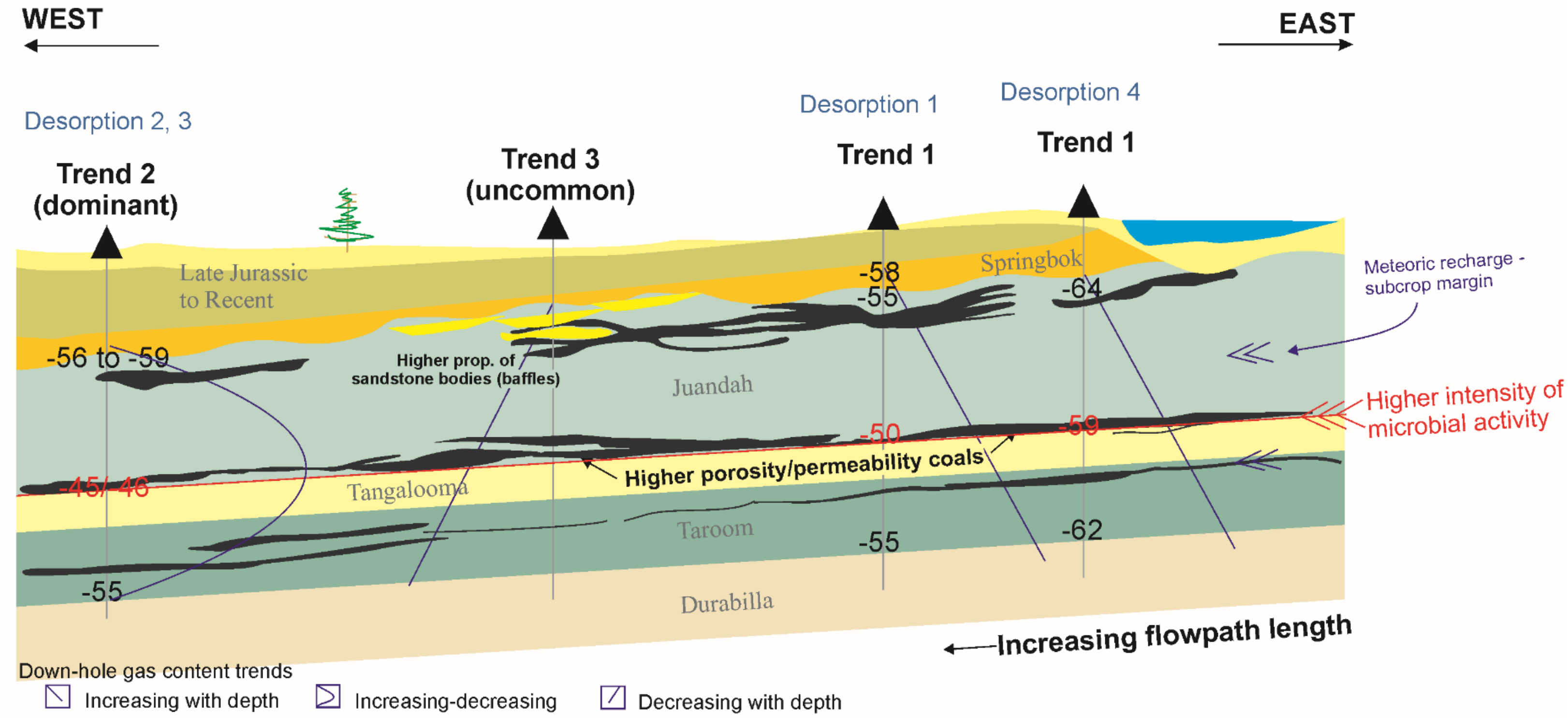
Greater ^{18}O and D depletion with increasing depth reflect the infiltration and increasing age of meteoric water down-dip.

Above GMWL = preferential use of light hydrogen over deuterium by methanogens

Fractionation factors are consistent with methanogenesis via CO_2-reduction

Baublys, K.A., Hamilton, S.K, Golding, S.D., Vink, S., Esterle, J., 2015. Microbial controls on the origin and evolution of coal seam gases and production waters of the Walloon Subgroup, Surat Basin, Australia. *International Journal of Coal Geology*, 147-148:85-104.

Conceptual model for spatial variability of methanogenesis

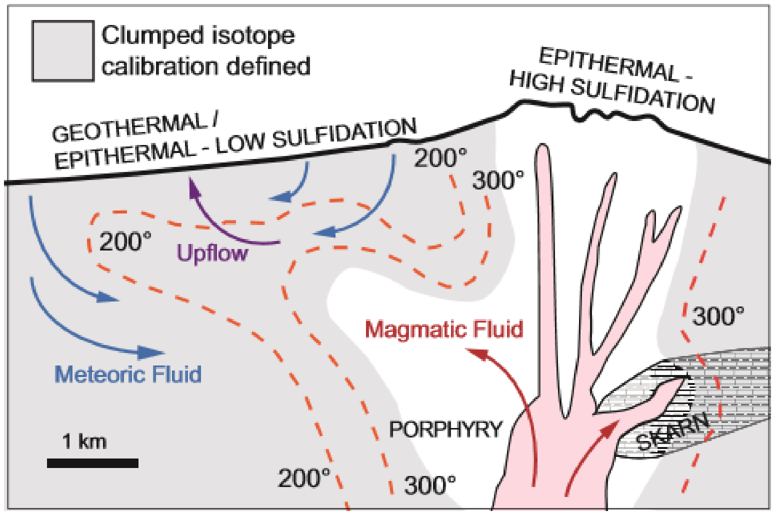


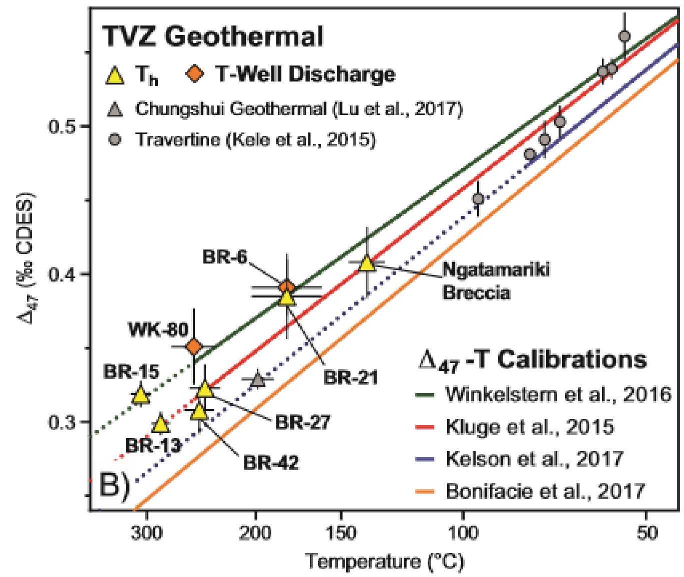
Changing gas content profiles and $\delta^{13}C-CH_4$ values reflect increased rates of microbial CO_2 reduction in central coal seams, and substrate depletion effects that become more pronounced with depth and distance from the basin margin.

Surat CBM isotope geochemistry

- Coupled ^{13}C-enrichment in methane and CO_2, H isotope composition of methane and dry gas compositions are evidence that Walloon CSG is dominated by secondary biogenic methane generated by the reduction of CO_2.
- Stratigraphic variations in gas content mainly reflect the extent of microbial methanogenesis.
- Methanogenesis in the Walloon Subgroup is geologically young; hence in situ bioreactors could potentially provide significant sources of gas.

New developments – clumped isotopes





Carbonate clumped isotopes provide an independent estimate of temperature so are able to delineate the heat footprint of hydrothermal systems and reconstruct the thermal history of sedimentary basins (e.g., Mering et al., 2018).

Methane clumped isotopes distinguish between microbial and thermogenic gas and can provide an independent estimate of formation temperature for natural gases (e.g., Douglas et al., 2017).

New developments – In Situ U-Pb dating

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The onset of the Dead Sea transform based on calcite age-strain analyses

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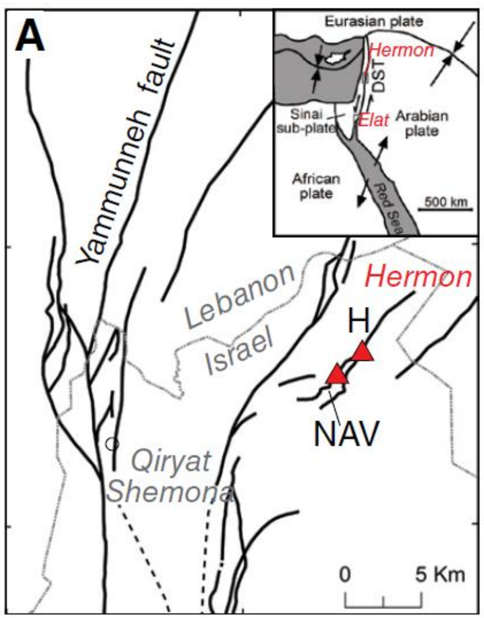
[3]Department of Earth Science, University of California, Santa Barbara, California 93106, USA
[4]Department of Geology, Macalester College, St. Paul, Minnesota 55105, USA



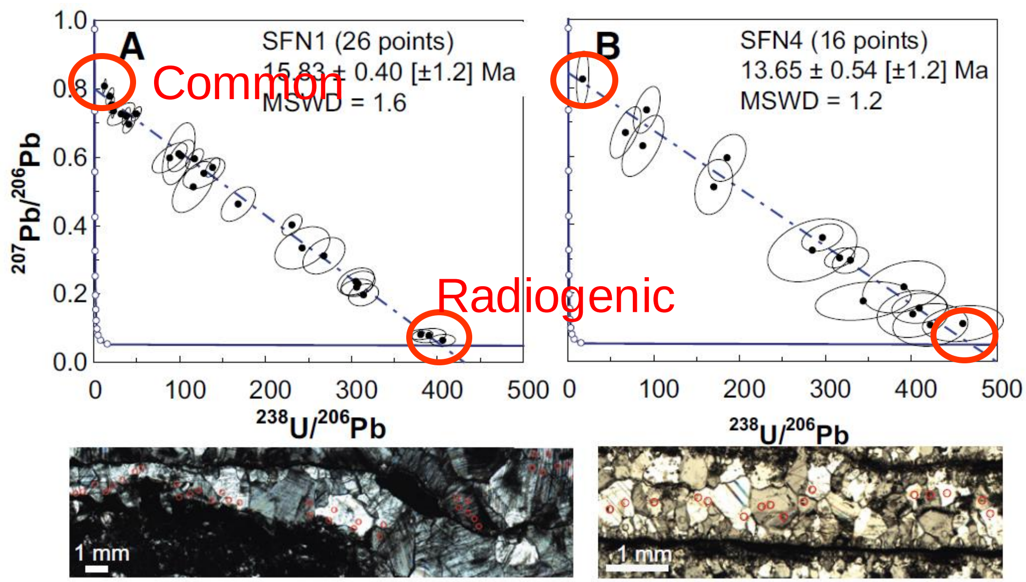
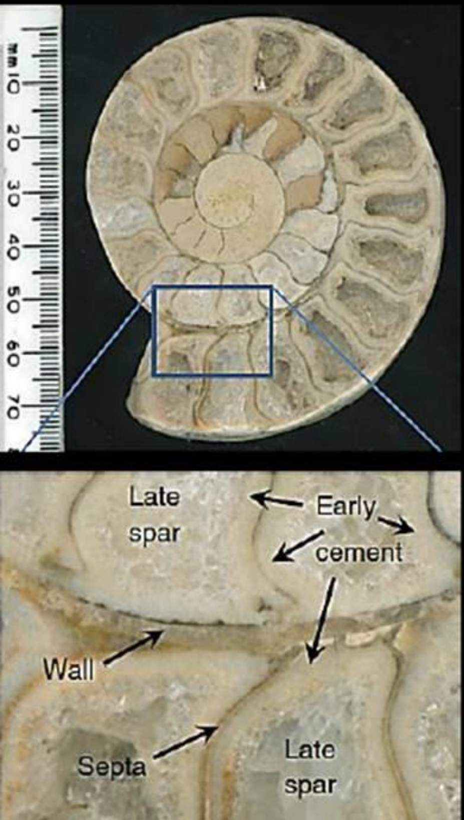


Figure 3. U-Pb Tera-Wasserburg concordia plots for samples SFN1 and SFN4 from Shelomo fault zone, Israel. Locations of laser ablation spot analyses (red circles) are indicated on cross-polarized microscopy images. Additional Tera-Wasserburg plots are given in Figure DR2 (see footnote 1). MSWD—mean square of weighted deviates.

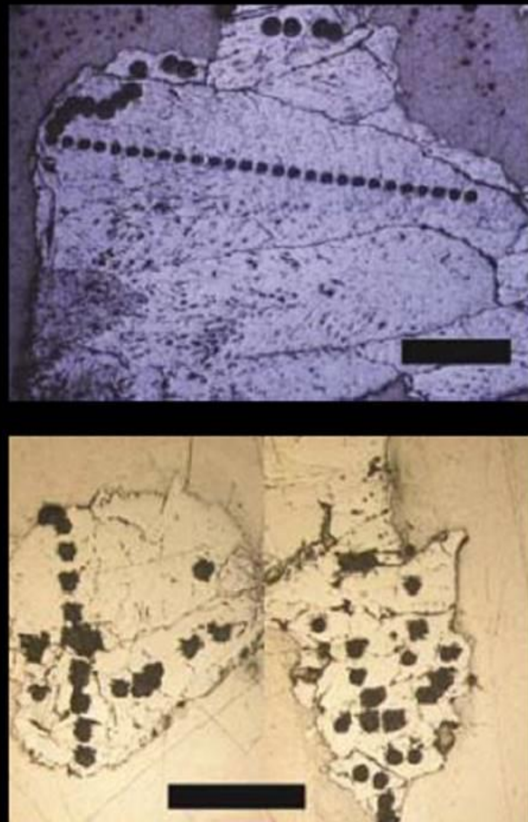
Carbonate Laser Ablation U-Pb dating

Early cement



Li et al., 2014

Hydrothermal



Coogan et al., 2014

Fault zone

Ring et al., 2016
Roberts et al., 2017
Nuriel et al., 2017
Hansman et al., 2018

Diagenesis

Godeau et al., 2018